

## Article

# Ferrocenylmethylphosphanes and the Alpha Process for Methoxycarbonylation: A Hidden Past.

Kevin M. Fortune,<sup>1</sup> Christa Castel,<sup>1</sup> Craig M. Robertson,<sup>2</sup> Peter N. Horton,<sup>3</sup> Mark Light,<sup>3</sup> Simon J. Coles,<sup>3</sup> Mark Waugh,<sup>4</sup> William Clegg,<sup>5</sup> Ross W. Harrington,<sup>5</sup> and Ian R. Butler.<sup>1,2\*</sup>

<sup>1</sup> Department of Chemistry, Bangor University, Bangor, Gwynedd, U.K. LL57 2UW.

<sup>2</sup> Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, U.K.

<sup>3</sup> Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, U.K.

<sup>4</sup> Mitsubishi Chemical U.K. Limited (formerly Lucite International UK Limited) The Wilton Centre, Redcar, TS10 4RF.

<sup>5</sup> Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU.

\* Correspondence: i.r.butler@hotmail.co.uk; Tel.: +44 01248-370405

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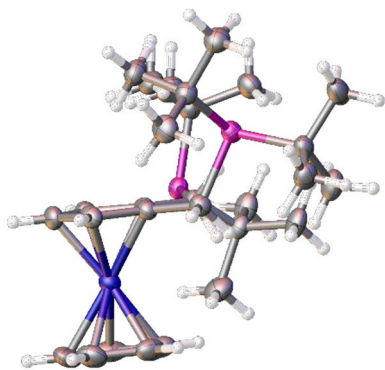
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## Crystallography Additional Information

**Compound 2a:** 00src159: CCDC 236436 (CSD code **RADYEB**).

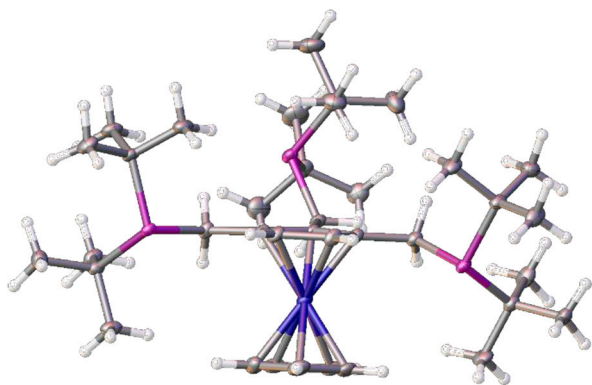
From Article DOI: 10.1016/j.inoche.2004.07.009. I.R. Butler, P.K. Baker, G.R. Eastham, K.M. Fortune, P.N. Horton, M.B. Hursthouse, Ferrocenylmethylphosphines ligands in the palladium-catalysed synthesis of methyl propionate, *Inorg.Chem.Commun.* (**2004**), 7, 1049-1052.  
<https://doi.org/10.1016/j.inoche.2004.07.009>



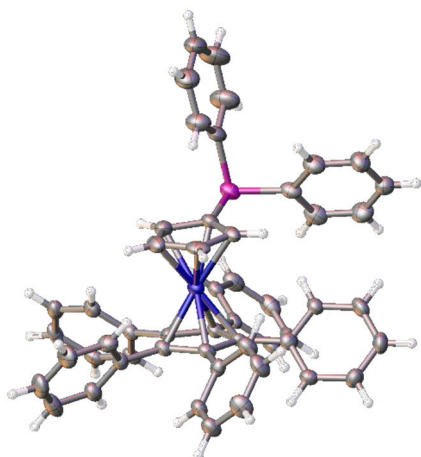
**Compound 8:** 02src0627: CCDC 233766 (CSD code: **XACTIF**)

From Article DOI: 10.1016/j.inoche.2004.04.006.

I.R. Butler, P.N. Horton, K.M. Fortune, K. Morris, C.H. Greenwell, G.R. Eastham, M.B. Hursthouse, The first 1,2,3-tris(phosphinomethyl)ferrocene, *Inorg. Chem. Commun.* (**2004**), 7, 923-928.



**Compound 10:** 02src530: CCDC 2077527

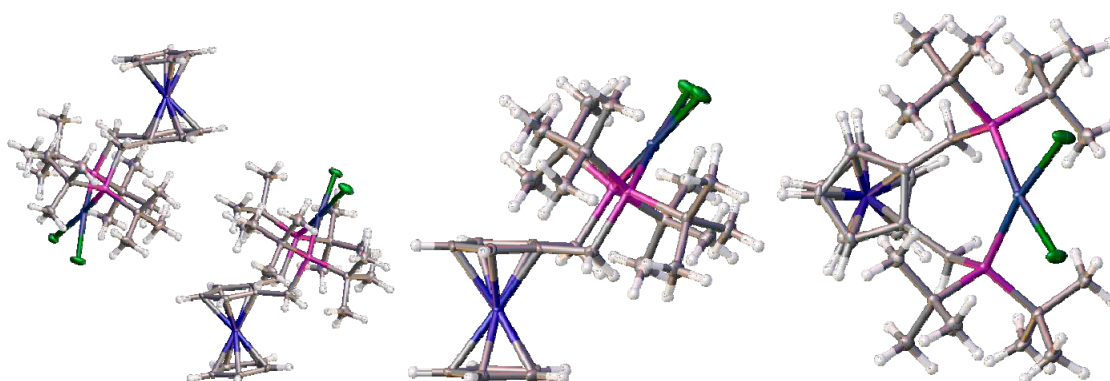


Structure of 1',2',3',4',5'-pentaphenyl-1-diphenylphosphinoferrocene

**Sample 2aPdCl<sub>2</sub>:** 2015NCS0574: CCDC 2077530

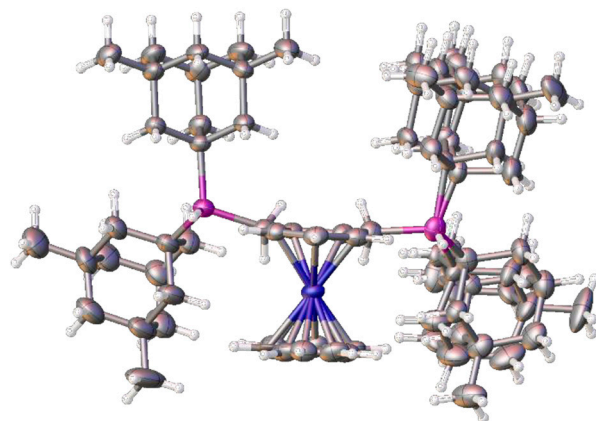
Previous structure: **04src0550**, see page S27-S37 had chloroform as the solvent, while this structure is dichloromethane solvated.

Full view and then side and top view

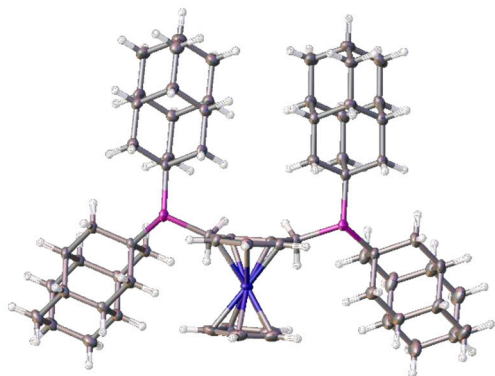


**Compound 2aPdCl<sub>2</sub>:** 2015NCS0574: CCDC 2077530, full view and then side and top view.

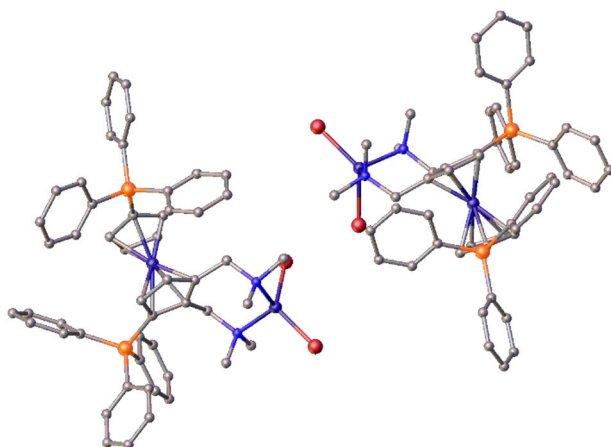
**Compound 2c:** sse1335: CCDC 1965611 (CSD code **MORYUQ**)



**Sample 2e:** sse1336; CCDC 1965612 (CSD code: **MORZAX**)

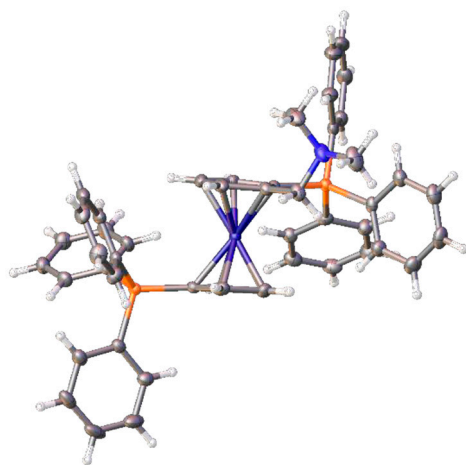


**Compound 24.NiBr<sub>2</sub>**: 2006src0791/ssf0791 (NiBr<sub>2</sub> complex with Fc structure); CCDC 1965846 CSD code **MOTLUF**



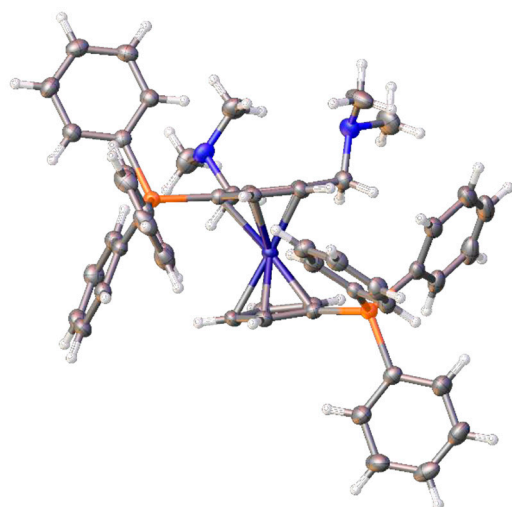
Compound **24.NiBr<sub>2</sub>**: both molecules; side view.

**Compound 23:** 2006src1007; CCDC 2077528



Olex 2 drawing of bis-2,1'-triphenylsilyl-NN-dimethylamiomethylferrocene, compound **23**.

**Compound 24:** 2006src1008; CCDC 2077529



Olex 2 drawing of 3,1'-bis-(triphenylsilyl)-bis-1,2-(N,N dimethylaminomethyl)ferrocene, compound **24**.

#### Experimental Crystallography for X-ray crystallography **10**, **23**, **24** and **2aPdCl<sub>2</sub>**

Suitable crystals were selected, and the crystallographic data for **10**, **23**, and **24** were collected on a Bruker Nonius Kappa CCD area detector ( $\phi$  scans and  $\omega$  scans to fill the asymmetric unit sphere) at the window of a Bruker Nonius FR591 rotating anode ( $\lambda_{\text{Mo-K}\alpha} = 0.71073 \text{ \AA}$ ). using *DirAx*<sup>i</sup> (cell determination), *Collect* (data collection), and *Denzo*<sup>ii</sup> (data reduction and cell refinement) and *SADABS*<sup>iii</sup> (absorption correction).

Crystallographic data for **2aPdCl<sub>2</sub>** were collected on a Rigaku FRE+ diffractometer equipped with HF Varimax confocal mirrors (100 $\mu\text{m}$  focus), an AFC12 goniometer and HG Saturn 724+ detector. Data were measured using profile data from  $\omega$ -scans using *MoK $\alpha$*  radiation. Cell determination and data collection were carried out using *CrystalClear*<sup>iv</sup>. With the data reduction, cell refinement and absorption correction using *CrystalisPro*<sup>v</sup>.

Using *Olex2*<sup>vi</sup>, the structures were solved with either *SHELXS-97*<sup>vii</sup> or *ShelXT*<sup>viii</sup> structure solution program, and the models were refined with *ShelX*<sup>ix</sup>. First, all non-hydrogen atoms were refined anisotropically. Then, all hydrogen atoms were placed geometrically using a standard riding model. Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC2077527-2077530 (for **10**, **23**, **24**, **2aPdCl<sub>2</sub>** respectively). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk)

Table S1: Crystal Data **10**, **23**, **24**, **2aPdCl<sub>2</sub>**

	<b>10</b>	<b>23</b>	<b>24</b>	<b>2a.PdCl<sub>2</sub></b>
Empirical Formula	C <sub>54</sub> H <sub>44</sub> FeO <sub>0.5</sub> P	C <sub>49</sub> H <sub>45</sub> FeNSi <sub>2</sub>	C <sub>52</sub> H <sub>52</sub> FeN <sub>2</sub> Si <sub>2</sub>	C <sub>29</sub> H <sub>50</sub> Cl <sub>4</sub> FeP <sub>2</sub> Pd
Formula Weight	787.71	759.89	816.98	764.68
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Temp (K)	120(2)	120(2)	120(2)	100(2)
Crystal System	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	P-1	P2 <sub>1</sub> /c	I2/a	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	12.142(5)	10.9639(2)	26.1977(5)	16.98450(10)
b (Å)	12.764(5)	26.5729(5)	11.9917(3)	18.5301(2)
c (Å)	16.578(5)	14.4019(2)	27.7143(6)	20.7859(2)
α (°)	93.032(5)	90	90	90
β (°)	107.990(5)	109.7270(10)	94.677(2)	90
γ (°)	116.730(5)	90	90	90
Volume (Å <sup>3</sup> )	2126.1(14)	3949.64(12)	8677.6(3)	6541.83(10)
Z	2	4	8	8
D <sub>calcd</sub> (mg m <sup>-3</sup> )	1.230	1.278	1.251	1.553
μ(mm <sup>-1</sup> )	0.429	0.478	0.441	1.437
F(000)	826	1600	3456	3152
Crystal Size (mm)	0.20 x 0.14 x 0.04	0.12 x 0.05 x 0.02	0.14 x 0.10 x 0.08	0.17 x 0.12 x 0.03
Crystal Shape, Colour	Rod, orange	Block, orange	Block, orange	Cut Block, red
Data/restraints/parameters	7282/50/532	9041/0/480	9948/0/518	14902/0/692
Goodness-of-fit on F <sup>2</sup>	0.914	1.027	1.021	1.031
Final R indices [ <i>I</i> > 2σ( <i>I</i> ): R <sub>1</sub> , wR <sub>2</sub>	0.0651, 0.1115	0.0470, 0.1034	0.0442, 0.0918	0.0260, 0.0537
R indices (all data) R <sub>1</sub> , wR <sub>2</sub>	0.1436, 0.1852	0.0643, 0.1110	0.0648, 0.1004	0.0297, 0.0550
Largest Diff. Peak, Hole	0.519, -0.329	0.528, -0.459	0.306, -0.285	0.397, -0.275

<sup>i</sup> R. W. W. Hoof, *Nonius B.V.*, 1998, 94:2

<sup>ii</sup> Z. Otwinowski and W. Minor, in *Macromolecular Crystallography, Pt A*, eds. C. W. Carter Jr. and R. M. Sweet, Academic Press, New York, 1997, 276, 307-326.

<sup>iii</sup> G. M. Sheldrick, Bruker-AXS Inc., Madison, WI, 2003, 26, Absorption correction

<sup>iv</sup> Rigaku, *CrystalClear- SM Expert 3.1 b27*, **2013**

<sup>v</sup> CrysAlisPro Software System, Rigaku Oxford Diffraction, Yarnton, Oxford, UK (**2017**).

<sup>vi</sup> Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., and Puschmann, H., Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), 42, 339-341.

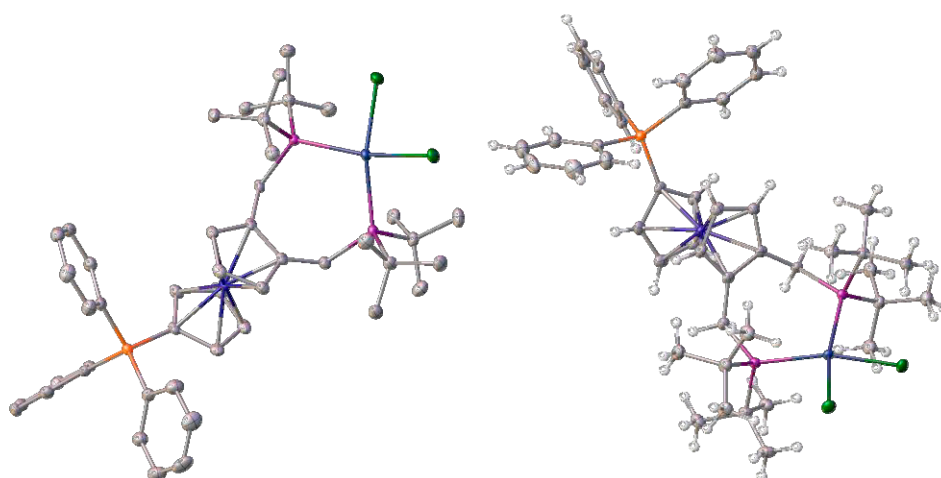
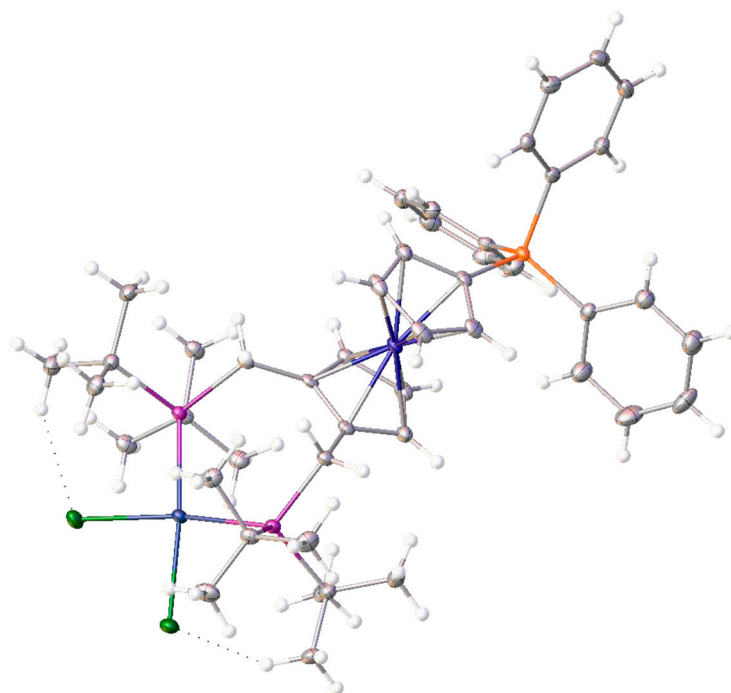
<sup>vii</sup> Sheldrick, G.M. *Acta Cryst.*, (**2008**), A64, 112-122.

<sup>viii</sup> Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), A71, 3-8.

<sup>ix</sup> Sheldrick, G.M., Crystal structure refinement with *ShelXL*, *Acta Cryst.*, (**2015**), C27, 3-8.



Crystallographic Data for compound **20**.PdCl<sub>2</sub> CCDC 2077837



Drawings of structure of the complex compound **20**.PdCl<sub>2</sub>

**Compound Code: final (20.PdCl<sub>2</sub>) CCDC 2077837**

Table S2: Crystal data and structure refinement for final.

Identification code	final
Empirical formula	C <sub>93</sub> H <sub>125</sub> Cl <sub>7</sub> Fe <sub>2</sub> P <sub>4</sub> Pd <sub>2</sub> Si <sub>2</sub>
Formula weight	1995.63
Temperature/K	100.02
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	23.733(2)
b/Å	14.6371(16)
c/Å	29.969(3)
α/°	90
β/°	112.935(2)
γ/°	90
Volume/Å <sup>3</sup>	9587.6(17)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.383
μ/mm <sup>-1</sup>	0.995
F(000)	4136.0
Crystal size/mm <sup>3</sup>	0.5 × 0.5 × 0.446
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.652 to 52.868
Index ranges	-22 ≤ h ≤ 29, -18 ≤ k ≤ 18, -37 ≤ l ≤ 36
Reflections collected	102423
Independent reflections	19529 [R <sub>int</sub> = 0.0402, R <sub>sigma</sub> = 0.0255]
Data/restraints/parameters	19529/0/1015
Goodness-of-fit on F <sup>2</sup>	1.050
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0304, wR <sub>2</sub> = 0.0686
Final R indexes [all data]	R <sub>1</sub> = 0.0366, wR <sub>2</sub> = 0.0721
Largest diff. peak/hole / e Å <sup>-3</sup>	0.77/-0.78

Table S3 Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for final.  $U_{\text{eq}}$  is defined as 1/3 of of the trace of the orthogonalised  $U_{ij}$  tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Pd <sub>4</sub>	7309.4(2)	2294.3(2)	2347.9(2)	11.31(4)
Pd <sub>3</sub>	7285.7(2)	2024.8(2)	-2436.1(2)	11.63(4)
Fe <sub>2</sub>	7018.1(2)	4901.9(2)	780.6(2)	12.15(7)
Fe <sub>1</sub>	8081.3(2)	-409.4(2)	-736.8(2)	11.67(7)
Cl <sub>10</sub>	5095.6(5)	543.0(6)	-726.4(4)	59.6(3)
Cl <sub>12</sub>	8028.4(3)	1139.3(4)	2730.0(2)	18.02(11)
Cl <sub>1</sub>	6375.0(3)	2638.4(4)	-3011.4(2)	21.03(12)
Cl <sub>11</sub>	6729.7(3)	1580.7(4)	2726.3(2)	19.47(12)
Cl <sub>9</sub>	7754.7(3)	3171.4(4)	-2726.2(2)	17.40(11)
Cl <sub>2</sub>	4625.4(4)	1962.5(6)	-306.0(3)	47.0(2)
Cl <sub>3</sub>	5881.6(4)	2012.0(7)	-198.3(3)	50.6(2)
P <sub>7</sub>	6421.3(3)	3079.1(4)	1890.8(2)	11.01(11)
P <sub>8</sub>	8074.5(3)	3045.4(4)	2185.5(2)	11.95(11)
P <sub>6</sub>	6674.1(3)	1256.3(4)	-2115.0(2)	11.80(11)
P <sub>5</sub>	8245.3(3)	1336.0(4)	-2057.2(2)	11.14(11)
Si <sub>13</sub>	8525.5(3)	-1281.5(4)	466.5(2)	12.35(12)
Si <sub>14</sub>	6595.4(3)	5852.8(4)	-393.9(2)	12.24(12)
C <sub>49</sub>	8631.7(11)	2842.8(16)	-1457.4(9)	18.7(5)
C <sub>105</sub>	8838.7(12)	3005.0(17)	3199.8(9)	22.9(5)
C <sub>58</sub>	5993.6(11)	2883.5(16)	-2081.0(9)	21.2(5)
C <sub>57</sub>	5815.2(11)	-235.5(16)	-2336.2(9)	19.4(5)
C <sub>107</sub>	9080.9(11)	4204.0(17)	2708.8(9)	21.5(5)
C <sub>106</sub>	8140.3(11)	4308.9(16)	2893.3(8)	17.9(5)
C <sub>85</sub>	6142.4(10)	7218.0(16)	-1133.4(8)	17.0(5)
C <sub>24</sub>	7596.8(11)	731.4(15)	-739.1(8)	15.2(4)
C <sub>53</sub>	6001.7(10)	586.9(15)	-2571.2(8)	14.8(4)
C <sub>18</sub>	7631.0(11)	-1602.4(15)	-1010.3(8)	17.0(5)
C <sub>31</sub>	9135.2(10)	-390.6(15)	729.9(8)	14.9(4)
C <sub>45</sub>	8900.5(10)	2139.6(15)	-1704.4(8)	14.2(4)
C <sub>40</sub>	6833.3(11)	-437.3(18)	810.6(9)	22.8(5)
C <sub>38</sub>	7618.6(11)	-62.0(16)	523.4(9)	19.9(5)
C <sub>61</sub>	6887.0(10)	5925.1(14)	276.1(8)	13.3(4)
C <sub>62</sub>	6566.9(11)	6124.4(15)	587.1(8)	17.0(5)
C <sub>65</sub>	7523.3(11)	5850.9(15)	593.1(8)	17.2(5)
C <sub>81</sub>	8041.6(12)	5827.9(19)	-849.2(10)	27.2(6)
C <sub>16</sub>	8636.5(11)	-1530.5(15)	-486.9(8)	15.4(5)
C <sub>72</sub>	5433.5(11)	5182.9(16)	-488.0(8)	17.2(5)

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C <sub>93</sub>	5993.8(10)	3640.1(15)	2248.7(8)	14.8(4)
C <sub>37</sub>	7855.5(10)	-950.1(16)	615.8(8)	14.7(4)
C <sub>101</sub>	8557.9(11)	2305.3(16)	1947.7(8)	17.0(5)
C <sub>100</sub>	8563.4(10)	3654.3(15)	2767.4(8)	15.1(4)
C <sub>42</sub>	7566.0(11)	-1571.7(16)	809.7(8)	18.1(5)
C <sub>71</sub>	5910.0(10)	5074.6(15)	-648.8(8)	14.5(4)
C <sub>70</sub>	7449.2(11)	3690.7(15)	810.5(8)	15.1(4)
C <sub>41</sub>	7062.4(11)	-1318.5(17)	908.5(9)	21.8(5)
C <sub>55</sub>	6219.5(11)	213.2(16)	-2955.7(8)	19.1(5)
C <sub>15</sub>	8279.2(10)	-1393.6(15)	-201.0(8)	13.3(4)
C <sub>43</sub>	8338.7(10)	377.7(15)	-1627.2(8)	13.0(4)
C <sub>103</sub>	8117.1(11)	1611.4(17)	1600.4(9)	21.4(5)
C <sub>39</sub>	7113.1(12)	191.0(17)	618.0(9)	23.3(5)
C <sub>69</sub>	7382.6(10)	3857.4(14)	1260.1(8)	13.0(4)
C <sub>32</sub>	9516.8(11)	-110.2(17)	497.4(8)	19.9(5)
C <sub>88</sub>	6148.7(10)	8633.7(16)	-518.4(9)	18.3(5)
C <sub>47</sub>	9180.4(11)	2643.9(16)	-2018.4(9)	18.4(5)
C <sub>25</sub>	8827.9(10)	-2426.1(16)	741.0(8)	14.9(4)
C <sub>90</sub>	6478.3(10)	4080.2(14)	1527.9(7)	12.4(4)
C <sub>22</sub>	8183.5(10)	568.9(14)	-1194.7(8)	13.1(4)
C <sub>63</sub>	6996.5(12)	6162.1(15)	1075.3(8)	19.5(5)
C <sub>59</sub>	6089.7(11)	1668.1(17)	-1473.4(9)	20.7(5)
C <sub>96</sub>	5369.3(10)	2720.0(16)	1045.5(8)	18.0(5)
C <sub>60</sub>	6998.7(11)	2624.8(16)	-1426.5(9)	19.8(5)
C <sub>98</sub>	5623.9(11)	4482.5(16)	1987.6(9)	18.6(5)
C <sub>80</sub>	8237.7(12)	4929.8(19)	-786.4(10)	29.4(6)
C <sub>92</sub>	5928.0(10)	2237.8(15)	1421.5(8)	14.5(4)
C <sub>77</sub>	7234.7(10)	5465.3(16)	-569.6(8)	15.6(5)
C <sub>19</sub>	7651.6(10)	-1440.9(15)	-536.3(8)	15.0(4)
C <sub>76</sub>	5830.2(11)	4417.8(17)	-1005.4(9)	20.6(5)
C <sub>79</sub>	7940.9(13)	4297.4(19)	-612.8(11)	31.4(6)
C <sub>23</sub>	7575.9(10)	558.7(15)	-1216.1(8)	14.0(4)
C <sub>66</sub>	6854.0(11)	3672.5(15)	434.9(8)	16.8(5)
C <sub>89</sub>	6334.4(10)	7759.2(15)	-335.6(8)	15.3(4)
C <sub>75</sub>	5297.2(11)	3894.6(17)	-1194.2(9)	23.1(5)
C <sub>64</sub>	7585.6(11)	5989.5(15)	1077.3(8)	19.6(5)
C <sub>17</sub>	8241.3(11)	-1659.8(15)	-980.4(8)	17.7(5)
C <sub>83</sub>	6338.7(10)	7033.0(15)	-636.6(8)	13.8(4)
C <sub>67</sub>	6420.3(10)	3835.2(15)	643.7(8)	14.3(4)
C <sub>46</sub>	8395.7(11)	708.4(15)	-2554.0(8)	15.5(5)
C <sub>68</sub>	6744.2(10)	3934.1(14)	1155.7(8)	12.2(4)

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C <sub>21</sub>	8583.6(11)	742.3(15)	-701.7(8)	15.8(5)
C <sub>91</sub>	7862.6(10)	4021.1(15)	1759.2(8)	14.2(4)
C <sub>86</sub>	5967.7(11)	8087.5(17)	-1317.5(8)	19.6(5)
C <sub>20</sub>	8221.1(11)	856.2(15)	-423.9(8)	16.6(5)
C <sub>87</sub>	5971.7(11)	8797.6(16)	-1008.7(9)	19.9(5)
C <sub>56</sub>	5423.4(10)	1162.6(17)	-2816.2(9)	20.0(5)
C <sub>48</sub>	9433.8(10)	1639.5(16)	-1310.0(8)	18.2(5)
C <sub>54</sub>	6414.7(11)	2131.3(15)	-1767.0(8)	16.0(5)
C <sub>82</sub>	7549.0(11)	6087.9(17)	-741.1(9)	20.2(5)
C <sub>102</sub>	8852.4(11)	2869.8(17)	1660.2(9)	21.3(5)
C <sub>44</sub>	7022.4(10)	342.3(15)	-1663.8(8)	13.2(4)
C <sub>29</sub>	9199.0(11)	-3449.8(18)	1437.4(9)	25.3(6)
C <sub>97</sub>	5539.4(11)	3005.4(16)	2346.7(9)	19.5(5)
C <sub>52</sub>	7880.0(11)	4.8(17)	-2775.1(9)	20.6(5)
C <sub>36</sub>	9242.0(11)	5.7(16)	1181.2(8)	18.9(5)
C <sub>26</sub>	8904.9(12)	-3133.9(17)	461.8(9)	23.9(5)
C <sub>35</sub>	9708.6(11)	637.2(17)	1391.7(9)	23.5(5)
C <sub>78</sub>	7445.4(12)	4561.5(17)	-507.5(10)	24.8(5)
C <sub>51</sub>	8375.8(13)	1330.8(17)	-2970.6(9)	24.6(6)
C <sub>30</sub>	8982.2(11)	-2604.6(17)	1236.3(9)	20.3(5)
C <sub>33</sub>	9980.6(11)	519.5(18)	708.7(9)	24.0(5)
C <sub>50</sub>	9012.8(11)	209.7(17)	-2355.5(9)	23.0(5)
C <sub>108</sub>	5140.2(12)	1697.5(19)	-574.7(10)	29.1(6)
C <sub>95</sub>	6331.2(11)	1817.5(16)	1176.1(8)	17.8(5)
C <sub>99</sub>	6488.4(11)	3962.5(17)	2733.1(8)	19.2(5)
C <sub>94</sub>	5697.0(11)	1423.2(15)	1626.4(9)	18.3(5)
C <sub>34</sub>	10077.6(11)	896.9(17)	1153.9(9)	23.9(5)
C <sub>104</sub>	9085.0(11)	1804.0(17)	2345.3(9)	21.4(5)
C <sub>28</sub>	9273.8(13)	-4136.3(19)	1149.2(10)	30.8(6)
C <sub>73</sub>	4905.5(11)	4659.4(17)	-670.1(8)	20.3(5)
C <sub>27</sub>	9127.5(14)	-3982.0(19)	661.8(10)	32.5(6)
C <sub>74</sub>	4838.2(11)	4009.0(16)	-1025.5(9)	20.9(5)

Table S4 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for final. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$ .

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Pd <sub>4</sub>	12.15(8)	9.97(8)	10.85(8)	2.12(6)	3.45(6)	0.76(6)
Pd <sub>3</sub>	12.39(8)	10.59(8)	11.93(8)	2.62(6)	4.75(6)	1.32(6)
Fe <sub>2</sub>	15.42(16)	9.99(15)	9.93(14)	1.12(11)	3.73(12)	-1.46(12)
Fe <sub>1</sub>	12.86(15)	11.61(15)	10.51(14)	2.02(11)	4.53(12)	-0.48(12)
Cl <sub>10</sub>	65.8(6)	29.9(4)	68.9(6)	-18.9(4)	10.8(5)	8.6(4)
Cl <sub>12</sub>	19.6(3)	15.4(3)	19.0(3)	5.7(2)	7.4(2)	5.7(2)
Cl <sub>1</sub>	16.0(3)	25.3(3)	21.0(3)	10.8(2)	6.3(2)	5.3(2)
Cl <sub>11</sub>	18.9(3)	20.3(3)	20.1(3)	8.2(2)	8.5(2)	0.7(2)
Cl <sub>9</sub>	18.5(3)	15.1(3)	18.0(3)	5.0(2)	6.5(2)	-1.3(2)
Cl <sub>2</sub>	45.5(5)	50.4(5)	55.1(5)	-5.7(4)	30.3(4)	5.1(4)
Cl <sub>3</sub>	31.3(4)	73.4(6)	35.7(4)	-1.0(4)	0.7(3)	-15.6(4)
P <sub>7</sub>	11.5(3)	9.7(3)	11.3(3)	1.1(2)	3.8(2)	0.0(2)
P <sub>8</sub>	11.5(3)	11.5(3)	11.6(3)	1.1(2)	3.2(2)	1.1(2)
P <sub>6</sub>	11.5(3)	11.1(3)	12.9(3)	1.4(2)	4.9(2)	1.4(2)
P <sub>5</sub>	12.3(3)	10.4(3)	11.2(3)	1.7(2)	5.1(2)	0.5(2)
Si <sub>13</sub>	11.9(3)	13.8(3)	11.6(3)	2.2(2)	4.8(2)	0.0(2)
Si <sub>14</sub>	14.0(3)	11.7(3)	11.3(3)	1.3(2)	5.3(2)	0.7(2)
C <sub>49</sub>	17.5(12)	17.0(12)	20.4(12)	-2.6(9)	6.1(10)	-1.8(9)
C <sub>105</sub>	23.7(13)	20.7(12)	16.1(12)	-0.2(9)	-1.0(10)	3.3(10)
C <sub>58</sub>	22.1(13)	17.3(12)	24.4(12)	1.7(10)	9.4(10)	7.4(10)
C <sub>57</sub>	16.5(11)	17.6(12)	23.1(12)	-0.6(9)	6.5(10)	-3.7(9)
C <sub>107</sub>	16.0(12)	21.6(12)	25.2(13)	-5.3(10)	6.0(10)	-2.6(10)
C <sub>106</sub>	16.9(11)	18.2(12)	16.5(11)	-4.2(9)	4.2(9)	-1.0(9)
C <sub>85</sub>	16.4(11)	19.2(12)	18.0(11)	0.5(9)	9.6(9)	1.5(9)
C <sub>24</sub>	19.8(12)	12.2(11)	16.2(11)	2.5(8)	9.7(9)	3.2(9)
C <sub>53</sub>	12.1(11)	14.3(11)	16.2(11)	0.0(9)	3.8(9)	-0.5(9)
C <sub>18</sub>	19.7(12)	13.4(11)	14.7(11)	1.1(9)	3.3(9)	-4.5(9)
C <sub>31</sub>	12.6(11)	14.0(11)	15.2(11)	2.7(8)	2.1(9)	2.6(9)
C <sub>45</sub>	12.3(11)	14.0(11)	14.5(10)	1.0(8)	3.3(9)	-2.9(8)
C <sub>40</sub>	20.4(12)	27.3(13)	24.4(13)	-6.4(10)	12.8(10)	-1.0(10)
C <sub>38</sub>	20.1(12)	18.8(12)	23.0(12)	3.0(10)	10.6(10)	-0.2(10)
C <sub>61</sub>	18.3(11)	8.1(10)	13.6(10)	2.4(8)	6.4(9)	-0.3(8)
C <sub>62</sub>	23.9(12)	12.8(11)	16.3(11)	1.8(9)	10.1(10)	1.4(9)
C <sub>65</sub>	19.4(12)	11.3(11)	20.0(11)	2.4(9)	6.8(10)	-5.4(9)
C <sub>81</sub>	24.9(14)	27.4(14)	33.8(14)	-0.7(11)	16.3(12)	-4.3(11)
C <sub>16</sub>	16.5(11)	13.6(11)	17.4(11)	3.0(9)	7.9(9)	0.4(9)
C <sub>72</sub>	18.5(12)	17.8(11)	15.1(11)	-0.2(9)	6.3(9)	1.5(9)
C <sub>93</sub>	15.8(11)	14.6(11)	15.7(11)	0.0(9)	7.9(9)	1.1(9)

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C <sub>37</sub>	13.8(11)	19.9(11)	9.9(10)	-1.2(8)	4.0(8)	-1.2(9)
C <sub>101</sub>	17.6(12)	17.0(11)	18.5(11)	1.0(9)	9.2(9)	3.9(9)
C <sub>100</sub>	13.7(11)	14.9(11)	13.1(10)	-0.4(8)	1.4(9)	0.3(9)
C <sub>42</sub>	19.2(12)	15.6(11)	19.8(12)	-0.5(9)	7.8(10)	-0.6(9)
C <sub>71</sub>	14.3(11)	12.6(11)	14.6(10)	3.3(8)	3.5(9)	1.5(8)
C <sub>70</sub>	19.1(12)	12.8(11)	14.8(11)	1.2(8)	8.1(9)	1.6(9)
C <sub>41</sub>	21.4(12)	24.6(13)	23.9(12)	-3.6(10)	13.8(10)	-5.7(10)
C <sub>55</sub>	18.4(12)	19.0(12)	18.7(11)	-2.2(9)	5.7(9)	-0.9(9)
C <sub>15</sub>	15.2(11)	10.5(10)	15.2(11)	3.1(8)	7.0(9)	1.0(8)
C <sub>43</sub>	14.0(11)	11.6(10)	13.1(10)	3.4(8)	5.0(9)	1.8(8)
C <sub>103</sub>	22.8(13)	20.8(12)	22.2(12)	-5.5(10)	10.7(10)	1.7(10)
C <sub>39</sub>	24.7(13)	18.3(12)	28.0(13)	-0.7(10)	11.6(11)	4.3(10)
C <sub>69</sub>	16.7(11)	7.8(10)	14.0(10)	2.4(8)	5.4(9)	0.8(8)
C <sub>32</sub>	20.1(12)	22.5(12)	15.4(11)	2.7(9)	5.0(9)	-1.8(10)
C <sub>88</sub>	14.7(11)	15.3(11)	24.4(12)	-0.9(9)	6.9(10)	-1.1(9)
C <sub>47</sub>	17.6(12)	14.6(11)	22.7(12)	3.2(9)	7.5(10)	-2.6(9)
C <sub>25</sub>	9.0(10)	17.9(11)	16.5(11)	4.1(9)	3.4(9)	-1.0(9)
C <sub>90</sub>	14.3(11)	9.6(10)	11.6(10)	2.0(8)	3.2(8)	0.6(8)
C <sub>22</sub>	15.9(11)	8.9(10)	13.9(10)	3.3(8)	5.2(9)	0.2(8)
C <sub>63</sub>	35.0(14)	10.8(11)	13.0(11)	-1.2(8)	9.8(10)	-3.5(10)
C <sub>59</sub>	22.9(13)	20.8(12)	23.1(12)	0.4(10)	14.1(10)	4.8(10)
C <sub>96</sub>	15.7(11)	18.2(12)	16.7(11)	1.9(9)	2.6(9)	-1.9(9)
C <sub>60</sub>	22.7(12)	14.8(11)	20.9(12)	-2.9(9)	7.5(10)	1.3(9)
C <sub>98</sub>	18.1(12)	17.9(12)	22.8(12)	0.3(9)	11.1(10)	3.3(9)
C <sub>80</sub>	18.8(13)	34.7(15)	39.8(16)	-13.0(12)	17.0(12)	-1.5(11)
C <sub>92</sub>	15.6(11)	10.2(10)	15.2(11)	-1.2(8)	3.4(9)	-1.6(8)
C <sub>77</sub>	14.5(11)	19.7(12)	13.3(10)	-1.0(9)	6.0(9)	0.4(9)
C <sub>19</sub>	15.4(11)	12.7(11)	17.6(11)	2.4(9)	7.1(9)	-2.2(9)
C <sub>76</sub>	19.8(12)	20.6(12)	21.1(12)	-3.0(10)	7.5(10)	2.3(10)
C <sub>79</sub>	29.3(15)	19.6(13)	47.0(17)	-4.5(12)	16.7(13)	5.3(11)
C <sub>23</sub>	17.3(11)	11.2(10)	13.3(10)	3.2(8)	6.0(9)	0.3(9)
C <sub>66</sub>	24.5(12)	11.4(11)	14.0(11)	-1.4(8)	7.0(9)	-2.5(9)
C <sub>89</sub>	13.1(11)	17.9(11)	15.6(11)	1.9(9)	6.2(9)	-2.3(9)
C <sub>75</sub>	23.9(13)	16.1(12)	26.0(13)	-5.7(10)	6.2(11)	1.6(10)
C <sub>64</sub>	25.0(13)	12.6(11)	16.7(11)	1.5(9)	3.1(10)	-6.5(9)
C <sub>17</sub>	28.1(13)	11.1(11)	16.6(11)	0.9(9)	11.5(10)	1.0(9)
C <sub>83</sub>	10.8(10)	14.8(11)	16.3(11)	2.5(9)	5.8(9)	0.1(8)
C <sub>67</sub>	15.8(11)	12.2(10)	13.2(10)	0.3(8)	3.7(9)	-2.8(9)
C <sub>46</sub>	20.1(12)	12.8(11)	16.8(11)	-0.9(9)	10.7(9)	-0.1(9)
C <sub>68</sub>	15.8(11)	6.0(10)	13.7(10)	2.4(8)	4.6(9)	-0.6(8)
C <sub>21</sub>	16.7(11)	14.0(11)	14.8(11)	1.6(8)	4.4(9)	-4.2(9)

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C <sub>91</sub>	14.9(11)	11.4(10)	15.9(11)	2.7(8)	5.5(9)	0.7(8)
C <sub>86</sub>	16.7(12)	26.0(13)	16.0(11)	7.4(9)	6.4(9)	2.0(10)
C <sub>20</sub>	23.7(12)	11.2(11)	14.1(11)	0.8(8)	6.5(9)	-0.3(9)
C <sub>87</sub>	15.2(11)	15.2(11)	28.9(13)	8.4(10)	8.3(10)	1.5(9)
C <sub>56</sub>	12.7(11)	21.9(12)	22.6(12)	1.5(10)	3.7(9)	1.3(9)
C <sub>48</sub>	12.5(11)	20.2(12)	20.0(12)	3.3(9)	4.1(9)	-1.6(9)
C <sub>54</sub>	18.3(12)	12.8(11)	18.8(11)	-0.4(9)	9.4(9)	3.5(9)
C <sub>82</sub>	20.4(12)	18.6(12)	22.8(12)	0.0(10)	9.8(10)	-0.1(10)
C <sub>102</sub>	19.3(12)	26.3(13)	21.6(12)	5.0(10)	11.4(10)	5.6(10)
C <sub>44</sub>	12.6(10)	13.0(11)	13.7(10)	2.5(8)	4.6(9)	1.2(8)
C <sub>29</sub>	18.8(12)	31.7(14)	21.2(12)	10.7(11)	3.4(10)	1.5(11)
C <sub>97</sub>	19.0(12)	19.6(12)	22.4(12)	1.5(10)	10.8(10)	-0.3(10)
C <sub>52</sub>	24.6(13)	20.6(12)	19.0(12)	-4.9(9)	10.9(10)	-4.8(10)
C <sub>36</sub>	14.5(11)	21.5(12)	21.2(12)	-1.1(10)	7.6(9)	2.5(9)
C <sub>26</sub>	32.0(14)	19.7(12)	22.9(13)	5.6(10)	13.8(11)	7.2(11)
C <sub>35</sub>	20.1(12)	21.9(13)	24.4(13)	-7.1(10)	4.3(10)	3.2(10)
C <sub>78</sub>	24.4(13)	20.1(13)	34.5(14)	0.3(11)	16.5(11)	0.4(10)
C <sub>51</sub>	39.7(16)	20.9(13)	19.5(12)	0.0(10)	18.4(11)	-2.2(11)
C <sub>30</sub>	19.0(12)	23.3(13)	17.3(11)	3.1(10)	5.5(10)	0.0(10)
C <sub>33</sub>	18.8(12)	25.6(13)	27.3(13)	6.1(11)	8.7(10)	-4.5(10)
C <sub>50</sub>	22.3(13)	23.2(13)	25.3(13)	-5.0(10)	11.2(11)	3.0(10)
C <sub>108</sub>	25.3(14)	29.4(15)	27.5(14)	-6.0(11)	4.8(11)	1.1(11)
C <sub>95</sub>	21.3(12)	12.7(11)	17.9(11)	-2.7(9)	6.0(10)	-0.9(9)
C <sub>99</sub>	20.8(12)	20.9(12)	17.9(11)	-3.7(9)	9.8(10)	0.0(10)
C <sub>94</sub>	18.0(12)	13.4(11)	21.2(12)	0.7(9)	5.1(10)	-4.0(9)
C <sub>34</sub>	15.7(12)	16.8(12)	31.5(14)	-1.2(10)	0.8(10)	-2.0(9)
C <sub>104</sub>	18.8(12)	22.0(13)	24.5(12)	3.6(10)	9.5(10)	8.3(10)
C <sub>28</sub>	30.0(15)	24.7(14)	35.4(15)	14.7(12)	10.3(12)	9.9(11)
C <sub>73</sub>	17.5(12)	25.0(13)	19.6(12)	5.4(10)	8.6(10)	2.4(10)
C <sub>27</sub>	42.6(17)	22.8(14)	35.0(15)	3.9(12)	18.2(13)	9.6(12)
C <sub>74</sub>	17.9(12)	16.3(12)	24.6(12)	3.1(10)	4.1(10)	-2.1(9)



Table S5 Bond Lengths for **20**.PdCl<sub>2</sub>, final.

<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Atom</b>	<b>Length/Å</b>
Pd <sub>4</sub>	Cl <sub>12</sub>	2.3575(6)	C <sub>45</sub>	C <sub>48</sub>	1.539(3)
Pd <sub>4</sub>	Cl <sub>11</sub>	2.3424(6)	C <sub>40</sub>	C <sub>41</sub>	1.386(4)
Pd <sub>4</sub>	P <sub>7</sub>	2.3213(6)	C <sub>40</sub>	C <sub>39</sub>	1.385(4)
Pd <sub>4</sub>	P <sub>8</sub>	2.3304(6)	C <sub>38</sub>	C <sub>37</sub>	1.400(3)
Pd <sub>3</sub>	Cl <sub>1</sub>	2.3550(6)	C <sub>38</sub>	C <sub>39</sub>	1.386(3)
Pd <sub>3</sub>	Cl <sub>9</sub>	2.3594(6)	C <sub>61</sub>	C <sub>62</sub>	1.443(3)
Pd <sub>3</sub>	P <sub>6</sub>	2.3208(6)	C <sub>61</sub>	C <sub>65</sub>	1.441(3)
Pd <sub>3</sub>	P <sub>5</sub>	2.3402(6)	C <sub>62</sub>	C <sub>63</sub>	1.421(3)
Fe <sub>2</sub>	C <sub>61</sub>	2.064(2)	C <sub>65</sub>	C <sub>64</sub>	1.415(3)
Fe <sub>2</sub>	C <sub>62</sub>	2.050(2)	C <sub>81</sub>	C <sub>80</sub>	1.383(4)
Fe <sub>2</sub>	C <sub>65</sub>	2.051(2)	C <sub>81</sub>	C <sub>82</sub>	1.383(4)
Fe <sub>2</sub>	C <sub>70</sub>	2.031(2)	C <sub>16</sub>	C <sub>15</sub>	1.435(3)
Fe <sub>2</sub>	C <sub>69</sub>	2.045(2)	C <sub>16</sub>	C <sub>17</sub>	1.422(3)
Fe <sub>2</sub>	C <sub>63</sub>	2.054(2)	C <sub>72</sub>	C <sub>71</sub>	1.400(3)
Fe <sub>2</sub>	C <sub>66</sub>	2.037(2)	C <sub>72</sub>	C <sub>73</sub>	1.386(3)
Fe <sub>2</sub>	C <sub>64</sub>	2.051(2)	C <sub>93</sub>	C <sub>98</sub>	1.539(3)
Fe <sub>2</sub>	C <sub>67</sub>	2.041(2)	C <sub>93</sub>	C <sub>97</sub>	1.536(3)
Fe <sub>2</sub>	C <sub>68</sub>	2.065(2)	C <sub>93</sub>	C <sub>99</sub>	1.543(3)
Fe <sub>1</sub>	C <sub>24</sub>	2.026(2)	C <sub>37</sub>	C <sub>42</sub>	1.396(3)
Fe <sub>1</sub>	C <sub>18</sub>	2.045(2)	C <sub>101</sub>	C <sub>103</sub>	1.536(3)
Fe <sub>1</sub>	C <sub>16</sub>	2.054(2)	C <sub>101</sub>	C <sub>102</sub>	1.544(3)
Fe <sub>1</sub>	C <sub>15</sub>	2.071(2)	C <sub>101</sub>	C <sub>104</sub>	1.537(3)
Fe <sub>1</sub>	C <sub>22</sub>	2.062(2)	C <sub>42</sub>	C <sub>41</sub>	1.389(3)
Fe <sub>1</sub>	C <sub>19</sub>	2.039(2)	C <sub>71</sub>	C <sub>76</sub>	1.395(3)
Fe <sub>1</sub>	C <sub>23</sub>	2.041(2)	C <sub>70</sub>	C <sub>69</sub>	1.437(3)
Fe <sub>1</sub>	C <sub>17</sub>	2.060(2)	C <sub>70</sub>	C <sub>66</sub>	1.422(3)
Fe <sub>1</sub>	C <sub>21</sub>	2.044(2)	C <sub>15</sub>	C <sub>19</sub>	1.437(3)
Fe <sub>1</sub>	C <sub>20</sub>	2.044(2)	C <sub>43</sub>	C <sub>22</sub>	1.505(3)
Cl <sub>10</sub>	C <sub>108</sub>	1.742(3)	C <sub>69</sub>	C <sub>68</sub>	1.427(3)
Cl <sub>2</sub>	C <sub>108</sub>	1.749(3)	C <sub>69</sub>	C <sub>91</sub>	1.505(3)
Cl <sub>3</sub>	C <sub>108</sub>	1.742(3)	C <sub>32</sub>	C <sub>33</sub>	1.385(3)
P <sub>7</sub>	C <sub>93</sub>	1.924(2)	C <sub>88</sub>	C <sub>89</sub>	1.395(3)
P <sub>7</sub>	C <sub>90</sub>	1.861(2)	C <sub>88</sub>	C <sub>87</sub>	1.383(3)
P <sub>7</sub>	C <sub>92</sub>	1.893(2)	C <sub>25</sub>	C <sub>26</sub>	1.388(3)
P <sub>8</sub>	C <sub>101</sub>	1.907(2)	C <sub>25</sub>	C <sub>30</sub>	1.408(3)
P <sub>8</sub>	C <sub>100</sub>	1.899(2)	C <sub>90</sub>	C <sub>68</sub>	1.496(3)
P <sub>8</sub>	C <sub>91</sub>	1.850(2)	C <sub>22</sub>	C <sub>23</sub>	1.418(3)
P <sub>6</sub>	C <sub>53</sub>	1.917(2)	C <sub>22</sub>	C <sub>21</sub>	1.434(3)
P <sub>6</sub>	C <sub>54</sub>	1.899(2)	C <sub>63</sub>	C <sub>64</sub>	1.418(4)

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P <sub>6</sub>	C <sub>44</sub>	1.852(2)	C <sub>59</sub>	C <sub>54</sub>	1.535(3)
P <sub>5</sub>	C <sub>45</sub>	1.907(2)	C <sub>96</sub>	C <sub>92</sub>	1.537(3)
P <sub>5</sub>	C <sub>43</sub>	1.859(2)	C <sub>60</sub>	C <sub>54</sub>	1.543(3)
P <sub>5</sub>	C <sub>46</sub>	1.898(2)	C <sub>80</sub>	C <sub>79</sub>	1.382(4)
Si <sub>13</sub>	C <sub>31</sub>	1.878(2)	C <sub>92</sub>	C <sub>95</sub>	1.544(3)
Si <sub>13</sub>	C <sub>37</sub>	1.876(2)	C <sub>92</sub>	C <sub>94</sub>	1.537(3)
Si <sub>13</sub>	C <sub>15</sub>	1.860(2)	C <sub>77</sub>	C <sub>82</sub>	1.396(3)
Si <sub>13</sub>	C <sub>25</sub>	1.881(2)	C <sub>77</sub>	C <sub>78</sub>	1.401(3)
Si <sub>14</sub>	C <sub>61</sub>	1.854(2)	C <sub>76</sub>	C <sub>75</sub>	1.396(3)
Si <sub>14</sub>	C <sub>71</sub>	1.886(2)	C <sub>79</sub>	C <sub>78</sub>	1.386(4)
Si <sub>14</sub>	C <sub>77</sub>	1.877(2)	C <sub>23</sub>	C <sub>44</sub>	1.501(3)
Si <sub>14</sub>	C <sub>83</sub>	1.881(2)	C <sub>66</sub>	C <sub>67</sub>	1.418(3)
C <sub>49</sub>	C <sub>45</sub>	1.544(3)	C <sub>89</sub>	C <sub>83</sub>	1.397(3)
C <sub>105</sub>	C <sub>100</sub>	1.533(3)	C <sub>75</sub>	C <sub>74</sub>	1.378(4)
C <sub>58</sub>	C <sub>54</sub>	1.537(3)	C <sub>67</sub>	C <sub>68</sub>	1.431(3)
C <sub>57</sub>	C <sub>53</sub>	1.544(3)	C <sub>46</sub>	C <sub>52</sub>	1.538(3)
C <sub>107</sub>	C <sub>100</sub>	1.535(3)	C <sub>46</sub>	C <sub>51</sub>	1.531(3)
C <sub>106</sub>	C <sub>100</sub>	1.537(3)	C <sub>46</sub>	C <sub>50</sub>	1.534(3)
C <sub>85</sub>	C <sub>83</sub>	1.402(3)	C <sub>21</sub>	C <sub>20</sub>	1.421(3)
C <sub>85</sub>	C <sub>86</sub>	1.385(3)	C <sub>86</sub>	C <sub>87</sub>	1.389(3)
C <sub>24</sub>	C <sub>23</sub>	1.433(3)	C <sub>29</sub>	C <sub>30</sub>	1.384(3)
C <sub>24</sub>	C <sub>20</sub>	1.425(3)	C <sub>29</sub>	C <sub>28</sub>	1.381(4)
C <sub>53</sub>	C <sub>55</sub>	1.536(3)	C <sub>36</sub>	C <sub>35</sub>	1.391(3)
C <sub>53</sub>	C <sub>56</sub>	1.532(3)	C <sub>26</sub>	C <sub>27</sub>	1.390(4)
C <sub>18</sub>	C <sub>19</sub>	1.422(3)	C <sub>35</sub>	C <sub>34</sub>	1.380(4)
C <sub>18</sub>	C <sub>17</sub>	1.419(3)	C <sub>33</sub>	C <sub>34</sub>	1.378(4)
C <sub>31</sub>	C <sub>32</sub>	1.402(3)	C <sub>28</sub>	C <sub>27</sub>	1.382(4)
C <sub>31</sub>	C <sub>36</sub>	1.401(3)	C <sub>73</sub>	C <sub>74</sub>	1.390(3)
C <sub>45</sub>	C <sub>47</sub>	1.536(3)			

Table S6 Bond Angles for final.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl <sub>11</sub>	Pd <sub>4</sub>	Cl <sub>12</sub>	84.01(2)	C <sub>39</sub>	C <sub>40</sub>	C <sub>41</sub>	119.6(2)
P <sub>7</sub>	Pd <sub>4</sub>	Cl <sub>12</sub>	163.82(2)	C <sub>39</sub>	C <sub>38</sub>	C <sub>37</sub>	121.3(2)
P <sub>7</sub>	Pd <sub>4</sub>	Cl <sub>11</sub>	86.37(2)	Si <sub>14</sub>	C <sub>61</sub>	Fe <sub>2</sub>	129.64(11)
P <sub>7</sub>	Pd <sub>4</sub>	P <sub>8</sub>	104.21(2)	C <sub>62</sub>	C <sub>61</sub>	Fe <sub>2</sub>	68.93(12)
P <sub>8</sub>	Pd <sub>4</sub>	Cl <sub>12</sub>	87.96(2)	C <sub>62</sub>	C <sub>61</sub>	Si <sub>14</sub>	129.99(17)
P <sub>8</sub>	Pd <sub>4</sub>	Cl <sub>11</sub>	164.56(2)	C <sub>65</sub>	C <sub>61</sub>	Fe <sub>2</sub>	69.03(12)
Cl <sub>1</sub>	Pd <sub>3</sub>	Cl <sub>9</sub>	83.63(2)	C <sub>65</sub>	C <sub>61</sub>	Si <sub>14</sub>	124.23(17)
P <sub>6</sub>	Pd <sub>3</sub>	Cl <sub>1</sub>	86.83(2)	C <sub>65</sub>	C <sub>61</sub>	C <sub>62</sub>	105.64(19)
P <sub>6</sub>	Pd <sub>3</sub>	Cl <sub>9</sub>	163.47(2)	C <sub>61</sub>	C <sub>62</sub>	Fe <sub>2</sub>	69.99(13)
P <sub>6</sub>	Pd <sub>3</sub>	P <sub>5</sub>	103.74(2)	C <sub>63</sub>	C <sub>62</sub>	Fe <sub>2</sub>	69.91(13)
P <sub>5</sub>	Pd <sub>3</sub>	Cl <sub>1</sub>	164.03(2)	C <sub>63</sub>	C <sub>62</sub>	C <sub>61</sub>	109.0(2)
P <sub>5</sub>	Pd <sub>3</sub>	Cl <sub>9</sub>	88.60(2)	C <sub>61</sub>	C <sub>65</sub>	Fe <sub>2</sub>	69.97(12)
C <sub>61</sub>	Fe <sub>2</sub>	C <sub>68</sub>	155.13(9)	C <sub>64</sub>	C <sub>65</sub>	Fe <sub>2</sub>	69.81(13)
C <sub>62</sub>	Fe <sub>2</sub>	C <sub>61</sub>	41.08(9)	C <sub>64</sub>	C <sub>65</sub>	C <sub>61</sub>	109.2(2)
C <sub>62</sub>	Fe <sub>2</sub>	C <sub>65</sub>	68.16(10)	C <sub>82</sub>	C <sub>81</sub>	C <sub>80</sub>	120.0(2)
C <sub>62</sub>	Fe <sub>2</sub>	C <sub>63</sub>	40.53(9)	C <sub>15</sub>	C <sub>16</sub>	Fe <sub>1</sub>	70.25(12)
C <sub>62</sub>	Fe <sub>2</sub>	C <sub>64</sub>	68.12(10)	C <sub>17</sub>	C <sub>16</sub>	Fe <sub>1</sub>	69.98(13)
C <sub>62</sub>	Fe <sub>2</sub>	C <sub>68</sub>	120.83(9)	C <sub>17</sub>	C <sub>16</sub>	C <sub>15</sub>	109.6(2)
C <sub>65</sub>	Fe <sub>2</sub>	C <sub>61</sub>	40.99(9)	C <sub>73</sub>	C <sub>72</sub>	C <sub>71</sub>	122.0(2)
C <sub>65</sub>	Fe <sub>2</sub>	C <sub>63</sub>	67.97(10)	C <sub>98</sub>	C <sub>93</sub>	P <sub>7</sub>	112.26(15)
C <sub>65</sub>	Fe <sub>2</sub>	C <sub>68</sub>	162.83(9)	C <sub>98</sub>	C <sub>93</sub>	C <sub>99</sub>	107.91(19)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>61</sub>	126.53(9)	C <sub>97</sub>	C <sub>93</sub>	P <sub>7</sub>	114.24(16)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>62</sub>	166.67(9)	C <sub>97</sub>	C <sub>93</sub>	C <sub>98</sub>	106.13(19)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>65</sub>	105.37(9)	C <sub>97</sub>	C <sub>93</sub>	C <sub>99</sub>	109.79(19)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>69</sub>	41.29(8)	C <sub>99</sub>	C <sub>93</sub>	P <sub>7</sub>	106.38(15)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>63</sub>	149.45(9)	C <sub>38</sub>	C <sub>37</sub>	Si <sub>13</sub>	120.34(17)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>66</sub>	40.93(9)	C <sub>42</sub>	C <sub>37</sub>	Si <sub>13</sub>	122.09(18)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>64</sub>	115.09(10)	C <sub>42</sub>	C <sub>37</sub>	C <sub>38</sub>	117.5(2)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>67</sub>	68.89(9)	C <sub>103</sub>	C <sub>101</sub>	P <sub>8</sub>	106.19(16)
C <sub>70</sub>	Fe <sub>2</sub>	C <sub>68</sub>	68.73(9)	C <sub>103</sub>	C <sub>101</sub>	C <sub>102</sub>	108.21(19)
C <sub>69</sub>	Fe <sub>2</sub>	C <sub>61</sub>	163.55(9)	C <sub>103</sub>	C <sub>101</sub>	C <sub>104</sub>	110.1(2)
C <sub>69</sub>	Fe <sub>2</sub>	C <sub>62</sub>	151.99(9)	C <sub>102</sub>	C <sub>101</sub>	P <sub>8</sub>	111.95(16)
C <sub>69</sub>	Fe <sub>2</sub>	C <sub>65</sub>	124.50(9)	C <sub>104</sub>	C <sub>101</sub>	P <sub>8</sub>	114.08(16)
C <sub>69</sub>	Fe <sub>2</sub>	C <sub>63</sub>	116.35(9)	C <sub>104</sub>	C <sub>101</sub>	C <sub>102</sub>	106.24(19)
C <sub>69</sub>	Fe <sub>2</sub>	C <sub>64</sub>	104.43(9)	C <sub>105</sub>	C <sub>100</sub>	P <sub>8</sub>	113.07(16)
C <sub>69</sub>	Fe <sub>2</sub>	C <sub>68</sub>	40.63(9)	C <sub>105</sub>	C <sub>100</sub>	C <sub>107</sub>	108.98(19)
C <sub>63</sub>	Fe <sub>2</sub>	C <sub>61</sub>	68.99(9)	C <sub>105</sub>	C <sub>100</sub>	C <sub>106</sub>	106.44(19)
C <sub>63</sub>	Fe <sub>2</sub>	C <sub>68</sub>	108.43(9)	C <sub>107</sub>	C <sub>100</sub>	P <sub>8</sub>	111.77(16)
C <sub>66</sub>	Fe <sub>2</sub>	C <sub>61</sub>	108.91(9)	C <sub>107</sub>	C <sub>100</sub>	C <sub>106</sub>	109.26(19)

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C <sub>66</sub>	Fe <sub>2</sub>	C <sub>62</sub>	130.70(9)	C <sub>106</sub>	C <sub>100</sub>	P <sub>8</sub>	107.11(15)
C <sub>66</sub>	Fe <sub>2</sub>	C <sub>65</sub>	118.37(9)	C <sub>41</sub>	C <sub>42</sub>	C <sub>37</sub>	121.3(2)
C <sub>66</sub>	Fe <sub>2</sub>	C <sub>69</sub>	68.99(9)	C <sub>72</sub>	C <sub>71</sub>	Si <sub>14</sub>	118.48(17)
C <sub>66</sub>	Fe <sub>2</sub>	C <sub>63</sub>	168.54(10)	C <sub>76</sub>	C <sub>71</sub>	Si <sub>14</sub>	124.38(18)
C <sub>66</sub>	Fe <sub>2</sub>	C <sub>64</sub>	150.40(10)	C <sub>76</sub>	C <sub>71</sub>	C <sub>72</sub>	117.1(2)
C <sub>66</sub>	Fe <sub>2</sub>	C <sub>67</sub>	40.69(9)	C <sub>69</sub>	C <sub>70</sub>	Fe <sub>2</sub>	69.86(12)
C <sub>66</sub>	Fe <sub>2</sub>	C <sub>68</sub>	68.43(9)	C <sub>66</sub>	C <sub>70</sub>	Fe <sub>2</sub>	69.75(13)
C <sub>64</sub>	Fe <sub>2</sub>	C <sub>61</sub>	68.92(9)	C <sub>66</sub>	C <sub>70</sub>	C <sub>69</sub>	107.9(2)
C <sub>64</sub>	Fe <sub>2</sub>	C <sub>65</sub>	40.35(9)	C <sub>40</sub>	C <sub>41</sub>	C <sub>42</sub>	120.1(2)
C <sub>64</sub>	Fe <sub>2</sub>	C <sub>63</sub>	40.43(10)	Si <sub>13</sub>	C <sub>15</sub>	Fe <sub>1</sub>	130.85(12)
C <sub>64</sub>	Fe <sub>2</sub>	C <sub>68</sub>	126.12(9)	C <sub>16</sub>	C <sub>15</sub>	Fe <sub>1</sub>	69.04(12)
C <sub>67</sub>	Fe <sub>2</sub>	C <sub>61</sub>	120.89(9)	C <sub>16</sub>	C <sub>15</sub>	Si <sub>13</sub>	130.03(17)
C <sub>67</sub>	Fe <sub>2</sub>	C <sub>62</sub>	111.43(9)	C <sub>16</sub>	C <sub>15</sub>	C <sub>19</sub>	105.55(19)
C <sub>67</sub>	Fe <sub>2</sub>	C <sub>65</sub>	153.86(9)	C <sub>19</sub>	C <sub>15</sub>	Fe <sub>1</sub>	68.36(12)
C <sub>67</sub>	Fe <sub>2</sub>	C <sub>69</sub>	68.89(9)	C <sub>19</sub>	C <sub>15</sub>	Si <sub>13</sub>	124.19(16)
C <sub>67</sub>	Fe <sub>2</sub>	C <sub>63</sub>	129.90(10)	C <sub>22</sub>	C <sub>43</sub>	P <sub>5</sub>	116.97(15)
C <sub>67</sub>	Fe <sub>2</sub>	C <sub>64</sub>	165.62(9)	C <sub>40</sub>	C <sub>39</sub>	C <sub>38</sub>	120.1(2)
C <sub>67</sub>	Fe <sub>2</sub>	C <sub>68</sub>	40.79(8)	C <sub>70</sub>	C <sub>69</sub>	Fe <sub>2</sub>	68.84(12)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>18</sub>	119.69(10)	C <sub>70</sub>	C <sub>69</sub>	C <sub>91</sub>	129.9(2)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>16</sub>	160.40(9)	C <sub>68</sub>	C <sub>69</sub>	Fe <sub>2</sub>	70.42(12)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>15</sub>	122.20(9)	C <sub>68</sub>	C <sub>69</sub>	C <sub>70</sub>	107.64(19)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>22</sub>	68.85(9)	C <sub>68</sub>	C <sub>69</sub>	C <sub>91</sub>	122.22(19)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>19</sub>	105.24(9)	C <sub>91</sub>	C <sub>69</sub>	Fe <sub>2</sub>	121.90(15)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>23</sub>	41.27(9)	C <sub>33</sub>	C <sub>32</sub>	C <sub>31</sub>	121.3(2)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>17</sub>	156.06(10)	C <sub>87</sub>	C <sub>88</sub>	C <sub>89</sub>	119.7(2)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>21</sub>	68.85(9)	C <sub>26</sub>	C <sub>25</sub>	Si <sub>13</sub>	121.24(17)
C <sub>24</sub>	Fe <sub>1</sub>	C <sub>20</sub>	40.98(9)	C <sub>26</sub>	C <sub>25</sub>	C <sub>30</sub>	117.1(2)
C <sub>18</sub>	Fe <sub>1</sub>	C <sub>16</sub>	67.96(9)	C <sub>30</sub>	C <sub>25</sub>	Si <sub>13</sub>	121.64(18)
C <sub>18</sub>	Fe <sub>1</sub>	C <sub>15</sub>	69.01(9)	C <sub>68</sub>	C <sub>90</sub>	P <sub>7</sub>	118.11(15)
C <sub>18</sub>	Fe <sub>1</sub>	C <sub>22</sub>	120.34(9)	C <sub>43</sub>	C <sub>22</sub>	Fe <sub>1</sub>	125.14(15)
C <sub>18</sub>	Fe <sub>1</sub>	C <sub>17</sub>	40.44(10)	C <sub>23</sub>	C <sub>22</sub>	Fe <sub>1</sub>	68.99(12)
C <sub>16</sub>	Fe <sub>1</sub>	C <sub>15</sub>	40.72(9)	C <sub>23</sub>	C <sub>22</sub>	C <sub>43</sub>	123.00(19)
C <sub>16</sub>	Fe <sub>1</sub>	C <sub>22</sub>	124.91(9)	C <sub>23</sub>	C <sub>22</sub>	C <sub>21</sub>	107.57(19)
C <sub>16</sub>	Fe <sub>1</sub>	C <sub>17</sub>	40.44(9)	C <sub>21</sub>	C <sub>22</sub>	Fe <sub>1</sub>	68.87(12)
C <sub>22</sub>	Fe <sub>1</sub>	C <sub>15</sub>	161.69(9)	C <sub>21</sub>	C <sub>22</sub>	C <sub>43</sub>	129.4(2)
C <sub>19</sub>	Fe <sub>1</sub>	C <sub>18</sub>	40.75(9)	C <sub>62</sub>	C <sub>63</sub>	Fe <sub>2</sub>	69.56(13)
C <sub>19</sub>	Fe <sub>1</sub>	C <sub>16</sub>	67.94(9)	C <sub>64</sub>	C <sub>63</sub>	Fe <sub>2</sub>	69.65(13)
C <sub>19</sub>	Fe <sub>1</sub>	C <sub>15</sub>	40.94(9)	C <sub>64</sub>	C <sub>63</sub>	C <sub>62</sub>	107.9(2)
C <sub>19</sub>	Fe <sub>1</sub>	C <sub>22</sub>	155.83(9)	C <sub>79</sub>	C <sub>80</sub>	C <sub>81</sub>	119.6(2)
C <sub>19</sub>	Fe <sub>1</sub>	C <sub>23</sub>	119.82(9)	C <sub>96</sub>	C <sub>92</sub>	P <sub>7</sub>	110.68(15)
C <sub>19</sub>	Fe <sub>1</sub>	C <sub>17</sub>	68.22(9)	C <sub>96</sub>	C <sub>92</sub>	C <sub>95</sub>	110.58(18)

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C <sub>19</sub>	Fe <sub>1</sub>	C <sub>21</sub>	160.78(9)	C <sub>96</sub>	C <sub>92</sub>	C <sub>94</sub>	108.01(18)
C <sub>19</sub>	Fe <sub>1</sub>	C <sub>20</sub>	123.10(9)	C <sub>95</sub>	C <sub>92</sub>	P <sub>7</sub>	107.13(15)
C <sub>23</sub>	Fe <sub>1</sub>	C <sub>18</sub>	103.82(9)	C <sub>94</sub>	C <sub>92</sub>	P <sub>7</sub>	114.94(15)
C <sub>23</sub>	Fe <sub>1</sub>	C <sub>16</sub>	158.21(9)	C <sub>94</sub>	C <sub>92</sub>	C <sub>95</sub>	105.37(18)
C <sub>23</sub>	Fe <sub>1</sub>	C <sub>15</sub>	157.25(9)	C <sub>82</sub>	C <sub>77</sub>	Si <sub>14</sub>	120.81(18)
C <sub>23</sub>	Fe <sub>1</sub>	C <sub>22</sub>	40.44(9)	C <sub>82</sub>	C <sub>77</sub>	C <sub>78</sub>	116.8(2)
C <sub>23</sub>	Fe <sub>1</sub>	C <sub>17</sub>	120.42(9)	C <sub>78</sub>	C <sub>77</sub>	Si <sub>14</sub>	122.26(18)
C <sub>23</sub>	Fe <sub>1</sub>	C <sub>21</sub>	68.57(9)	C <sub>18</sub>	C <sub>19</sub>	Fe <sub>1</sub>	69.83(13)
C <sub>23</sub>	Fe <sub>1</sub>	C <sub>20</sub>	68.87(9)	C <sub>18</sub>	C <sub>19</sub>	C <sub>15</sub>	109.2(2)
C <sub>17</sub>	Fe <sub>1</sub>	C <sub>15</sub>	68.86(9)	C <sub>15</sub>	C <sub>19</sub>	Fe <sub>1</sub>	70.70(12)
C <sub>17</sub>	Fe <sub>1</sub>	C <sub>22</sub>	107.18(9)	C <sub>71</sub>	C <sub>76</sub>	C <sub>75</sub>	121.3(2)
C <sub>21</sub>	Fe <sub>1</sub>	C <sub>18</sub>	158.20(9)	C <sub>80</sub>	C <sub>79</sub>	C <sub>78</sub>	120.1(3)
C <sub>21</sub>	Fe <sub>1</sub>	C <sub>16</sub>	111.21(9)	C <sub>24</sub>	C <sub>23</sub>	Fe <sub>1</sub>	68.79(12)
C <sub>21</sub>	Fe <sub>1</sub>	C <sub>15</sub>	125.63(9)	C <sub>24</sub>	C <sub>23</sub>	C <sub>44</sub>	127.4(2)
C <sub>21</sub>	Fe <sub>1</sub>	C <sub>22</sub>	40.88(8)	C <sub>22</sub>	C <sub>23</sub>	Fe <sub>1</sub>	70.57(12)
C <sub>21</sub>	Fe <sub>1</sub>	C <sub>17</sub>	124.53(10)	C <sub>22</sub>	C <sub>23</sub>	C <sub>24</sub>	108.28(19)
C <sub>21</sub>	Fe <sub>1</sub>	C <sub>20</sub>	40.69(9)	C <sub>22</sub>	C <sub>23</sub>	C <sub>44</sub>	124.26(19)
C <sub>20</sub>	Fe <sub>1</sub>	C <sub>18</sub>	157.50(10)	C <sub>44</sub>	C <sub>23</sub>	Fe <sub>1</sub>	123.51(15)
C <sub>20</sub>	Fe <sub>1</sub>	C <sub>16</sub>	126.17(9)	C <sub>70</sub>	C <sub>66</sub>	Fe <sub>2</sub>	69.32(13)
C <sub>20</sub>	Fe <sub>1</sub>	C <sub>15</sub>	109.11(9)	C <sub>67</sub>	C <sub>66</sub>	Fe <sub>2</sub>	69.81(13)
C <sub>20</sub>	Fe <sub>1</sub>	C <sub>22</sub>	68.64(9)	C <sub>67</sub>	C <sub>66</sub>	C <sub>70</sub>	108.4(2)
C <sub>20</sub>	Fe <sub>1</sub>	C <sub>17</sub>	161.51(10)	C <sub>88</sub>	C <sub>89</sub>	C <sub>83</sub>	121.7(2)
C <sub>93</sub>	P <sub>7</sub>	Pd <sub>4</sub>	115.91(7)	C <sub>74</sub>	C <sub>75</sub>	C <sub>76</sub>	120.4(2)
C <sub>90</sub>	P <sub>7</sub>	Pd <sub>4</sub>	118.59(7)	C <sub>65</sub>	C <sub>64</sub>	Fe <sub>2</sub>	69.84(13)
C <sub>90</sub>	P <sub>7</sub>	C <sub>93</sub>	99.43(10)	C <sub>65</sub>	C <sub>64</sub>	C <sub>63</sub>	108.2(2)
C <sub>90</sub>	P <sub>7</sub>	C <sub>92</sub>	104.06(10)	C <sub>63</sub>	C <sub>64</sub>	Fe <sub>2</sub>	69.92(13)
C <sub>92</sub>	P <sub>7</sub>	Pd <sub>4</sub>	105.84(7)	C <sub>18</sub>	C <sub>17</sub>	Fe <sub>1</sub>	69.21(13)
C <sub>92</sub>	P <sub>7</sub>	C <sub>93</sub>	112.59(10)	C <sub>18</sub>	C <sub>17</sub>	C <sub>16</sub>	107.5(2)
C <sub>101</sub>	P <sub>8</sub>	Pd <sub>4</sub>	116.19(8)	C <sub>16</sub>	C <sub>17</sub>	Fe <sub>1</sub>	69.58(13)
C <sub>100</sub>	P <sub>8</sub>	Pd <sub>4</sub>	106.06(7)	C <sub>85</sub>	C <sub>83</sub>	Si <sub>14</sub>	120.75(17)
C <sub>100</sub>	P <sub>8</sub>	C <sub>101</sub>	111.64(10)	C <sub>89</sub>	C <sub>83</sub>	Si <sub>14</sub>	122.13(17)
C <sub>91</sub>	P <sub>8</sub>	Pd <sub>4</sub>	118.95(7)	C <sub>89</sub>	C <sub>83</sub>	C <sub>85</sub>	117.1(2)
C <sub>91</sub>	P <sub>8</sub>	C <sub>101</sub>	102.81(10)	C <sub>66</sub>	C <sub>67</sub>	Fe <sub>2</sub>	69.50(13)
C <sub>91</sub>	P <sub>8</sub>	C <sub>100</sub>	100.15(10)	C <sub>66</sub>	C <sub>67</sub>	C <sub>68</sub>	108.1(2)
C <sub>53</sub>	P <sub>6</sub>	Pd <sub>3</sub>	115.67(7)	C <sub>68</sub>	C <sub>67</sub>	Fe <sub>2</sub>	70.49(12)
C <sub>54</sub>	P <sub>6</sub>	Pd <sub>3</sub>	106.84(7)	C <sub>52</sub>	C <sub>46</sub>	P <sub>5</sub>	107.49(15)
C <sub>54</sub>	P <sub>6</sub>	C <sub>53</sub>	112.23(10)	C <sub>51</sub>	C <sub>46</sub>	P <sub>5</sub>	113.33(16)
C <sub>44</sub>	P <sub>6</sub>	Pd <sub>3</sub>	118.65(7)	C <sub>51</sub>	C <sub>46</sub>	C <sub>52</sub>	106.29(19)
C <sub>44</sub>	P <sub>6</sub>	C <sub>53</sub>	99.33(10)	C <sub>51</sub>	C <sub>46</sub>	C <sub>50</sub>	108.7(2)
C <sub>44</sub>	P <sub>6</sub>	C <sub>54</sub>	103.54(10)	C <sub>50</sub>	C <sub>46</sub>	P <sub>5</sub>	111.67(16)
C <sub>45</sub>	P <sub>5</sub>	Pd <sub>3</sub>	115.62(7)	C <sub>50</sub>	C <sub>46</sub>	C <sub>52</sub>	109.14(19)

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C <sub>43</sub>	P <sub>5</sub>	Pd <sub>3</sub>	119.48(7)	C <sub>69</sub>	C <sub>68</sub>	Fe <sub>2</sub>	68.94(12)
C <sub>43</sub>	P <sub>5</sub>	C <sub>45</sub>	103.29(10)	C <sub>69</sub>	C <sub>68</sub>	C <sub>90</sub>	124.63(19)
C <sub>43</sub>	P <sub>5</sub>	C <sub>46</sub>	99.82(10)	C <sub>69</sub>	C <sub>68</sub>	C <sub>67</sub>	107.94(19)
C <sub>46</sub>	P <sub>5</sub>	Pd <sub>3</sub>	105.83(7)	C <sub>90</sub>	C <sub>68</sub>	Fe <sub>2</sub>	128.46(15)
C <sub>46</sub>	P <sub>5</sub>	C <sub>45</sub>	111.80(10)	C <sub>67</sub>	C <sub>68</sub>	Fe <sub>2</sub>	68.72(12)
C <sub>31</sub>	Si <sub>13</sub>	C <sub>25</sub>	109.53(10)	C <sub>67</sub>	C <sub>68</sub>	C <sub>90</sub>	127.4(2)
C <sub>37</sub>	Si <sub>13</sub>	C <sub>31</sub>	107.82(10)	C <sub>22</sub>	C <sub>21</sub>	Fe <sub>1</sub>	70.25(12)
C <sub>37</sub>	Si <sub>13</sub>	C <sub>25</sub>	109.90(10)	C <sub>20</sub>	C <sub>21</sub>	Fe <sub>1</sub>	69.68(13)
C <sub>15</sub>	Si <sub>13</sub>	C <sub>31</sub>	112.41(10)	C <sub>20</sub>	C <sub>21</sub>	C <sub>22</sub>	108.4(2)
C <sub>15</sub>	Si <sub>13</sub>	C <sub>37</sub>	109.82(10)	C <sub>69</sub>	C <sub>91</sub>	P <sub>8</sub>	117.39(15)
C <sub>15</sub>	Si <sub>13</sub>	C <sub>25</sub>	107.35(10)	C <sub>85</sub>	C <sub>86</sub>	C <sub>87</sub>	119.9(2)
C <sub>61</sub>	Si <sub>14</sub>	C <sub>71</sub>	111.83(10)	C <sub>24</sub>	C <sub>20</sub>	Fe <sub>1</sub>	68.82(13)
C <sub>61</sub>	Si <sub>14</sub>	C <sub>77</sub>	108.64(10)	C <sub>21</sub>	C <sub>20</sub>	Fe <sub>1</sub>	69.63(13)
C <sub>61</sub>	Si <sub>14</sub>	C <sub>83</sub>	107.11(10)	C <sub>21</sub>	C <sub>20</sub>	C <sub>24</sub>	107.9(2)
C <sub>77</sub>	Si <sub>14</sub>	C <sub>71</sub>	111.57(10)	C <sub>88</sub>	C <sub>87</sub>	C <sub>86</sub>	119.9(2)
C <sub>77</sub>	Si <sub>14</sub>	C <sub>83</sub>	110.15(10)	C <sub>58</sub>	C <sub>54</sub>	P <sub>6</sub>	114.79(16)
C <sub>83</sub>	Si <sub>14</sub>	C <sub>71</sub>	107.44(10)	C <sub>58</sub>	C <sub>54</sub>	C <sub>60</sub>	105.76(19)
C <sub>86</sub>	C <sub>85</sub>	C <sub>83</sub>	121.6(2)	C <sub>59</sub>	C <sub>54</sub>	P <sub>6</sub>	111.08(16)
C <sub>23</sub>	C <sub>24</sub>	Fe <sub>1</sub>	69.94(12)	C <sub>59</sub>	C <sub>54</sub>	C <sub>58</sub>	108.37(19)
C <sub>20</sub>	C <sub>24</sub>	Fe <sub>1</sub>	70.20(13)	C <sub>59</sub>	C <sub>54</sub>	C <sub>60</sub>	110.50(19)
C <sub>20</sub>	C <sub>24</sub>	C <sub>23</sub>	107.9(2)	C <sub>60</sub>	C <sub>54</sub>	P <sub>6</sub>	106.19(15)
C <sub>57</sub>	C <sub>53</sub>	P <sub>6</sub>	112.33(15)	C <sub>81</sub>	C <sub>82</sub>	C <sub>77</sub>	121.9(2)
C <sub>55</sub>	C <sub>53</sub>	P <sub>6</sub>	106.68(15)	C <sub>23</sub>	C <sub>44</sub>	P <sub>6</sub>	119.10(15)
C <sub>55</sub>	C <sub>53</sub>	C <sub>57</sub>	107.74(19)	C <sub>28</sub>	C <sub>29</sub>	C <sub>30</sub>	119.6(2)
C <sub>56</sub>	C <sub>53</sub>	P <sub>6</sub>	113.70(16)	C <sub>35</sub>	C <sub>36</sub>	C <sub>31</sub>	121.7(2)
C <sub>56</sub>	C <sub>53</sub>	C <sub>57</sub>	106.56(18)	C <sub>25</sub>	C <sub>26</sub>	C <sub>27</sub>	121.6(2)
C <sub>56</sub>	C <sub>53</sub>	C <sub>55</sub>	109.68(19)	C <sub>34</sub>	C <sub>35</sub>	C <sub>36</sub>	120.1(2)
C <sub>19</sub>	C <sub>18</sub>	Fe <sub>1</sub>	69.42(13)	C <sub>79</sub>	C <sub>78</sub>	C <sub>77</sub>	121.6(2)
C <sub>17</sub>	C <sub>18</sub>	Fe <sub>1</sub>	70.36(13)	C <sub>29</sub>	C <sub>30</sub>	C <sub>25</sub>	121.6(2)
C <sub>17</sub>	C <sub>18</sub>	C <sub>19</sub>	108.1(2)	C <sub>34</sub>	C <sub>33</sub>	C <sub>32</sub>	120.8(2)
C <sub>32</sub>	C <sub>31</sub>	Si <sub>13</sub>	122.37(17)	Cl <sub>10</sub>	C <sub>108</sub>	Cl <sub>2</sub>	110.67(16)
C <sub>36</sub>	C <sub>31</sub>	Si <sub>13</sub>	120.88(18)	Cl <sub>3</sub>	C <sub>108</sub>	Cl <sub>10</sub>	111.63(16)
C <sub>36</sub>	C <sub>31</sub>	C <sub>32</sub>	116.7(2)	Cl <sub>3</sub>	C <sub>108</sub>	Cl <sub>2</sub>	110.72(15)
C <sub>49</sub>	C <sub>45</sub>	P <sub>5</sub>	106.08(15)	C <sub>33</sub>	C <sub>34</sub>	C <sub>35</sub>	119.3(2)
C <sub>47</sub>	C <sub>45</sub>	P <sub>5</sub>	114.24(15)	C <sub>29</sub>	C <sub>28</sub>	C <sub>27</sub>	120.1(2)
C <sub>47</sub>	C <sub>45</sub>	C <sub>49</sub>	109.37(18)	C <sub>72</sub>	C <sub>73</sub>	C <sub>74</sub>	119.8(2)
C <sub>47</sub>	C <sub>45</sub>	C <sub>48</sub>	106.05(18)	C <sub>28</sub>	C <sub>27</sub>	C <sub>26</sub>	119.9(3)
C <sub>48</sub>	C <sub>45</sub>	P <sub>5</sub>	112.41(15)	C <sub>75</sub>	C <sub>74</sub>	C <sub>73</sub>	119.5(2)
C <sub>48</sub>	C <sub>45</sub>	C <sub>49</sub>	108.58(18)				

Table S7 Hydrogen Atom Coordinates ( $\text{\AA} \times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **20**.PdCl<sub>2</sub>, final.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H <sub>49A</sub>	8317	3206	-1705	28
H <sub>49B</sub>	8958	3247	-1250	28
H <sub>49C</sub>	8449	2522	-1259	28
H <sub>10A</sub>	8509	2667	3247	34
H <sub>10B</sub>	9068	3359	3492	34
H <sub>10C</sub>	9115	2573	3137	34
H <sub>58A</sub>	6184	3164	-2285	32
H <sub>58B</sub>	5929	3350	-1871	32
H <sub>58C</sub>	5599	2616	-2287	32
H <sub>57A</sub>	6157	-667	-2212	29
H <sub>57B</sub>	5460	-541	-2579	29
H <sub>57C</sub>	5710	-21	-2069	29
H <sub>10D</sub>	9346	3791	2621	32
H <sub>10E</sub>	9321	4511	3015	32
H <sub>10F</sub>	8906	4661	2453	32
H <sub>10G</sub>	7977	4769	2637	27
H <sub>10H</sub>	8373	4612	3202	27
H <sub>10I</sub>	7802	3963	2920	27
H <sub>85</sub>	6129	6735	-1349	20
H <sub>24</sub>	7255	758	-649	18
H <sub>18</sub>	7271	-1662	-1297	20
H <sub>40</sub>	6486	-265	875	27
H <sub>38</sub>	7808	376	393	24
H <sub>62</sub>	6138	6216	482	20
H <sub>65</sub>	7849	5728	493	21
H <sub>81</sub>	8245	6266	-967	33
H <sub>16</sub>	9071	-1534	-365	18
H <sub>72</sub>	5473	5628	-247	21
H <sub>42</sub>	7716	-2179	875	22
H <sub>70</sub>	7824	3608	771	18
H <sub>41</sub>	6875	-1750	1044	26
H <sub>55A</sub>	6329	723	-3118	29
H <sub>55B</sub>	5890	-144	-3195	29
H <sub>55C</sub>	6578	-179	-2800	29
H <sub>43A</sub>	8080	-136	-1810	16
H <sub>43B</sub>	8769	170	-1508	16
H <sub>10J</sub>	7962	1198	1784	32
H <sub>10K</sub>	8334	1258	1439	32

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H <sub>10L</sub>	7774	1936	1357	32
H <sub>39</sub>	6958	796	551	28
H <sub>32</sub>	9456	-357	189	24
H <sub>88</sub>	6144	9115	-307	22
H <sub>47A</sub>	9397	2206	-2142	28
H <sub>47B</sub>	9468	3108	-1823	28
H <sub>47C</sub>	8854	2939	-2291	28
H <sub>90A</sub>	6062	4334	1361	15
H <sub>90B</sub>	6726	4553	1756	15
H <sub>63</sub>	6905	6282	1351	23
H <sub>59A</sub>	5706	1395	-1695	31
H <sub>59B</sub>	6002	2123	-1269	31
H <sub>59C</sub>	6354	1190	-1268	31
H <sub>96A</sub>	5121	2988	1208	27
H <sub>96B</sub>	5123	2276	803	27
H <sub>96C</sub>	5507	3204	886	27
H <sub>60A</sub>	7293	2174	-1225	30
H <sub>60B</sub>	6894	3051	-1218	30
H <sub>60C</sub>	7180	2964	-1620	30
H <sub>98A</sub>	5903	4949	1957	28
H <sub>98B</sub>	5400	4729	2175	28
H <sub>98C</sub>	5333	4306	1664	28
H <sub>80</sub>	8575	4749	-862	35
H <sub>19</sub>	7305	-1375	-454	18
H <sub>76</sub>	6145	4324	-1122	25
H <sub>79</sub>	8077	3681	-566	38
H <sub>66</sub>	6763	3569	101	20
H <sub>89</sub>	6461	7655	2	18
H <sub>75</sub>	5251	3457	-1440	28
H <sub>64</sub>	7958	5970	1356	24
H <sub>17</sub>	8364	-1765	-1242	21
H <sub>67</sub>	5989	3872	473	17
H <sub>21</sub>	9017	775	-581	19
H <sub>91A</sub>	7718	4523	1909	17
H <sub>91B</sub>	8238	4238	1724	17
H <sub>86</sub>	5845	8198	-1655	24
H <sub>20</sub>	8369	992	-88	20
H <sub>87</sub>	5853	9395	-1134	24
H <sub>56A</sub>	5257	1338	-2576	30
H <sub>56B</sub>	5118	805	-3074	30
H <sub>56C</sub>	5525	1713	-2955	30



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H <sub>48A</sub>	9292	1378	-1071	27
H <sub>48B</sub>	9766	2073	-1149	27
H <sub>48C</sub>	9583	1150	-1459	27
H <sub>82</sub>	7421	6708	-785	24
H <sub>10M</sub>	8531	3123	1369	32
H <sub>10N</sub>	9121	2475	1565	32
H <sub>10O</sub>	9093	3369	1863	32
H <sub>44A</sub>	6702	109	-1559	16
H <sub>44B</sub>	7133	-166	-1832	16
H <sub>29</sub>	9296	-3557	1772	30
H <sub>97A</sub>	5193	2877	2042	29
H <sub>97B</sub>	5391	3302	2573	29
H <sub>97C</sub>	5744	2432	2488	29
H <sub>52A</sub>	7900	-449	-2529	31
H <sub>52B</sub>	7928	-301	-3049	31
H <sub>52C</sub>	7483	316	-2888	31
H <sub>36</sub>	8989	-161	1348	23
H <sub>26</sub>	8803	-3037	126	29
H <sub>35</sub>	9773	890	1700	28
H <sub>78</sub>	7244	4119	-390	30
H <sub>51A</sub>	7977	1635	-3109	37
H <sub>51B</sub>	8438	964	-3221	37
H <sub>51C</sub>	8700	1791	-2848	37
H <sub>30</sub>	8936	-2133	1438	24
H <sub>33</sub>	10235	693	545	29
H <sub>50A</sub>	9341	651	-2199	35
H <sub>50B</sub>	9081	-91	-2622	35
H <sub>50C</sub>	9010	-250	-2118	35
H <sub>108</sub>	5021	2059	-881	35
H <sub>95A</sub>	6503	2307	1044	27
H <sub>95B</sub>	6082	1412	913	27
H <sub>95C</sub>	6664	1467	1415	27
H <sub>99A</sub>	6707	3431	2919	29
H <sub>99B</sub>	6294	4296	2919	29
H <sub>99C</sub>	6778	4366	2669	29
H <sub>94A</sub>	6046	1102	1866	27
H <sub>94B</sub>	5470	1004	1363	27
H <sub>94C</sub>	5427	1644	1781	27
H <sub>34</sub>	10395	1331	1296	29
H <sub>10P</sub>	9398	2247	2531	32
H <sub>10Q</sub>	9265	1356	2196	32

H <sub>10R</sub>	8928	1489	2562	32
H <sub>28</sub>	9426	-4716	1286	37
H <sub>73</sub>	4591	4745	-553	24
H <sub>27</sub>	9179	-4455	464	39
H <sub>74</sub>	4478	3646	-1151	25

Table S8 Solvent masks information for **20**.PdCl<sub>2</sub>, final.

Number	X	Y	Z	Volume	Electron count	Content
1	0.000	0.500	1.000	445.6	113.7	?
2	0.500	0.000	0.500	445.6	113.7	?

## Experimental

Single crystals of C<sub>93</sub>H<sub>125</sub>Cl<sub>7</sub>Fe<sub>2</sub>P<sub>4</sub>Pd<sub>2</sub>Si<sub>2</sub> presented for single crystal determination. A suitable crystal was selected and mounted on a MiTeGen tip using fomblin oil and placed on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100 K during data collection. Using Olex2,<sup>1</sup> the structure was solved with the ShelXS<sup>2</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>3</sup> refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.*, **2009**, 42, 339-341.
2. Sheldrick, G.M. *Acta Cryst.*, **2008**, A64, 112-122.
3. Sheldrick, G.M., *Acta Cryst.*, **2015**, C71, 3-8.

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 Crystal structure determination of  $C_{93}H_{125}Cl_7Fe_2P_4Pd_2Si_2$  [final]

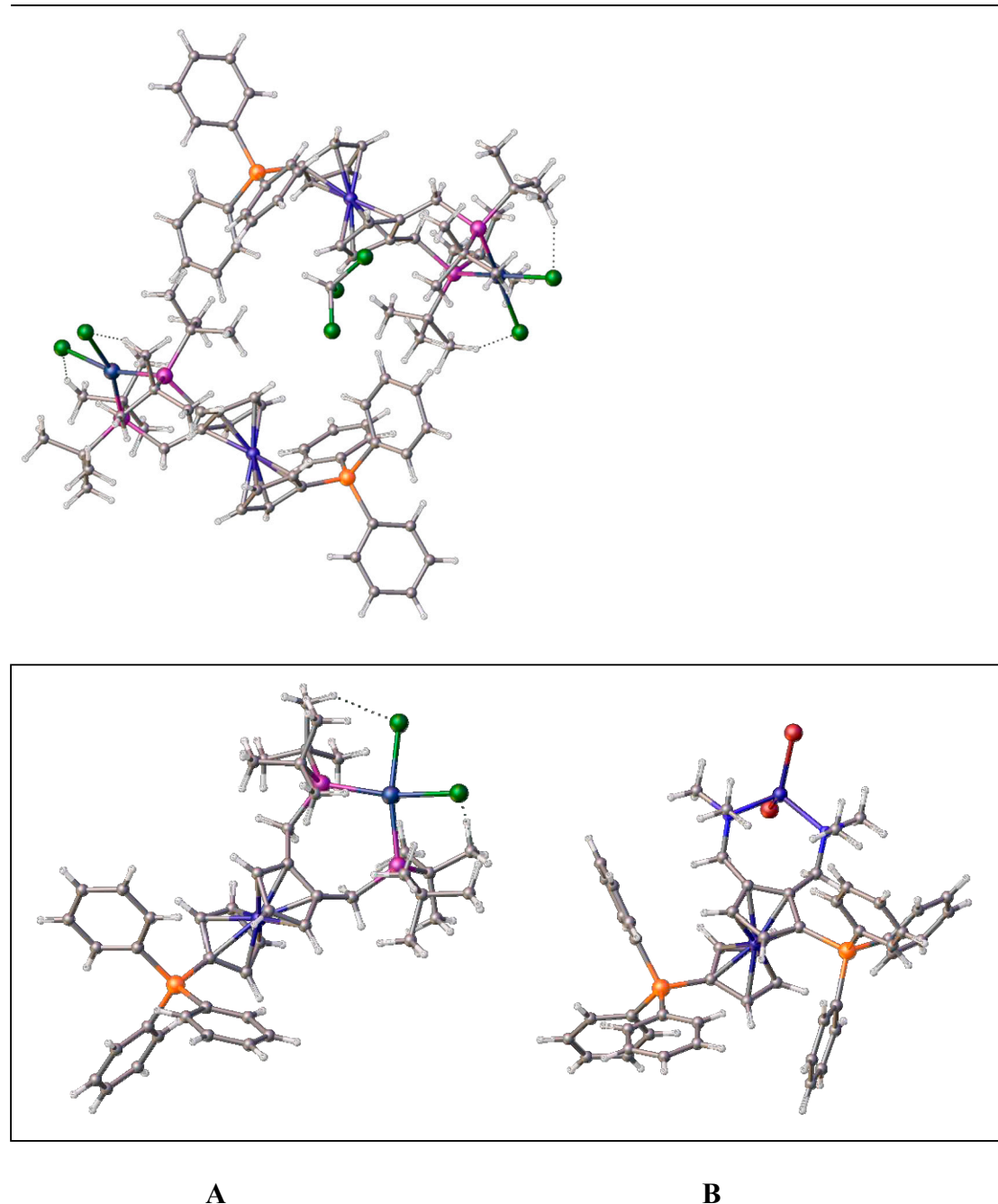
**Crystal Data** for  $C_{93}H_{125}Cl_7Fe_2P_4Pd_2Si_2$  ( $M=1995.63$  g/mol): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 23.733(2)$  Å,  $b = 14.6371(16)$  Å,  $c = 29.969(3)$  Å,  $\beta = 112.935(2)^\circ$ ,  $V = 9587.6(17)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 100.02$  K,  $\mu(MoK\alpha) = 0.995$  mm<sup>-1</sup>,  $D_{calc} = 1.383$  g/cm<sup>3</sup>, 102423 reflections measured ( $4.652^\circ \leq 2\theta \leq 52.868^\circ$ ), 19529 unique ( $R_{int} = 0.0402$ ,  $R_{sigma} = 0.0255$ ) which were used in all calculations. The final  $R_1$  was 0.0304 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0721 (all data).

## Refinement model description

Number of restraints - 0, number of constraints - unknown.

## Details:

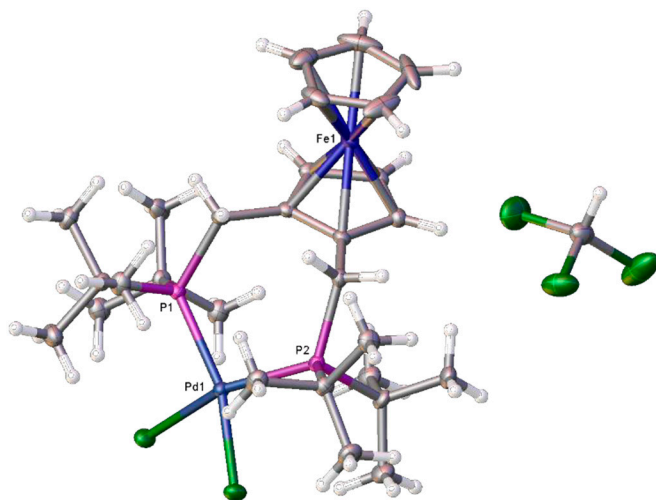
1. Fixed Uiso
  - At 1.2 times of:
    - All C(H) groups, All C(H,H) groups
  - At 1.5 times of:
    - All C(H,H,H) groups
- 2.a Ternary CH refined with riding coordinates:
  - C108 (H108)
- 2.b Secondary CH2 refined with riding coordinates:
  - C43 (H43A, H43B), C90 (H90A, H90B), C91 (H91A, H91B), C44 (H44A, H44B)
- 2.c Aromatic/amide H refined with riding coordinates:
  - C85 (H85), C24 (H24), C18 (H18), C40 (H40), C38 (H38), C62 (H62), C65 (H65), C81 (H81), C16 (H16), C72 (H72), C42 (H42), C70 (H70), C41 (H41), C39 (H39), C32 (H32), C88 (H88), C63 (H63), C80 (H80), C19 (H19), C76 (H76), C79 (H79), C66 (H66), C89 (H89), C75 (H75), C64 (H64), C17 (H17), C67 (H67), C21 (H21), C86 (H86), C20 (H20), C87 (H87), C82 (H82), C29 (H29), C36 (H36), C26 (H26), C35 (H35), C78 (H78), C30 (H30), C33 (H33), C34 (H34), C28 (H28), C73 (H73), C27 (H27), C74 (H74)
- 2.d Idealised Me refined as rotating group:
  - C49 (H49A, H49B, H49C), C105 (H10A, H10B, H10C), C58 (H58A, H58B, H58C), C57 (H57A, H57B, H57C), C107 (H10D, H10E, H10F), C106 (H10G, H10H, H10I), C55 (H55A, H55B, H55C), C103 (H10J, H10K, H10L), C47 (H47A, H47B, H47C), C59 (H59A, H59B, H59C), C96 (H96A, H96B, H96C), C60 (H60A, H60B, H60C), C98 (H98A, H98B, H98C), C56 (H56A, H56B, H56C), C48 (H48A, H48B, H48C), C102 (H10M, H10N, H10O), C97 (H97A, H97B, H97C), C52 (H52A, H52B, H52C), C51 (H51A, H51B, H51C), C50 (H50A, H50B, H50C), C95 (H95A, H95B, H95C), C99 (H99A, H99B, H99C), C94 (H94A, H94B, H94C), C104 (H10P, H10Q, H10R)



**Figure S1:** showing side by side views of diposphine complex **20**.PdCl<sub>2</sub> and diamine **24**.NiBr<sub>2</sub>. A comparison between tetrahedral (Ni) and square planar coordination (Pd).

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Crystal Data and Experimental **2a**PdCl<sub>2</sub> (chloroform solvate, 2004 version; comparison purposes only).



**Experimental.** Single orange shard crystals of **04src0550** were used as supplied. A suitable crystal with dimensions  $0.320 \times 0.260 \times 0.100$  mm<sup>3</sup> was selected and mounted on a Bruker-Nonius 95mm CCD camera on  $\kappa$ -goniostat diffractometer. The crystal was kept at a steady  $T = 120(2)$  K during data collection. The structure was solved with the ShelXS-97 (Sheldrick, 1997a) solution program and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on  $F^2$ .

**Crystal Data.** C<sub>29</sub>H<sub>49</sub>Cl<sub>5</sub>FeP<sub>2</sub>Pd,  $M_r = 799.12$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 11.5254(9)$  Å,  $b = 14.3958(11)$  Å,  $c = 20.4783(12)$  Å,  $\beta = 95.396(6)^\circ$ ,  $\alpha = \gamma = 90^\circ$ ,  $V = 3382.6(4)$  Å<sup>3</sup>,  $T = 120(2)$  K,  $Z = 4$ ,  $Z' = 1$ ,  $\mu(\text{MoK}\alpha) = 1.469$  mm<sup>-1</sup>, 33024 reflections measured, 7727 unique ( $R_{\text{int}} = 0.0568$ ) which were used in all calculations. The final  $wR_2$  was 0.0876 (all data) and  $R_1$  was 0.0389 ( $I \geq 2 \sigma(I)$ ).

Compound	2aPdCl2
Formula	C <sub>29</sub> H <sub>49</sub> Cl <sub>5</sub> FeP <sub>2</sub> Pd
$D_{calc}/\text{g cm}^{-3}$	1.569
$\mu/\text{mm}^{-1}$	1.469
Formula Weight	799.12
Colour	orange
Shape	shard
Size/mm <sup>3</sup>	0.320×0.260×0.100
$T/\text{K}$	120(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
$a/\text{\AA}$	11.5254(9)
$b/\text{\AA}$	14.3958(11)
$c/\text{\AA}$	20.4783(12)
$\alpha/^\circ$	90
$\beta/^\circ$	95.396(6)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	3382.6(4)
$Z$	4
$Z'$	1
Wavelength/ $\text{\AA}$	0.71073
Radiation type	MoK $\alpha$
$\theta_{min}/^\circ$	3.133
$\theta_{max}/^\circ$	27.483
Measured Refl's.	33024
Indep't Refl's	7727
Refl's $I \geq 2 \sigma(I)$	5710
$R_{int}$	0.0568
Parameters	355
Restraints	0
Largest Peak	0.963
Deepest Hole	-1.163
GooF	1.015
$wR_2$ (all data)	0.0876
$wR_2$	0.0783
$R_1$ (all data)	0.0675
$R_1$	0.0389

### Structure Quality Indicators

<b>Reflections:</b>	d min (Mo) 2 $\theta$ =55.0°	0.77	$I/\sigma(I)$	15.7	$R_{int}$	5.68%	Full 50.5°	99.7
<b>Refinement:</b>	Shift	0.001	Max Peak	1.0	Min Peak	-1.2	GooF	1.015

A orange shard-shaped crystal with dimensions  $0.320 \times 0.260 \times 0.100 \text{ mm}^3$  was mounted. Data were collected using a Bruker-Nonius 95mm CCD camera on  $\kappa$ -goniostat diffractometer equipped with an Oxford Cryosystems low-temperature device operating at  $T = 120(2) \text{ K}$ .

Data were measured using  $\phi$  &  $\omega$  scans using MoK $\alpha$  radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program COLLECT (Hooft, R.W.W., 1998). The maximum resolution that was achieved was  $\theta = 27.483^\circ$  (0.77 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the

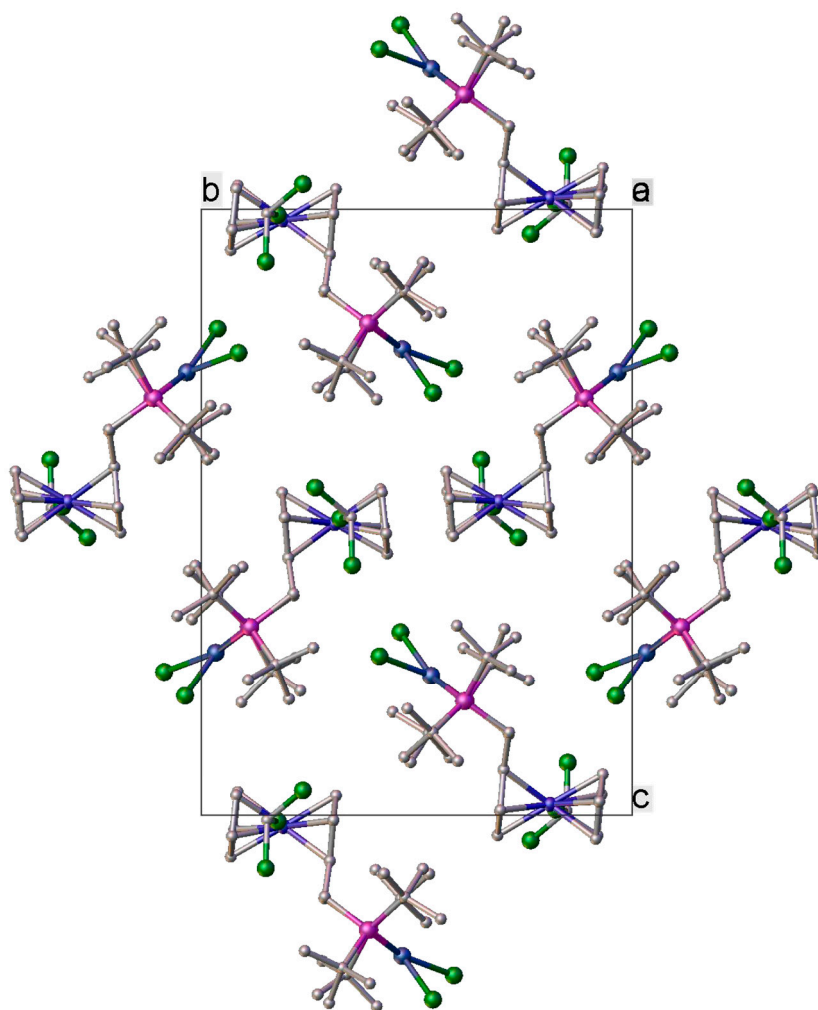
strategy calculation from the program COLLECT (Hooft, R.W.W., 1998). The unit cell was refined using DENZO (Otwinowski & Minor, 1997) on 7711 reflections, 23% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using DENZO (Otwinowski & Minor, 1997). The final completeness is 99.70 % out to  $27.483^\circ$  in  $\theta$ . A multi-scan absorption correction was performed using SADABS V2.10 (Sheldrick, G.M., 2003). The absorption coefficient  $\mu$  of this material is  $1.469 \text{ mm}^{-1}$  at this wavelength ( $\lambda = 0.71073 \text{ \AA}$ ) and the minimum and maximum transmissions are 0.651 and 0.867.

The structure was solved and the space group  $P2_1/n$  (# 14) determined by the ShelXS-97 (Sheldrick, 1997a) structure solution program and refined by full matrix least squares minimisation on  $F^2$  using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

*\_exptl\_absorpt\_process\_details*: SADABS V2.10 (Sheldrick, G.M., 2003)

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.



**Figure S2:** Packing diagram of 04src0550, PdCl<sub>2</sub>.

## Reflection Statistics

Total reflections (after filtering)	33695	Unique reflections	7727
Completeness	0.998	Mean $I/\sigma$	14.46
$hkl_{\max}$ collected	(12, 18, 26)	$hkl_{\min}$ collected	(-14, -17, -26)
$hkl_{\max}$ used	(14, 18, 26)	$hkl_{\min}$ used	(-14, 0, 0)
Lim $d_{\max}$ collected	99.0	Lim $d_{\min}$ collected	0.77
$d_{\max}$ used	6.8	$d_{\min}$ used	0.77
Friedel pairs	8965	Friedel pairs merged	1
Inconsistent equivalents	0	$R_{\text{int}}$	0.0568
$R_{\text{sigma}}$	0.0635	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT $hkl$ )	6
Multiplicity	(14250, 7078, 1781, 4)	Maximum multiplicity	10
Removed systematic absences	665	Filtered off (Shel/OMIT)	70

**Table S8:** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **04src0550**.  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$ .

Atom	x	y	z	$U_{eq}$
C1	1989(3)	7018.3(19)	751.5(15)	15.9(7)
C2	3220(3)	7016.1(19)	744.9(15)	14.2(7)
C3	3486(3)	6935(2)	77.1(15)	17.7(7)
C4	2417(3)	6877(2)	-327.0(16)	19.3(7)
C5	1487(3)	6941(2)	86.7(16)	18.9(7)
C6	2417(4)	9315(2)	676.7(18)	30.1(9)
C7	3418(3)	9290(2)	345(2)	41.6(12)
C8	3041(5)	9189(2)	-331(2)	55.1(15)
C9	1820(5)	9157(2)	-385(2)	47.9(13)
C10	1461(3)	9237(2)	229(2)	36.5(10)
C11	1389(3)	7142.6(19)	1365.4(15)	14.9(7)
C12	4068(3)	7138(2)	1336.3(15)	15.1(7)
C13	119(3)	5364(2)	1367.2(16)	17.2(7)
C14	822(3)	4712(2)	961.2(17)	22.5(7)
C15	-685(3)	5955(2)	896.0(16)	22.4(8)
C16	-688(3)	4784(2)	1758.9(17)	22.6(8)
C17	581(3)	6636(2)	2611.3(15)	16.3(7)
C18	300(3)	5931(2)	3135.4(17)	25.6(8)
C19	1498(3)	7298(2)	2944.0(16)	21.1(7)
C20	-522(3)	7186(2)	2395.3(17)	20.6(7)
C21	5137(3)	5276(2)	1343.0(16)	18.2(7)
C22	5746(3)	4443(2)	1703.2(17)	24.7(8)
C23	6040(3)	5761(2)	953.7(16)	22.7(8)
C24	4151(3)	4858(2)	875.6(17)	24.4(8)
C25	5541(3)	6727(2)	2507.0(15)	17.5(7)
C26	4861(3)	7034(2)	3083.3(16)	21.6(7)
C27	6549(3)	6090(2)	2764.2(17)	24.5(8)
C28	6095(3)	7599(2)	2228.4(17)	22.4(7)
P1	1235.9(7)	6097.7(5)	1882.5(4)	13.58(18)
P2	4431.2(7)	6134.9(5)	1885.2(4)	13.83(18)



Cl1	1715.5(7)	4136.7(5)	2629.9(4)	21.53(18)
Cl2	4374.3(7)	4622.3(5)	3027.9(4)	22.09(18)
Fe1	2503.7(4)	8091.3(3)	182.9(2)	16.20(11)
Pd1	2927.5(2)	5334.0(2)	2309.6(2)	13.55(7)
C31	7643(3)	8475(2)	77.9(18)	28.6(8)
Cl31	6159.3(9)	8226.1(8)	97.4(7)	56.1(3)
Cl32	8360.1(10)	8503.9(7)	869.3(5)	46.5(3)
Cl33	8272.6(11)	7643.4(10)	-410.8(6)	68.1(4)

**Table S9:** Anisotropic Displacement Parameters ( $\times 10^4$ ) for **04src0550**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C1	18.8(18)	10.7(14)	18.1(17)	2.5(13)	0.7(14)	-0.5(12)
C2	17.0(17)	12.7(14)	12.9(16)	2.5(12)	0.7(13)	0.0(12)
C3	20.0(18)	16.1(15)	17.3(17)	-0.3(13)	4.3(14)	-0.4(12)
C4	26(2)	16.5(15)	14.9(17)	-1.8(13)	1.1(15)	-4.4(13)
C5	18.1(18)	15.2(15)	22.6(18)	2.1(14)	-1.7(15)	-3.9(12)
C6	56(3)	15.0(16)	19.9(19)	3.4(15)	5.4(19)	3.7(16)
C7	20(2)	11.2(16)	90(4)	-1(2)	-10(2)	-3.0(14)
C8	104(4)	14.3(18)	57(3)	5(2)	64(3)	1(2)
C9	87(4)	19.8(19)	31(2)	5.6(18)	-26(3)	1(2)
C10	26(2)	18.6(18)	64(3)	8.6(19)	5(2)	3.3(15)
C11	14.4(17)	11.8(14)	18.4(17)	3.6(13)	0.8(14)	-0.2(12)
C12	14.8(17)	14.8(14)	16.3(17)	-0.8(13)	4.7(14)	-1.4(12)
C13	13.9(17)	18.5(15)	18.9(17)	-1.7(14)	0.5(14)	-5.2(12)
C14	20.6(19)	22.8(17)	24.1(19)	-6.2(15)	1.4(15)	-3.3(14)
C15	15.1(18)	27.0(17)	24.6(19)	4.7(15)	-0.6(15)	-6.1(13)
C16	20.1(19)	22.2(17)	25.2(19)	-1.8(15)	0.8(15)	-6.1(13)
C17	16.9(17)	14.6(15)	17.4(17)	-1.3(13)	2.2(14)	0.5(12)
C18	32(2)	23.9(17)	22.2(19)	1.6(15)	10.0(16)	1.7(15)
C19	21.4(19)	24.8(17)	16.9(18)	-6.0(14)	0.3(15)	-2.0(14)
C20	15.7(18)	20.6(16)	25.9(19)	-6.0(15)	3.0(15)	0.5(13)
C21	16.8(17)	18.9(16)	19.4(17)	-3.0(14)	4.8(14)	5.7(13)
C22	28(2)	17.7(16)	29(2)	-1.8(15)	4.8(16)	6.0(14)
C23	21.5(19)	25.3(17)	22.9(19)	-1.0(15)	9.6(15)	2.7(14)
C24	28(2)	20.2(17)	25(2)	-5.1(15)	3.9(16)	2.1(14)
C25	16.0(17)	17.9(15)	18.2(17)	-1.1(14)	0.3(14)	-1.2(12)
C26	20.1(19)	24.9(17)	19.2(18)	-4.3(14)	-1.8(15)	0.6(14)
C27	17.3(19)	27.2(18)	28(2)	-0.8(16)	-3.4(15)	1.5(14)
C28	20.1(18)	21.4(16)	25.6(19)	-2.5(15)	0.8(15)	-5.8(14)
P1	13.5(4)	12.5(4)	14.9(4)	0.6(3)	2.3(3)	-0.3(3)
P2	13.0(4)	13.8(4)	14.8(4)	-0.6(3)	2.0(3)	0.8(3)
Cl1	20.4(4)	15.9(4)	28.5(5)	5.7(3)	3.8(4)	-1.7(3)
Cl2	20.0(4)	21.6(4)	24.0(4)	7.2(3)	-1.4(4)	2.1(3)
Fe1	20.0(3)	14.6(2)	14.1(2)	1.76(18)	2.2(2)	-0.85(18)
Pd1	13.49(14)	12.12(11)	15.22(14)	1.43(10)	2.34(10)	0.40(9)
C31	23(2)	28.4(19)	34(2)	8.0(17)	0.8(17)	-2.2(15)
Cl31	31.2(6)	53.3(7)	85.1(9)	15.1(6)	11.8(6)	-9.6(5)
Cl32	59.9(7)	39.8(5)	37.2(6)	2.7(5)	-9.6(5)	14.5(5)
Cl33	61.1(8)	102.5(10)	38.7(7)	-9.5(7)	-5.7(6)	46.5(7)

**Table S10:** Bond Lengths in Å for **04src0550**.

Atom	Atom	Length/Å
C1	C2	1.421(4)
C1	C5	1.432(4)
C1	C11	1.501(4)
C1	Fe1	2.055(3)
C2	C3	1.434(4)
C2	C12	1.493(4)
C2	Fe1	2.055(3)
C3	C4	1.420(5)
C3	Fe1	2.036(3)
C4	C5	1.430(4)
C4	Fe1	2.034(3)
C5	Fe1	2.028(3)
C6	C7	1.394(5)
C6	C10	1.370(5)
C6	Fe1	2.038(3)
C7	C8	1.417(6)
C7	Fe1	2.033(3)
C8	C9	1.402(7)
C8	Fe1	2.028(4)
C9	C10	1.363(6)
C9	Fe1	2.038(4)
C10	Fe1	2.048(4)
C11	P1	1.857(3)
C12	P2	1.853(3)
C13	C14	1.535(4)
C13	C15	1.532(4)
C13	C16	1.532(4)
C13	P1	1.905(3)
C17	C18	1.534(4)
C17	C19	1.534(4)
C17	C20	1.527(4)
C17	P1	1.900(3)
C21	C22	1.542(4)
C21	C23	1.536(4)
C21	C24	1.538(5)
C21	P2	1.895(3)
C25	C26	1.542(4)
C25	C27	1.535(4)
C25	C28	1.542(4)
C25	P2	1.917(3)
P1	Pd1	2.3354(8)
P2	Pd1	2.3177(8)
Cl1	Pd1	2.3505(8)
Cl2	Pd1	2.3521(8)
C31	Cl31	1.752(4)
C31	Cl32	1.749(4)
C31	Cl33	1.760(4)

**Table S11:** Bond Angles in ° for **04src0550**.

Atom	Atom	Atom	Angle/°
C2	C1	C5	107.8(3)
C2	C1	C11	123.2(3)
C2	C1	Fe1	69.78(17)
C5	C1	C11	129.0(3)
C5	C1	Fe1	68.43(17)
C11	C1	Fe1	124.4(2)
C1	C2	C3	108.2(3)
C1	C2	C12	124.8(3)
C1	C2	Fe1	69.77(17)
C3	C2	C12	126.9(3)
C3	C2	Fe1	68.75(17)
C12	C2	Fe1	124.3(2)
C2	C3	Fe1	70.22(17)
C4	C3	C2	108.0(3)
C4	C3	Fe1	69.50(17)
C3	C4	C5	108.0(3)
C3	C4	Fe1	69.64(17)
C5	C4	Fe1	69.15(17)
C1	C5	Fe1	70.49(17)
C4	C5	C1	108.1(3)
C4	C5	Fe1	69.62(17)
C7	C6	Fe1	69.8(2)
C10	C6	C7	108.7(4)
C10	C6	Fe1	70.8(2)
C6	C7	C8	106.7(4)
C6	C7	Fe1	70.2(2)
C8	C7	Fe1	69.4(2)
C7	C8	Fe1	69.8(2)
C9	C8	C7	107.1(4)
C9	C8	Fe1	70.2(2)
C8	C9	Fe1	69.4(2)
C10	C9	C8	108.3(4)
C10	C9	Fe1	70.9(2)
C6	C10	Fe1	70.0(2)
C9	C10	C6	109.3(4)
C9	C10	Fe1	70.1(2)
C1	C11	P1	117.2(2)
C2	C12	P2	119.6(2)
C14	C13	P1	106.0(2)
C15	C13	C14	108.5(3)
C15	C13	C16	105.7(3)
C15	C13	P1	112.2(2)
C16	C13	C14	109.1(2)
C16	C13	P1	115.1(2)
C18	C17	C19	106.4(3)
C18	C17	P1	113.9(2)
C19	C17	P1	107.1(2)
C20	C17	C18	108.7(3)
C20	C17	C19	109.1(2)

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C20	C17	P1	111.4(2)
C22	C21	P2	115.3(2)
C23	C21	C22	107.5(3)
C23	C21	C24	110.6(3)
C23	C21	P2	110.9(2)
C24	C21	C22	105.6(3)
C24	C21	P2	106.7(2)
C26	C25	C28	107.9(2)
C26	C25	P2	106.3(2)
C27	C25	C26	109.4(3)
C27	C25	C28	106.7(3)
C27	C25	P2	113.5(2)
C28	C25	P2	112.9(2)
C11	P1	C13	103.22(14)
C11	P1	C17	100.56(13)
C11	P1	Pd1	118.29(10)
C13	P1	Pd1	116.30(10)
C17	P1	C13	111.34(14)
C17	P1	Pd1	106.10(10)
C12	P2	C21	103.74(14)
C12	P2	C25	98.91(13)
C12	P2	Pd1	118.75(10)
C21	P2	C25	112.50(14)
C21	P2	Pd1	105.82(10)
C25	P2	Pd1	116.59(10)
C2	Fe1	C1	40.45(12)
C3	Fe1	C1	68.85(12)
C3	Fe1	C2	41.04(12)
C3	Fe1	C6	144.38(15)
C3	Fe1	C9	138.05(17)
C3	Fe1	C10	176.19(16)
C4	Fe1	C1	69.03(12)
C4	Fe1	C2	68.77(12)
C4	Fe1	C3	40.86(13)
C4	Fe1	C6	174.38(15)
C4	Fe1	C9	110.88(15)
C4	Fe1	C10	135.65(15)
C5	Fe1	C1	41.07(12)
C5	Fe1	C2	68.73(13)
C5	Fe1	C3	69.14(13)
C5	Fe1	C4	41.24(12)
C5	Fe1	C6	134.38(15)
C5	Fe1	C7	174.39(16)
C5	Fe1	C8	142.03(19)
C5	Fe1	C9	111.75(16)
C5	Fe1	C10	109.05(14)
C6	Fe1	C1	109.77(13)
C6	Fe1	C2	114.13(13)
C6	Fe1	C10	39.19(15)
C7	Fe1	C1	135.94(17)
C7	Fe1	C2	111.91(15)
C7	Fe1	C3	115.23(14)
C7	Fe1	C4	144.38(16)
C7	Fe1	C6	40.04(16)
C7	Fe1	C9	67.72(17)
C7	Fe1	C10	66.81(15)
C8	Fe1	C1	176.75(17)
C8	Fe1	C2	138.71(19)
C8	Fe1	C3	112.46(15)

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C8	Fe1	C4	113.98(15)
C8	Fe1	C6	67.37(15)
C8	Fe1	C7	40.86(18)
C8	Fe1	C9	40.35(19)
C8	Fe1	C10	66.72(17)
C9	Fe1	C1	140.54(18)
C9	Fe1	C2	178.90(18)
C9	Fe1	C6	66.31(15)
C9	Fe1	C10	38.99(17)
C10	Fe1	C1	112.19(14)
C10	Fe1	C2	141.97(15)
P1	Pd1	Cl1	87.28(3)
P1	Pd1	Cl2	163.14(3)
P2	Pd1	P1	104.64(3)
P2	Pd1	Cl1	162.64(3)
P2	Pd1	Cl2	86.57(3)
Cl1	Pd1	Cl2	84.90(3)
Cl31	C31	Cl33	109.2(2)
Cl32	C31	Cl31	111.2(2)
Cl32	C31	Cl33	111.03(19)

**Table S12:** Torsion Angles in ° for **04src0550**.

Atom	Atom	Atom	Atom	Angle/°
C1	C2	C3	C4	-0.7(3)
C1	C2	C3	Fe1	58.8(2)
C1	C2	C12	P2	80.6(3)
C1	C11	P1	C13	-70.1(3)
C1	C11	P1	C17	174.8(2)
C1	C11	P1	Pd1	59.9(3)
C2	C1	C5	C4	0.8(3)
C2	C1	C5	Fe1	-58.9(2)
C2	C1	C11	P1	-82.4(3)
C2	C3	C4	C5	1.2(3)
C2	C3	C4	Fe1	59.9(2)
C2	C12	P2	C21	62.9(3)
C2	C12	P2	C25	178.8(2)
C2	C12	P2	Pd1	-54.1(3)
C3	C2	C12	P2	-103.5(3)
C3	C4	C5	C1	-1.3(3)
C3	C4	C5	Fe1	59.0(2)
C5	C1	C2	C3	-0.1(3)
C5	C1	C2	C12	176.4(3)
C5	C1	C2	Fe1	58.0(2)
C5	C1	C11	P1	101.7(3)
C6	C7	C8	C9	0.0(4)
C6	C7	C8	Fe1	-60.6(2)
C7	C6	C10	C9	0.4(4)
C7	C6	C10	Fe1	59.7(2)
C7	C8	C9	C10	0.2(4)
C7	C8	C9	Fe1	-60.3(2)
C8	C9	C10	C6	-0.4(4)

C8	C9	C10	Fe1	-59.6(3)
C10	C6	C7	C8	-0.2(4)
C10	C6	C7	Fe1	-60.3(2)
C11	C1	C2	C3	-176.8(2)
C11	C1	C2	C12	-0.2(4)
C11	C1	C2	Fe1	-118.6(3)
C11	C1	C5	C4	177.2(3)
C11	C1	C5	Fe1	117.5(3)
C12	C2	C3	C4	-177.1(3)
C12	C2	C3	Fe1	-117.7(3)
C22	C21	P2	C12	168.7(2)
C22	C21	P2	C25	62.8(3)
C22	C21	P2	Pd1	-65.5(2)
C23	C21	P2	C12	46.2(3)
C23	C21	P2	C25	-59.7(3)
C23	C21	P2	Pd1	172.0(2)
C24	C21	P2	C12	-74.3(2)
C24	C21	P2	C25	179.8(2)
C24	C21	P2	Pd1	51.4(2)
Fe1	C1	C2	C3	-58.1(2)
Fe1	C1	C2	C12	118.4(3)
Fe1	C1	C5	C4	59.7(2)
Fe1	C1	C11	P1	-
				169.43(16)
Fe1	C2	C3	C4	-59.5(2)
Fe1	C2	C12	P2	168.54(16)
Fe1	C3	C4	C5	-58.7(2)
Fe1	C4	C5	C1	-60.3(2)
Fe1	C6	C7	C8	60.1(2)
Fe1	C6	C10	C9	-59.3(3)
Fe1	C7	C8	C9	60.6(3)
Fe1	C8	C9	C10	60.6(3)
Fe1	C9	C10	C6	59.3(2)

**Table S13:** Hydrogen Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **04src0550**.  $U_{eq}$  is defined as  $1/3$  of the trace of the orthogonalised  $U_{ij}$ .

Atom	x	y	z	$U_{eq}$
H3	4243.95	6923.28	-69.41	21
H4	2334.64	6807.72	-790.4	23
H5	678.38	6932.88	-54.74	23
H6	2399.97	9375.61	1137.6	36
H7	4200.88	9332.03	534.08	50
H8	3524.55	9151.59	-680.75	66
H9	1326.92	9089.88	-780.51	57
H10	673.55	9238.7	329.29	44
H11A	599.76	7392.81	1239.31	18
H11B	1821.52	7619.36	1638.66	18
H12A	3765.95	7637.65	1605.76	18
H12B	4806.45	7366.94	1183.75	18
H14A	287.15	4346.16	662.54	34
H14B	1293.42	4292.82	1255.61	34
H14C	1335.01	5079.6	706.22	34
H15A	-219.78	6286.25	593.91	34
H15B	-1101.03	6404.74	1147.23	34
H15C	-1249.07	5551.41	645.45	34

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H16A	-1168.87	4378.08	1459.69	34
H16B	-1193.39	5198.81	1985.3	34
H16C	-219.67	4405.53	2082.17	34
H18A	1009.66	5591.01	3290.71	38
H18B	-289.57	5493.18	2946.23	38
H18C	1.5	6258.81	3504.25	38
H19A	1211.85	7557.9	3340.98	32
H19B	1646.29	7803.01	2641.64	32
H19C	2223.24	6956.22	3061.86	32
H20A	-1097.03	6773.53	2162.51	31
H20B	-331.09	7691.61	2103.05	31
H20C	-844.79	7446.39	2781.66	31
H22A	6011.21	4006.93	1381.27	37
H22B	5196.93	4129.43	1966.76	37
H22C	6417.64	4663.99	1990.57	37
H23A	6650.77	6035.77	1259	34
H23B	5657.21	6249.82	679.03	34
H23C	6388.28	5305.08	674.82	34
H24A	4483.8	4443.05	562.78	37
H24B	3718.7	5358.14	636.78	37
H24C	3621.22	4505.03	1129.68	37
H26A	4559.33	6485.56	3294.48	32
H26B	4210.12	7434.39	2918.89	32
H26C	5381.76	7378.61	3403.03	32
H27A	7049.38	6415.49	3103.69	37
H27B	7006.63	5920.03	2402.27	37
H27C	6235.49	5526.33	2950.88	37
H28A	5494.79	8074.98	2133.29	34
H28B	6439.63	7436.78	1823.92	34
H28C	6702.9	7839.95	2551.03	34
H31	7717.93	9100.13	-127.39	34

## Citations

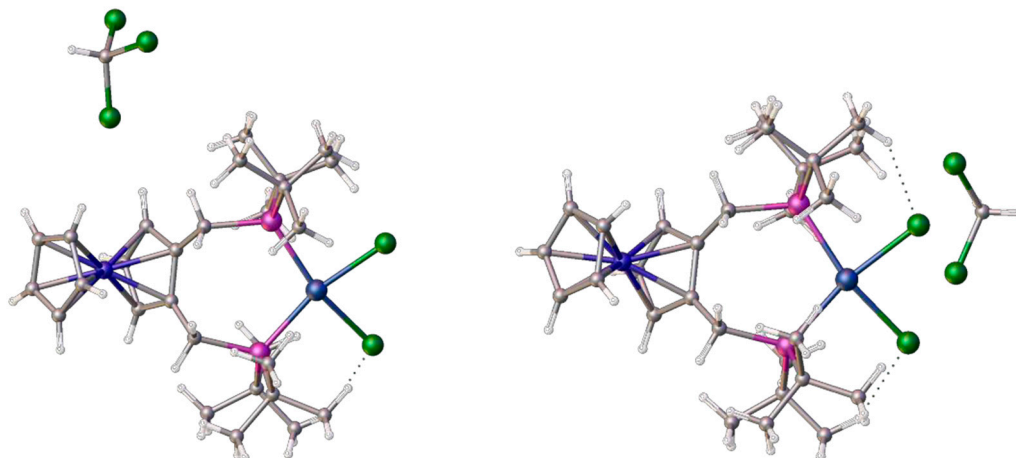
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**Figure S3:** Comparison of chloroform solvated (2004) structure with dichloromethane solvated, **2aPdCl<sub>2</sub>**.



**Figure S4:** Structure of compound **26** together with Olex 2 drawing of the 2 molecules present in the structural determination at an angle of 53° to each other.

This meant that despite every effort to separate them out most attempts at collecting single crystal X-ray diffraction data resulted in diffraction from multiple components. The crystal used (0.18 x 0.03 x 0.02 mm<sup>3</sup>) appeared to be single and produces a suitable structure. However, during refining there was always an area of large residual electron density just 1.4 Å away from the Ru atom. Attempts at modelling the crystal as either a merohedral or non-merohedral twin gave no improvement and a second crystal domain was not apparent from the diffraction images. What worked was refining a second molecule (at 15% occupancy) at a 53° angle to the first, with the second Ru atom sitting 1.4 Å away from the first.

**Crystal Data for RuN2\_2005src0328. Compound 26.** C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>Ru, *M<sub>r</sub>* = 345.44, orthorhombic, *Pbca* (No. 61), *a* = 7.747(9) Å, *b* = 15.519(18) Å, *c* = 25.745(8) Å, *a* = *b* = *g* = 90°, *V* = 3095(5) Å<sup>3</sup>, *T* = 120(2) K, *Z* = 8, *Z'* = 1, *m*(MoK<sub>α</sub>) = 1.002 mm<sup>-1</sup>, 13347 reflections measured, 3400 unique (*R*<sub>int</sub> = 0.1639) which were used in all calculations. The final *wR*<sub>2</sub> was 0.2317 (all data) and *R*<sub>1</sub> was 0.1086 (*I* ≥ 2 *s*(*I*)). NCS Code RuN2\_2005src0328 and CCDC code of 2080218.

code **RuN2\_2005src0328** and CCDC code of 2080218.



RuN2\_2005src0328. RuN2\_checkcif.pdf cif



## Synthesis Experimental Section: Materials and Methods

All solvents used were freshly dried and distilled using standard laboratory methods. NMR spectra were run on either Bruker AC 250, at 250 MHz, or Bruker Avance 500, at 500 MHz. Reagents were obtained from commercial sources and purified and standardised before use (For further details and preparative information for the additional compounds, see supplementary information). Ligand synthesis experiments were performed under an argon atmosphere with work-ups carried out under standard laboratory conditions unless otherwise indicated. All reaction solvents were predried using conventional methods, whereas work-up (i.e. extractions and so on.) solvents were laboratory grade reagents. All ferrocene reagents were prepared from ferrocene. Other compounds were obtained from commercial sources and were used without any further purification.

### Preparation of 1,2-bis-dimethylaminomethylferrocene, (*damf*), 5.

A solution of *n*-butyl lithium (33.67 cm<sup>3</sup>, 1.6 M in hexanes) was added to dimethylaminomethyl ferrocene (10.82 g, 48.97 mmol) in diethyl ether (80 cm<sup>3</sup>), and the reaction stirred at RT under N<sub>2</sub> for 4 hours. The red reaction solution was cooled in a dry ice / IMS bath, and Eschenmoser's salt (9.06 g, 48.97 mmol) added. The solution was returned to RT and stirring continued for another 18 h. The reaction mixture was quenched with dilute NaOH and stirred for a further 15 minutes. The ethereal layer containing the product was separated, and the aqueous layer was further extracted several times with diethyl ether. The combined ether fractions were dried over MgSO<sub>4</sub> and then filtered through celite. The ether solvent was removed in vacuo to yield an orange solid. The product was recrystallised from petrol at -17°C, and the resulting crystals were washed with cold petrol and dried in vacuo. Further purification was achieved by sublimation onto a cold finger at 60 - 70°C under vacuum. Orange crystals suitable for X-ray crystallography were obtained by sublimation.

F.W. 300.07 g.mol<sup>-1</sup>; yield: 13.2 g (74%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 2.17 (s, 12 H; 4 × CH<sub>3</sub>), δ 3.20 (d, 2H, 12.817 Hz; NCH<sub>2</sub> AB quartet), δ 3.32 (d, 2 H, 12.817 Hz; NCH<sub>2</sub> AB quartet), δ 4.00 (s, 5 H; cp-5), δ 4.06 (t, 1 H, 2.441 Hz; cp-β H), δ 4.16 (d, 2 H, 2.441 Hz; cpα-H). <sup>13</sup>C NMR (62 MHz, CDCl<sub>3</sub>): δ, 45.32 (s; CH<sub>3</sub>), δ 57.36 (s; NCH<sub>2</sub>), δ 66.70 (cpβ-C), δ 69.22 (cp5), δ 70.14 (cpα-C), δ 84.02 (s; cpγ C). Melting point: 73–76 °C. Elemental analysis, calculated for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>Fe; C 64.0%, H 8.1%, N 9.4%. Found, C 63.7%, H 7.9%, N 9.5%.

### Preparation of bis-1,2-(di-*tert*-butylphosphanomethyl)ferrocene, *butphos*, 2a, from bis-1,2-dimethylaminomethylferrocene, 5. Method 1.

To bis-1,2-dimethylaminomethyl ferrocene (0.50 g, 1.66 mmol) in anhydrous acetic acid (100 cm<sup>3</sup>) and under nitrogen was added di-*tert*-butylphosphane (0.616 cm<sup>3</sup>, 3.33 mmol). The reaction was stirred at 80°C for 72 hours, and the solvent removed in vacuo at approximately 70°C. The product was dissolved into refluxing ethanol and then cooled to -17°C. The resulting yellow crystals were washed with small quantities of cold ethanol.

F.W. 502.48 g.mol<sup>-1</sup>. Formula: C<sub>28</sub>H<sub>48</sub>FeP<sub>2</sub>. Yield 83%. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 1.12 (18 H, d, J<sub>HP</sub> = 10.681 Hz), δ 1.171 (18 H, d, J<sub>HP</sub> = 10.986 Hz), δ, 2.674 (2 H, dd, J<sub>HH</sub> = 15.87 Hz, J<sub>HP</sub> = 2.441 Hz), δ 2.860 (2 H, dm, J<sub>HH</sub> = 15.87 Hz), δ 3.837 (1 H, t, J = 2 Hz), δ 4.022 (5 H, s), δ 3.346 (2 H, d, J = 2 Hz). <sup>13</sup>C NMR (120 MHz, CDCl<sub>3</sub>): δ 21.02 (dd, 1J<sub>PC</sub> (inner): 23.83 Hz, 4J<sub>PC</sub> (outer) = 3.67 Hz; CH<sub>2</sub>P), δ 29.90 (d, 2J<sub>PC</sub> = 13.75 Hz; CH<sub>3</sub> (inner)), δ 29.86 (d, 2J<sub>PC</sub> = 12.83 Hz; CH<sub>3</sub> (outer)), δ 31.34 (d, 1J<sub>PC</sub> = 22.00 Hz; PCMe<sub>3</sub> (inner)), δ 31.92 (d, 1J<sub>PC</sub> = 22.91 Hz; PCMe<sub>3</sub> (outer)), δ 63.75 (s; cpβ-C); δ 69.47 (s; cp5); δ 70.08 (d, 3J<sub>PC</sub> = 4.41 Hz; cpα-C); δ 86.73 (d, 2J<sub>PC</sub> = 5.46 Hz; cpγ-C). <sup>13</sup>C DEPT (120 MHz, CDCl<sub>3</sub>) δ 21.01 (dd, ↓CH<sub>2</sub>), δ 29.90 (d, ↑CH<sub>3</sub>), δ 31.45 (d, ↑CH<sub>3</sub>), δ 63.74 (s, ↑CH), δ 69.46 (s, ↑CH), δ 70.04 (↑CH), δ 70.13 (s, ↑CH). <sup>31</sup>P (101.25 MHz, CDCl<sub>3</sub>): δ 22.90 (s). Elemental analysis, calculated for C<sub>28</sub>H<sub>48</sub>FeP<sub>2</sub>: C 66.9%, H 9.6% Found C 66.8%, H 9.6%.

### Preparation of 1-(hydroxymethyl)-2-(dimethylaminomethyl)ferrocene, 6.

To DMAMF (1.0 g, 4.12 mmol) in diethyl ether (20 ml) under argon, was added *n*-butyl lithium (5.14 ml, 8.24 mmol) in 2:1 excess. The reaction was stirred for 3 hours, taking on a reddish colour. After cooling the solution in a dry ice / IMS bath, we added calcined para-formaldehyde (0.247 g) in 2 times excess. Stirring continued overnight (17 hours). The reaction was quenched with water, extracted with diethyl ether, dried over MgSO<sub>4</sub>, filtered over celite, and the solvent removed in vacuo. TLC analysis (alumina plate, light petrol/diethyl ether (9:1)) showed two compounds to be present. <sup>1</sup>H NMR confirmed these to be the starting material DMAMF, and the desired product 1-hydroxy-2-dimethylaminomethyl ferrocene, present in a 1:2 ratio. The crude product was eluted through a neutral alumina column. First, DMAMF came off with petrol/diethyl ether (9:1 ratio), and the

polarity was increased substantially by using pure ethyl acetate to elute the hydroxyl product. After the removal of ethyl acetate in vacuo, tiny crystals started to appear. These were separated and washed with diethyl ether. The remaining material was purged with a vacuum for several hours to leave the analytically pure product as orange oil. The material continued to crystallise, and we used the oil and crystal mixture in a subsequent reaction.

F.W. 273.02 g.mol<sup>-1</sup> Formula: C<sub>14</sub>H<sub>19</sub>NFeO, Yield 0.2 g (18%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 2.13 (s, 6 H; 2 × CH<sub>3</sub>), δ 2.74 (d, 1 H, 12.51 Hz; NCH<sub>2</sub> AB couple), δ 3.85 (d, 1 H, 12.51 Hz; NCH<sub>2</sub> AB couple), δ 3.98 (dd, 1 H, 2.16 Hz; cp H3), δ 4.04 (s, 5 H; cp-5), δ 4.06 (dd, 1 H, 2.14 Hz; cp-H5), δ 4.07 (d, 1 H, 12.21 Hz; CH<sub>2</sub>OH AB couple), δ 4.15 (m, 1 H; cp-H4), δ 4.73 (d, 1 H, 12.21 Hz; CH<sub>2</sub>OH AB couple). <sup>13</sup>C NMR (61 MHz, CDCl<sub>3</sub>) δ 44.38 (s; 2 × CH<sub>3</sub>), δ 58.27 (s; NCH<sub>2</sub>), δ 60.04 (s; CH<sub>2</sub>O), δ 65.33 (s; cp C4), δ 68.82 (s; cp-5), δ 69.56 (s; cp C3), δ 70.58 (s; cp C5), δ 84.47 (s; cp C2), δ 87.65 (s; cp C1). COSY 2D <sup>1</sup>H NMR, partly obscured doublet in 1D spectrum at 4.071 ppm and its coupling to the doublet at 4.73 ppm confirmed. Infrared spectra (CHCl<sub>3</sub>, thin film NaCl plates) 3378 cm<sup>-1</sup> ν(OH), 2954 cm<sup>-1</sup>, 2861 cm<sup>-1</sup>, 2826 cm<sup>-1</sup>, 2783 cm<sup>-1</sup>, 1105 cm<sup>-1</sup>, ν(C-O): 1351 cm<sup>-1</sup>, O-H bending: 1030 cm<sup>-1</sup>. Elemental analysis, calculated for C<sub>14</sub>H<sub>19</sub>NFeO, C 61.5%, H 7.0% N 5.1%; Found C 61.3%, H 7.3%, N 4.8%.

#### Method 2: Preparation of bis-(1,2-di-tert-butylphosphanomethyl)ferrocene, *butphos*, 2a.

To 1-dimethylaminomethyl-2-hydroxymethyl ferrocene (0.2 g, 0.753 mmol) in acetic acid (15 mL) stirred under argon, was added 4-equivalents of di-tert-butylphosphane (0.54 mL, 2.93 mmol), followed by 1 equivalent acetic anhydride. The reaction solution turned from orange to yellow within 1 minute. The system was then heated to 80°C and stirred for 72 hours. The solvent was removed in vacuo to leave orange oil. The crude product recrystallised from refluxing ethanol (4 ml) to yield 0.23g orange crystals. Yield: 0.23 g (53 %). N.B. On subsequent scale-up yields, starting with 5.0 g of the precursor compound, yields increased to >80%.

#### Preparation of 1-(hydroxymethyl)-2,3-bis-(dimethylaminomethyl)ferrocene, 7.

To a stirred solution of 1,2-bis-dimethylaminomethyl ferrocene (0.70 g) in Et<sub>2</sub>O (15 cm<sup>3</sup>) under argon was added 1.2 equivalents n-butyl lithium (1.75 ml, 1.6 M) and the mixture stirred for three hours to yield a red solution. Cooling in a dry ice/IMS bath, calcined paraformaldehyde was added in 2:1 excess and stirring continued overnight (17 hours), followed by quenching with water. The product was extracted with diethyl ether, dried over MgSO<sub>4</sub>, filtered through celite, and the solvent then removed in vacuo, leaving an orange oil that partially crystallised on cooling.

F.W. 330.08 g.mol<sup>-1</sup> Formula: C<sub>17</sub>H<sub>26</sub>N<sub>2</sub>FeO, Yield 0.70 g (91%). <sup>1</sup>H (250 MHz, CDCl<sub>3</sub>): δ 2.13 (s, 6 H; NCH<sub>3</sub>), δ 2.17 (s, 6 H; NCH<sub>3</sub>), δ 2.91 (d, 1 H, J = 12.82 Hz; NCH<sub>2</sub> inner), δ 3.00 (d, 1 H, 12.51 Hz; NCH<sub>2</sub> outer), δ 3.43 (d, 1 H, 12.82 Hz; NCH<sub>2</sub> inner), δ 3.81 (d, 1 H, 12.51 Hz; NCH<sub>2</sub> outer), δ 3.96 (s, 5 H; cp-5), δ 3.99 (d, 1 H, 12.21 Hz; OCH<sub>2</sub>) (partly obscured by large cp-ring peak at δ 3.96), δ 4.07 (d, 1 H, δ 2.14 Hz; cp H4), δ 4.13 (d, 1 H, δ 2.14 Hz; cp H5), δ 4.78 (d, 1 H, 12.21 Hz; OCH<sub>2</sub>). <sup>13</sup>C (62 MHz, CDCl<sub>3</sub>): δ 44.53 (s; N-CH<sub>3</sub> outer), δ 45.28 (s; NCH<sub>3</sub> inner), δ 55.80 (s; NCH<sub>2</sub> outer), δ 57.90 (s; NCH<sub>2</sub> inner), δ 60.27 (s; OCH<sub>2</sub>), δ 67.94 (s; cp C4), δ 68.28 (s; cp C5), δ 69.60 (s; cp 5), δ 84.77 (s; cp C3), δ 84.84 (s; cp C2), δ 88.32 (s; cp C1). Infrared spectra (CHCl<sub>3</sub> / thin film NaCl plates) ν (OH) (hydrogen bonded): 3381 cm<sup>-1</sup> (br), 2956 cm<sup>-1</sup> (m), 2863 cm<sup>-1</sup>, 2826 cm<sup>-1</sup> (m), 2774 cm<sup>-1</sup> (m), ν(C-O): 1354 cm<sup>-1</sup> (m), 1105 cm<sup>-1</sup> (m), O-H bending 1039 cm<sup>-1</sup> (m), 1008 cm<sup>-1</sup> (s). Elemental analysis, calculated for C<sub>17</sub>H<sub>26</sub>N<sub>2</sub>FeO: C 61.8%, H 7.9%, N 8.5%. Found, C 62.3%, H 7.8%, N 8.8%.

#### Preparation of 1,2,3-tris-(di-tert-butyl-phosphanyl-methyl)ferrocene, 8.

To 1-hydroxymethyl-2,3-bis-dimethylaminomethyl ferrocene (0.70 g, 2.12 mmol) stirring in acetic acid freshly distilled from acetic anhydride (25 cm<sup>3</sup>), under argon, was added di-tert-butylphosphane (2.60 mL, 13.98 mmol) as 3 equivalents in 2 x excess. Together with acetic anhydride (0.24 mL, 2.33 mmol), the solution was then stirred at 80°C for seven days, during which time the solution darkened its orange colouration. Removal of the solvent in vacuo, recrystallisation from refluxing ethanol and cooling to 17°C overnight furnished orange crystals. These were filtered off and washed with cold ethanol. Volatiles were removed in vacuo to yield the analytically pure product as a yellow/orange powder.

O.W. 660.336 g.mol<sup>-1</sup>. Formula: C<sub>37</sub>H<sub>67</sub>FeP<sub>3</sub>. Yield: 0.43 g (31 %). <sup>1</sup>H (250 MHz, CDCl<sub>3</sub>) δ 1.12 (dd – pseudo triplet, 36 H, 12.1 Hz; CH<sub>3</sub> outer), δ 1.26 (d, 18H, <sup>3</sup>JPH = 10.7 Hz; CH<sub>3</sub> inner), δ 2.68 (d, 2 H, 17.7 Hz; CH<sub>2</sub> outer), δ 2.95 (s, 2 H; CH<sub>2</sub> outer), δ 3.07 (m, 2 H; CH<sub>2</sub> inner), δ 4.01 (s, 5 H; cp 5) δ 4.33 (s, 2 H; cpγ-H). <sup>13</sup>C {<sup>1</sup>H} (CDCl<sub>3</sub>, 125.77 MHz):

$\delta$  21.38 (d,  $^1J_{CP}$  = 20.16 Hz; CH<sub>2</sub>-inner),  $\delta$  21.43 (d, 25.66 Hz; CH<sub>2</sub>; - outer),  $\delta$  29.73 (d,  $^2J_{CP}$  = 13.7 Hz; 2  $\times$  CH<sub>3</sub>-inner),  $\delta$  29.95 (d,  $^2J_{CP}$  = 25.6 Hz; -outer down),  $\delta$  30.05 (d,  $^2J_{CP}$  = 25.6 Hz; -outer up),  $\delta$  31.54 (d,  $^1J_{CP}$  = 19.25 Hz; tert-C inner),  $\delta$  31.64 (d,  $^1J_{CP}$  = 24.74 Hz; tert-C outer down),  $\delta$  32.18 (d,  $^1J_{CP}$  = 22.00 Hz; tert-C outer up),  $\delta$  67.97 (s; CH),  $\delta$  70.32 (s; cp5),  $\delta$  86.21 (d,  $^2J_{CP}$  = 17.41 Hz; Cp-subst).  $^{13}C\{^1H\}$  DEPT (CDCl<sub>3</sub>, 125.77 MHz)  $\delta$  21.3 (CH<sub>2</sub>),  $\delta$  21.4 (CH<sub>2</sub>),  $\delta$  29.73 (d) (CH<sub>3</sub>),  $\delta$  29.95 (d) (CH<sub>3</sub>),  $\delta$  30.05 (d) (CH<sub>3</sub>),  $\delta$  67.97 (s) (CH),  $\delta$  70.32 (s) (cp5).  $^{31}P$  NMR (202.4 MHz, CDCl<sub>3</sub>):  $\delta$  20.58 (s, 2 P),  $\delta$  21.35 (s, 1 P). Infrared spectra (CHCl<sub>3</sub>/ thin film NaCl plates)  $\nu$ (C-H): 2939 cm<sup>-1</sup>, 2897 cm<sup>-1</sup>, 2863 cm<sup>-1</sup>, 2357 cm<sup>-1</sup>  $\nu$ (C-P): 1470 cm<sup>-1</sup>,  $\nu$ (C-P): 1366 cm<sup>-1</sup>. m.p. 115–118°C. Elemental analysis, calculated for C<sub>37</sub>H<sub>67</sub>FeP<sub>3</sub>: C 67.2%, H 10.2%, Found: C 67.4%, H 10.2%.

#### Preparation of 1-bromo-1'-dimethylaminomethylferrocene, 15.

To dibromo ferrocene (10.02 g, 29.14 mmol) in dry THF (250 ml) under nitrogen, and cooled to -78°C (dry ice/acetone bath) was added n-butyllithium (11.10 ml, 27.69 mmol, 0.95 eq). The reaction was kept cool and stirred for a further two hours, resulting in the formation of an orange precipitate. After adding Eschenmoser's salt (6.47 g, 34.97 mmol, 1.2 eq), the solution was allowed to warm up to room temperature and stirring continued for twelve hours. The reaction was quenched with water and extracted with diethyl ether. The product was isolated using an acid/base extraction; 10% Phosphoric acid was added to the ethereal layer, and the aqueous layer was isolated and washed with diethyl ether. Any unreacted starting material or by-products remained in the organic layer, while the product located in the aqueous layer due to the presence of the amine. After mixing the aqueous layer with pure diethyl ether, we added sodium hydroxide (2 M) until the layer was slightly alkaline. This organic layer was then extracted with diethyl ether, dried over magnesium sulphate and filtered over celite. The solvent was removed in vacuo using a rotary evaporator, to furnish purified product as an orange oil (2.00 g, 21% yield).

C<sub>13</sub>H<sub>16</sub>NFeBr, F.W. 322.03 g.mol<sup>-1</sup>.  $^1H$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.11 (s, 6H, 2  $\times$  CH<sub>3</sub>),  $\delta$  3.23 (s, 2H, CpCH<sub>2</sub>N),  $\delta$  3.98 (t, 1.89 Hz; 2  $\times$  CH),  $\delta$  4.04 (t, 1.89 Hz; 2  $\times$  CH),  $\delta$  4.09 (t, 1.89 Hz; 2  $\times$  CH),  $\delta$  4.25 (t, 1.89 Hz; 2  $\times$  CH).  $^{13}C$  NMR (62.5 MHz, CDCl<sub>3</sub>)  $\delta$  30.84 (s; NCH<sub>3</sub>),  $\delta$  45.58 (CpCH<sub>2</sub>N),  $\delta$  65.61 (s; Cp  $\beta$ -C),  $\delta$  67.35 (s; CpBr  $\beta$ -C),  $\delta$  67.73 (s; Cp  $\alpha$ -C),  $\delta$  68.24 (s; CpBr  $\alpha$ -C),  $\delta$  69.32 (s; Cp ipso-C),  $\delta$  70.52 (s; CpBr ipso-C). Elemental analysis, calculated for C<sub>13</sub>H<sub>16</sub>NFeBr: C 48.5%, H 5.0%, N 4.3%. Found C 47.2%, H 4.8%, N 4.1%.

#### Preparation of 1-dimethylaminomethyl-1'-trimethylsilyl ferrocene, 16.

To 1-bromo-1'-trimethylsilylferrocene (5.52 g, 16.37 mmol) in dry diethyl ether (100 ml) was added n-butyllithium (7.2 ml, 18.01 mmol, 1.1 eq) and the reaction was stirred under N<sub>2</sub> for 1 hour at room temperature. We added dry THF (100 ml) before cooling the solution to -78°C (dry ice/acetone bath) and then quenched with Eschenmoser's salt (3.33 g, 18 mmol, 1 eq). The solution was allowed to warm up to room temperature and stirred for twelve hours, resulting in a yellow solution. The reaction was then quenched with water and stirred for a further fifteen minutes. The ethereal layer, containing the product was separated, and the aqueous layer was further extracted several times with diethyl ether. The combined ether fractions were dried over magnesium sulphate and filtered through celite. The ether solvent was then removed by rotary evaporator to leave a red oil. The product was purified by column chromatography. Starting material was removed with 9:1 petrol/Et<sub>2</sub>O, and the product was obtained as an orange band, using 1:1 petrol/Et<sub>2</sub>O (5% triethylamine). Drying the final product with vacuum furnished a red oil: (4.09 g, 79% yield).

C<sub>16</sub>H<sub>25</sub>NSiFe, F.W. 315.31 g.mol<sup>-1</sup>.  $^1H$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.00 (s, 9H, 3  $\times$  CH<sub>3</sub>)  $\delta$  1.94 (s, 6H, 2  $\times$  CH<sub>3</sub>),  $\delta$  3.04 (s, 2H, CpCH<sub>2</sub>N),  $\delta$  3.79 (t, 2.00 Hz; 2  $\times$  CH),  $\delta$  3.84 (t, 1.89 Hz; 2  $\times$  CH),  $\delta$  3.91 (t, 1.90 Hz; 2  $\times$  CH),  $\delta$  4.04 (t, 1.89 Hz; 2  $\times$  CH).  $^{13}C$  NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.00 (s; SiCH<sub>3</sub>),  $\delta$  44.94 (s; NCH<sub>3</sub>),  $\delta$  59.38 (CpCH<sub>2</sub>N),  $\delta$  68.42 (s; CpSiMe<sub>3</sub>,  $\beta$ -C),  $\delta$  70.39 (s;  $\beta$ -C),  $\delta$  71.59 (s; CpSiMe<sub>3</sub>  $\alpha$ -C),  $\delta$  72.43 (s;  $\alpha$ -C),  $\delta$  73.49 (s; CpSiMe<sub>3</sub> ipso-C),  $\delta$  83.43 (s; ipso-C). MS (EI) m/z (rel. int): 316 (M + H)<sup>+</sup> (78%), 271 (100%). Elemental analysis, calculated for C<sub>16</sub>H<sub>25</sub>NSiFe: C 61.0%, H 8.0%, N 4.4%; Found: C 60.7%, H 7.93%, N 4.5%.

#### Preparation of 1,2-bis-(dimethylaminomethyl)-1'-trimethylsilylferrocene, 17.

To 1-dimethylaminomethyl-1'-trimethylsilyl ferrocene (3.86 g, 12.24 mmol) in dry diethyl ether (100 ml) was added n-butyllithium (5.88 ml, 14.69 mmol, 1.2 eq) and the reaction was stirred under N<sub>2</sub> for 1 hour at room temperature. Dry THF (100 ml) was added, and the solution was cooled to -78°C (dry ice/acetone bath) and

quenched with Eschenmoser's salt (2.50 g, 13.47 mmol, 1.1 eq). The solution was allowed to warm to room temperature and was stirred for twelve hours, resulting in an orange solution. The reaction was quenched with water and stirred for a further fifteen minutes. The ethereal layer, containing the product, was separated, and the aqueous layer was further extracted several times with diethyl ether. The combined ether fractions were dried over magnesium sulphate and filtered over celite. The ether solvent was removed by rotary evaporator to furnish a red oil. The product was purified by column chromatography. The starting material was removed with 9:1 petrol/Et<sub>2</sub>O, and the product was obtained with 1:1 petrol/Et<sub>2</sub>O (5% triethylamine). The resulting red oil was dried in vacuo: (4.33g, 95% yield) C<sub>19</sub>H<sub>33</sub>N<sub>2</sub>SiFe.

F.W. 373.42 g.mol<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 0.00 (s, 9H, 3 × CH<sub>3</sub>), δ1.97 (s, 12H, 4 × CH<sub>3</sub>), δ2.99 (d, 2H, 12.92 Hz; NCH<sub>2</sub>Cp), δ3.13 (d, 2H, 12.93 Hz; NCH<sub>2</sub>Cp), δ3.76 (t, 2H, 2 × CH), δ3.87 (t, 2H, 2 × CH), δ3.81 (t, 1H, 2.84 Hz; 1 × CH), δ3.97 (d, 2H, 2.21 Hz; 2 × CH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 0.00 (s; SiCH<sub>3</sub>), δ45.33 (s; NCH<sub>3</sub>), δ57.49 (CpCH<sub>2</sub>N), δ67.32 (s; CpSiMe<sub>3</sub> β-C), δ68.37 (s; β-C), δ70.78 (s; CpSiMe<sub>3</sub> α-C), δ73.15 (s; α-C), δ73.91 (s; CpSiMe<sub>3</sub> ipso-C), δ83.92 (s; ipso-C). MS (EI) m/z (rel. int): 373 M<sup>+</sup> (100%), 227 (25%). Elemental analysis, calculated for C<sub>19</sub>H<sub>33</sub>N<sub>2</sub>SiFe: C 61.1%, H 8.9%, N 7.5%. Found: C 59.8%, H 8.7%, N 7.4%.

#### Preparation of 1-dimethylaminomethyl-2,1'-bis-trimethylsilyl ferrocene, 21.

To dimethylaminomethylferrocene (30.0g, 123.39mmol) in dry diethyl ether (200 ml) was added n-butyllithium (123.39 ml, 308.48 mmol, 2.5 eq) and TMEDA (20.48 ml, 135.73 mmol, 1.1 eq) and the reaction was stirred under N<sub>2</sub> for 12 hours at room temperature. The solution was then cooled to -78°C (dry ice/acetone bath) and quenched with chlorotrimethylsilane (34.45 ml, 271.46 mmol, 2.2 eq). The solution was allowed to warm to room temperature and stirred for twelve hours, resulting in an orange solution. The reaction was quenched with water and stirred for a further fifteen minutes. The ethereal layer, containing the product was separated, and the aqueous layer was further extracted several times with diethyl ether. The combined ether fractions were dried over magnesium sulphate and filtered through celite. The ether solvent was removed by rotary evaporator, resulting in red oil. The product was purified by column chromatography. After removing small amounts of starting material with petrol and 5% triethylamine, the product was obtained using 1:1 petrol/Et<sub>2</sub>O (5% triethylamine). The resulting red oil was dried under vacuum: (40.1 g, 84% yield).

C<sub>19</sub>H<sub>33</sub>NSi<sub>2</sub>Fe, F.W. 387.49 g.mol<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 0.25 (s, 9H, 3 × CH<sub>3</sub>), δ0.30 (s, 9H, 3 × CH<sub>3</sub>), δ2.11 (s, 6H, 2 × CH<sub>3</sub>), δ3.00 (d, 1H, 12.45 Hz; NCH<sub>2</sub>Cp), δ3.45 (d, 1H, 12.45 Hz; NCH<sub>2</sub>Cp), δ3.98 (t, 2H, 1.26 Hz; 2 × CH), δ4.06 (t, 2H, 1.26 Hz; 2 × CH), δ4.19 (t, 1H, 1.74 Hz; 1 × CH), δ4.27 (d, 1H, 1.74 Hz; 1 × CH), δ4.29 (d, 1H, 1.74 Hz; 1 × CH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ0.00 (s; SiCH<sub>3</sub>), δ0.41 (s; SiCH<sub>3</sub>), δ45.03 (s; NCH<sub>3</sub>), δ59.72 (CpCH<sub>2</sub>N), δ70.03 (s; CpSiMe<sub>3</sub> β-C), δ71.77 (s; β-C), δ72.01 (s; CpSiMe<sub>3</sub> α-C), δ72.68 (s; α-C), δ72.88 (s; α-C), δ74.00 (s; CpSiMe<sub>3</sub> ipso-C), δ74.25 (s; ipso-C), δ89.97 (s; ipso-C). Elemental analysis, calculated for C 58.9%, H 8.6%, N 3.6%. Found: C 58.6%, H 8.4%, N 3.6%.

#### Preparation of 1,2-bis-dimethylaminomethyl-5,1'-bis-trimethylsilyl ferrocene, 22.

To 1-dimethylaminomethyl-5,1'-bis-trimethylsilyl ferrocene (30.0 g, 77.42 mmol) in dry diethyl ether (200 ml) was added n-butyllithium (37.2 ml, 92.91 mmol, 1.2 eq) and the reaction was stirred under N<sub>2</sub> for 20 hours at room temperature. Dry THF (250 mL) was added, and the solution cooled to -78°C (dry ice/acetone bath) then quenched with Eschenmoser's salt (17.18 g, 92.91 mmol, 1.2 eq). The solution was allowed to warm up to room temperature. Stirring continued another 12 hours to furnish a red solution. The reaction was quenched with water and stirred for fifteen minutes. The ethereal layer, containing the product, was separated and the aqueous layer further extracted several times with diethyl ether. The combined ether fractions were dried over magnesium sulphate and filtered through celite. The ether solvent was removed by rotary evaporator, resulting in red oil. The product was purified by column chromatography, using a large scale column. Small amounts of starting material were removed with petrol and 5% triethylamine, and the product was obtained with 1:1 petrol/Et<sub>2</sub>O (5% triethylamine). The resulting red oil was dried under vacuum: (32.11 g, 93% yield).

C<sub>22</sub>H<sub>40</sub>N<sub>2</sub>Si<sub>2</sub>Fe, F.W. 444.59 g.mol<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 0.00 (s, 9H, 3 × CH<sub>3</sub>), δ0.03 (s, 9H, 3 × CH<sub>3</sub>), δ1.86 (s, 6H, 2 × CH<sub>3</sub>), δ1.93 (s, 6H, 2 × CH<sub>3</sub>), δ2.97 (d, 2H, 12.77 Hz; NCH<sub>2</sub>Cp), δ3.24 (d, 2H, 12.77 Hz; NCH<sub>2</sub>Cp), δ3.74 (t, 2H, 1.26 Hz; 2 × CH), δ3.81 (t, 2H, 1.26 Hz; 2 × CH), δ3.95 (d, 1H, 2.37 Hz; 1 × CH), δ4.08 (d, 1H, 2.37 Hz; 1 × CH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 0.00 (s; SiCH<sub>3</sub>), δ0.09 (s; SiCH<sub>3</sub>), δ44.43 (s; NCH<sub>3</sub>), δ57.31 (CpCH<sub>2</sub>N), δ69.73 (s; CpSiMe<sub>3</sub> β-C), δ71.43 (s; CpSiMe<sub>3</sub> α-C), δ72.62 (s; α-C), δ72.83 (s; α-C), δ73.68 (s; CpSiMe<sub>3</sub> ipso-C), δ74.94 (s;

ipso-C),  $\delta$  87.25 (s; ipso-C),  $\delta$  89.68 (s; ipso-C). Elemental analysis, calculated for C 59.4%, H 9.1%, N 6.3%. Found: C 57.2%, H 8.6%, N 6.0%.

#### Preparation of 1-dimethylaminomethyl-5,1'-bis-triphenylsilyl ferrocene, 23.

To dimethylaminomethylferrocene (20.0 g, 82.26 mmol) in dry diethyl ether (300 ml) was added *n*-butyllithium (82.26 ml, 205.65 mmol, 2.5 eq) and TMEDA (13.66 ml, 90.49 mmol, 1.1 eq). The reaction was stirred under N<sub>2</sub> for 12 hours at room temperature. We cooled the solution to -78°C with a dry ice/acetone bath and quenched it with water before stirring for a further fifteen minutes. We combined the ethereal layer containing the product, with chlorotriphenylsilane (50.94 g, 172.75 mmol, 2.1 eq) dissolved in dry THF (200 ml). The solution was warmed to room temperature and stirred for twelve hours, resulting in a red solution. The mixture was extracted several times with diethyl ether. The ether fractions were combined and dried over magnesium sulphate, and filtered over celite. The ether solvent was removed by rotary evaporator to furnish a red oil. This product was purified by layering the oil with petrol and diethyl ether and leaving it to crystallise overnight. After decanting the orange/red crystals, they were dried under vacuum. A second crop of orange/red crystals was obtained by the layering the decanted liquid and repeating the process: (42.75g, 68% yield).

C<sub>49</sub>H<sub>45</sub>NSi<sub>2</sub>Fe, F.W. 759.98 g.mol<sup>-1</sup>. M.P. 154-157°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.71 (s, 6H, 2 × CH<sub>3</sub>),  $\delta$  2.59 (d, 1H, 12.46 Hz; NCH<sub>2</sub>Cp),  $\delta$  2.93 (d, 1H, 12.46 Hz; NCH<sub>2</sub>Cp),  $\delta$  3.99 (t, 1H, 1.74 Hz; 1 × CH),  $\delta$  4.01 (t, 2H, 1.10 Hz; 2 × CH),  $\delta$  4.05 (t, 2H, 1.10 Hz; 2 × CH),  $\delta$  4.21 (d, 1H, 1 × CH),  $\delta$  4.28 (d, 1H, 1.74 Hz; 1 × CH)  $\delta$  7.38 (t, 6H, 1.58 Hz),  $\delta$  7.39 (t, 3H, 1.26 Hz),  $\delta$  7.42 (t, 6H, 1.57 Hz),  $\delta$  7.47 (t, 3H, 1.26 Hz),  $\delta$  7.60 (t, 6H, 1.57 Hz),  $\delta$  7.68 (t, 6H, 1.26 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 44.61 (s; NCH<sub>3</sub>),  $\delta$  58.43 (CpCH<sub>2</sub>N),  $\delta$  66.86 (s; CpSiPh<sub>3</sub>  $\beta$ -C),  $\delta$  72.36 (s;  $\beta$ -C),  $\delta$  73.34 (s; CpSiPh<sub>3</sub>  $\alpha$ -C),  $\delta$  74.67 (s;  $\alpha$ -C),  $\delta$  74.77 (s;  $\alpha$ -C),  $\delta$  75.66 (s; CpSiPh<sub>3</sub> ipso-C),  $\delta$  75.75 (s; ipso-C),  $\delta$  91.09 (s; ipso-C)  $\delta$  127.52 (Ar CH),  $\delta$  127.79 (Ar CH),  $\delta$  129.24 (Ar CH),  $\delta$  129.51 (Ar CH), 135.52 (Ar CH),  $\delta$  135.69 (Ar CH),  $\delta$  135.98 (Ar ipso-C),  $\delta$  136.46 (Ar ipso-C). MS (EI) *m/z* (rel. int): 759 M<sup>+</sup> (8%), 715 (100%). Elemental analysis, calculated for C 77.5%, H 6.0%, N 1.8%. Found: C 77.6%, H 6.0%, N 1.8%.

#### Preparation of 1,2-bis-dimethylaminomethyl-5,1'-bis-triphenylsilyl ferrocene, 24.

To 1-dimethylaminomethyl-5,1'-bis-triphenylsilyl ferrocene (40.0 g, 52.63 mmol) in dry diethyl ether (400 ml) was added *n*-butyllithium (25.26 ml, 63.16 mmol, 1.2 eq) and the reaction was stirred under N<sub>2</sub> for 20 hours at room temperature. Dry THF (250 ml) was then added, and the solution was cooled to -78°C (dry ice/acetone bath) and quenched with Eschenmoser's salt (12.65 g, 68.42 mmol, 1.3 eq). The solution was allowed to warm up to room temperature and stirred for twelve hours, resulting in an orange solution. It was then quenched with water and stirred for a further fifteen minutes. The ethereal layer containing the product was separated, and the aqueous layer was further extracted several times with diethyl ether. The combined ether fractions were dried over magnesium sulphate and filtered over celite. The ether solvent was removed by rotary evaporator to furnish a red oil. The oil was purified by layering with minimal amounts of diethyl ether and petrol and leaving to crystallise overnight. After decanting the liquid residue, the red crystals were dried under vacuum. A second crop of crystals was obtained by layering the decanted liquid and repeating the process: (21.50g, 50 % yield).

C<sub>52</sub>H<sub>52</sub>N<sub>2</sub>Si<sub>2</sub>Fe F.W. 817.09 g.mol<sup>-1</sup>. m.p. 150-154°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.69 (s, 6H, 2 × CH<sub>3</sub>),  $\delta$  2.08 (s, 6H, 2 × CH<sub>3</sub>),  $\delta$  2.81 (d, 2H, 12.30 Hz; NCH<sub>2</sub>Cp),  $\delta$  3.40 (d, 2H, 12.30 Hz; NCH<sub>2</sub>Cp),  $\delta$  4.05 (t, 2H, 1.42 Hz; 2 × CH),  $\delta$  4.08 (t, 2H, 1.42 Hz; 2 × CH),  $\delta$  4.27 (d, 1H, 2.40 Hz; 1 × CH),  $\delta$  4.38 (d, 1H, 2.40 Hz; 1 × CH),  $\delta$  7.45 (t, 6H, 1.26 Hz),  $\delta$  7.47 (t, 3H, 1.57 Hz),  $\delta$  7.70 (t, 6H, 1.26 Hz),  $\delta$  7.71 (t, 3H, 1.57 Hz),  $\delta$  7.81 (t, 6H, 1.26 Hz),  $\delta$  7.83 (t, 6H, 1.57 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 45.22 (s; NCH<sub>3</sub>),  $\delta$  56.67 (CpCH<sub>2</sub>N),  $\delta$  67.43 (s; CpSiPh<sub>3</sub>  $\beta$ -C),  $\delta$  68.63 (s; CpSiPh<sub>3</sub>  $\alpha$ -C),  $\delta$  74.02 (s;  $\alpha$ -C),  $\delta$  75.07 (s;  $\alpha$ -C),  $\delta$  76.21 (s; CpSiPh<sub>3</sub> ipso-C),  $\delta$  77.95 (s; ipso-C),  $\delta$  88.31 (s; ipso-C),  $\delta$  90.73 (s; ipso-C),  $\delta$  127.45 (Ar CH),  $\delta$  127.94 (Ar CH),  $\delta$  129.07 (Ar CH),  $\delta$  129.61 (Ar CH),  $\delta$  135.53 (Ar CH),  $\delta$  136.07 (Ar CH),  $\delta$  136.17 (Ar ipso-C),  $\delta$  136.55 (Ar ipso-C). MS (EI) *m/z* (rel. int): 817 M<sup>+</sup> (34%), 772 (100%). Elemental analysis, calculated for C 76.5%, H 6.4%, N 3.4%. Found: C 74.6%, H 6.2%, N 3.1%.

#### Preparation of dimethylaminomethylruthenocene, 25. (see ref 69, main paper)

Ruthenocene (3.97 g, 17 mmol) and potassium *tert*-butoxide (250 mg, 2.13 mmol) was dissolved in dry THF (350 ml) and cooled to -78°C. *t*-Butyllithium (14.7ml, 25.5 mmol, 1.7 M solution in pentane) was added over 10 min and stirred for a further 30 min at temperature below -70°C. After adding Eschenmoser's salt (4.81 g, 26 mmol), the mixture was stirred for 12 h as it warmed to room temperature. The reaction was quenched with HCl (20 ml, 1 M), and the reaction treated with NaOH until the aqueous phase was at pH 10. After removing the organic

layer, the aqueous phase was washed with diethyl ether (2 x 75 ml). The organic portions were combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the solvent removed in vacuo. The crude mixture was purified by column chromatography on deactivated alumina. We removed un-reacted ruthenocene (0.66 g) by eluting with hexane and hexane/ $\text{Et}_2\text{O}$  (70:30). Recrystallisation from hexane at  $-15^\circ\text{C}$  yielded the product as cream crystals. The product was dried under high vacuum: (1.71 g, 35% yield).

$\text{C}_{13}\text{H}_{17}\text{NRu}$  F.W. 288.35  $\text{g}\cdot\text{mol}^{-1}$ .  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.22 (s, 6H, 2 x  $\text{CH}_3$ ),  $\delta$  3.10 (s, 2H,  $\text{CpCH}_2\text{N}$ ),  $\delta$  4.52 (s, 5H, Cp),  $\delta$  4.53 (2H, Cp),  $\delta$  4.60 (2H, Cp).  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{CDCl}_3$ )  $\delta$  = 44.76 (s;  $\text{NCH}_3$ ),  $\delta$  58.97 ( $\text{CpCH}_2\text{N}$ ), 70.23 ( $\text{Cp}\alpha\text{-C}$ ),  $\delta$  70.52 ( $\text{Cp}5$ ),  $\delta$  72.37 ( $\text{Cp}\beta\text{-C}$ ),  $\delta$  86.96 (Cp *ipso*-C). MS (EI)  $m/z$  (rel. int): 290  $\text{M}^+$  (100%), 245 (23%). Elemental analysis, calculated for  $\text{C}_{13}\text{H}_{17}\text{NRu}$ : C, 54.2%, H 5.9%, N 4.8%. Found: C 53.5%, H 5.7%, N 4.5%. M.P.  $38\text{--}40^\circ\text{C}$  (lit.  $39\text{--}42^\circ\text{C}$ ).

#### Preparation of 1,2-bis-dimethylaminomethylruthenocene, 26.

To dimethylaminomethyl ruthenocene, **25**, (1.61 g, 5.58 mmol) in dry diethyl ether (80ml) was added *t*-butyllithium (4.60 ml, 7.82 mmol, 1.4 eq), and the reaction stirred under  $\text{N}_2$  for four hours. The yellow reaction solution was cooled to  $-78^\circ\text{C}$  (dry ice/acetone bath), and Eschenmoser's salt (1.45g, 7.82mmol) was added. The cloudy white solution was then warmed to room temperature and stirred for eighteen hours. The reaction was then quenched with dilute sodium hydroxide and stirred for fifteen minutes. The ethereal layer, containing product, was separated, and the aqueous layer was extracted several times with diethyl ether. The combined ether fractions were dried over magnesium sulphate and filtered over celite. The ether solvent was removed by rotary evaporator to give a yellow oil, and the crude product was placed in the freezer overnight. The product was recrystallised from petrol at  $-17^\circ\text{C}$ , and the white crystals were washed with cold petrol and dried in vacuo: (1.78g, 92% yield).

$\text{C}_{16}\text{H}_{24}\text{N}_2\text{Ru}$  F.W. 345.45  $\text{g}\cdot\text{mol}^{-1}$   $\text{C}_{16}\text{H}_{24}\text{N}_2\text{Ru}$ ,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.24 (s, 12H, 4 x  $\text{CH}_3$ ), 3.05 (d, 2H, 13.13 Hz;  $\text{NCH}_2\text{Cp}$ ),  $\delta$  3.26 (d, 2H, 13.13 Hz;  $\text{NCH}_2\text{Cp}$ ),  $\delta$  4.45 (s, 5H, Cp5),  $\delta$  4.48 (t, 1H, 1.99 Hz;  $\text{Cp}\beta\text{-H}$ ),  $\delta$  4.64 (d, 2H, 1.99 Hz;  $\text{Cp}\alpha\text{-H}$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 45.50 (s,  $\text{NCH}_3$ ),  $\delta$  57.28 (s,  $\text{NCH}_2$ ),  $\delta$  70.53 ( $\text{Cp}\alpha\text{-C}$ ),  $\delta$  71.32 ( $\text{Cp}5$ ),  $\delta$  72.57 ( $\text{Cp}\beta\text{-C}$ ),  $\delta$  88.21 (Cp *ipso*-C). MS (EI)  $m/z$  (rel. int): 346  $\text{M}^+$  (10%), 343 (52%), 315 (60%), 300 (100%). M.P.  $47\text{--}50^\circ\text{C}$ . Elemental analysis, calculated for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{Ru}$ : C 55.6%, H 7.0%, N 8.1%. Found: C 55.6%, H 7.1%, N 8.0%.

### S1.3 Additional Synthetic Details of Ferrocenylmethylphosphanes; *in situ* methods. (Work carried out at Lucite International)

#### General Information

Unless stated to the contrary all manipulations were performed under an atmosphere of nitrogen using standard Schlenk line, cannula and glovebox techniques. All chemicals were obtained from Aldrich except di-*tert*-butylphosphane (STREM), 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane (CYTEC) and congressane (Lachema). All NMR experiments were performed using CDCl<sub>3</sub> as the solvent.

#### Bulk preparation of 1,2-bis(di-*tert*-butyl)phosphanomethyl)ferrocene, 2a.

Into a 500ml Schlenk flask was added di-*tert*-butylphosphane (25.0g, 171mmol) and the 1,2-bis-dimethylaminomethylferrocene, (*damf*), **5**, (25.65g, 85.5mmol) (**1**) in a glovebox. This was then suspended in a mixture of acetic acid: acetic anhydride (100ml: 10ml). The suspension was then heated to 130°C and kept at this temperature for two hours. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue suspended in ethanol (50ml). The ethanol suspension was heated until all the phosphane had dissolved. The solution was then allowed to cool to room temperature before being placed in the freezer at -20°C. This gave orange crystals. The ethanol mother liquor was removed by cannula and the crystals dried under vacuum. This gave orange crystals which was isolated in the glovebox. Yield 31.0 g, 72 %. <sup>31</sup>P NMR: δ = 23.6 ppm, 100 % pure. FW = 500.4635

#### Preparation of di-(1-adamantyl)phosphinic chloride, Ad<sub>2</sub>P(O)Cl .

Phosphorus trichloride (83, 0.98 mol) was added rapidly to a combination of aluminium chloride (25.0 g, 0.19 mol) and adamantane (27.2g, 0.20 mol) affording a tan suspension. The reaction was heated to reflux (~80°C). After 10 minutes, a yellow-orange suspension was formed. The reaction was refluxed for a total of 16 h. The excess PCl<sub>3</sub> was removed under vacuum to give an orange / red solid. Chloroform (250 cm<sup>3</sup>) was added yielding an orange suspension, which was cooled to 0 °C. Water (100 cm<sup>3</sup>) was added slowly: initially the suspension viscosity increased, but on full addition of water the viscosity lessened. The suspension was then filtered through a frit to remove the orange solid impurity. The filtrate consisted of a two phase (water / chloroform) system. The lower phase (chloroform) was collected by separation and dried over Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then filtered and the filtrate dried under vacuum to give an off-white powder. Yield 32.5 g, 99 %. <sup>31</sup>P NMR: δ = 87.2 ppm, 99 % pure. FW = 352.88.

#### Preparation of di-(1-adamantyl)phosphine, Ad<sub>2</sub>PH, **A** (Goerlich and Schmutzler)<sup>51</sup>

LiAlH<sub>4</sub> (1M in THF, 185mmol, 185ml) was added over 90 minutes to a chilled (-10 °C) solution of Ad<sub>2</sub>P(O)Cl (27.6 g, 78.1mmol) (**2**) in THF (100cm<sup>3</sup>). The reaction was allowed to warm to ambient temperature then stirred for 16 h. The solution was then cooled to 0 °C and HCl (15ml conc.) in water (15ml, degassed) was added slowly. The upper phase was removed via flat ended cannula, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered via cannula. The volatiles were removed under vacuum affording the product as an off-white solid. Yield 16.8 g, 71 %. <sup>31</sup>P NMR: δ = 18.6 ppm, analytically pure. FW = 302.44.

#### Preparation of the 1,2-bis(di-1-adamantyl)phosphanomethyl)ferrocene, 2b.

Into a 500ml Schlenk flask was added the phosphane (16.8g, 55.5mmol) (**A**) and the diamine (8.3g, 27.8mmol) (**4**) in a glovebox. This was then suspended in a mixture of acetic acid: acetic anhydride (170ml, 17ml). The suspension was then heated to 130°C and kept at this temperature for 90 minutes. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue washed with ethanol (50ml). The ethanol washings were then removed by cannula and the residue dried under vacuum. This gave a free-flowing yellow/orange solid which was isolated in the glovebox. Yield 16.1g, 71.2 %. No <sup>31</sup>P NMR due to lack of solubility in CDCl<sub>3</sub>, FW = 814.94.

#### Preparation of Dimethyladamantylphosphinic chloride, (Me<sub>2</sub>Ad)<sub>2</sub>P(O)Cl

Phosphorous trichloride (183ml, 980mmol) was added rapidly to a combination of aluminium chloride (24.4g, 182.6mmol) and 2,5-dimethyladamantane (30.0g, 182.6mmol) affording a tan suspension. The reaction was

heated to reflux ( $\sim 80^\circ\text{C}$ ). After 10 minutes, a yellow-orange suspension was formed. The reaction was refluxed for a total of 16 h. The excess  $\text{PCl}_3$  was removed under vacuum to give an orange / red solid. Chloroform ( $250\text{ cm}^3$ ) was added yielding an orange suspension, which was cooled to  $0^\circ\text{C}$ . Water ( $100\text{ cm}^3$ ) was added slowly: initially the suspension viscosity increased, but on full addition of water the viscosity lessened. The suspension was then filtered through a frit to remove the orange solid impurity. The filtrate consisted of a two phase (water / chloroform) system. The lower phase (chloroform) was collected by separation and dried over  $\text{Na}_2\text{SO}_4$ . The organic layer was then filtered and the filtrate dried under vacuum to give an off-white powder. Yield 35.2 g, 94 %.  $^{31}\text{P}$  NMR:  $\delta = 87.0\text{ ppm}$ , 99 % pure. FW = 408.98.

#### Preparation of Bis-(1,3-dimethyladamantyl)phosphine, $(\text{Me}_2\text{Ad})_2\text{PH}$ .

$\text{LiAlH}_4$  (1M in THF, 96mmol, 96ml) was added slowly to a solution of  $(\text{Me}_2\text{Ad})_2\text{P}(\text{O})\text{Cl}$  (35.5 g, 87mmol) (5) in THF ( $100\text{ cm}^3$ ). The reaction was allowed to warm to ambient temperature then stirred for 16 h. The solution was then cooled to  $0^\circ\text{C}$  and HCl (15ml conc.) in water (35ml, degassed) was added slowly. The upper phase was removed via flat ended cannula, dried over  $\text{Na}_2\text{SO}_4$  and filtered via cannula. The volatiles were removed *in-vacuo* affording the product as an off-white solid. Yield 21.3 g, 68 %.  $^{31}\text{P}$  NMR:  $\delta = 15.7\text{ ppm}$ , 99 % pure. FW = 358.54.

#### Synthesis of 1,2-Bis-[(di-1-(3,5-dimethyladamantyl)phosphanomethyl]ferrocene, 2c.

Into a 500ml Schlenk flask was added bis-(1,3-dimethyladamantyl)phosphane,  $(\text{Me}_2\text{Ad})_2\text{PH}$ , (13.1g, 38.3mmol) and 1,2-bis-dimethylaminomethylferrocene, (*damf*), **5**, (5.74g, 19.2mmol) (1) in the glovebox.. This was then suspended in a mixture of acetic acid: acetic anhydride (130ml: 13ml). The suspension was then heated to  $130^\circ\text{C}$  and kept at this temperature for 90 minutes. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue washed with ethanol (50ml). The ethanol washings were then removed by cannula and the residue dried under vacuum. This gave a free-flowing yellow/orange solid which was isolated in the glovebox. Yield 13.1 g, 74 %.  $^{31}\text{P}$  NMR:  $\delta = 18.9\text{ ppm}$ , 100 % pure. FW = 925.11.

#### Preparation of 3,5-Dimethyl-tert-butyladamantane, $\text{Me}_2\text{Bu}^t\text{Ad}$ .

Into a 500ml Schlenk flask was added 1-bromo-3,5-dimethyladamantane (50.0g, 205.65mmol), this was then dissolved in THF (100ml) and cooled to  $0^\circ\text{C}$ . To this was added tert-butyl lithium (1.7M in pentane, 145ml, 246.8mmol) dropwise. The resultant solution was then heated to reflux for three hours. The solution was then cooled to room temperature and methanol (100ml) added to quench the reaction. The volume was then removed under vacuum to give a sticky solid. Diethyl ether (300ml) was then added and the ether extract removed by cannula. The ether extract was then dried under vacuum to give a yellow sticky solid. Yield 23.7 g, 52.3 %. FW = 220.40.

#### Preparation of Bis-(3,5-dimethyl-1-tert-butyladamantyl)phosphinic chloride, $(\text{Me}_2\text{Bu}^t\text{Ad})_2\text{P}(\text{O})\text{Cl}$

Phosphorus trichloride ( $46.9\text{ cm}^3$ , 538.0 mmol) was added rapidly to a combination of aluminium chloride (14.3 g, 107.6mmol) and 3,5-dimethyl-tert-butyladamantane (23.7 g, 107.6mmol) affording a tan suspension. The reaction was heated to reflux ( $\sim 80^\circ\text{C}$ ). After 10 minutes, a yellow-orange suspension was formed. The reaction was refluxed for a total of 16 h. The excess  $\text{PCl}_3$  was removed under vacuum to give an orange / red solid. Chloroform ( $250\text{ cm}^3$ ) was added yielding an orange suspension, which was cooled to  $0^\circ\text{C}$ . Water ( $100\text{ cm}^3$ ) was added slowly: initially the suspension viscosity increased, but on full addition of water the viscosity lessened. The suspension was then filtered through a frit to remove the orange solid impurity. The filtrate consisted of a two phase (water / chloroform) system. The lower phase (chloroform) was collected by separation and dried over  $\text{Na}_2\text{SO}_4$ . The organic layer was then filtered and the filtrate dried under vacuum to give a sticky yellow solid. Yield 27.0 g, 49.2 %. FW = 458.19.

#### Preparation of $(\text{Me}_2\text{Bu}^t\text{Ad})_2\text{PH}$ .

$\text{LiAlH}_4$  (1M in THF, 106mmol, 106ml) was added over 90 minutes to a chilled ( $-10^\circ\text{C}$ ) solution of  $(\text{Me}_2\text{Bu}^t\text{Ad})_2\text{P}(\text{O})\text{Cl}$  (27.0 g, 53 mmol) (13) in THF ( $100\text{ cm}^3$ ). The reaction was left to warm to ambient temperature then stirred for 16 h. The solution was then cooled to  $0^\circ\text{C}$  and HCl (10ml conc.) in water (10ml, degassed) was added slowly. The upper phase was removed via flat ended cannula, dried over  $\text{Na}_2\text{SO}_4$  and



filtered using a cannula. The volatiles were removed *in-vacuo* affording the product as an off-white sticky solid. Yield 17.65 g, 70.8 %.  $^{31}\text{P}$  NMR:  $\delta$  = 14.5 ppm, 98 % pure. FW = 470.75.

#### Synthesis of 1,2-bis(di-1-(3,5-dimethyl-7-*tert*-butyladamantyl)phosphanomethyl)ferrocene, 2d.

Into a 500ml Schlenk flask was added the phosphane,  $(\text{Me}_2\text{Bu}^t\text{Ad})_2\text{PH}$ , (17.7g, 37.5mmol) and the 1,2-bis-dimethylaminomethylferrocene, (*damf*), **5**, (5.62g, 18.8mmol) (**4**) in a glovebox. This was then suspended in a mixture of acetic acid: acetic anhydride (180: 18ml). The suspension was then heated to 130°C and kept at this temperature for 90 minutes. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue washed with ethanol (50ml). The ethanol washings were then removed by cannula and the residue dried under vacuum. This gave a free-flowing yellow/orange solid which was isolated in the glovebox. Yield 13.3 g, 61 %.  $^{31}\text{P}$  NMR:  $\delta$  = 23.5 ppm, 90 % pure. FW = 1151.56. 3.22

#### Preparation of *tert*-butyladamantane. Bu<sup>t</sup>Ad

Into a 500ml Schlenk flask was added 1-bromoadamantane (32.9g, 153.0mmol), this was then dissolved in THF (100ml). To this was added *tert*-butyl lithium (1.7M in pentane, 100ml, 170mmol) dropwise. The resultant solution was then heated to reflux for three hours. The solution was then cooled to room temperature and methanol (100ml) added to quench the reaction. The volume was then removed under vacuum to give a sticky solid. Pentane (300ml) was then added, and the resultant suspension filtered. The filtrate was then removed under vacuum to give a white solid. Yield 19.0 g, 64.7%. FW=192.34.

#### Preparation of Bis-(1-*tert*-butyladamantyl)phosphinic chloride, $(\text{Bu}^t\text{Ad})_2\text{P}(\text{O})\text{Cl}$

Phosphorous trichloride (43ml, 316.8mmol) was added rapidly to a combination of aluminium chloride (13.2g, 99.0mmol) and *tert*-butyladamantane (19.0g, 99.0 mmol) affording a tan suspension. The reaction was heated to reflux (~80°C). After 10 mins, a yellow-orange suspension was formed. The reaction was refluxed for a total of 16 h. The excess  $\text{PCl}_3$  was removed under vacuum to give an orange / red solid. Chloroform (250 cm<sup>3</sup>) was added yielding an orange suspension, which was cooled to 0 °C. Water (100 cm<sup>3</sup>) was added slowly: initially the suspension viscosity increased, but on full addition of water the viscosity lessened. The suspension was then filtered through a frit to remove the orange solid impurity. The filtrate consisted of a two phase (water / chloroform) system. The lower phase (chloroform) was collected by separation and dried over  $\text{Na}_2\text{SO}_4$ . The organic layer was then filtered, and the filtrate dried under vacuum to give an off-white waxy solid. Yield 22.1 g, 96 %.  $^{31}\text{P}$  NMR:  $\delta$  = 87.1 ppm, 95 % pure. FW = 465.09.

#### Preparation of Bis-(1-*tert*-butyladamantyl)phosphane, $(\text{Bu}^t\text{Ad})_2\text{PH}$ .

$\text{LiAlH}_4$  (1M in THF, 125mmol, 125ml) was added over 90 minutes to a chilled (-10 °C) solution of  $(\text{Bu}^t\text{Ad})_2\text{P}(\text{O})\text{Cl}$  (23.8 g, 51 mmol) in THF (100cm<sup>3</sup>). The reaction was left to warm to ambient temperature and was then stirred for 16 h. The solution was then cooled to 0 °C and HCl (15ml conc.) in water (15ml, degassed) was added slowly. The upper phase was removed via flat ended cannula, dried over  $\text{Na}_2\text{SO}_4$  and filtered using a cannula. The volatiles were removed *in-vacuo* affording the product as an off-white solid. Yield 15.7 g, 74.1 %.  $^{31}\text{P}$  NMR:  $\delta$  = 18.2 ppm, 95 % pure. FW = 414.65

#### Synthesis of 1,2-bis(di-1-(5-*tert*-butyladamantyl)phosphanomethyl)ferrocene, 2e.

Into a 500ml Schlenk flask was added bis-(1-*tert*-butyladamantyl)phosphane,  $(\text{Bu}^t\text{Ad})_2\text{PH}$  (15.7g, 37.8mmol) (**10**) and the 1,2-bis-dimethylaminomethylferrocene, (*damf*), **5**, (5.64g, 18.3mmol) (**1**) in the glovebox.. This was then suspended in a mixture of acetic acid: acetic anhydride (160ml: 16ml). The suspension was then heated to 130°C and kept at this temperature for 90 minutes. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue washed with ethanol (50ml). The ethanol washings were then removed by cannula and the residue dried under vacuum. This gave a free- flowing yellow/orange solid which was isolated in the glovebox. Yield 16.4 g, 70 %.  $^{31}\text{P}$  NMR:  $\delta$  = 21.3 ppm, 95 % pure. FW = 1037.33. 3.12

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**Preparation of Dicongressanylphosphinic chloride, Cong<sub>2</sub>P(O)Cl** (congressane = diadamantane)

Phosphorus trichloride (116ml, 1.33 mol) was added rapidly to a combination of aluminium chloride (35.5 g, 0.27 mol) and di-adamantane (50.0g, 0.27 mol) affording a tan suspension. The reaction was heated to reflux (~80°C). After 10 mins, a yellow-orange suspension was formed. The reaction was refluxed for a total of 16 h. The excess PCl<sub>3</sub> was removed under vacuum to give an orange / red solid. Chloroform (250 cm<sup>3</sup>) was added yielding an orange suspension, which was cooled to 0 °C. Water (100 cm<sup>3</sup>) was added slowly: initially the suspension viscosity increased, but on full addition of water the viscosity lessened. The suspension was then filtered through a frit to remove the orange solid impurity. The filtrate consisted of a two phase (water / chloroform) system. The lower phase (chloroform) was collected by separation and dried over Na<sub>2</sub>SO<sub>4</sub>. The organic layer was then filtered and the filtrate dried under vacuum to give an off-white powder. Yield 61.1 g, 99%. <sup>31</sup>P NMR: δ = 87.2 ppm, 75 % pure. FW = 457.02.

**Preparation of Dicongressanylphosphosphine, Cong<sub>2</sub>PH.**

LiAlH<sub>4</sub> (1M in THF, 250mmol, 250ml) was added over 90 minutes to a chilled (-10 °C) solution of (Cong)<sub>2</sub>P(O)Cl (61.1 g, 134mmol) in THF (100cm<sup>3</sup>). The reaction was allowed to warm to ambient temperature then stirred for 16 h. The solution was then cooled to 0 °C and HCl (15ml conc.) in water (15ml, degassed) was added slowly. This gave a two-phase mixture with a large volume of white solid in the interphase. The upper phase was removed via flat ended cannula. The solid in the interphase was then extracted with THF (3\*250ml). The combined THF extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered via cannula. The volatiles were removed in-vacuo affording the product as an off-white solid. Yield 26.0 g, 48 %. <sup>31</sup>P NMR: δ = 13.5 ppm. FW = 406.58.

**Preparation of the 1,2-bis(di-1-congressylphosphanomethyl)ferrocene, 2f.**

Into a 500ml Schlenk flask was added dicongressanylphosphosphine, Cong<sub>2</sub>PH, (10.0g, 24.6mmol) and the 1,2-bis-dimethylaminomethylferrocene, (*damf*), **5**, (3.69g, 12.3mmol) (**4**) in the glovebox. This was then suspended in a mixture of acetic acid : acetic anhydride ( 300ml : 30ml ). The suspension was then heated to 150°C until the solid had fully dissolved. The solution was then cooled to 140°C and stirred for 5 hours. The resultant solution was then allowed to cool to ambient temperature which gave the precipitation of some yellow solid. The solution was then filtered, and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue washed with ethanol (50ml). The ethanol washings were then removed by cannula and the residue dried under vacuum. This gave a free-flowing yellow/orange solid which was isolated in the glovebox. Yield 10.1 g, 80.4 %. <sup>31</sup>P NMR: δ = 17.9 ppm, 88 % pure. FW = 1021.20.

**Preparation of the 1,2-bis(dicongressylphosphanomethyl)ferrocene-bis-methanesulfonate salt, 2f.sulfonate.**

Into a 500ml Schlenk flask was added the phosphane (8.6g, 8.4mmol) (**5E**) and this was suspended in methanol (50ml). Methane sulfonic acid (1.1ml, 16.8mmol) was added. This gave a red / orange solution with some insoluble material. The solution was then filtered and the filtrate concentrated under vacuum. Diethyl ether (30ml) was then added and the solution placed in the freezer overnight. This gave the formation of an orange / yellow crystalline solid. The solution was removed by cannula and the solid dried under vacuum. The solid was isolated in the glovebox. Yield 4.7 g, 46 %. <sup>31</sup>P NMR: δ = 33 ppm, 99.9 % pure. FW = 1213.41.

**Synthesis of 1,2-bis(di-1-(3,5-dimethyladamantyl)phosphanomethyl)-1'-(trimethylsilyl)ferrocene, 2g.**

The ferrocenyldiamine, **17**, (1.00g, 2.68mmol) was dissolved in acetic acid: acetic anhydride (18ml: 2ml) which had been degassed with nitrogen for 10 minutes. The diamine solution was then transferred by cannula into a 500ml Schlenk flask containing the phosphane (**B**) (1.98g, 5.36mmol). The resultant suspension was then heated to 130 ° C for five hours. The solution was then cooled to room temperature and the solvent removed under vacuum. The residue was suspended in methanol (50ml) and stirred for 20 minutes. The methanol was then removed under vacuum. The residue was then washed with ethanol (50ml) and the ethanol washings removed by cannula. The remaining solid was then dried under vacuum and isolated in the glovebox as a yellow / orange solid. Yield = 1.10g, 41%. 86% pure. <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 161.9MHz, δ); 18.7ppm

**Synthesis of 1,2-bis(di-1-(3,5-dimethyladamantyl)phosphanomethyl)-1'-(triphenylsilyl)ferrocene, 2h.**

The ferrocenyldiamine, **19**, (0.50g, 0.90mmol) was dissolved in acetic acid: acetic anhydride (18ml: 2ml) which had been degassed with nitrogen for 10 minutes. The diamine solution was then transferred by cannula into a 500ml schlenk flask containing the phosphane (B) (0.64g, 1.80mmol). The resultant suspension was then heated to 130 ° C for five hours. The solution was then cooled to room temperature and the solvent removed under vacuum. The residue was suspended in methanol (50ml) and stirred for 20 minutes. The methanol was then removed under vacuum. The residue was then washed with ethanol (50ml) and the ethanol washings removed by cannula. The remaining solid was then dried under vacuum and isolated in the glovebox as a yellow / orange solid. Yield = 0.20g, 19%. 66% pure.  $^{31}\text{P}$  { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ , 161.9MHz,  $\delta$ ); 18.5 (s).

**Preparation of 1,2-bis(1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantyl)phosphanomethyl)ferrocene, 2i.**

Into a 500ml Schlenk flask was added 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane (10.0g, 46.3mmol) and the diamine 1,2-bis-dimethylaminomethylferrocene (6.49g, 23.1mmol) (**1**) in the glovebox. This was then suspended in a mixture of acetic acid: acetic anhydride (100ml: 10ml). The suspension was then heated to 130°C and kept at this temperature for three hours. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue dissolved in ethanol (100ml), some warming was required. The ethanol solution was then placed in the freezer at -20°C and left overnight. This gave red/orange crystals. The ethanol solution was removed by cannula and the crystals dried under vacuum. These crystals were then isolated in the glovebox. Yield 5.1 g, 34 %.  $^{31}\text{P}$  NMR:  $\delta$  = -27.4, -29.0, -33.9 ppm, 99 % pure. FW = 640.46.

**Preparation of 1,2-bis-( $\alpha,\alpha$ -(P-(2,2,6,6-tetramethylphosphano-4-one))methyl)ferrocene, 2j.**

2,6-Dimethyl-2,5-heptadiene-4-one (14.60g, 0.106mol) was added to 1,2-bis(diphosphanomethyl)ferrocene (14.7g, 0.053mol) and the reaction mixture was heated to 120°C for 20 hrs. The reaction mixture was cooled to ambient temperature and the crude product was removed by filtration and subsequently washed with pentane (20ml) and dried under vacuum to give the title product as a yellow orange solid (24.9g, 85%).  $^1\text{H}$  NMR (250MHz),  $\delta$ : 4.32(1H, br m) 4.08(5H, s), 4.02 (1H br m), 3.94(1H, br m) 2.84(4H, br), 1.80-2.50(8H), 1.05-1.40(24).  $^{31}\text{P}$  NMR:  $\delta$ , 4.15 (d). Calcd. C, 64.26%, H, 7.88; Found C, 65.03%, H, 7.94.

**Notes:** It had been previously reported by Schleyer and co. workers<sup>52</sup> that the reaction of methyl Grignard reagents with bromoadamantane did not give 1-methyl-adamantane in high yield. Thus, another methodology was needed for its synthesis. The method that was employed was a derivative of that reported by Henkel<sup>53</sup> et.al. in which 1-adamantyl carboxylic acid was reduced to 1-adamantyl methanol, which was converted to the tosylate and then reduced with lithium aluminium hydride to the methyl complex. The mono-methyl complex was then converted to the phosphinic chloride and reduced to the secondary phosphane. The secondary phosphane was then reacted with (**4**) to give a bidentate phosphane. The synthesis of the bis(congressanylphosphano) ferrocenyl complex **2f** suffered from a number of problems relating to the bulk and solubility of the congressane ligand. The reaction of the congressane with phosphorus chloride and aluminium chloride gave after work-up under standard reaction conditions only 75% of the desired  $\text{R}_2\text{P}(\text{O})\text{Cl}$  product (the other 25% identified as the  $\text{RP}(\text{O})\text{Cl}_2$  complex from the  $^{31}\text{P}$  NMR). The reduction of the  $\text{R}_2\text{P}(\text{O})\text{Cl}$  to the  $\text{R}_2\text{PH}$  complex was limited by the poor solubility of the secondary phosphane in THF, giving an isolated yield of the secondary phosphane of only 45%.

**Additional ferrocenyl phosphines not used directly in catalysis experiments. Preparation of precursors used in the synthesis and 1,2-bis(di-1-(5-methyladamantyl)phosphanomethyl)ferrocene, 2k****Preparation of  $\text{AdCH}_2\text{OH}$** 

1-adamantyl carboxylic acid (35.0g, 194.2mmol) was dissolved in THF (100ml) and to this added lithium aluminium hydride (1M in THF, 240ml, 240mmol) dropwise over 90 minutes. The resultant white suspension was then heated to reflux for three hours before being cooled to room temperature and stirred overnight. The suspension was cooled to 0°C and HCl (20ml, conc.) was added dropwise. This gave gas evolution and a white precipitate formation. The precipitate was extracted with diethyl ether (3\*300ml) and the combined organic

extracts dried over  $\text{Na}_2\text{SO}_4$ . The organic extracts were then filtered and dried under vacuum. This gave a white crystalline solid. Yield = 25.5 g, 79.2%. FW=166.20.  $^1\text{H}$  NMR showed similar resonance to authentic sample of  $\text{AdCH}_2\text{OH}$  from Aldrich.

#### Preparation of $\text{AdCH}_2\text{OTs}$

1-Adamantyl methanol (25.5g, 153.6mmol) (16) was dissolved in pyridine (100ml) and cooled to  $0^\circ\text{C}$ . To this was added the p-toluene sulfonic chloride (34.6g, 181.5mmol) in pyridine (80ml) dropwise over 90 minutes. The solution was then stirred at this temperature for two hours which gave a large volume of white precipitate. The suspension was then allowed to warm to room temperature and stirred overnight. Into a 1L flask was added HCl (40ml, conc.) and water (360ml). This solution was then cooled to  $0^\circ\text{C}$  and the pyridine tosylate suspension added to it. The resultant clear solution was then extracted with diethyl ether (150ml) and the organic extract collected by separation. This was repeated three further times. The combined ether extracts were washed with a 10% solution of HCl which has been cooled to  $0^\circ\text{C}$ . The ether extracts were then washed with water (5\*100ml). The ether extracts were then dried over  $\text{Na}_2\text{SO}_4$  and filtered. The filtrate was then dried under vacuum to give a white solid. Yield = 43.8 g, 88.2%. FW=304.45.

#### Preparation of MeAd

The  $\text{AdCH}_2\text{OTs}$  (43.4g, 135mmol) (17) was suspended in THF (100ml) and cooled to  $0^\circ\text{C}$ , to this added lithium aluminium hydride (1M in THF, 150ml, 150mmol) dropwise over 90 minutes. The resultant solution was then heated to reflux for 18 hours. The white suspension formed was then cooled to  $0^\circ\text{C}$ . Water (150ml) was added dropwise. The product was extracted with diethyl ether (2X200ml) and the ether extracts collected by separation. The combined ether extracts were dried over  $\text{Na}_2\text{SO}_4$  and then filtered. The filtrate was then dried under vacuum. To the aqueous layer was then added hexane (400ml) and the hexane extract collected by separation. The hexane extract was then washed with water (2\*250ml) before being dried over  $\text{Na}_2\text{SO}_4$ . The hexane extract was then filtered and added to the diethyl ether extracted products and the hexane solvent removed under vacuum. This gave a sticky white solid. Yield = 7.1g, 35.0%. FW=150.26.

#### Preparation of $(\text{MeAd})_2\text{P(O)Cl}$

Phosphorus trichloride ( $20.6\text{ cm}^3$ , 236.6 mmol) was added rapidly to a combination of aluminium chloride (6.3 g, 47.3 mmol) and 1-methyladamantane (7.1g, 47.3mmol) (18) affording a tan suspension. The reaction was heated to reflux ( $\sim 80^\circ\text{C}$ ). After 10 mins, a yellow-orange suspension was formed. The reaction was refluxed for a total of 16 h. The excess  $\text{PCl}_3$  was removed under vacuum to give an orange / red solid. Chloroform ( $250\text{ cm}^3$ ) was added yielding an orange suspension, which was cooled to  $0^\circ\text{C}$ . Water ( $100\text{ cm}^3$ ) was added slowly: initially the suspension viscosity increased, but on full addition of water the viscosity lessened. The suspension was then filtered through a frit to remove the orange solid impurity. The filtrate consisted of a two phase (water / chloroform) system. The lower phase (chloroform) was collected by separation and dried over  $\text{Na}_2\text{SO}_4$ . The organic layer was then filtered and the filtrate dried under vacuum to give an off-white solid. Yield 8.5 g, 46.5 %.  $^{31}\text{P}$  NMR:  $\delta = 87.1\text{ ppm}$ , 95+ % pure. FW = 380.90

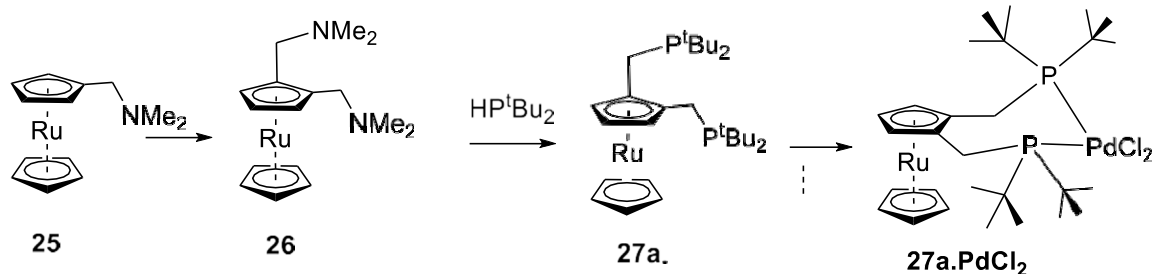
#### Preparation of $(\text{MeAd})_2\text{PH}$

$\text{LiAlH}_4$  (1M in THF, 44mmol, 44ml) was added over 90 minutes to a chilled ( $-10^\circ\text{C}$ ) solution of  $(1\text{-Ad})_2\text{P(O)Cl}$  (8.5g, 22 mmol) (19) in THF ( $50\text{ cm}^3$ ). The reaction was allowed to warm to room temperature and then stirred for 16 h. The solution was then cooled to  $0^\circ\text{C}$  and HCl (5ml conc.) in water (5ml, degassed) was added slowly. The upper phase was removed via flat ended cannula, dried over  $\text{Na}_2\text{SO}_4$  and filtered via cannula. The volatiles were removed *in-vacuo* affording the product an off-white solid, isolated in the glovebox. Yield 5.69 g, 78.2 %.  $^{31}\text{P}$  NMR:  $\delta = 16.2\text{ ppm}$ , 90 % pure. FW = 330.49.

#### Preparation of 1,2-bis(di-1-(5-methyladamantyl)phosphanomethyl)ferrocene, 2k

Into a 500ml Schlenk flask was added the phosphane,  $(\text{MeAd})_2\text{PH}$ , (5.69g, 17.22mmol) (20) and the 1,2-bis-dimethylaminomethylferrocene, (*damf*), **5**, (2.58g, 8.61mmol) (**4**) in the glovebox. This was then suspended in a mixture of acetic acid : acetic anhydride ( 60ml : 6ml ) which had been degassed for 30 minutes with  $\text{N}_2$ . The suspension was then heated to  $130^\circ\text{C}$  and kept at this temperature for 90minutes. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid

was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue washed with ethanol (50ml). The ethanol washings were then removed by cannula and the residue dried under vacuum. This gave a free-flowing orange solid which was isolated in the glovebox. Yield 3.1 g, 41.4%.  $^{31}\text{P}$  NMR:  $\delta = 19.5\text{ppm}$ , 90 % pure. FW = 869.00.



#### Synthesis of 1,2-bis(di-1-(3,5-dimethyladamantyl)phosphanomethyl)ruthenocene, **27b**.

Into a 500ml Schlenk flask was added the phosphane (3.32g, 9.2mmol) (**6**) and the diamine **26** (1.60g, 4.6mmol) (**1b**) in the glovebox. This was then suspended in a mixture of acetic acid: acetic anhydride (30ml: 5ml). The suspension was then heated to  $130^\circ\text{C}$  and kept at this temperature for 5 hours. The resultant solution was then allowed to cool to ambient temperature and the solvent removed under vacuum. The resultant sticky solid was suspended in methanol (50ml) and stirred for 30 minutes. The methanol was then removed under vacuum and the residue washed with ethanol (20ml). The ethanol washings were then removed by cannula and the residue dried under vacuum. This gave a free flowing off white solid which was isolated in the glovebox. Yield 2.55 g, 57%.  $^{31}\text{P}$  NMR:  $\delta = 19.2\text{ ppm}$ , 91 % pure. FW = 970.34.

#### Mo complexes (crystallographic data will be published separately)

The complex  $[\text{MoI}_2(\text{CO})_3(\text{NCCH}_3)_2]$  was prepared following literature methods. All other chemicals were obtained from commercial sources and used without further purification, unless otherwise described. Column chromatography was carried out using neutral alumina (150 mesh,  $158\text{\AA}$ , Brockman Grade 1) or silica gel (Kieselgel 230 – 400 mesh) support. Dichloromethane was dried by reflux over calcium hydride. Chloroform was dried over sodium wire, using benzophenone indicator. Acetonitrile was dried by stirring over potassium carbonate (24h) followed by storage over  $3\text{\AA}$  sieve (24h). Acetic acid was dried by distillation (B.P.  $118^\circ\text{C}$ ) with 3% acetic anhydride w/v. Methanol was dried by reflux over Mg turnings with  $\text{I}_2$ , and then stood over  $3\text{\AA}$  sieve (24h). THF was dried by distillation (B.P.  $66^\circ\text{C}$ ) over sodium benzophenone.

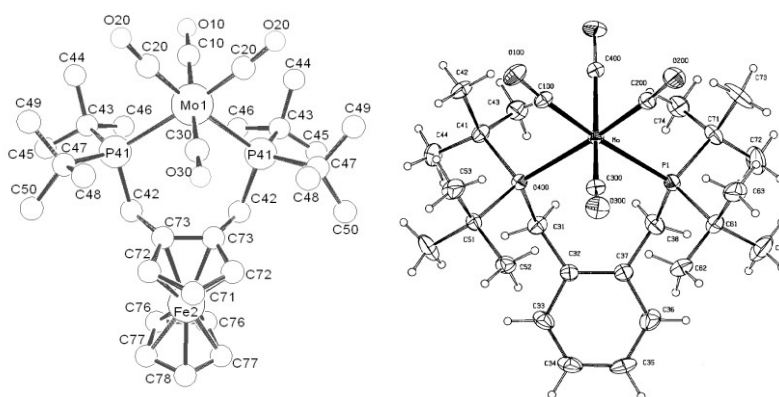
#### Preparation of $[\text{Mo}(\text{CO})_4(\text{P}^t\text{P})]$ ( $\text{P}^t\text{P} = \text{bis-(1,2-di-tert-butylphosphanomethyl)ferrocene}$ , *butphos*)

To  $[\text{Mo}(\text{CO})_4(\text{pip})_2]^{54}$  (0.112g, 0.318 mmol) in  $\text{CH}_2\text{Cl}_2$  ( $10\text{ cm}^3$ ) under argon at RT, was added *bis*-1,2-*tert*-butylphosphinomethyl ferrocene (0.16g, 0.318 mmol) and the reaction stirred for 3 h. The supernatant was removed, and yellow precipitate washed with cold dichloromethane then dried *in vacuo* to furnish the bright yellow powder product. A crystal suitable for X-ray analysis was obtained from cooling the supernatant to  $-11^\circ\text{C}$  for 1 month.

F.W.  $710.472\text{ gmol}^{-1}$  Formula:  $\text{C}_{32}\text{H}_{48}\text{FeMoO}_4\text{P}_2$  Yield: 0.15 g (65 %),  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$ 1.33 (18H, d, 11.60 Hz),  $\delta$ 1.43 (18H, d, 10.68 Hz),  $\delta$ 2.78 (2 H, d, 14.65 Hz),  $\delta$ 3.27 (2H, dd,  $J_{\text{HH}}$  14.65 Hz,  $J_{\text{H31P}}$  10.53 Hz),  $\delta$ 4.01 (5 H, s),  $\delta$ 4.02 (1H, m),  $\delta$ 4.02 (2H, d, 2.44 Hz).  $^{13}\text{C}$  NMR (62 MHz,  $\text{CDCl}_3$ ):  $\delta$ 24.35,  $\delta$ 29.67,  $\delta$ 30.67,  $\delta$ 31.67,  $\delta$ 36.48,  $\delta$ 37.16,  $\delta$ 53.42,  $\delta$ 65.56,  $\delta$ 69.84,  $\delta$ 70.34,  $\delta$ 84.06.  $^{31}\text{P}$  NMR (102 MHz,  $\text{CDCl}_3$ ):  $\delta$ 59.11(s), Infrared spectrum: ( $\text{CH}_2\text{Cl}_2$  / thin film NaCl plates)  $2007.3\text{ cm}^{-1}$ ,  $1903.0\text{ cm}^{-1}$ ,  $1882.6\text{ cm}^{-1}$ ,  $1850.2\text{ cm}^{-1}$ . Elemental analysis:  $\text{C}_{32}\text{H}_{48}\text{FeMoO}_4\text{P}_2$  (includes 0.25 eq  $\text{CH}_2\text{Cl}_2$ ) C, 52.9 %, H, 6.7 % Found: C, 53.0 %, H, 6.9 %

### Preparation of $[\text{Mo}(\text{CO})_4(\eta^2\text{-DtBPMB})](\text{DtBPMB} = 1,2\text{-di-}t\text{-butylphosphanomethyl benzene})$

To  $[\text{Mo}(\text{CO})_4(\text{pip})_2]$  (pip = piperidine) (0.50g, 1.32 mmol) in  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ) and under argon, was added 1,2-bis-[(di-*tert*-butyl-phosphanyl)-methyl] benzene (0.53g, 1.32 mmol) and the reaction refluxed for 3 ½ hours in an oil bath at 55° ~ 60°C. The resulting red / brown solution was filtered, and the solvent removed *in vacuo* to leave golden brown solid. This was washed with cold ethanol (3 x 10  $\text{cm}^3$ ). The crude product was then redissolved in refluxing dichloromethane (<1 $\text{cm}^3$ ) and cooled to -17°C. The resulting light brown powder was washed with diethyl ether and dried for several hours *in vacuo*. A small quantity was layered in  $\text{CH}_2\text{Cl}_2$  / diethyl ether (1: 5 ratio) and crystals suitable for X-ray crystallography analysis were obtained after 3 hours at -17°C. F.W. 602.54  $\text{gmol}^{-1}$  Formula:  $\text{C}_{28}\text{H}_{44}\text{MoO}_4\text{P}_2$  Yield: 0.67 g (84 %),  $^1\text{H}$  NMR:  $\delta$ 1.424 (d, 36H,  $J_{1\text{H}-31\text{P}}$  11.902 Hz),  $\delta$ 3.322 (d, 4H,  $J_{1\text{H}-31\text{P}}$  6.409 Hz),  $\delta$ 7.08 (m, 2H),  $\delta$ 7.30 (m, 2H)  $^{13}\text{C}$  NMR:  $\delta$ 29.84,  $\delta$ 31.16,  $\delta$ 37.48,  $\delta$ 37.55,  $\delta$ 37.59,  $\delta$ 126.20,  $\delta$ 133.16,  $\delta$ 136.82,  $\delta$ 212.90,  $\delta$ 214.89.  $^{31}\text{P}$  NMR:  $\delta$ 8.04 (s), satellites  $\delta$ 8.24,  $\delta$ 7.82 (107.575 Hz). Infrared spectrum ( $\text{CHCl}_3$  / thin film NaCl plates)  $\nu(\text{C}\equiv\text{O})$ : 2007.4  $\text{cm}^{-1}$ , 1901.4  $\text{cm}^{-1}$ , 1879.8  $\text{cm}^{-1}$  (+ low frequency shoulder). Elemental analysis:  $\text{C}_{28}\text{H}_{44}\text{MoO}_4\text{P}_2$ . Calcd for  $\text{C}_{28}\text{H}_{44}\text{MoO}_4\text{P}_2$ , C, 55.8 %, H, 7.4 %, Found, C, 56.2 %, H, 7.3 %



Comparison of Structures of  $\text{Mo}(\text{CO})_4$ -complexes of *but phos* 5 and *alpha* ligand.

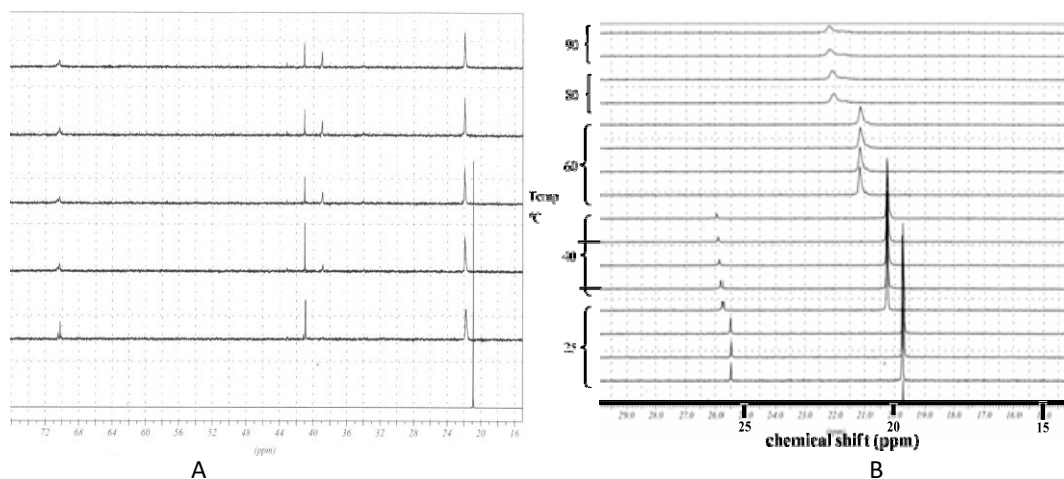
- S1. J. R Goerlich, R. Schmutzler, *Phosphorus, Sulphur and Silicon*, **1995**, 102, 211.
- S2. E. Osawa, Z. Majerski, P.Von R. Schleyer, *J. Org. Chem.*, **1971**, 36, 205.
- S3. J.G. Henkel, J.T. Hane, G. Gianutsos, *J. Med. Chem.* **1982**, 25, 51.
- S4. E.M. Armstrong, P.K. Baker, M.G.B. Drew, *Organometallics*, **1988**, 7, 319.

### 1',2',3',4',5'-Penta-phenyl(1-diphenylphosphino)ferrocene, 10

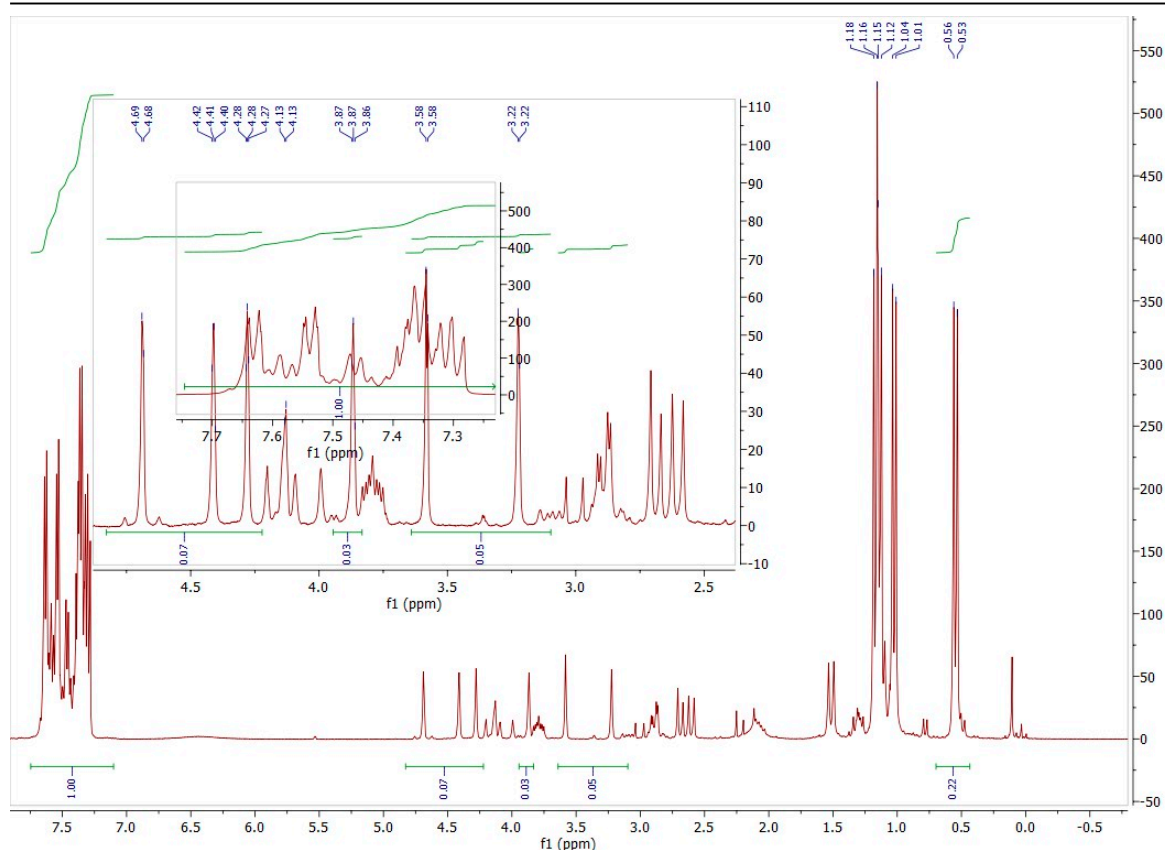
1',2',3',4',5'-Penta-phenyl(diphenylphosphino)ferrocene, **10** was prepared using the method of Hardwig et al, (see ref 58, paper) without modification except diphenylphosphinoferrocene was the precursor compound in chlorobenzene. The red product was purified by flash chromatography on silica gel in 22% yield. Structural data was provided by Peter Horton.



**Figure S5:** Sublimation of compound **5** as a means of purification.



**Figure S6:**  $^{31}\text{P}$  NMR spectra (original data) used to optimize reaction conditions for the preparation of ferrocenylmethylphosphanes from the ferrocenylmethylamine precursors. A:  $^{31}\text{P}$  NMR spectra of product (*ca* 22ppm) formation at set times from the lower to upper spectra: 0 min, 23 mins, 1h 23min, 2h 23min, 2h 57 mins, 3h. 23min (constant temperature of 80°C), showing the formation of by-products and oxidised products. B: variable temperature spectrum showing the formation of the product **2a** from **5** showing the presence of reaction intermediates which grow then disappear.



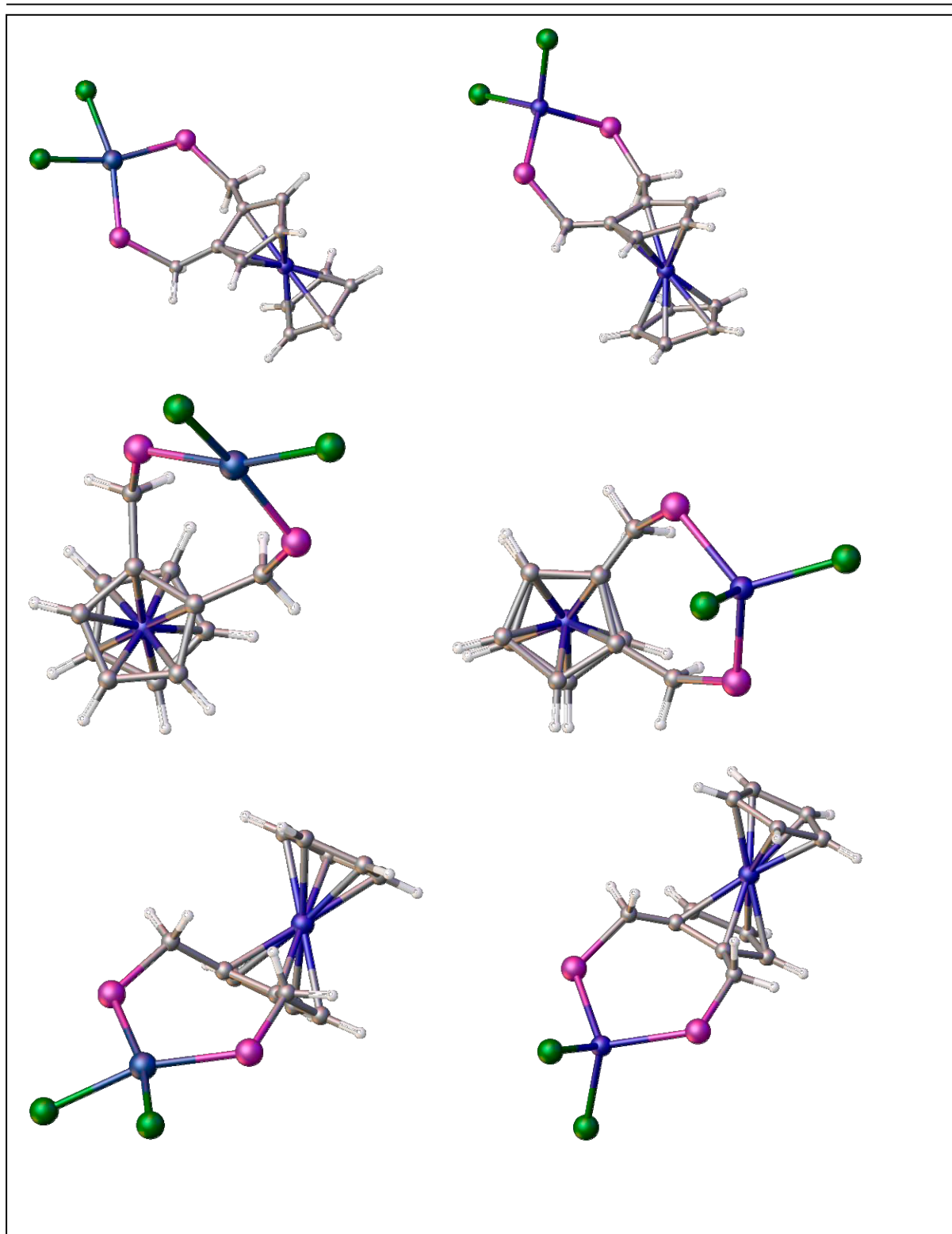
**Figure S7:** An example of ligand used after 10 years storage. NMR spectrum of bis-triphenylsilyl-substituted butphos. (note there is a little oxidation of the phosphine (ca 10%).

### Standard Catalysis Technical Details

The catalytic experiments were undertaken using a Batch Hastelloy autoclave system in the semi-technical building at the Wilton industrial site by Lucite International. The autoclave was pressure tested with nitrogen overnight. Standard reactions were carried out as follows:

The Pd(OAc)<sub>2</sub> (22mg, 0.1 mmol) and the respective phosphine ligand (0.5 mmol) were weighed out in an inert atmosphere glove box into a 500ml 3-neck round bottom flask. On removal, 300ml of degassed MeOH was added and the mixture stirred for 1 hour. To this solution methanesulphonic acid (140μl, 2 mmol) was added and the weight of the catalyst solution recorded. The autoclave was charged with the solution and heated to 100°C with stirring (3.0 bar vapour pressure) at 1000 rpm. The reaction was started by the introduction of CO/ethylene (1:1) gaseous mixture to the autoclave to a total pressure of 13.0 bars. This resulted in a 1:1 ratio of ethylene to CO with a total pressure of gasses of 10 bars above solvent vapour pressure. The temperature and pressure were maintained for 3 hours during which period these values were recorded. At the end of 3 hours the gases were isolated and the unit cooled to room temperature. The depressurized unit was emptied and the final weight of the MeP solution produced was taken.





**Figure S8:** Comparison of cutaways showing left ( $\text{PdCl}_2$ ) coordination and right ( $\text{NiCl}_2$ ) coordination to ferrocene-bis-methylenephosphines.