Synthesis, Structure, Theoretical Studies and Ligand Exchange Reactions of Monomeric, T-shaped Arylpalladium(II) Halide Complexes with an Additional, Weak Agostic Interaction

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Supporting Information

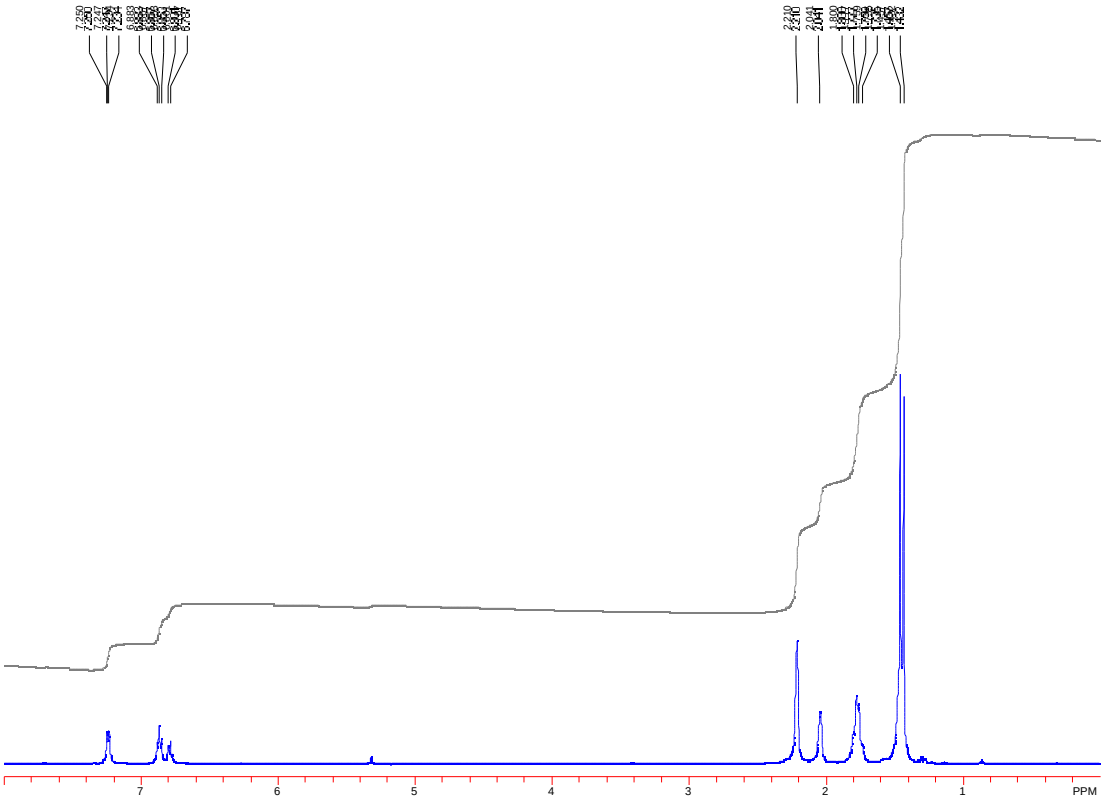

Figure 1. ^{1}H NMR spectrum of **3a**.

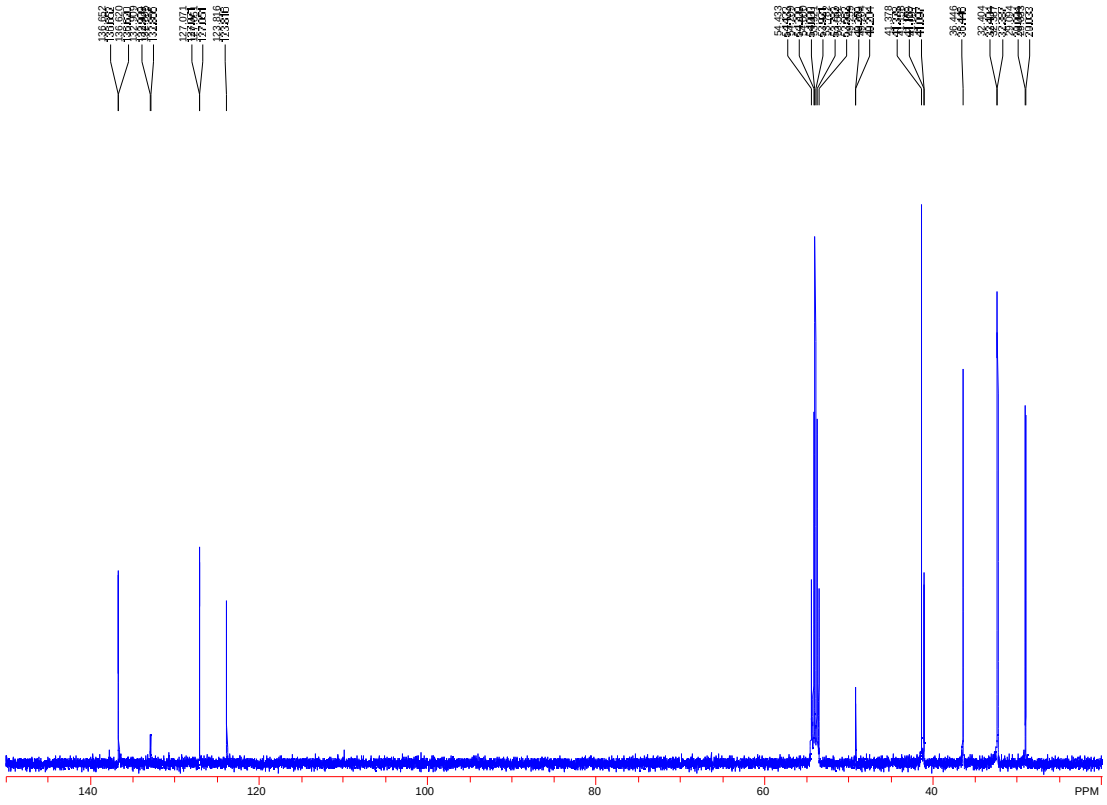

Figure 2. ^{13}C NMR spectrum of **3a**.

X-ray data for 5a.

Table 1. Crystal data and structure refinement for **5a**.

Identification code	hart10	
Empirical formula	C25 H38 F3 O3 P Pd S	
Formula weight	612.98	
Temperature	223(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	P2(1)/c	
	a = 9.933(9) Å	α= 90°.
	b = 16.926(16) Å	β= 105.77(2)°.
	c = 16.484(15) Å	γ= 90°.
Volume	2667(4) $Å^3$	
Z	4	
Density (calculated)	1.527 Mg/m^3	
Absorption coefficient	0.880 mm^{-1}	
F(000)	1264	
Crystal size	0.30 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.76 to 28.27°.	
Index ranges	-13<=h<=12, -22<=k<=22, -21<=l<=21	
Reflections collected	19314	
Independent reflections	6350 [R(int) = 0.0352]	
Completeness to theta = 28.27∞	95.9 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6350 / 0 / 308	
Goodness-of-fit on F^2	1.156	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0902	
R indices (all data)	R1 = 0.0408, wR2 = 0.0933	
Largest diff. peak and hole	0.843 and -0.347 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	9970(1)	1357(1)	906(1)	29(1)
S(1)	11690(1)	605(1)	2657(1)	40(1)
P(1)	9015(1)	2392(1)	93(1)	29(1)
F(1)	13975(2)	-120(2)	2606(2)	101(1)
F(2)	14167(2)	607(2)	3689(2)	129(1)
F(3)	14032(3)	1114(2)	2459(2)	126(1)
O(1)	11242(2)	500(1)	1745(1)	41(1)
O(2)	11366(3)	-35(2)	3116(2)	95(1)
O(3)	11454(3)	1384(1)	2913(2)	80(1)
C(1)	8341(2)	653(1)	722(1)	32(1)
C(2)	8060(3)	106(1)	74(2)	43(1)
C(3)	7043(3)	-467(2)	36(2)	57(1)
C(4)	6333(3)	-496(2)	633(2)	63(1)
C(5)	6628(3)	36(2)	1288(2)	56(1)
C(6)	7627(3)	611(2)	1337(2)	44(1)
C(7)	10555(2)	3057(1)	600(1)	28(1)
C(8)	10804(3)	3764(1)	72(2)	38(1)
C(9)	12122(3)	4211(1)	545(2)	46(1)
C(10)	13385(3)	3661(2)	713(2)	57(1)
C(11)	13181(3)	2980(2)	1277(2)	48(1)
C(12)	11861(3)	2515(1)	811(2)	37(1)
C(13)	10430(2)	3372(1)	1460(1)	30(1)
C(14)	11745(3)	3836(2)	1923(2)	41(1)
C(15)	11945(3)	4528(1)	1377(2)	46(1)
C(16)	13017(3)	3293(2)	2109(2)	49(1)
C(17)	7322(2)	2827(1)	220(2)	38(1)
C(18)	6070(3)	2376(2)	-330(2)	59(1)
C(19)	7155(3)	3714(1)	-5(2)	44(1)

C(20)	7269(3)	2724(2)	1132(2)	45(1)
C(21)	8882(3)	2254(2)	-1068(1)	51(1)
C(22)	8340(4)	2988(2)	-1609(2)	59(1)
C(23)	7900(5)	1549(2)	-1425(2)	77(1)
C(24)	10331(4)	2034(2)	-1167(2)	66(1)
C(25)	13577(3)	551(2)	2868(2)	67(1)

Table 3. Bond lengths [Å] and angles [°] for **5a**.

Pd(1)-C(1)	1.967(3)
Pd(1)-H(12)	2.0653
Pd(1)-O(1)	2.159(2)
Pd(1)-P(1)	2.2523(16)
S(1)-O(2)	1.408(2)
S(1)-O(3)	1.423(2)
S(1)-O(1)	1.458(2)
S(1)-C(25)	1.813(4)
P(1)-C(21)	1.897(3)
P(1)-C(17)	1.898(3)
P(1)-C(7)	1.901(3)
F(1)-C(25)	1.313(4)
F(2)-C(25)	1.325(4)
F(3)-C(25)	1.316(4)
C(1)-C(2)	1.384(3)
C(1)-C(6)	1.387(3)
C(2)-C(3)	1.390(4)
C(3)-C(4)	1.359(5)
C(4)-C(5)	1.374(5)
C(5)-C(6)	1.377(4)
C(7)-C(8)	1.539(3)
C(7)-C(12)	1.549(3)
C(7)-C(13)	1.550(3)
C(8)-C(9)	1.529(4)
C(9)-C(10)	1.527(4)
C(9)-C(15)	1.527(4)
C(10)-C(11)	1.527(4)
C(11)-C(16)	1.520(4)
C(11)-C(12)	1.543(4)
C(13)-C(14)	1.537(3)
C(14)-C(15)	1.523(4)
C(14)-C(16)	1.525(4)
C(17)-C(20)	1.528(4)
C(17)-C(18)	1.528(4)

C(17)-C(19)	1.544(3)
C(21)-C(24)	1.538(5)
C(21)-C(22)	1.539(4)
C(21)-C(23)	1.551(4)
C(1)-Pd(1)-H(12)	176.9
C(1)-Pd(1)-O(1)	90.29(10)
H(12)-Pd(1)-O(1)	87.2
C(1)-Pd(1)-P(1)	100.58(9)
H(12)-Pd(1)-P(1)	81.9
O(1)-Pd(1)-P(1)	169.12(5)
O(2)-S(1)-O(3)	118.29(18)
O(2)-S(1)-O(1)	114.27(15)
O(3)-S(1)-O(1)	112.88(13)
O(2)-S(1)-C(25)	103.50(17)
O(3)-S(1)-C(25)	103.57(17)
O(1)-S(1)-C(25)	101.62(14)
C(21)-P(1)-C(17)	109.76(13)
C(21)-P(1)-C(7)	110.12(12)
C(17)-P(1)-C(7)	110.70(12)
C(21)-P(1)-Pd(1)	113.99(9)
C(17)-P(1)-Pd(1)	118.60(8)
C(7)-P(1)-Pd(1)	92.31(9)
S(1)-O(1)-Pd(1)	122.74(11)
C(2)-C(1)-C(6)	119.6(2)
C(2)-C(1)-Pd(1)	120.61(18)
C(6)-C(1)-Pd(1)	118.74(19)
C(1)-C(2)-C(3)	119.5(3)
C(4)-C(3)-C(2)	120.4(3)
C(3)-C(4)-C(5)	120.3(3)
C(4)-C(5)-C(6)	120.3(3)
C(5)-C(6)-C(1)	119.8(3)
C(8)-C(7)-C(12)	109.52(19)
C(8)-C(7)-C(13)	108.35(18)
C(12)-C(7)-C(13)	105.59(18)
C(8)-C(7)-P(1)	116.48(17)
C(12)-C(7)-P(1)	105.83(16)

C(13)-C(7)-P(1)	110.52(14)
C(9)-C(8)-C(7)	110.1(2)
C(10)-C(9)-C(15)	110.0(3)
C(10)-C(9)-C(8)	109.8(2)
C(15)-C(9)-C(8)	109.9(2)
C(9)-C(10)-C(11)	109.4(2)
C(16)-C(11)-C(10)	110.6(2)
C(16)-C(11)-C(12)	109.9(2)
C(10)-C(11)-C(12)	108.5(2)
C(11)-C(12)-C(7)	110.9(2)
C(14)-C(13)-C(7)	111.18(19)
C(15)-C(14)-C(16)	110.4(2)
C(15)-C(14)-C(13)	109.2(2)
C(16)-C(14)-C(13)	109.7(2)
C(14)-C(15)-C(9)	109.0(2)
C(11)-C(16)-C(14)	108.3(2)
C(20)-C(17)-C(18)	106.7(2)
C(20)-C(17)-C(19)	108.5(2)
C(18)-C(17)-C(19)	109.0(2)
C(20)-C(17)-P(1)	109.43(16)
C(18)-C(17)-P(1)	110.1(2)
C(19)-C(17)-P(1)	112.97(17)
C(24)-C(21)-C(22)	108.9(2)
C(24)-C(21)-C(23)	106.5(3)
C(22)-C(21)-C(23)	108.4(3)
C(24)-C(21)-P(1)	109.03(19)
C(22)-C(21)-P(1)	113.75(18)
C(23)-C(21)-P(1)	110.0(2)
F(1)-C(25)-F(3)	106.4(3)
F(1)-C(25)-F(2)	108.0(3)
F(3)-C(25)-F(2)	110.7(3)
F(1)-C(25)-S(1)	111.6(2)
F(3)-C(25)-S(1)	110.3(3)
F(2)-C(25)-S(1)	109.9(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	37(1)	19(1)	28(1)	3(1)	6(1)	-2(1)
S(1)	41(1)	45(1)	35(1)	8(1)	10(1)	4(1)
P(1)	42(1)	20(1)	23(1)	1(1)	5(1)	-2(1)
F(1)	63(1)	101(2)	126(2)	-17(2)	2(1)	41(1)
F(2)	84(2)	158(3)	102(2)	-42(2)	-48(1)	9(2)
F(3)	70(2)	112(2)	205(3)	4(2)	50(2)	-36(2)
O(1)	51(1)	30(1)	36(1)	4(1)	1(1)	9(1)
O(2)	85(2)	114(2)	82(2)	59(2)	16(1)	-20(2)
O(3)	102(2)	78(2)	56(1)	-18(1)	18(1)	40(1)
C(1)	37(1)	19(1)	37(1)	4(1)	4(1)	-4(1)
C(2)	47(2)	25(1)	51(2)	-3(1)	3(1)	1(1)
C(3)	56(2)	28(1)	73(2)	-8(1)	-9(2)	-5(1)
C(4)	44(2)	41(2)	92(2)	18(2)	-2(2)	-14(1)
C(5)	47(2)	50(2)	71(2)	25(2)	17(1)	-5(1)
C(6)	54(2)	37(1)	40(1)	7(1)	13(1)	-4(1)
C(7)	34(1)	20(1)	31(1)	3(1)	12(1)	-1(1)
C(8)	52(2)	24(1)	42(1)	5(1)	20(1)	-3(1)
C(9)	52(2)	27(1)	64(2)	10(1)	24(1)	-7(1)
C(10)	47(2)	42(2)	90(2)	6(1)	33(2)	-9(1)
C(11)	32(1)	33(1)	80(2)	9(1)	16(1)	-1(1)
C(12)	42(1)	24(1)	49(1)	2(1)	20(1)	-1(1)
C(13)	36(1)	26(1)	30(1)	-2(1)	9(1)	-3(1)
C(14)	44(1)	32(1)	42(1)	-4(1)	4(1)	-6(1)
C(15)	44(2)	27(1)	62(2)	-3(1)	6(1)	-7(1)
C(16)	36(1)	41(2)	63(2)	4(1)	-1(1)	-11(1)
C(17)	35(1)	28(1)	44(1)	5(1)	0(1)	-1(1)
C(18)	45(2)	46(2)	72(2)	1(2)	-7(1)	-10(1)
C(19)	42(2)	32(1)	52(2)	9(1)	3(1)	8(1)
C(20)	40(1)	44(2)	55(2)	10(1)	18(1)	4(1)

C(21)	98(2)	28(1)	22(1)	1(1)	11(1)	1(1)
C(22)	108(3)	36(2)	26(1)	6(1)	7(1)	1(2)
C(23)	147(4)	40(2)	33(2)	-9(1)	4(2)	-17(2)
C(24)	118(3)	51(2)	36(1)	-2(1)	35(2)	17(2)
C(25)	46(2)	61(2)	80(2)	-10(2)	-7(2)	-5(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5a**.

	x	y	z	U(eq)
H(2A)	8554	122	-339	51
H(3A)	6845	-838	-406	69
H(4A)	5637	-880	598	75
H(5A)	6146	6	1706	67
H(6A)	7825	974	1785	52
H(8A)	10909	3576	-469	45
H(8B)	9996	4120	-40	45
H(9A)	12273	4660	194	55
H(10A)	14237	3953	989	69
H(10B)	13488	3452	178	69
H(11A)	14004	2626	1387	58
H(12)	11715	2076	1165	26(6)
H(12A)	11993	2294	289	31
H(13A)	9609	3716	1367	36
H(13B)	10297	2927	1811	36
H(14A)	11621	4040	2461	49
H(15A)	12775	4832	1670	55
H(15B)	11131	4879	1269	55
H(16A)	13858	3586	2407	59
H(16B)	12889	2853	2467	59
H(18A)	5211	2604	-262	88
H(18B)	6129	1826	-160	88
H(18C)	6077	2414	-916	88
H(19A)	6275	3903	68	66
H(19B)	7166	3787	-587	66
H(19C)	7921	4007	361	66
H(20A)	6404	2946	1197	68
H(20B)	8057	2995	1506	68
H(20C)	7312	2167	1272	68

H(22A)	8300	2877	-2193	88
H(22B)	8967	3428	-1410	88
H(22C)	7412	3120	-1566	88
H(23A)	7842	1481	-2018	116
H(23B)	6975	1655	-1361	116
H(23C)	8270	1072	-1120	116
H(24A)	10270	1961	-1759	98
H(24B)	10649	1548	-863	98
H(24C)	10989	2454	-940	98

X-Ray Structure Report for **2b**

Data Collection

A yellow-orange block crystal of $C_{18}H_{32}BrPPd$ having approximate dimensions of 0.25 x 0.25 x 0.25 mm was mounted with epoxy cement on the tip of a fine glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a =	8.7046(17) Å	α =	90 º
b =	17.837(4) Å	β =	93.54(3) º
c =	12.781(3) Å	γ =	90 º
V =	1980.6(7) Å^3		

For Z = 4 and F.W. = 465.72, the calculated density is 1.562 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P2_1/n$ (#14)

The data were collected at a temperature of 183(2) K to a maximum 2θ value of 54.74 º. Three omega scans consisting of 66, 57, and 18 data frames, respectively, were collected with a frame width of 1.8 ° and a detector-to-crystal distance, Dx, of 35 mm. Each frame was exposed twice (for the purpose of de-zingering) for a total of 54 seconds. The data frames were processed and scaled using the DENZO software package.[1]

Data Reduction

A total of 11601 reflections were collected of which 4147 were unique and observed (R_{int} = 0.0826). The linear absorption coefficient, μ, for Mo-Kα radiation is 30.29 cm^{-1} and _-scan absorption corrections were applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. The final cycle of full-matrix least-squares refinement[3] on F was based on 4147 observed reflections ($I > 2.00\sigma(I)$) and 191 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0574$$

$$R_W = [\, \Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2]^{1/2} = 0.1424$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 1.268 and –0.697 $e^-/Å^3$, respectively.

REFERENCES

(1) Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press.
(2) *Acta Cryst.* **A46** (1990) 467-473
(3) Least Squares function minimized:

$$\Sigma w(|F_O|-|F_C|)^2$$

Structural Description

The compound crystallized in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit and four in the unit cell. The geometry about the palladium atom is square planar with the fourth coordination site occupied by a hydrogen atom of C(12). Although the protons of C(12) were not located from the electron difference map the positions of H(12A-C) represent the most probable orientation. This feature is better illustrated in Figure 3. The Pd(1)-H(12B) distance is 2.18 Å and is comparable to a similar agostic interaction, 2.14 Å, in the previously solved JS03. The angles associated with this interaction are 79.2 ° [H(12B)-Pd(1)-P(1)], 87.9 ° [H(12B)-Pd(1)-Br(1)], and 175.4 ° [H(12B)-Pd(1)-C(13)]. The coordination plane of palladium, including H(12B), is planar (mean deviation = 0.050 Å) and the phenyl ring [C(13-18)] is offset from this plane by 87.4 °. There are no significant intermolecular contacts.

Table 6. Crystal data and structure refinement for **2b**.

Identification code	hartwig_js04	
Empirical formula	$C_{18} H_{32} Br P Pd$	
Formula weight	465.72	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.7046(17) Å	α= 90°.
	b = 17.837(4) Å	β= 93.54(3)°.
	c = 12.781(3) Å	γ = 90°.
Volume	1980.6(7) $Å^3$	
Z	4	
Density (calculated)	1.562 g/cm^3	
Absorption coefficient	30.29 cm^{-1}	
F(000)	944	
Crystal size	0.25 x 0.25 x 0.25 mm^3	
Theta range for data collection	13.27 to 27.87°.	
Index ranges	-11<=h<=9, -23<=k<=23, -11<=l<=16	
Reflections collected	11601	
Independent reflections	4147 [R(int) = 0.0826]	
Completeness to theta = 27.87°	87.8 %	
Absorption correction	psi-scans	
Max. and min. transmission	0.5181 and 0.5181	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4147 / 0 / 191	
Goodness-of-fit on F^2	1.093	
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.1424	
R indices (all data)	R1 = 0.0861, wR2 = 0.1555	
Largest diff. peak and hole	1.268 and -0.697 e.$Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	9313(1)	110(1)	7387(1)	33(1)
Br(1)	10113(1)	1427(1)	7318(1)	48(1)
P(1)	9143(1)	-1169(1)	7383(1)	30(1)
C(1)	7871(7)	-1580(3)	6267(4)	41(1)
C(2)	8420(20)	-1256(8)	5253(7)	110(5)
C(3)	6218(9)	-1368(7)	6395(9)	88(3)
C(4)	7960(10)	-2433(4)	6186(7)	67(2)
C(5)	8737(8)	-1638(3)	8672(4)	46(1)
C(6)	9486(17)	-1205(6)	9591(7)	93(3)
C(7)	9185(11)	-2461(4)	8735(6)	64(2)
C(8)	6986(11)	-1621(5)	8802(7)	72(2)
C(9)	11262(6)	-1307(3)	7089(6)	48(1)
C(10)	11753(9)	-2059(5)	6753(10)	80(3)
C(11)	12294(11)	-1206(7)	8178(10)	88(3)
C(12)	11688(11)	-659(6)	6435(8)	76(2)
C(13)	7218(6)	368(3)	7784(4)	36(1)
C(14)	6078(7)	549(3)	7021(5)	45(1)
C(15)	4653(7)	784(4)	7311(6)	56(2)
C(16)	4336(8)	838(4)	8343(6)	55(2)
C(17)	5483(8)	697(4)	9106(6)	55(2)
C(18)	6914(8)	451(3)	8827(5)	46(1)

Table 8. Bond lengths [Å] and angles [°] for **2b**.

Pd(1)-C(13)	1.977(5)	C(2)-C(1)-P(1)	107.1(5)
Pd(1)-P(1)	2.2854(13)	C(4)-C(1)-P(1)	114.0(4)
Pd(1)-Br(1)	2.4537(8)	C(7)-C(5)-C(6)	110.7(7)
P(1)-C(1)	1.898(5)	C(7)-C(5)-C(8)	105.4(6)
P(1)-C(5)	1.902(6)	C(6)-C(5)-C(8)	106.6(8)
P(1)-C(9)	1.921(6)	C(7)-C(5)-P(1)	114.2(5)
C(1)-C(3)	1.507(11)	C(6)-C(5)-P(1)	110.6(5)
C(1)-C(2)	1.521(14)	C(8)-C(5)-P(1)	108.8(4)
C(1)-C(4)	1.527(10)	C(10)-C(9)-C(12)	117.1(7)
C(5)-C(7)	1.519(10)	C(10)-C(9)-C(11)	101.3(8)
C(5)-C(6)	1.519(12)	C(12)-C(9)-C(11)	104.6(7)
C(5)-C(8)	1.543(12)	C(10)-C(9)-P(1)	118.1(5)
C(9)-C(10)	1.479(11)	C(12)-C(9)-P(1)	106.6(5)
C(9)-C(12)	1.488(13)	C(11)-C(9)-P(1)	107.8(6)
C(9)-C(11)	1.620(14)	C(18)-C(13)-C(14)	118.9(5)
C(13)-C(18)	1.383(9)	C(18)-C(13)-Pd(1)	120.4(4)
C(13)-C(14)	1.386(8)	C(14)-C(13)-Pd(1)	120.3(4)
C(14)-C(15)	1.382(10)	C(15)-C(14)-C(13)	119.9(6)
C(15)-C(16)	1.368(12)	C(16)-C(15)-C(14)	121.1(6)
C(16)-C(17)	1.375(12)	C(15)-C(16)-C(17)	119.4(6)
C(17)-C(18)	1.389(10)	C(16)-C(17)-C(18)	120.0(6)
C(13)-Pd(1)-P(1)	99.92(15)	C(13)-C(18)-C(17)	120.6(6)
C(13)-Pd(1)-Br(1)	93.14(15)		
P(1)-Pd(1)-Br(1)	166.88(4)	Symmetry transformations used to generate equivalent atoms	
C(1)-P(1)-C(5)	110.5(3)		
C(1)-P(1)-C(9)	109.0(3)		
C(5)-P(1)-C(9)	110.2(3)		
C(1)-P(1)-Pd(1)	115.00(19)		
C(5)-P(1)-Pd(1)	116.9(2)		
C(9)-P(1)-Pd(1)	93.79(19)		
C(3)-C(1)-C(2)	110.3(9)		
C(3)-C(1)-C(4)	108.1(7)		
C(2)-C(1)-C(4)	107.5(8)		
C(3)-C(1)-P(1)	109.7(4)		

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	31(1)	25(1)	44(1)	-1(1)	5(1)	1(1)
Br(1)	47(1)	28(1)	70(1)	-1(1)	15(1)	-2(1)
P(1)	27(1)	25(1)	38(1)	-3(1)	2(1)	1(1)
C(1)	40(3)	42(3)	40(3)	-7(2)	-5(2)	-7(2)
C(2)	169(12)	110(7)	47(4)	7(5)	-28(5)	-61(8)
C(3)	39(4)	106(7)	116(7)	-60(6)	-24(4)	15(4)
C(4)	61(4)	52(4)	86(5)	-30(4)	-16(3)	5(3)
C(5)	64(4)	38(3)	36(3)	10(2)	4(2)	0(3)
C(6)	143(10)	80(5)	51(4)	14(4)	-28(5)	-23(6)
C(7)	80(5)	44(3)	71(4)	16(3)	23(3)	17(3)
C(8)	81(5)	69(5)	70(4)	21(4)	36(4)	13(4)
C(9)	27(2)	31(3)	85(4)	-7(3)	12(3)	-1(2)
C(10)	41(3)	46(4)	156(8)	-12(4)	35(4)	4(3)
C(11)	57(5)	90(6)	117(7)	5(5)	0(5)	-10(5)
C(12)	65(5)	68(5)	96(6)	-3(4)	25(4)	-6(4)
C(13)	32(2)	27(2)	49(3)	1(2)	3(2)	2(2)
C(14)	40(3)	43(3)	50(3)	5(2)	-4(2)	5(2)
C(15)	38(3)	38(3)	92(5)	9(3)	-11(3)	4(3)
C(16)	45(3)	39(3)	83(5)	2(3)	20(3)	1(3)
C(17)	55(4)	46(3)	66(4)	-2(3)	23(3)	3(3)
C(18)	45(3)	41(3)	52(3)	-10(2)	5(2)	2(2)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2b**.

	x	y	z	U(eq)
H(2A)	7783	-1457	4657	165
H(2B)	9495	-1394	5184	165
H(2C)	8321	-709	5266	165
H(3A)	5565	-1582	5819	132
H(3B)	6119	-820	6386	132
H(3C)	5895	-1562	7064	132
H(4A)	7273	-2606	5598	101
H(4B)	7644	-2659	6838	101
H(4C)	9019	-2583	6070	101
H(6A)	9272	-1457	10248	139
H(6B)	9068	-695	9593	139
H(6C)	10601	-1183	9525	139
H(7A)	8931	-2664	9415	96
H(7B)	10293	-2510	8658	96
H(7C)	8619	-2738	8172	96
H(8A)	6762	-1871	9459	108
H(8B)	6450	-1881	8212	108
H(8C)	6634	-1099	8820	108
H(10A)	12855	-2050	6634	120
H(10B)	11170	-2199	6102	120
H(10C)	11561	-2426	7300	120
H(11A)	13384	-1274	8049	133
H(11B)	11987	-1580	8686	133
H(11C)	12137	-702	8458	133
H(12A)	12767	-705	6267	113
H(12B)	11547	-192	6822	113
H(12C)	11030	-652	5784	113
H(14A)	6277	511	6300	53
H(15A)	3879	912	6784	68
H(16A)	3333	970	8531	66

H(17A)	5296	769	9824	66
H(18A)	7693	338	9358	55

X-Ray Structure Report for **2d**.

Data Collection

A red-orange blade crystal of $C_{54}H_{52}BrFePPd$ having approximate dimensions of 0.15 x 0.15 x 0.10 mm was mounted with epoxy cement on the tip of a fine glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a =	15.380(3) Å	α =	90 °
b =	18.945(4) Å	β =	116.14(3) °
c =	17.221(3) Å	γ =	90 °
V =	4504.4(16) Å^3		

For Z = 4 and F.W. = 974.09, the calculated density is 1.436 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P2_1/n$ (#14)

The data were collected at a temperature of 183(2) K to a maximum 2θ value of 56.62 °. Five omega scans consisting of 54, 43, 48, 43, and 14 data frames, respectively, were collected with a frame width of 1.4 ° and a detector-to-crystal distance, Dx, of 35 mm. Each frame was exposed twice (for the purpose of de-zingering) for a total of 203 seconds. The data frames were processed and scaled using the DENZO software package.[1]

Data Reduction

A total of 19779 reflections were collected of which 11161 were unique and observed (R_{int} = 0.0651). The linear absorption coefficient, μ, for Mo-Kα radiation is 16.80 cm^{-1} and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. The final cycle of full-matrix least-squares refinement[3] on F was based on 11161 observed reflections (I > 2.00σ(I)) and 523 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0531$$

$$R_W = \{\Sigma[w (F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2} = 0.0981$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 0.717 and –0.724 $e^-/Å^3$, respectively.

REFERENCES

(1) Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press.

(2) *Acta Cryst.* **A46** (1990) 467-473

(3) Least Squares function minimized:

$$\Sigma w(F_o^2 - F_c^2)^2$$

Structural Description

The compound crystallized in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit and four molecules in the unit cell. The geometry about Pd(1) is square planar with the final coordination site filled by an agostically bound hydrogen, H(46C), of a neighboring ^{t}Bu group. Although refined in idealize locations the hydrogen atoms of C(46) were initially located from the electron difference map. The experimental coordinates compared well with the calculated coordinates and the atoms were idealized for ease of refinement. The Pd(1) – H(46C) distance is 2.13 Å and, more significantly, the Pd(1) – C(46) distance is ~ 2.78 Å. The coordination plane of Pd(1) possesses a mean deviation of 0.077 Å and the coordinated phenyl ring, C(49-54), is offset by 98.3 °. This phenyl ring is skewed slightly from the H(46C)-Pd(1)-C(49) vector by 17.3 ° and is a direct effect of the steric demands of the phosphine ligand. This feature is better illustrated in Figures **3** and **4**.

The five phenyl rings of the substituted ferrocene are oriented in a "paddlewheel" geometry with offsetting angles between the rings and the central Cp ring ranging from 44.0 – 55.5 °. Fe(1) is equidistant from both Cp-centroids, ~ 1.67 Å, and Fe – C distances range from 2.049(4) – 2.098(3) Å for C(2-10). Phosphine substitution in the top Cp ring results in an elongated Fe(1) – C(1) distance of 2.125(3) Å. The two Cp rings are offset from one another by 16.0 ° producing a Cent-Fe-Cent angle of 190.2 °. This large angle is directed towards Pd(1) and the Fe – Pd separation is ~ 4.91 Å.

There are no significant intermolecular contacts.

Table 11. Crystal data and structure refinement for **2d**.

Identification code	hartwig_js05	
Empirical formula	C_{54} H_{52} Br Fe P Pd	
Formula weight	974.09	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 15.380(3) Å	α= 90°.
	b = 18.945(4) Å	β= 116.14(3)°.
	c = 17.221(3) Å	γ = 90°.
Volume	4504.4(16) $Å^3$	
Z	4	
Density (calculated)	1.436 g/cm^3	
Absorption coefficient	16.80 cm^{-1}	
F(000)	1992	
Crystal size	0.15 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.15 to 28.31°.	
Index ranges	-20<=h<=20, -25<=k<=22, -22<=l<=22	
Reflections collected	19779	
Independent reflections	11161 [R(int) = 0.0651]	
Completeness to theta = 28.31°	99.4 %	
Absorption correction	None	
Max. and min. transmission	0.8500 and 0.7867	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11161 / 0 / 523	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.0981	
R indices (all data)	R1 = 0.1103, wR2 = 0.1135	
Largest diff. peak and hole	0.717 and -0.724 $e.Å^{-3}$	

Table 12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **2d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1999(1)	5807(1)	7606(1)	31(1)
Br(1)	1117(1)	6904(1)	7070(1)	41(1)
Fe(1)	4387(1)	4386(1)	7125(1)	24(1)
P(1)	2465(1)	4671(1)	7911(1)	29(1)
C(1)	3532(3)	4378(2)	7814(2)	25(1)
C(2)	3780(3)	3676(2)	7672(2)	29(1)
C(3)	4801(3)	3612(2)	8055(2)	30(1)
C(4)	5204(3)	4277(2)	8433(2)	29(1)
C(5)	4431(3)	4749(2)	8267(2)	29(1)
C(6)	3940(2)	4993(2)	6011(2)	26(1)
C(7)	3927(2)	4257(2)	5792(2)	25(1)
C(8)	4888(3)	3981(2)	6287(2)	28(1)
C(9)	5494(3)	4545(2)	6788(2)	28(1)
C(10)	4911(3)	5173(2)	6628(2)	26(1)
C(11)	3147(3)	5504(2)	5564(2)	28(1)
C(12)	2826(3)	5979(2)	5998(2)	35(1)
C(13)	2136(3)	6490(2)	5552(3)	43(1)
C(14)	1764(3)	6531(2)	4674(3)	41(1)
C(15)	2059(3)	6058(2)	4225(2)	38(1)
C(16)	2740(3)	5548(2)	4667(2)	31(1)
C(17)	3111(3)	3893(2)	5072(2)	28(1)
C(18)	3286(3)	3527(2)	4456(2)	33(1)
C(19)	2515(3)	3252(2)	3720(2)	44(1)
C(20)	1583(3)	3337(2)	3604(2)	44(1)
C(21)	1407(3)	3693(2)	4223(2)	42(1)
C(22)	2165(3)	3967(2)	4945(2)	35(1)
C(23)	5191(3)	3249(2)	6205(2)	27(1)
C(24)	5949(3)	3149(2)	5993(2)	37(1)

C(25)	6219(3)	2476(2)	5861(3)	49(1)
C(26)	5732(3)	1899(2)	5954(3)	53(1)
C(27)	4973(3)	1985(2)	6165(3)	46(1)
C(28)	4697(3)	2656(2)	6286(2)	34(1)
C(29)	6566(3)	4503(2)	7341(2)	30(1)
C(30)	7170(3)	5023(2)	7288(2)	36(1)
C(31)	8163(3)	4984(3)	7765(3)	49(1)
C(32)	8578(3)	4424(3)	8308(3)	56(1)
C(33)	7982(3)	3890(2)	8368(3)	51(1)
C(34)	6989(3)	3926(2)	7886(2)	37(1)
C(35)	5245(3)	5899(2)	6970(2)	29(1)
C(36)	5845(3)	6017(2)	7848(2)	36(1)
C(37)	6175(3)	6686(2)	8144(3)	44(1)
C(38)	5917(3)	7257(2)	7579(3)	49(1)
C(39)	5319(3)	7145(2)	6720(3)	46(1)
C(40)	4990(3)	6473(2)	6413(2)	34(1)
C(41)	2681(3)	4290(2)	8996(2)	36(1)
C(42)	3706(3)	4504(2)	9656(2)	43(1)
C(43)	2611(3)	3478(2)	8972(3)	49(1)
C(44)	1958(3)	4605(2)	9302(3)	49(1)
C(45)	1337(3)	4303(2)	7014(2)	36(1)
C(46)	1074(3)	4848(2)	6272(2)	44(1)
C(47)	495(3)	4308(3)	7268(3)	61(1)
C(48)	1406(3)	3564(2)	6674(3)	46(1)
C(49)	3003(3)	6284(2)	8622(2)	32(1)
C(50)	2802(3)	6496(2)	9299(2)	43(1)
C(51)	3451(4)	6919(2)	9945(3)	49(1)
C(52)	4304(4)	7124(2)	9935(3)	52(1)
C(53)	4507(3)	6919(2)	9262(3)	45(1)
C(54)	3852(3)	6498(2)	8598(2)	38(1)

Table 13. Bond lengths [Å] and angles [°] for **2d**.

Pd(1)-C(49)	1.969(3)	C(11)-C(16)	1.390(5)
Pd(1)-H(46C)	2.1282	C(11)-C(12)	1.392(5)
Pd(1)-P(1)	2.2567(10)	C(12)-C(13)	1.390(5)
Pd(1)-Br(1)	2.4292(6)	C(13)-C(14)	1.362(5)
Fe(1)-Cent(1)	1.683(4)	C(14)-C(15)	1.385(6)
Fe(1)-Cent(2)	1.677(4)	C(15)-C(16)	1.381(5)
Fe(1)-C(9)	2.049(4)	C(17)-C(22)	1.379(5)
Fe(1)-C(4)	2.049(3)	C(17)-C(18)	1.390(5)
Fe(1)-C(10)	2.053(3)	C(18)-C(19)	1.399(5)
Fe(1)-C(3)	2.054(3)	C(19)-C(20)	1.367(6)
Fe(1)-C(8)	2.060(3)	C(20)-C(21)	1.386(6)
Fe(1)-C(5)	2.056(3)	C(21)-C(22)	1.377(5)
Fe(1)-C(6)	2.077(3)	C(23)-C(24)	1.379(5)
Fe(1)-C(2)	2.084(3)	C(23)-C(28)	1.396(5)
Fe(1)-C(7)	2.098(3)	C(24)-C(25)	1.391(5)
Fe(1)-C(1)	2.125(3)	C(25)-C(26)	1.374(6)
P(1)-C(1)	1.807(4)	C(26)-C(27)	1.376(6)
P(1)-C(45)	1.877(4)	C(27)-C(28)	1.385(5)
P(1)-C(41)	1.891(4)	C(29)-C(30)	1.383(5)
C(1)-C(2)	1.435(5)	C(29)-C(34)	1.401(5)
C(1)-C(5)	1.436(5)	C(30)-C(31)	1.382(5)
C(2)-C(3)	1.415(5)	C(31)-C(32)	1.373(6)
C(3)-C(4)	1.427(5)	C(32)-C(33)	1.399(6)
C(4)-C(5)	1.413(5)	C(33)-C(34)	1.381(5)
C(6)-C(10)	1.442(5)	C(35)-C(40)	1.388(5)
C(6)-C(7)	1.441(5)	C(35)-C(36)	1.399(5)
C(6)-C(11)	1.481(5)	C(36)-C(37)	1.376(5)
C(7)-C(8)	1.441(5)	C(37)-C(38)	1.391(6)
C(7)-C(17)	1.488(5)	C(38)-C(39)	1.370(6)
C(8)-C(9)	1.431(5)	C(39)-C(40)	1.385(5)
C(8)-C(23)	1.490(5)	C(41)-C(42)	1.537(6)
C(9)-C(10)	1.440(5)	C(41)-C(43)	1.542(5)
C(9)-C(29)	1.499(5)	C(41)-C(44)	1.545(5)
C(10)-C(35)	1.494(5)	C(45)-C(48)	1.540(5)

C(45)-C(47)	1.539(6)	C(5)-Fe(1)-C(6)	123.79(14)
C(45)-C(46)	1.551(5)	C(9)-Fe(1)-C(2)	144.81(14)
C(49)-C(50)	1.392(5)	C(4)-Fe(1)-C(2)	67.56(14)
C(49)-C(54)	1.385(5)	C(10)-Fe(1)-C(2)	173.56(14)
C(50)-C(51)	1.377(6)	C(3)-Fe(1)-C(2)	39.99(14)
C(51)-C(52)	1.375(6)	C(8)-Fe(1)-C(2)	117.18(14)
C(52)-C(53)	1.383(6)	C(5)-Fe(1)-C(2)	67.44(14)
C(53)-C(54)	1.395(5)	C(6)-Fe(1)-C(2)	137.97(14)
		C(9)-Fe(1)-C(7)	68.20(14)
C(49)-Pd(1)-H(46C)	176.6	C(4)-Fe(1)-C(7)	159.90(14)
C(49)-Pd(1)-P(1)	100.71(11)	C(10)-Fe(1)-C(7)	68.48(13)
H(46C)-Pd(1)-P(1)	79.9	C(3)-Fe(1)-C(7)	127.61(14)
C(49)-Pd(1)-Br(1)	91.94(11)	C(8)-Fe(1)-C(7)	40.54(13)
H(46C)-Pd(1)-Br(1)	87.8	C(5)-Fe(1)-C(7)	159.81(14)
P(1)-Pd(1)-Br(1)	166.16(3)	C(6)-Fe(1)-C(7)	40.38(13)
Cent(1)-Fe(1)-Cent(2)	169.8(3)	C(2)-Fe(1)-C(7)	114.67(14)
C(9)-Fe(1)-C(4)	98.22(14)	C(9)-Fe(1)-C(1)	162.84(13)
C(9)-Fe(1)-C(10)	41.12(14)	C(4)-Fe(1)-C(1)	67.43(14)
C(4)-Fe(1)-C(10)	111.59(14)	C(10)-Fe(1)-C(1)	133.70(13)
C(9)-Fe(1)-C(3)	108.43(15)	C(3)-Fe(1)-C(1)	67.36(14)
C(4)-Fe(1)-C(3)	40.70(13)	C(8)-Fe(1)-C(1)	154.62(13)
C(10)-Fe(1)-C(3)	143.10(14)	C(5)-Fe(1)-C(1)	40.13(13)
C(9)-Fe(1)-C(8)	40.76(14)	C(6)-Fe(1)-C(1)	119.03(13)
C(4)-Fe(1)-C(8)	119.67(14)	C(2)-Fe(1)-C(1)	39.86(13)
C(10)-Fe(1)-C(8)	69.01(14)	C(7)-Fe(1)-C(1)	128.11(13)
C(3)-Fe(1)-C(8)	101.42(14)	C(1)-P(1)-C(45)	110.97(17)
C(9)-Fe(1)-C(5)	122.72(14)	C(1)-P(1)-C(41)	101.68(17)
C(4)-Fe(1)-C(5)	40.27(13)	C(45)-P(1)-C(41)	111.58(18)
C(10)-Fe(1)-C(5)	107.58(14)	C(1)-P(1)-Pd(1)	118.68(11)
C(3)-Fe(1)-C(5)	67.95(14)	C(45)-P(1)-Pd(1)	94.52(12)
C(8)-Fe(1)-C(5)	158.41(14)	C(41)-P(1)-Pd(1)	119.57(12)
C(9)-Fe(1)-C(6)	68.55(14)	C(2)-C(1)-C(5)	106.3(3)
C(4)-Fe(1)-C(6)	149.78(14)	C(2)-C(1)-P(1)	128.4(3)
C(10)-Fe(1)-C(6)	40.86(13)	C(5)-C(1)-P(1)	119.8(2)
C(3)-Fe(1)-C(6)	167.96(14)	C(2)-C(1)-Fe(1)	68.53(19)
C(8)-Fe(1)-C(6)	68.43(13)	C(5)-C(1)-Fe(1)	67.34(19)

P(1)-C(1)-Fe(1)	149.29(18)	C(29)-C(9)-Fe(1)	129.1(2)
C(3)-C(2)-C(1)	108.8(3)	C(9)-C(10)-C(6)	107.5(3)
C(3)-C(2)-Fe(1)	68.9(2)	C(9)-C(10)-C(35)	127.4(3)
C(1)-C(2)-Fe(1)	71.61(19)	C(6)-C(10)-C(35)	124.9(3)
C(2)-C(3)-C(4)	107.9(3)	C(9)-C(10)-Fe(1)	69.31(19)
C(2)-C(3)-Fe(1)	71.1(2)	C(6)-C(10)-Fe(1)	70.46(19)
C(4)-C(3)-Fe(1)	69.46(19)	C(35)-C(10)-Fe(1)	129.4(2)
C(5)-C(4)-C(3)	107.9(3)	C(16)-C(11)-C(12)	117.7(3)
C(5)-C(4)-Fe(1)	70.12(18)	C(16)-C(11)-C(6)	118.8(3)
C(3)-C(4)-Fe(1)	69.84(19)	C(12)-C(11)-C(6)	123.4(3)
C(4)-C(5)-C(1)	108.9(3)	C(13)-C(12)-C(11)	121.2(3)
C(4)-C(5)-Fe(1)	69.61(19)	C(14)-C(13)-C(12)	119.8(4)
C(1)-C(5)-Fe(1)	72.53(19)	C(13)-C(14)-C(15)	120.2(4)
C(10)-C(6)-C(7)	108.3(3)	C(16)-C(15)-C(14)	120.0(4)
C(10)-C(6)-C(11)	125.2(3)	C(15)-C(16)-C(11)	121.0(4)
C(7)-C(6)-C(11)	125.6(3)	C(22)-C(17)-C(18)	118.3(3)
C(10)-C(6)-Fe(1)	68.68(18)	C(22)-C(17)-C(7)	121.9(3)
C(7)-C(6)-Fe(1)	70.59(18)	C(18)-C(17)-C(7)	119.5(3)
C(11)-C(6)-Fe(1)	134.7(2)	C(17)-C(18)-C(19)	120.4(4)
C(8)-C(7)-C(6)	107.7(3)	C(20)-C(19)-C(18)	120.3(4)
C(8)-C(7)-C(17)	126.3(3)	C(19)-C(20)-C(21)	119.5(4)
C(6)-C(7)-C(17)	125.2(3)	C(22)-C(21)-C(20)	120.2(4)
C(8)-C(7)-Fe(1)	68.32(18)	C(17)-C(22)-C(21)	121.3(4)
C(6)-C(7)-Fe(1)	69.04(17)	C(24)-C(23)-C(28)	118.5(3)
C(17)-C(7)-Fe(1)	136.0(2)	C(24)-C(23)-C(8)	119.3(3)
C(9)-C(8)-C(7)	108.1(3)	C(28)-C(23)-C(8)	122.1(3)
C(9)-C(8)-C(23)	127.2(3)	C(23)-C(24)-C(25)	121.2(4)
C(7)-C(8)-C(23)	124.4(3)	C(26)-C(25)-C(24)	119.5(4)
C(9)-C(8)-Fe(1)	69.22(19)	C(27)-C(26)-C(25)	120.4(4)
C(7)-C(8)-Fe(1)	71.14(19)	C(26)-C(27)-C(28)	120.1(4)
C(23)-C(8)-Fe(1)	130.0(2)	C(27)-C(28)-C(23)	120.4(4)
C(8)-C(9)-C(10)	108.4(3)	C(30)-C(29)-C(34)	118.2(3)
C(8)-C(9)-C(29)	125.8(3)	C(30)-C(29)-C(9)	120.1(3)
C(10)-C(9)-C(29)	125.6(3)	C(34)-C(29)-C(9)	121.6(3)
C(8)-C(9)-Fe(1)	70.0(2)	C(31)-C(30)-C(29)	121.5(4)
C(10)-C(9)-Fe(1)	69.57(19)	C(32)-C(31)-C(30)	120.4(4)

C(31)-C(32)-C(33)	119.2(4)
C(34)-C(33)-C(32)	120.4(4)
C(33)-C(34)-C(29)	120.4(4)
C(40)-C(35)-C(36)	118.1(3)
C(40)-C(35)-C(10)	120.4(3)
C(36)-C(35)-C(10)	121.4(3)
C(37)-C(36)-C(35)	120.6(4)
C(36)-C(37)-C(38)	120.7(4)
C(39)-C(38)-C(37)	119.0(4)
C(38)-C(39)-C(40)	120.8(4)
C(39)-C(40)-C(35)	120.9(3)
C(42)-C(41)-C(43)	108.7(3)
C(42)-C(41)-C(44)	107.6(3)
C(43)-C(41)-C(44)	110.0(3)
C(42)-C(41)-P(1)	107.8(3)
C(43)-C(41)-P(1)	112.0(3)
C(44)-C(41)-P(1)	110.5(3)
C(48)-C(45)-C(47)	108.7(3)
C(48)-C(45)-C(46)	109.2(3)
C(47)-C(45)-C(46)	106.5(3)
C(48)-C(45)-P(1)	117.2(3)
C(47)-C(45)-P(1)	110.6(3)
C(46)-C(45)-P(1)	104.0(2)
C(50)-C(49)-C(54)	120.0(3)
C(50)-C(49)-Pd(1)	120.0(3)
C(54)-C(49)-Pd(1)	119.3(3)
C(51)-C(50)-C(49)	119.7(4)
C(52)-C(51)-C(50)	120.7(4)
C(51)-C(52)-C(53)	120.0(4)
C(52)-C(53)-C(54)	119.9(4)
C(49)-C(54)-C(53)	119.6(4)

Table 14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	29(1)	28(1)	33(1)	-3(1)	10(1)	3(1)
Br(1)	40(1)	32(1)	45(1)	-2(1)	11(1)	9(1)
Fe(1)	26(1)	23(1)	24(1)	1(1)	10(1)	-1(1)
P(1)	30(1)	26(1)	30(1)	-3(1)	13(1)	0(1)
C(1)	27(2)	25(2)	24(2)	4(1)	12(2)	1(2)
C(2)	37(2)	22(2)	32(2)	3(2)	19(2)	2(2)
C(3)	34(2)	28(2)	30(2)	5(2)	15(2)	4(2)
C(4)	32(2)	31(2)	22(2)	5(2)	8(2)	3(2)
C(5)	35(2)	29(2)	26(2)	-1(2)	16(2)	0(2)
C(6)	29(2)	26(2)	24(2)	2(2)	14(2)	-3(2)
C(7)	27(2)	26(2)	19(2)	0(1)	9(2)	-3(2)
C(8)	31(2)	29(2)	24(2)	1(2)	13(2)	-3(2)
C(9)	27(2)	31(2)	29(2)	3(2)	15(2)	-2(2)
C(10)	31(2)	26(2)	20(2)	1(1)	11(2)	-5(2)
C(11)	32(2)	24(2)	28(2)	0(2)	14(2)	-5(2)
C(12)	47(2)	29(2)	31(2)	2(2)	20(2)	0(2)
C(13)	49(3)	31(2)	55(3)	3(2)	29(2)	7(2)
C(14)	33(2)	38(2)	53(3)	13(2)	18(2)	9(2)
C(15)	31(2)	43(2)	37(2)	12(2)	12(2)	1(2)
C(16)	31(2)	29(2)	32(2)	4(2)	14(2)	3(2)
C(17)	34(2)	22(2)	26(2)	3(2)	12(2)	-5(2)
C(18)	31(2)	35(2)	32(2)	-2(2)	13(2)	1(2)
C(19)	61(3)	41(2)	32(2)	-10(2)	22(2)	-8(2)
C(20)	44(3)	39(2)	35(2)	-2(2)	5(2)	-13(2)
C(21)	32(2)	40(2)	46(2)	-1(2)	10(2)	-4(2)
C(22)	33(2)	37(2)	35(2)	-6(2)	15(2)	-4(2)
C(23)	27(2)	28(2)	24(2)	1(2)	9(2)	4(2)
C(24)	33(2)	35(2)	44(2)	-2(2)	18(2)	-2(2)
C(25)	46(3)	48(3)	63(3)	1(2)	35(2)	12(2)

C(26)	64(3)	37(3)	60(3)	2(2)	29(3)	19(2)
C(27)	54(3)	30(2)	56(3)	2(2)	26(2)	-5(2)
C(28)	34(2)	32(2)	42(2)	2(2)	22(2)	2(2)
C(29)	27(2)	36(2)	28(2)	-6(2)	11(2)	-5(2)
C(30)	32(2)	40(2)	36(2)	-3(2)	16(2)	-4(2)
C(31)	29(2)	66(3)	53(3)	-11(2)	19(2)	-13(2)
C(32)	24(2)	81(4)	54(3)	-8(3)	7(2)	-1(2)
C(33)	40(3)	57(3)	47(3)	7(2)	11(2)	8(2)
C(34)	25(2)	44(2)	39(2)	1(2)	11(2)	-3(2)
C(35)	33(2)	24(2)	34(2)	-3(2)	18(2)	-5(2)
C(36)	39(2)	36(2)	33(2)	-3(2)	16(2)	-9(2)
C(37)	51(3)	48(3)	36(2)	-12(2)	22(2)	-17(2)
C(38)	61(3)	34(2)	58(3)	-17(2)	32(2)	-19(2)
C(39)	54(3)	34(2)	51(3)	1(2)	25(2)	-9(2)
C(40)	36(2)	31(2)	36(2)	0(2)	16(2)	-5(2)
C(41)	43(2)	36(2)	33(2)	4(2)	20(2)	1(2)
C(42)	55(3)	47(2)	28(2)	6(2)	19(2)	2(2)
C(43)	64(3)	38(2)	51(3)	10(2)	33(2)	1(2)
C(44)	52(3)	56(3)	50(3)	-5(2)	34(2)	-2(2)
C(45)	25(2)	39(2)	40(2)	-6(2)	10(2)	-6(2)
C(46)	41(2)	39(2)	39(2)	-5(2)	6(2)	4(2)
C(47)	34(3)	89(4)	60(3)	-20(3)	21(2)	-12(2)
C(48)	50(3)	38(2)	42(2)	-6(2)	14(2)	-10(2)
C(49)	31(2)	27(2)	31(2)	-3(2)	9(2)	0(2)
C(50)	47(3)	38(2)	41(2)	-5(2)	18(2)	0(2)
C(51)	66(3)	39(2)	39(2)	-3(2)	21(2)	4(2)
C(52)	64(3)	29(2)	36(2)	-5(2)	-2(2)	6(2)
C(53)	36(2)	30(2)	51(3)	3(2)	2(2)	2(2)
C(54)	36(2)	29(2)	43(2)	-4(2)	13(2)	2(2)

Table 15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3})for **2d**.

_	x	y	z	U(eq)
H(2A)	3308	3294	7354	35
H(3A)	5174	3176	8071	36
H(4A)	5909	4387	8762	35
H(5A)	4499	5254	8453	34
H(12A)	3083	5954	6610	42
H(13A)	1925	6809	5859	51
H(14A)	1300	6885	4370	50
H(15A)	1793	6085	3612	46
H(16A)	2934	5222	4353	37
H(18A)	3932	3463	4535	40
H(19A)	2641	3005	3300	53
H(20A)	1060	3153	3102	52
H(21A)	761	3749	4150	50
H(22A)	2035	4211	5364	42
H(24A)	6291	3547	5935	44
H(25A)	6737	2415	5707	58
H(26A)	5919	1438	5872	64
H(27A)	4639	1584	6228	55
H(28A)	4168	2714	6425	41
H(30A)	6895	5415	6916	43
H(31A)	8562	5348	7717	59
H(32A)	9260	4398	8639	68
H(33A)	8262	3500	8743	61
H(34A)	6591	3558	7925	45
H(36A)	6027	5633	8242	43
H(37A)	6584	6758	8742	53
H(38A)	6151	7717	7784	59
H(39A)	5128	7533	6331	55
H(40A)	4585	6405	5814	41
H(42A)	3836	4313	10226	65

H(42B)	3755	5020	9689	65
H(42C)	4181	4315	9474	65
H(43A)	2727	3302	9545	73
H(43B)	3099	3281	8811	73
H(43C)	1964	3334	8546	73
H(44A)	2080	4403	9865	73
H(44B)	1295	4494	8880	73
H(44C)	2041	5118	9357	73
H(46A)	487	4694	5769	66
H(46B)	1610	4885	6111	66
H(46C)	960	5310	6466	66
H(47A)	-86	4111	6795	91
H(47B)	366	4794	7382	91
H(47C)	670	4022	7790	91
H(48A)	775	3431	6211	69
H(48B)	1597	3221	7147	69
H(48C)	1891	3569	6449	69
H(50A)	2220	6351	9316	51
H(51A)	3308	7071	10402	58
H(52A)	4753	7407	10391	63
H(53A)	5093	7065	9252	55
H(54A)	3987	6359	8132	45