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Synthesis of Bis(phosphine)-1,2-dihydroplatina(II)cyclobutabenzenes. Molecular Structure of the 1,2-Dihydroplatina(II)cyclobutabenzene $Pt(CH_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$

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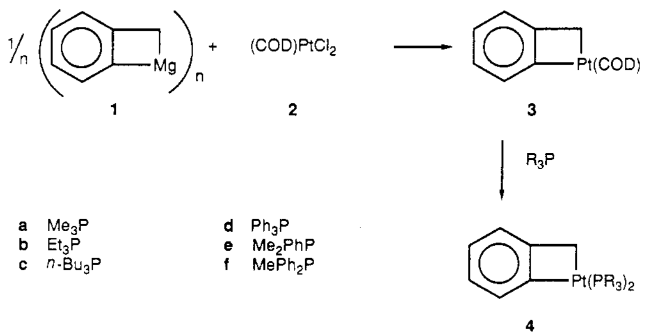
The reaction of 1,2-dihydro-1-magnesacyclobutabenzene (**1**) with dichloro(1,5-η^2-cyclooctadiene)platinum(II) (**2**) gave the thermally unstable 1-(1,5-η^2-cyclooctadiene)-1,2-dihydro-1-platina(II)cyclobutabenzene (**3**). The diene ligand can be replaced by tertiary phosphine ligands, yielding stable bis(phosphine)-1,2-dihydroplatina(II)cyclobutabenzenes. The molecular structure of 1,1-bis(trimethylphosphine)-1,2-dihydro-1-platina(II)cyclobutabenzene $Pt(CH_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$ (**4a**) has been determined by X-ray crystal structure analysis. Crystals of **4a** are monoclinic, space group $P2_1/n$ ($Z = 4$), with $a = 15.317$ (3) Å, $b = 11.559$ (2) Å, $c = 9.093$ (1) Å, and $\beta = 93.77$ (3)°. The structure was refined to $R = 0.036$ ($R_w = 0.035$). The molecule is almost planar; the Pt–C(aryl) and Pt–C(benzyl) bond lengths are 2.060 (8) and 2.112 (7) Å, respectively.

Introduction

1,2-Dihydro-1-metallacyclobutabenzenes can be considered as derivatives of metallacyclobutenes, of which only representatives of silacyclobutene,[1] titanacyclobutene,[2] and iridacyclobutene[3] are known. On the contrary, many dihydrometallacyclobutabenzenes with main group[4] as well as transition metals[5] have been prepared. However, for platinum, the smallest benzo-annelated platinacycloalkenes are 2,3-dihydro-1*H*-2-platina(II)cyclopentabenzenes.[6] Recently, we have prepared bis(phosphine)-1,2-dihydroplatina(II)cyclobutanes by reacting the 1,3-di-Grignard reagent 1,3-bis(bromomagnesio)-2,2-dimethylpropane with dichloro(1,5-η^2-cyclooctadiene)platinum(II) (**2**), followed by displacement of the diene ligand by monodentate tertiary phosphines.[7] We now report that with (oligomeric) 1,2-dihydro-1-magnesacyclobutabenzene (**1**)[4e,8] as the 1,3-di-Grignard equivalent, bis(phosphine)-1,2-dihydroplatina(II)cyclobutabenzenes can be prepared in a similar fashion.

Scheme I



Results and Discussion

When **1** was reacted with **2** in THF at −70 °C, a yellow solution containing **3** and a white precipitate (magnesium

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Table I. ^{31}P NMR Data for $\overline{Pt(CH_2\text{-}o\text{-}C_6H_4})L_2$ (4)

compd	L	θ^a	δ^b (^1J(Pt-P))^c P$_1$	P$_2$	$^1\bar{J}$(Pt-P)^d	^2J(P-P)^c
4a	Me_3P	118	-23.7 (1936)	-18.7 (1813)	1875	9
4b	Et_3P	132	6.6 (2009)	13.1 (1845)	1927	9
4c	n-Bu_3P	132	-1.0 (1997)	5.1 (1833)	1915	9
4d	Ph_3P	145	26.1 (2058)	22.5 (1837)	1948	7
4e	Me_2PhP	122	-15.2 (1938)	-10.9 (1797)	1868	8

^{a}From ref 14a. $^b\delta$ (ppm), relative to external H_3PO_4. ^{c}In Hz. $^d\,^1\bar{J}$(Pt-P) = 0.5[^1J(Pt-P$_1$) + ^1J(Pt-P$_2$)] (Hz).

dichloride) were obtained. The solvent was evaporated at -20 °C, leaving a yellow residue, and **3** was extracted from this residue with n-pentane at -20 °C. Compound **3** appeared to be thermally unstable; at room temperature a black precipitate, presumably Pt(0), was formed. Therefore, **3** was not isolated for spectroscopic identification but immediately treated with an excess of a tertiary phosphine, yielding thermally stable bis(phosphine)-1,2-dihydroplatina(II)cyclobutabenzenes in variable yields (Scheme I).

Trimethylphosphine or triethylphosphine yielded **4a** and **4b**, respectively, in almost pure form. Crystals of **4a** were obtained from toluene/n-heptane (1/1) at -80 °C; **4b** was purified by short-path distillation (95 °C, 10^{-6} mbar) and isolated as a colorless oil, which solidified after being left standing at room temperature for several days. With the other phosphines, complex mixtures were obtained, which contained, besides **4c–e**, unidentified byproducts. The platinacycles **4c–e** could not be separated from these impurities and were identified by their ^{31}P NMR spectra only (Table I). With dimethylphenylphosphine, mainly tetrakis(dimethylphenylphosphine)platinum(0)[9] was obtained. When the ligand displacement was performed with diphenylmethylphosphine, no NMR signals attributable to **4f** could be detected.

NMR Spectra of 4. The benzylic protons of both **4a** and **4b** appear as a doublet of doublets, flanked by Pt satellites, with ^2J(Pt-H) = 67.9 Hz for **4a** and ^2J(Pt-H) = 78.3 Hz for **4b**, respectively. These coupling constants are comparable to those found for platina(II)cyclobutanes[7,10] and for $\overline{Pt(CH_2\text{-}o\text{-}C_6H_4CH_2})(PEt_3)_2$.[6a] The magnetic equivalency of the benzylic protons was established by recording $^1H\{^{31}P\}$ NMR spectra. From the two distinguishable ^3J(P-H) coupling constants (**4a**, ^3J(P-H) = 4.4, 6.4 Hz; **4b**, ^3J(P-H) = 5.2, 6.5 Hz) and from the equivalency of the benzylic protons, it can be deduced that platinum occurs in the expected square-planar coordination mode. The chemical shifts of the benzylic protons of **4a** (δ 2.06 (benzene-d_6), 1.13 (dioxane-d_8)), **4b** (δ 1.57 (benzene-d_6)), and **4d** (δ 1.61 (benzene-d_6)) are more shielded with regard to those of $\overline{Pt(CH_2\text{-}o\text{-}C_6H_4CH_2})$-(PEt$_3$)$_2$ (δ 3.55).[6a]

Similar phenomena are observed in the ^{13}C NMR spectrum of **4a**. Thus, the signal of the benzylic carbon has two couplings with phosphorus (^2J(P-C) = 5, 87 Hz). The ^1J(Pt-C) for **4a** (396 Hz) is much smaller than that for $\overline{Pt(CH_2\text{-}o\text{-}C_6H_4CH_2})(PEt_3)_2$ (620 Hz);[6a] this is in line with the expectation that the platinum–carbon bonds in the four-membered ring of **4a** have more p character. The benzylic carbon of **4a** is more shielded (δ -9.9 (dioxane-d_8)) than in the five-membered platinacycle (δ 36.1).[6a]

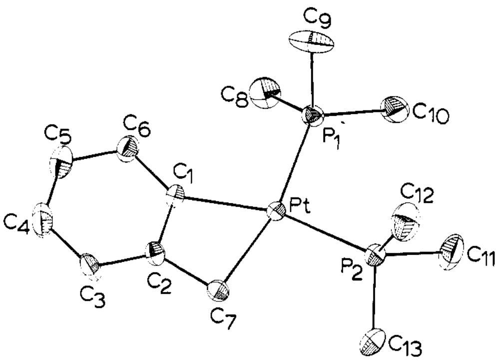

Figure 1. ORTEP structure of **4a**.

The ^{31}P NMR spectra of 4 (Table I) show an AX spin system with Pt satellites, as is expected for platinum(II) complexes with two nonequivalent phosphine ligands. The ^1J(Pt-P) coupling constants are normal, although their magnitude (1797–2058 Hz) is generally larger than that observed for the analogous cis-bis(phosphine)platinum(II) complexes $(Et_3P)_2PtPh_2$ (δ 2.6 (^1J(Pt-P) = 1776 Hz)),[11] (n-Bu$_3$P)$_2$PtPh$_2$ (δ 4.9 (^1J(Pt-P) = 1758 Hz)),[12] $(Ph_3P)_2PtPh_2$ (δ 18.1 (^1J(Pt-P) = 1763 Hz)), and $(Ph_3P_2)PtMes_2$ (δ 22.4 (^1J(Pt-P) = 1736 Hz)).[11]

The assignment of the ^{31}P signals to the phosphorus nuclei P$_1$ and P$_2$ is based on the magnitude of the ^1J(Pt-P) coupling constants. According to general experience, the trans effect of the phenyl group is larger than that of the benzyl group, resulting in a smaller ^1J(Pt-P) for a phosphine ligand trans to a phenyl group. A relevant illustration may be found in a comparison of (DPPM)PtPh$_2$ (^1J(Pt-P) = 1394 Hz) with (DPPM)Pt(CH$_2$Ph)$_2$ (^1J(Pt-P) = 1570 Hz).[13] Accordingly, we assign P$_1$ with the larger platinum–phosphorus coupling constant to the phosphorus trans to the benzylic carbon atom and P$_2$ to that trans to the aryl carbon of 4 (Table I). There is a roughly linear relationship between ^1J(Pt-P) and the cone angle θ^{14} of the phosphine ligands; this correlation is better for the mean value $^1\bar{J}$(Pt-P) = 0.5[^1J(Pt-P$_1$) + ^1J(Pt-P$_2$)] than for P$_1$ or P$_2$ separately. However, the clear-cut trend earlier found for platina(II)cyclobutanes is not followed, and effects other than the s character of the phosphorus lone pair must play an important role. It should be pointed out that in general, $\delta(^{31}P_1) < \delta(^{31}P_2)$, with the exception of **4d**; in this case, an anisotropic effect by the phenyl groups of the neighboring triphenylphosphine ligands on each other may cause the reverse.

Molecular Structure of 4a. Only for one

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Table II. Fractional Atomic Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters for 4a

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eq), Å²
Pt	0.11805 (3)	0.12346 (4)	0.13931 (4)	0.0378 (2)
P1	0.1227 (2)	0.1277 (3)	−0.1124 (3)	0.049 (1)
P2	0.2233 (2)	−0.0115 (3)	0.1986 (4)	0.054 (2)
C1	0.0286 (7)	0.2540 (9)	0.164 (1)	0.043 (6)
C2	0.0281 (7)	0.250 (1)	0.316 (1)	0.047 (6)
C3	−0.0168 (9)	0.327 (1)	0.398 (2)	0.074 (9)
C4	−0.064 (1)	0.416 (1)	0.319 (2)	0.09 (1)
C5	−0.0646 (10)	0.423 (1)	0.165 (2)	0.09 (1)
C6	−0.0168 (9)	0.343 (1)	0.084 (2)	0.066 (8)
C7	0.0867 (8)	0.148 (1)	0.361 (1)	0.053 (7)
C8	0.0158 (10)	0.149 (2)	−0.209 (2)	0.09 (1)
C9	0.189 (1)	0.244 (2)	−0.185 (2)	0.11 (1)
C10	0.159 (1)	0.001 (1)	−0.217 (2)	0.09 (1)
C11	0.240 (1)	−0.141 (1)	0.086 (2)	0.10 (1)
C12	0.334 (1)	0.048 (2)	0.210 (2)	0.11 (1)
C13	0.215 (1)	−0.076 (2)	0.380 (2)	0.12 (2)

Table III. Bond Lengths (Å) for 4a with Standard Deviations in Parentheses

Pt–P1	2.295 (2)	P2–C13	1.82 (1)
Pt–P2	2.282 (3)	C1–C2	1.38 (1)
Pt–C1	2.060 (8)	C1–C6	1.42 (1)
Pt–C7	2.122 (7)	C2–C3	1.37 (1)
P1–C8	1.82 (1)	C2–C7	1.52 (1)
P1–C9	1.83 (1)	C3–C4	1.42 (2)
P1–C10	1.85 (1)	C4–C5	1.40 (2)
P2–C11	1.84 (1)	C5–C6	1.42 (1)
P2–C12	1.83 (1)		

Table IV. Bond Angles (deg) for 4a with Standard Deviations in Parentheses

P1–Pt–P2	100.5 (1)	C11–P2–C12	100.1 (9)
P1–Pt–C1	99.1 (3)	C11–P2–C13	101.0 (9)
P1–Pt–C7	165.6 (2)	C12–P2–C13	102.9 (9)
P2–Pt–C1	159.9 (2)	Pt–C1–C2	97.6 (7)
P2–Pt–C7	93.9 (3)	Pt–C1–C6	141.6 (6)
C1–Pt–C7	66.7 (4)	C2–C1–C6	120.2 (9)
Pt–P1–C8	113.4 (4)	C1–C2–C3	123.8 (9)
Pt–P1–C9	115.4 (4)	C1–C2–C7	104.6 (8)
Pt–P1–C10	121.7 (4)	C3–C2–C7	131.6 (9)
C8–P1–C9	103.2 (9)	C2–C3–C4	117 (1)
C8–P1–C10	98.6 (8)	C3–C4–C5	121 (1)
C9–P1–C10	101.7 (9)	C4–C5–C6	121 (1)
Pt–P2–C11	123.1 (5)	C1–C6–C5	117 (1)
Pt–P2–C12	113.2 (6)	Pt–C7–C2	90.8 (7)
Pt–P2–C13	113.8 (6)		

dihydrometallacyclobutabenzene, i.e. for $\overline{\mathrm{Ni(CH_2\text{-}\mathit{o}\text{-}C_6H_4)}}\mathrm{(TMEDA)}$, has the X-ray structure been determined.[5j] For that reason it was of interest to obtain more detailed information about the molecular structure of **4a**. Furthermore, it was desirable to confirm the square-planar coordination of the platinum atom, as derived from the NMR data. Finally, a comparison of the structure of **4a** with those reported for platina(II)cyclobutanes[10c,15] would reveal the influence of the annelated benzene ring on the platinacyclobutane moiety.

The molecular structure of **4a** is presented in Figure 1. The final values for all refined atomic coordinates are given in Table II. Selected bond lengths and angles are listed in Table III and IV.

The platinacyclobutene ring is slightly puckered and is almost coplanar with the benzene ring. The benzene ring itself is completely planar; the C–C bonds are practically nonalternating and have normal lengths. The structure of **4a** is similar to that reported for $\overline{\mathrm{Ni(CH_2\text{-}\mathit{o}\text{-}C_6H_4)}}\mathrm{(TMEDA)}$;[5j] the C–M–C angle is normal. Because platinum–carbon bond lengths are larger than nickel–carbon bond lengths, the C–M–C angle in **4a** (66.7°) is smaller than in $\overline{\mathrm{Ni(CH_2\text{-}\mathit{o}\text{-}C_6H_4)}}\mathrm{(TMEDA)}$ (71.7°).[5j] As a consequence, the angle at the benzylic carbon in **4a** (90.8°) is larger than that in the nickel complex (85.3°). With regard to platina(II)cyclobutanes, the C–Pt–C angle in **4a** is slightly smaller ($\overline{\mathrm{PtCH_2CH_2CH_2}}\mathrm{(bpy)}$, 69.9°;[10c] $\overline{\mathrm{PtCH_2CMe_2CH_2}}\mathrm{(PEt_3)_2}$, 67.3°[15]); this is a straightforward consequence of the presence of sp²-hybridized carbon atoms in the four-membered ring of **4a**.

The platinum–carbon bonds are longer than those normally encountered for platinum–C(aryl) and platinum–C(alkyl) bonds. The benzylic Pt–C distance in **4a** (2.122 (7) Å) is significantly longer than that found for the Pt–C bonds in $\overline{\mathrm{PtCH_2CH_2CH_2}}\mathrm{(bpy)}$ (2.03 (1) and 2.04 (1) Å)[10e] and in $\overline{\mathrm{PtCH_2CMe_2CH_2}}\mathrm{(PEt_3)_2}$ (2.080 (6) and 2.086 (6) Å).[15] The Pt–C(aryl) bond length in **4a** (2.060 (8) Å) is only slightly longer compared to that in *cis*-$\mathrm{(PPh_3)_2Pt(C_6H_4\text{-}\mathit{o}\text{-}MeO)_2}$[16] (2.03 (1) Å) and comparable to that in *cis*-$\mathrm{(PEt_3)_2Pt(C_6H_5\text{-}\mathit{p}\text{-}Me)Cl}$ (2.05 (3) Å).[17] Slightly longer bonds in four-membered ring systems seem to be a general phenomenon in carbo- and metallacycles as compared to acyclic analogues.[18]

Experimental Section

Solvents were distilled from sodium–potassium alloy. 1,2-Dihydro-1-magnesacyclobutabenzene (**1**)[4e,5e,8] and dichloro(1,5-η^2-cyclooctadiene)platinum(II) (**2**)[19] were prepared according to literature procedures. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WM 250 spectrometer. All experiments were performed in a completely sealed and evacuated glass apparatus.[20]

1,1-Bis(trimethylphosphine)-1,2-dihydro-1-platina(II)-cyclobutabenzene (4a). To a suspension of **2** (175 mg, 0.47 mmol) in THF (25 mL) was added at −70 °C a suspension of **1** (0.47 mmol) in THF (25 mL). After the reaction mixture was stirred for 0.5 h at −70 °C, it was allowed to warm to −20 °C in 0.5 h. A yellow solution and a white precipitate (magnesium dichloride) were obtained. At −20 °C, the solvent was evaporated, and to the yellow residue of **3** thus obtained (not characterized) was added *n*-pentane (20 mL). After filtration, an excess of trimethylphosphine was added at −20 °C to the yellow filtrate. After the mixture was stirred for 0.5 h at −20 °C and for 0.5 h at room temperature, a colorless solution was obtained. After evaporation of the solvent, a colorless solid was isolated, which was recrystallized from toluene/*n*-heptane (1/1) at −80 °C, yielding 105 mg (51%) of colorless crystals of **4a**: mp 139–140 °C; ^{1}H NMR (dioxane-d_8) δ 1.13 (dd, 2 H, ^3J(P–H) = 4.4 Hz, 6.4 Hz, ^2J(Pt–H) = 67.9 Hz, CH_2), 1.55 (d, 9 H, ^2J(P–H) = 8.5 Hz, ^3J(Pt–H) = 23.4 Hz, PMe_3), 1.71 (d, 9 H, ^2J(P–H) = 8.5 Hz, ^3J(Pt–H) = 21.6 Hz, PMe_3), 6.48 (d, 1 H, ^3J(H,H) = 3.9 Hz, arom), 6.93 (m, 2 H, arom), 7.34 (dd, 1 H, ^3J(H–H) = 4.8 Hz, ^4J(P–H) 8.6 Hz, ^3J(Pt–H) = 62.5 Hz, arom); ^{1}H NMR (benzene-d_6, 90 MHz) δ 0.99 (d, 9 H, ^2J(P–H) = 8.4 Hz, ^3J(Pt–H) = 23.5 Hz, PMe_3), 1.17 (d, 9 H,

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^2J(P–H) = 8.4 Hz, ^3J(Pt–H) = 21.7 Hz, PMe_3), 2.06 (dd, 2 H, CH_2), 7.12 (m, 1 H, arom), 7.40 (m, 2 H, arom), 7.50 (m, 1 H, arom); ^{13}C NMR (dioxane-d_8) δ -9.9 (tdd, ^1J(C–H) = 132 Hz, ^2J(P–C) = 4.8 Hz, 87.2 Hz, ^1J(Pt–C) = 395 Hz, CH_2), 17.0 (qdd), ^1J(C–H) = 130 Hz, ^1J(P–C) = 29 Hz, ^3J(P–C) = 2 Hz, ^2J(Pt–C) = 32 Hz), 19.1 (qdd, ^1J(C–H) = 128 Hz, ^1J(P–C) = 27 Hz, ^3J(P–C) = 3 Hz, ^2J(Pt–C) = 34 Hz), 123.8 (ddd, ^1J(C–H) = 158 Hz, ^3J(C–H) = 8 Hz, ^3J(P–C) = 9 Hz, ^2J(Pt–C) = 72 Hz), 124.3 (d, ^1J(C–H) = 155 Hz), 124.4 (d, ^1J(C–H) = 157 Hz), 129.1 (d, ^1J(C–H) = 164 Hz), 129.5 (b s), 163.4 (b s).

1,1-Bis(triethylphosphine)-1,2-dihydro-1-platina(II)-cyclobutabenzene (4b). Compound **4b** was prepared via **3** by the procedure described for **4a**, using triethylphosphine instead of trimethylphosphine; **4b** was isolated as a yellow oil (50%). After short-path distillation (95 °C, 10^{-6} mbar), a colorless oil was obtained, which solidified on standing at room temperature after several days: ^{1}H NMR (benzene-d_6) δ 0.94 (td, 9 H, ^3J(H–H) = 7.7 Hz, ^3J(P–H) = 15.4 Hz, CH_3), 0.95 (td, 9 H, ^3J(H–H) = 7.8 Hz, ^3J(H–H) = 7.8 Hz, ^3J(P–H) = 15.6 Hz, CH_3), 1.51 (qd, 6 H, ^3J(H–H) = 7.7 Hz, ^2J(P–H) = 7.5 Hz, ^3J(Pt–H) = 19.1 Hz, PCH_2), 1.57 (dd, 2 H, ^3J(P–H) = 5.2 Hz, 6.5 Hz, ^2J(Pt–H) = 78.3 Hz, CH_2), 1.72 (qd, 6 H, ^3J(H–H) = 7.8 Hz, ^2J(P–H) = 7.6 Hz, PCH_2), 6.68 (ddd, 1 H, ^3J(H–H) = 4.9 Hz, ^4J(H–H) = 1.0 Hz, ^4J(P–H) = 4.9 Hz, ^3J(Pt–H) = 52.1 Hz arom), 7.03 (m, 2 H, arom), 7.38 (dd, ^3J(H–H) = 5.6 Hz, ^4J(H–H) = 1.5 Hz, arom). Anal. Calcd for $C_{19}H_{36}P_2Pt$: C, 43.76; H, 6.96. Found: C, 43.90; H, 6.88.

Reactions of 3 with Other Phosphines. The reactions were performed as described for **4a**, using tri-n-butylphosphine, triphenylphosphine, dimethylphenylphosphine, or diphenylmethylphosphine, instead of trimethylphosphine. From these reactions, mixtures of **4c**, **4d**, or **4e** and of unidentified products were isolated. It was not possible to separate **4c–e** from the impurities. Therefore, **4c** and **4e** were only identified by ^{31}P NMR spectroscopy and **4d** by its ^{31}P NMR spectrum and ^{1}H NMR spectrum. For ^{31}P NMR data, see Table I **4d**: ^{1}H NMR (benzene-d_6) δ 1.61 (dd, 2 H, ^3J(P–H) = 5.1 Hz, 6.0 Hz, CH_2), 6.73–7.73 (m, 34 H, arom); ^{31}P NMR of the impurities (benzene-d_6) δ 53.9, 42.0, -18.2, -31.3, -36.4 (with n-Bu$_3$P), 23.4, -4.1 ($\nu_{1/2}$ = 57 Hz) (with Ph$_3$P), -33.7 (^1J(Pt–P) = 3806 Hz) (with Me$_2$PhP; this product was identified as (Me$_2$PhP)$_4$Pt(0)[9]), -26.3, 4.8 (^1J(Pt–P) = 1838 Hz) (with MePh$_2$P).

Crystal Data of 4a. Crystals of **4a** are monoclinic, space group $P2_1/n$, with Z = 4, a = 15.317 (3) Å, b = 11.559 (2) Å, c = 9.093 (1) Å, β = 93.77 (3)°, V = 1597.00 (3) Å^3, D_{calcd} = 1.77 g·cm^{-3}, and μ(Mo Kα) = 90.5 cm^{-1}. Reflection intensities were recorded at ambient temperature on a Nonius CAD-4 diffractometer using graphite-monochromated radiation; 5093 were below the 2.5σ (I) level and were treated as unobserved. The structure was solved by means of the heavy-atom method. The lighter atoms (P, C) were solved by use of the Fourier difference method.

After isotropic block diagonal least-squares refinement, an empirical absorption correction was applied (DIFABS[21]). Continued anisotropic refinement converged to R = 0.036 and R_w = 0.039 (2311 reflections). Weighting scheme [$w = 1/(5.9 + F_o + 0.021F_o^2)$] was used, and the anomalous dispersion of Pt was taken into account. The hydrogen atoms were found, but their positions did not refine.

The calculations were carried out with X-ray 76.[22] The scattering factors were taken from Cromer and Mann;[23] the dispersion correction was taken from ref 24.

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Supplementary Material Available: Tables of distances of atoms from planes, dihedral angles, and anisotropic thermal parameters (Tables V–VII) (3 pages); a listing of structure factors (Table VIII) (16 pages). Ordering information is given on any current masthead page.

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