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Synthesis and Structure of a Cationic Diplatinum *μ*-Alkylidene *μ*-Hydride Complex

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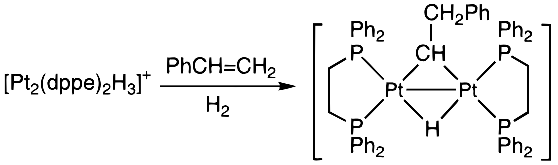
The dinuclear *μ*-alkylidene *μ*-hydride cation [$Pt_2(dppf)_2(\mu\text{-}CHCH_2Ar)(\mu\text{-}H)$][Br] (**2**, dppf = $Ph_2PC_5H_4FeC_5H_4PPh_2$, Ar = *p*-$MeOC_6H_4$) was obtained unexpectedly from reaction of *p*-methoxybromostyrene (**3**) with $Pt(dppf)Cl_2/NaBH_4$/norbornene and crystallographically characterized. Solutions of the hydride $[Pt(dppf)H]_2$ (**7**), prepared by deprotonation of the known cation $[Pt_2(dppf)_2H_3]^+$ (**6**) or by treatment of $Pt(dppf)Cl_2$ with two equiv of $LiBEt_3H$, deposit an insoluble precipitate formulated as $[Pt(dppf)H]_n$ (**11**), which also gives **2** on treatment with **3**.

Although many dinuclear platinum complexes are known, a particularly rare class of these compounds contains bridging alkylidene and hydride ligands.[1] Minghetti and co-workers reported the unusual reaction shown in Scheme 1 to give what, so far, is the unique example $[Pt_2(dppe)_2(\mu\text{-}CHCH_2Ph)(\mu\text{-}H)]^+$ (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$).[2] We report here a new synthetic route to the closely related complex $[Pt_2(dppf)_2(\mu\text{-}CHCH_2Ar)(\mu\text{-}H)]^+$ (**2**, dppf = $Ph_2PC_5H_4FeC_5H_4PPh_2$, Ar = *p*-$MeOC_6H_4$) and its spectroscopic and crystallographic characterization.

Complex **2** was initially obtained in poor yield (Scheme 2) as an unexpected product from the reaction of *p*-methoxybromostyrene (**3**) with a material generated in situ from $Pt(dppf)Cl_2$, $NaBH_4$, and norbornene in CH_2Cl_2/EtOH, according to a procedure for the preparation of Pt(dppf)(CH=CHAr)Br (**4**) reported by Brown and Cooley.[3] Complex **2** was prepared reproducibly several times (see Experimental section). The original preparation of **4** reported the use of dry solvents, and we used absolute ethanol without further purification, but this does not explain our results since the expected Pt(II) oxidative addition product **4** could also be made under very similar conditions (see Experimental Section). Although we do not understand the reason for these observations, we have developed an alternative reproducible synthesis of **2** (see below).

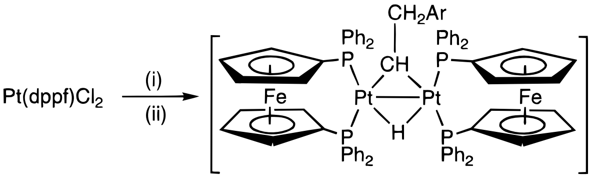
Scheme 1[a]



1

[a] dppe = $Ph_2PCH_2CH_2PPh_2$. Reference 2.

Scheme 2[a]



2

[a] Ar = *p*-$MeOC_6H_4$. Reagents: (i) 2 equiv of $NaBH_4$, norbornene, CH_2Cl_2/EtOH; (ii) *p*-methoxybromostyrene (**3**).

Complex **2** was identified spectroscopically in comparison to **1** and the *μ*-carbonyl complex[4] $[Pt_2(dppf)_2(\mu\text{-}CO)(\mu\text{-}H)]^+$ (**5**). The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, Figure 1) shows two multiplets at δ 22.2 ($^1J_{Pt-P} = 4690$, trans to H), and 11.9 ($^1J_{Pt-P} = 2403$, trans to C). The fine structure in the spectrum could be reproduced by simulation (Figure 1a,b, see Figure 2 for atom labeling) using the coupling constants above in addition to $J_{14} = 3$, $J_{15} = 230$, $J_{34} = 2$, $J_{35} = 16$, $J_{56} = 43$.[5] These results are similar to those for **1** (for P trans to H, $^1J_{Pt-P} = 4350$, $^3J_{Pt-P} = 173$; for P trans to C, $^1J_{Pt-P} = 2082$) and for **5** at low temperature ($^1J_{Pt-P} = 4927$, $^3J_{Pt-P} = 600$ (P trans to H); $^1J_{Pt-P} = 2892$ (P trans to C)). In all three compounds, both $^1J_{Pt-P}$ and $^3J_{Pt-P}$ values for P trans to the *μ*-hydride are much larger than those for P trans to the *μ*-alkylidene or *μ*-carbonyl, reflecting the relative trans influences of these ligands.

In the ^1H NMR spectrum (CD_2Cl_2) the hydride resonance appears at δ −3.31 (tt, $^2J_{P-H} = 13, 79$, $^1J_{Pt-H} = 566$), which is very similar to the results for **1** ($^2J_{P-H} = 7.8, 76$, $^1J_{Pt-H} = 578$) and **5** at low temperature ($^2J_{P-H}$

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[1] For a review, see: Anderson, G. K. *Adv. Organomet. Chem.* **1993**, *35*, 1−39.

[2] Minghetti, G.; Albinati, A.; Bandini, A. L.; Banditelli, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 120−121.

[3] Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353−359.

[4] Bandini, A. L.; Banditelli, G.; Cinellu, M. A.; Sanna, G.; Minghetti, G.; Demartin, F.; Manassero, M. *Inorg. Chem.* **1989**, *28*, 404−410.

[5] Simulation with gNMR (Cherwell Scientific). $J_{12} = 200$ was used in the simulation, but the spectrum was not sensitive to this coupling constant.

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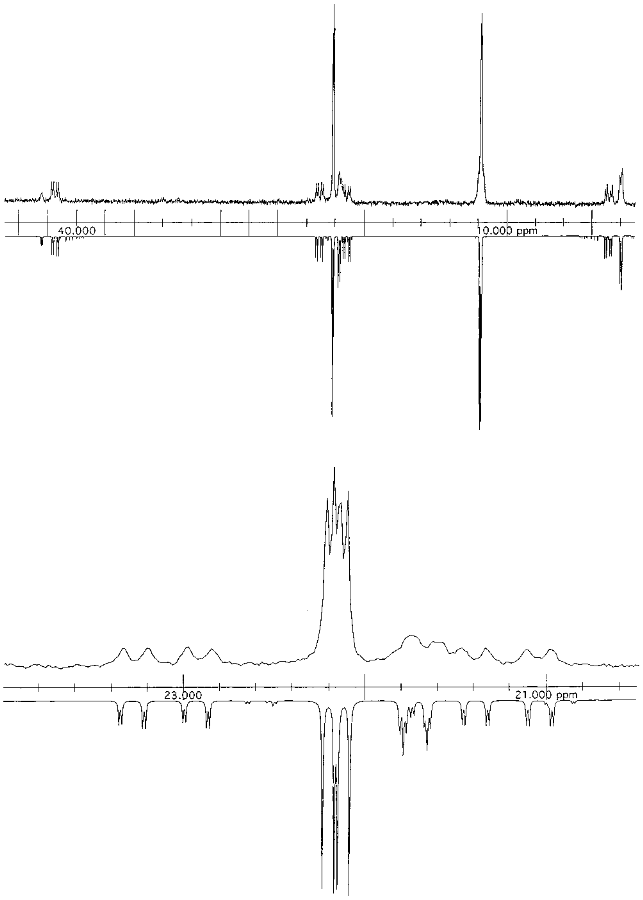


Figure 1. Experimental (top) and simulated (bottom) $^{31}P\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2. (a) full spectrum, (b) expansion.

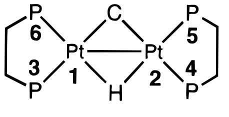


Figure 2. Atom labeling for complex **2**.

= 16, 82, $^1J_{Pt-H}$ = 453).[2,4] The protons of the alkylidene ligand give rise to broad (even at −60 °C) peaks at δ 1.33 (CH_2) and 4.87 (CH); these are coupled to each other in the $^1H-^1H$ COSY spectrum, and C−H correlation spectra obtained with the HMQC sequence show they are attached to carbons with ^{13}C NMR signals at 44.5 and 135.8 ppm, respectively. For comparison, the μ-CH ^{13}C NMR signal in **1** appears at δ 124.5; the rest of the ^1H and ^{13}C NMR spectra were not reported.[2]

The crystal structure of **2** as the bromide salt, with cocrystallized CH_2Cl_2 and water, is shown in Figure 3. Figure S1 in the Supporting Information shows the structure from a different angle. Data collection and structure refinement are summarized in Table 1, selected bond lengths and angles appear in the figure caption, and additional details are given in the Experimental Section and the Supporting Information. The metal hydride was not observed. The C−C bond length in the alkylidene ligand (1.522(11) Å) confirms reduction of the C=C double bond and is similar to that in **1** (1.52(2) Å).[2] The geometry of the Pt_2C triangle compares well with those in the related complexes **1** and **5**: Pt−Pt distances for these three compounds are 2.7314(4), 2.735(1), and 2.790(1) Å, while the Pt−C−Pt angles are 82.5(3)°, 84.1(6)°, and 87.3(3)°. The Pt−C bond lengths are also very similar: 2.065(7) and 2.076(8), 2.02(2) and 2.07(2), and 2.039(8) and 2.004(7) Å. The Pt−P(dppf) distances in **2** and **5** (for P trans to H, 2.246(2) and 2.259(2) Å in **2**, 2.300(2) and 2.293(2) Å in **5**; for P trans to C, 2.337(2) and 2.311(2) Å in **2**, 2.358(2) and 2.359(2)Å in **5**) are also similar. This indicates, consistent with the ^{31}P NMR results, that the trans influence of the bridging carbonyl and alkylidene ligands is similar and larger than that of the μ-H ligand.[6] Finally, the bite

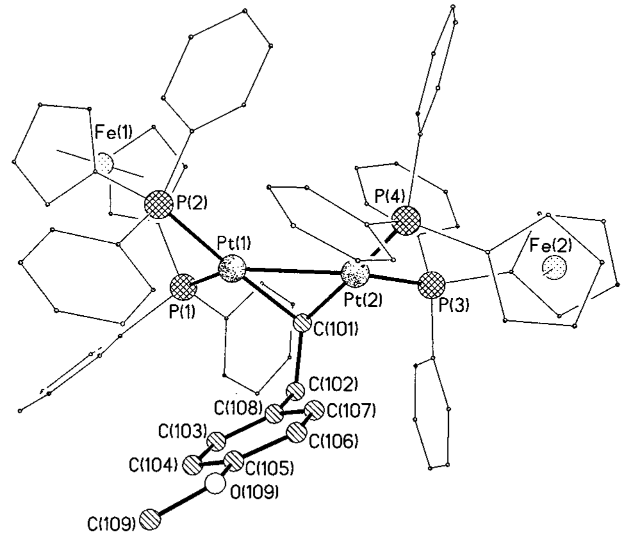
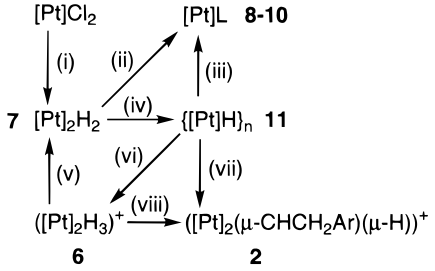


Figure 3. ORTEP diagram of $2\cdot0.5CH_2Cl_2\cdot0.5H_2O$. For clarity, the bromide counterion and cocrystallized solvents are not shown. Selected bond lengths (Å) and angles (deg): Pt(1)−C(101) 2.065(7), Pt(1)−P(1) 2.246(2), Pt(1)−P(2) 2.337(2), Pt(1)−Pt(2) 2.7314(4), Pt(2)−C(101) 2.076(8), Pt(2)−P(3) 2.259(2), Pt(2)−P(4) 2.311(2), C(101)−C(102) 1.522(11); Pt(1)−C(101)−Pt(2) 82.5(3), C(101)−Pt(1)−P(1) 90.1(2), C(101)−Pt(1)−P(2) 169.0(2), P(1)−Pt(1)−P(2) 100.60(7), C(101)−Pt(1)−Pt(2) 48.9(2), P(1)−Pt(1)−Pt(2) 134.93(5), P(2)−Pt(1)−Pt(2) 121.61(6), C(101)−Pt(2)−P(3) 86.5(2), C(101)−Pt(2)−P(4) 170.3(2), P(3)−Pt(2)−P(4) 102.20(7), C(101)−Pt(2)−Pt(1) 48.6(2), P(3)−Pt(2)−Pt(1) 126.28(6), P(4)−Pt(2)−Pt(1) 125.91(5).

Table 1. Crystal Data and Structure Refinement

empirical formula	$C_{77.5}H_{69}BrClFe_2O_{1.5}P_4Pt_2$
fw	1765.58
temp	223(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimensions	a = 23.69760(10) Å, α = 90° b = 13.8429(2) Å, β = 91.4520(10)° c = 41.73820(10) Å, γ = 90°
volume, *Z*	13687.5(2) Å^3, 8
density (calcd)	1.711 mg/m^3
abs coeff	5.253 mm^{-1}
F(000)	6912
cryst color, size	yellow block, 0.50 × 0.50 × 0.40 mm
θ range for data collection	0.98−28.49°
limiting indices	$-31 \le h \le 31, 0 \le k \le 16, 0 \le l \le 55$
no. of reflns collected	26 044
no. of indep reflns	14 352 (R_{int} = 0.0427)
abs corr	empirical from DIFABS
max and min transmission	1.000 and 0.798
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	14343/0/813
goodness-of-fit on F^2	1.348
final *R* indices [$I > 2\sigma > (I)$]	R1 = 0.0591, wR2 = 0.1161
R indices (all data)	R1 = 0.0844, wR2 = 0.1305
largest diff peak and hole	3.710 and −4.126 e Å^{-3}

Scheme 3[a]



[a] [Pt] = Pt(dppf), Ar = *p*-$MeOC_6H_4$. Reagents: (i) 2 equiv of $LiBEt_3H$ (ii) 1 equiv of L per Pt, L = *trans*-stilbene (for **8**), bromostyrene **3** (for **9**), or dppf (for **10**); (iii) 1 equiv of L per Pt, L = *trans*-stilbene or dppf; (iv) THF, room temperature, ca. 1 h (v) KOt-Bu or $LiN(SiMe_3)_2$; (vi) $HBF_4{\cdot}Me_2O$; (vii) bromostyrene **3**; (viii) bromostyrene **3** in CH_2Cl_2, then KOt-Bu or $LiN(SiMe_3)_2$

angle of the dppf ligands in **2** (100.60(7)° and 102.20(7)°) is similar to that in carbonyl complex **5** (103.68(6) and 103.64(6)°).

The unexpected formation of **2** suggested the intermediacy of a platinum hydride. Therefore, treatment of $Pt(dppf)Cl_2$ with $NaBH_4$ in CH_2Cl_2/EtOH *without norbornene* was investigated. The IR (KBr) spectrum of the insoluble yellow solid formed showed an absorption at 2019 cm^{-1} assigned to a Pt−H stretch. When this material was treated with $AgBF_4$ in CH_2Cl_2, it dissolved and ^{31}P NMR showed that an ~1:1 mixture of the known cations $[Pt(dppf)(\mu\text{-}OH)]_2^{2+}$ and $[Pt_2(dppf)_2H_3]^+$ (**6**) was present.[4] The insoluble material on treatment with bromostyrene **3** gave dinuclear **2** plus several other products after heating in CH_2Cl_2 at 60 °C for 3 days, according to ^{31}P NMR.

To investigate the role of trihydride cation **6** further, it was prepared independently and treated with bromostyrene **3** in CH_2Cl_2 (Scheme 3). No reaction occurred even on heating to 55 °C for 3 days. However, when this reaction mixture was treated with $NaBH_4$ in EtOH, KOt-Bu, or $LiN(SiMe_3)_2$, dinuclear **2** was formed. These observations suggested the intermediacy of the neutral hydride $[Pt(dppf)H]_2$ (**7**), generated by deprotonation of cation **6**. Indeed, treatment of **6** with KOt-Bu or $LiN(SiMe_3)_2$ in THF gave **7** as a red solution whose ^{31}P NMR spectrum (δ 37.3, $^1J_{Pt-P} = 4184$, $^3J_{Pt-P} = 218$, $^2J_{P-P} = 40$) is similar to that of related hydride dimers (Scheme 3).[7] When the deprotonation was carried out in THF-d_8, the hydride resonance for **7** was observed by ^1H NMR as a broad signal at −3.4 ppm. Complex **7** could also be prepared conveniently by reaction of $Pt(dppf)Cl_2$ with 2 equiv of $LiBEt_3H$ in THF (Scheme 3), which gave a dark solution whose ^{31}P NMR spectrum was the same as that described above. THF solutions of **7** generated by deprotonation of cation **6** reacted immediately (Scheme 3) with *trans*-stilbene, bromostyrene **3**, and dppf to give Pt(dppf)(*trans*-stilbene) (**8**), Pt(dppf)(**3**) (**9**), and $Pt(dppf)_2$ (**10**), respectively; these known compounds were identified by ^{31}P NMR.[8] Thus, as previously reported for the analogous $[Pt(dppe)H]_2$,[9] complex **7** is a convenient source of Pt(0).

When hydride **7** was generated by either of these methods, a yellow solid (**11**) rapidly precipitated from solution (Scheme 3). Unfortunately, the formation of this solid prevented us from acquiring low-temperature NMR spectra of **7**. The precipitate was insoluble in the common solvents and could not be recrystallized. Presumably, it is oligomeric with bridging dppf ligands;[10] elemental analysis and IR ($\nu_{Pt-H} = 2018$ cm^{-1}, KBr) are consistent with the composition $[Pt(dppf)H]_n$. The deuteride $[Pt(dppf)D]_n$ was prepared similarly from $LiBEt_3D$ ($\nu_{Pt-D} = 1494$ cm^{-1}, KBr). Addition of $HBF_4{\cdot}Me_2O$ to a CH_2Cl_2 slurry of **11** gave a yellow-orange solution of trihydride cation **6** (Scheme 3). Similarly, treatment of THF slurries of **11** with *trans*-stilbene or dppf slowly led to the formation of the zero-valent complexes **8** and **10**.

Reaction of a THF slurry of **11** with bromostyrene **3** reproducibly led to the formation of dinuclear cation **2**; in one case (see Experimental Section), it was isolated after recrystallization in 42% yield. However, this reaction sometimes gave, in addition to **2**, the bromostyrene π-complex **9** and the oxidative addition product Pt(dppf)(CH=CHAr)Br (**4**). In CH_2Cl_2, **2** and **4** were observed (Scheme 3). Despite the occasional formation of these byproducts, this procedure is the best and most reproducible way to make **2**. These results and the physical properties of **7** and **11** are consistent with the idea that these compounds have different structures and hence different reactivity.

These observations suggest that a Pt hydride is involved in the formation of **2**, presumably via bromostyrene insertion into a Pt−H bond followed by Pt−C bond formation with the loss of bromide ion. However, the details of the mechanism and the factors responsible for the varied yields of the products in either of the syntheses of **2** remain unclear. It is possible that the insoluble material formed in the initial $Pt(dppf)Cl_2$/$NaBH_4$ mixture contains **11**, as suggested by the similarity of their IR spectra. However, since neither of these materials could be purified, further mechanistic speculation seems imprudent.

In conclusion, the unusual μ-alkylidene μ-hydride cation **2** has been prepared and spectroscopically and crystallographically characterized. The new hydrides $[Pt(dppf)H]_2$ (**7**) and $[Pt(dppf)H]_n$ (**11**) were prepared; although **11** reacts with bromostyrene **3** to give **2**, the mechanism of this reaction remains unclear. Finally, the synthesis of **2** by reaction of a bromostyrene deriva-

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(6) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

(7) ^{31}P NMR data for a series of $[Pt(diphos)H]_2$ dimers (diphos = dippe ($(i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2$), dcpe ($Cy_2PCH_2CH_2PCy_2$; Cy = cyclo-$C_6H_{11}$), dtbpe ($(t\text{-}Bu)_2PCH_2CH_2P(t\text{-}Bu)_2$), dppe) is given in Schwartz, D. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4014−4025 and references therein. A referee pointed out that the Pt−P coupling constants in **7** compare better with those of the dfepe analog (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$), see Bennett, B. L.; Roddick, D. M. *Inorg. Chem.* **1996**, *35*, 4703−4707) than with these examples.

(8) Pt(dppf)(*trans*-stilbene) (**8**) has been prepared independently by treatment of a mixture of $Pt(dppf)Cl_2$ and *trans*-stilbene with 2 equiv of $LiBEt_3H$ in THF. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.5 ($^1J_{Pt-P} = 3763$). Full details of the synthesis and characterization will be reported separately. For the bromostyrene π-complex (**9**), see ref 3. For $Pt(dppf)_2$ (**10**), see: Fang, Z.-G.; Low, P. M. N.; Ng, S.-C.; Hor, T. S. A. *J. Organomet. Chem.* **1994**, *483*, 17−20. Treatment of a mixture of **6** and **3** in THF with KOt-Bu also gave the π-complex **9**, but a similar experiment in CH_2Cl_2 gave cation **2** plus vinyl bromide complex **4**.

(9) Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1554−1556.

(10) For a review of dppf coordination chemistry with examples of μ-dppf coordination, see: Gan, K.-S.; Hor, T. S. A. In *Ferrocenes. Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T.; Eds.; VCH: Weinheim, Germany, 1995; pp 3−104.

tive with a metal hydride is novel and may provide a general route to μ-alkylidene complexes.

Experimental Section

General Considerations. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, and toluene were dried and distilled before use by employing Na/benzophenone. CH_2Cl_2 was distilled from CaH_2. Absolute ethanol was used as purchased without further purification.

Unless otherwise noted, all NMR spectra were recorded on a Varian 300 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are reported relative to Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported relative to H_3PO_4 (85%), used as an external reference. Unless otherwise noted, peaks in the NMR spectra are singlets. Coupling constants are reported in hertz. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR instrument and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. Unless otherwise noted, reagents were from commercial suppliers. The following compounds were made by the literature procedures: $Pt(dppf)Cl_2$,[4] p-$MeOC_6H_4$-$CH{=}CHBr$,[11] $[Pt_2(dppf)_2H_3][BF_4]$.[4]

[$Pt_2(dppf)_2(\mu$-$CHCH_2Ar)(\mu$-$H)$][Br] (2, Ar = pMeOC$_6$H$_4$). To a solution of $Pt(dppf)Cl_2$ (prepared from $Pt(COD)Cl_2$ and dppf and recrystallized from CH_2Cl_2/ether, 189 mg, 0.23 mmol, COD = 1,5-cyclooctadiene) in CH_2Cl_2 (5 mL) was added a solution of norbornene (113 mg, 1.20 mmol) in absolute ethanol (5 mL), which was purged with nitrogen for 60 min. When solid $NaBH_4$ (39 mg, 1.0 mmol) was added, the solution bubbled, then changed color from yellow to dark orange and then to olive/khaki. After 3 h of stirring, the solution was filtered. The solid was washed with ether (2 × 5 mL) and dried in vacuum. The solid was suspended in CH_2Cl_2 (5 mL) and p-$MeOC_6H_4CH{=}CHBr$ (**3**, 60 mg, 0.28 mmol) was added to afford, after 2 days of stirring, a dark yellow solution. The solution was filtered, and the solvent was removed. The solid residue was redissolved in CH_2Cl_2 and recrystallized with ether at −20 °C to give the product as a dark yellow solid in ~30% yield. Subsequent additional recrystallizations afforded dark orange crystals of X-ray quality. This preparation could be reproduced several times, but a separate batch of $Pt(dppf)Cl_2$, which was not recrystallized, gave the reported Pt(dppf)(CH=CHAr)Br (**4**).[3] We have not been able to discover the reason(s) for the success or failure of these syntheses.

^1H NMR (CD_2Cl_2, 500 MHz): δ 7.71 (4H, m, Ar), 7.53 (2H, m, Ar), 7.4−7.1 (24H, m, Ar), 7.0−6.8 (12H, m, Ar), 6.61 (2H, m, Ar), 4.87 (br, 1H, CH), 4.63 (2H, CH), 4.46 (2H, CH), 4.41 (2H, CH), 4.39 (2H, CH), 4.34 (2H, CH), 4.20 (2H, CH), 3.81 (3H, Me), 3.77 (2H, CH), 3.60 (2H, CH), 1.33 (2H, br, CH_2), −3.31 (1H, tt, $^2J_{P-H} = 13$, $^2J_{P-H} = 79$, $^1J_{Pt-H} = 566$, Pt-H). ^{13}C NMR (CD_2Cl_2): δ 157.8 (Ar), 135.8 (CH), 135.2 (m, Ar), 134.1 (m, Ar), 133.3 (m, Ar), 131.8 (Ar), 130.7 (m, Ar), 128.5 (m, Ar), 113.0 (Ar), 76.0 (m, Cp), 75.1 (m, Cp), 73.8 (m, Cp), 72.9 (m, Cp), 55.4 (OMe), 44.5 (CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.2 (m, $^1J_{Pt-P} = 4690$), 11.9 (m, $^1J_{Pt-P} = 2403$). IR (KBr): 3050, 1508, 1480, 1435, 1385, 1306, 1243, 1166, 1097, 1030, 748, 696. Anal. Calcd for $C_{77}H_{67}BrFe_2OP_4Pt_2$: C, 53.96; H, 3.94. Found: C, 53.57; H, 4.55.

Crystallographic Structural Determination for 2·0.5CH$_2$Cl$_2$·0.5H$_2$O. Crystal, data collection, and refinement parameters are given in Table 1. The systematic absences in the diffraction data are consistent with the space groups *Cc* or *C*2/*c*. The E-statistics and the value of *Z* indicated the centrosymmetric space group, which was verified by the chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. An empirical absorption correction was applied, based on a Fourier series in the polar angles of the incident and diffracted beam paths and was used to model an absorption surface for the difference between the observed and calculated structure factors.[12] The asymmetric unit contains one cation, a bromide anion on a 2-fold axis, a bromide anion disordered over an inversion center, one-half of a molecule of dichloromethane, and one-half of a molecule of water. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms, except those on the water molecule, which were omitted, were treated as idealized contributions. One significant peak remained on the difference map (3.71 e/Å^3) but was in a chemically unreasonable position (<0.5 Å from Pt) and was considered noise.

All software and sources of the scattering factors are contained in the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Reaction of Pt(dppf)Cl$_2$ with NaBH$_4$. To a stirred solution of $Pt(dppf)Cl_2$ (50 mg, 0.06 mmol) in CH_2Cl_2 (15 mL) was added an excess of $NaBH_4$ (8 mg, 0.21 mmol) in ethanol (10 mL). The color of the solution changed from yellow to dark orange, and after 1 h of stirring a yellow solid formed. The solution was decanted, and the solid residue was washed with petroleum ether (2 × 7 mL) and dried under vacuum to give an insoluble yellow solid. IR (KBr): 3049, 2970, 2295, 2019 (ν_{Pt-H}), 1479, 1434, 1166, 1095, 1028, 744. This solid is probably a mixture of compounds, as indicated by the following experiments.

(a) A sample of this material (50 mg) was suspended in CH_2Cl_2, and an excess of $AgBF_4$ (20 mg, 0.1 mmol) was added. After 15 min of stirring, the dark green solution was filtered. The ^{31}P NMR spectrum of the solution showed a mixture of the known[4] hydroxide $[Pt_2(dppf)_2(\mu\text{-}OH)_2][BF_4]_2$ and trihydride cation **6** in approximately equal amounts.

(b) A sample of this material (20 mg) was placed into an NMR tube with excess of bromostyrene **3** (9 mg, 0.05 mmol) in CH_2Cl_2, and the solution was heated at 60 °C. After 3 days, the solid dissolved to give a dark yellow solution; ^{31}P NMR showed **2** was the major product.

Complex 2 via [Pt$_2$(dppf)$_2$H$_3$][BF$_4$] (6). $[Pt_2(dppf)_2H_3][BF_4]$ (144 mg, 0.09 mmol) was dissolved in CH_2Cl_2. Bromostyrene **3** (20 mg, 0.15 mmol) was added as a CH_2Cl_2 solution, and the reaction was monitored by ^{31}P NMR. After 6 days of stirring, no reaction occurred. $LiN(SiMe_3)_2$ was added to the solution in excess, and the solution was stirred for 5 days. The major product, **2**, was identified by ^{31}P NMR.

[Pt(dppf)H]$_2$ (7) and [Pt(dppf)H]$_n$ (11). To a stirred solution of $Pt(dppf)Cl_2$ (113 mg, 0.13 mmol) in THF (5 mL) was added Super-Hydride ($LiBEt_3H$, 0.27 mL of 1M THF solution, 0.27 mmol) to afford a dark red solution. At this point, the $^{31}P\{^1H\}$ NMR spectrum showed a peak at δ 37.3 ($^1J_{Pt-P} = 4184$, $^3J_{Pt-P} = 218$, $^2J_{P-P} = 40$), plus minor impurities. After 1 h of stirring, a yellow solid precipitated out of the solution. The solution was decanted, and the solid was washed with THF and dried in vacuum to give 89 mg (78% yield) of **11** as insoluble yellow powder. IR (KBr): 3050, 2925, 2018 (Pt-H), 1479, 1434, 1166, 1096, 1067, 1029, 822, 745, 695. Anal. Calcd. for $C_{68}H_{58}P_4Fe_2Pt_2$: C, 54.41; H, 3.89%. Found: C, 54.13; H, 4.39%.

[Pt(dppf)D]$_n$ (11−D) was prepared following a similar procedure as that for the hydride, using Super-Deuteride, and was isolated as a brown solid, which did not give satisfactory elemental analyses. IR (KBr): 3051, 2923, 1494, 1480, 1435, 1097, 1067, 823, 747, 696.

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Deprotonation of 6: Formation of 7 and its Reactions with *trans*-Stilbene, dppf, and Bromostyrene 3. To an orange slurry of trihydride cation **6** (30 mg, 0.019 mmol) in THF-d_8 (0.5 mL) was added a solution of KOt-Bu (5 mg, 0.05 mmol) in 0.3 mL of THF-d_8. On mixing, a red solution formed; some suspended solid remained. The $^{31}P\{^1H\}$ NMR spectrum was the same as that described above in the synthesis from Pt(dppf)Cl_2 and $LiBEt_3H$. ^1H NMR (THF-d_8): δ 7.66 (br, 14H), 7.30 (4H), 7.11 (apparent t, "*J*" = 7, 8H), 6.93 (apparent t, "*J*" = 7, 14H), 4.21 (8H), 4.15 (8H), −3.4 (br, 2H). After 1 h, most of the material had precipitated out as an orange-brown solid, which turned yellow over several hours.

In related experiments, hydride **7** was generated as a red THF solution by addition of KOt-Bu (2 mg, 0.02 mmol) to 10 mg (0.006 mmol) of cation **6**. Addition of *trans*-stilbene (5 mg, 0.03 mmol) to one such mixture caused an immediate color change to yellow-orange; ^{31}P NMR confirmed the formation of Pt(dppf)(*trans*-stilbene) (**8**). Similarly, addition of dppf (10 mg, 0.02 mmol) in a separate experiment gave a yellow solution; ^{31}P NMR showed the presence of Pt(dppf)$_2$ (**10**) and excess dppf. In another experiment, 20 mg (0.012 mmol) of **6** was treated with 2 mg (0.02 mmol) of KOt-Bu. To the resulting orange-red slurry was added bromostyrene **3** (5 mg, 0.02 mmol). The color of the solution changed to yellow, and ^{31}P NMR showed that the π-complex Pt(dppf)(*p*-$MeOC_6H_4CH{=}CHBr$) (**9**) had formed.

Protonation of [Pt(dppf)H]$_n$ (11). Hydride complex **11** (40 mg, 0.03 mmol) was suspended in THF (2 mL). Upon addition of $HBF_4{\cdot}Me_2O$ (5 mg, 0.04 mmol) the solution acquired a yellow color. After 3 h of stirring, the color of the solution became orange and the solid dissolved completely. The solvent was removed, and the solid residue was redissolved in CH_2Cl_2 and filtered. The product $[Pt_2(dppf)_2H_3][BF_4]$ (**6**) was identified by ^{31}P NMR. This reaction can also be carried out on a larger scale in CH_2Cl_2.

Reactions of [Pt(dppf)(H)]$_n$ (11) with dppf and *trans*-Stilbene. A slurry of [Pt(dppf)(H)]$_n$ (20 mg, 0.01 mmol) and dppf (10 mg, 0.02 mmol) in 1 mL of THF was placed in an NMR tube. No visible reaction occurred. After 15 h, ^{31}P NMR showed that Pt(dppf)$_2$ (**10**) had formed; some dppf was also observed, as well as some remaining insoluble solid. In a similar experiment with *trans*-stilbene (6 mg, 0.03 mmol), Pt(dppf)(*trans*-stilbene) (**8**) was observed by ^{31}P NMR after 15 h; again, some insoluble solid remained.

Complex 2 via [Pt(dppf)H]$_n$ (11). Pt(dppf)Cl_2 (108 mg, 0.13 mmol) was suspended in THF (5 mL). Upon addition of Super-Hydride (0.27 mL of 1M solution in THF, 0.27 mmol), the yellow solid rapidly dissolved with bubbling to form a dark orange solution. After 1 h at room temperature a yellow precipitate formed. The solution was decanted, and the solid residue was washed with ether (3 × 5 mL) and dried. *p*-$MeOC_6H_4CH{=}CHBr$ (15 mg, 0.07 mmol) was added to the solid as a solution in THF (10 mL). After 2 days of stirring, the solution was filtered, the solvent was removed, and the solid residue was redissolved in CD_2Cl_2. The ^{31}P NMR spectrum showed mostly **2** with minor impurities of other unidentified compounds. Addition of ether and cooling to −20 °C gave 48 mg (42% yield) of **2**.

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Supporting Information Available: Tables of the crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and ORTEP diagram of $\mathbf{2}{\cdot}0.5H_2O{\cdot}0.5CH_2Cl_2$ (12 pages). Ordering information is given on any current masthead page.

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