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Synthesis and Reactivity of a Dimeric Platinum Phosphinidene Complex

Igor V. Kourkine and David S. Glueck*

6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

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The dimeric platinum phosphinidene complex [Pt(dppe)(μ-PMes)]$_2$ (**1**; dppe = $Ph_2PCH_2CH_2PPh_2$, Mes = 2,4,6-$Me_3C_6H_2$) was prepared by double deprotonation of [Pt(dppe)(μ-PHMes)]$_2$[BF_4]$_2$ (**3**); use of 1 equiv of base gives the monocationic complex [{Pt(dppe)}$_2$(μ-PHMes)(μ-PMes)][BF_4] (**2**), which can also be made from **1** and 1 equiv of HBF_4. NMR data suggest that complex **1** contains pyramidal μ-phosphinidene ligands, and it undergoes nucleophilic reactions typical of a tertiary phosphine. Alkylation with MeI affords [Pt(dppe){μ-P(Me)Mes}]$_2$[BF_4]$_2$ (**4**), BH_3•THF gives the borane adduct [Pt(dppe){μ-P(BH_3)Mes}]$_2$ (**5**), and air oxidation yields [Pt(dppe){μ-P(O)Mes}]$_2$ (**6**). However, reaction with sulfur gives the monomeric trithioxophosphorane complex Pt(dppe)(S_3PMes) (**7**), which was prepared independently from Pt(dppe)(*trans*-stilbene) and [MesPS_2]$_2$.

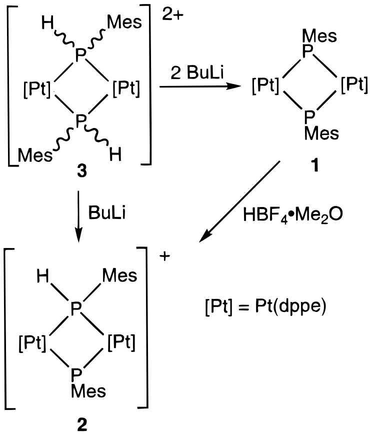
Introduction

Metal−ligand multiple bonds are common in early transition metal complexes of terminal oxo ligands and their isoelectronic analogs.[1] In contrast, related late metal compounds usually feature bridging ligands instead of metal−ligand multiple bonding. Mayer has suggested that these observations can be explained by the destabilizing influence of filled−filled pπ−dπ interactions, which were also proposed to account for the observed nucleophilicity of oxo and related ligands in late metal complexes.[2] A well-studied example of such effects is the series of oxo-[3] and sulfido-bridged[4] platinum(II) dimers [PtL_2(μ-E)]$_2$ (L = phosphine; E = S, O), whose nucleophilic reactivity has been described. We report here the preparation and a reactivity study of an isoelectronic platinum phosphinidene complex, which allows a comparison of the properties and reactivity of these bridging ligands at Pt centers.

Results and Discussion

In an extension of Sharp's synthesis[3] of μ-oxo Pt dimers from μ-hydroxo precursors, deprotonation of [Pt(dppe)(μ-PHMes)]$_2$[BF_4]$_2$ (**3**; dppe = $Ph_2PCH_2CH_2PPh_2$, Mes = 2,4,6-$Me_3C_6H_2$)[5] with 2 equiv of *n*-BuLi, LiN(SiMe_3)$_2$, or other strong base generates the platinum phosphinidene complex [Pt(dppe)(μ-PMes)]$_2$ (**1**; Scheme 1). Crystallization directly from the resulting solution affords neutral **1** as a red-orange air- and water-sensitive solid which cocrystallizes with 2 equiv of LiBF_4 and THF, as demonstrated by elemental analysis and the ^{1}H and ^{19}F NMR and IR spectra. Salt-free **1** is isolated by extraction with benzene. Since its ^{31}P and ^{1}H NMR spectra are identical to those of the LiBF_4-containing material, there is no P−Li interaction in **1**, in contrast to the spectroscopically and crystallographically observed Li−O interactions in the [PtL_2(μ-O)]$_2$•*n*LiBF_4 (*n* = 1, 2) complexes.[3c]

Scheme 1



Related μ-sulfido complexes contain either planar[6] or puckered[7] Pt_2S_2 rings. The complex [Pt(PPh_3)$_2$(μ-O)]$_2$•LiBF_4 contains a bent Pt_2O_2 ring, perhaps to enable chelation of lithium by the oxo ligands, while a similar ring is planar in Li$_2$[Pt(dppm-H)(μ-O)]$_2$•4THF.[3c] [Pt(PPh_3)$_2$(μ-Te)]$_2$[8] and the PEt_3 analog[9] contain planar Pt_2Te_2 rings. These examples and related experimental and theoretical results demonstrate that planar and hinged cores in such molecules are similar in energy.[10]

Several possible structures for **1** are illustrated in Figure 1.[11] Trigonal planar μ-PMes ligands (Figure 1a) could be stabilized by Pt−P π-bonding. Related π-interactions in Pt_2S_2 rings with sulfido and thiolato ligands have been proposed and their consequences for structure and reactivity discussed.[12] Pyramidal μ-PMes ligands could adopt the anti and syn geometries shown in Figure 1b,c. An alternative syn structure (Figure 1d), which features a puckered Pt_2P_2 ring and face-to-face Mes groups, is precedented in the crystal structure[13] of *syn*-[NiCp{μ-P(Me)Mes}]$_2$.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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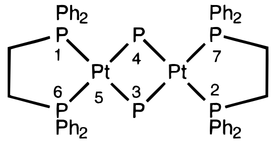
Table 1. ^{31}P NMR Data[a]



complex	$J_{1,2}$	$J_{1,3}$	$J_{1,5}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	δ_1	δ_3
$[PtL_2(\mu\text{-PMes})]_2$ (**1**)	20	50	2151	50	−55	805	45.8	−56.8
$[\{PtL_2\}_2(\mu\text{-PHMes})(\mu\text{-PMes})]^+$ (**2**)[b]	30	108	1874	63	−120	744	54.4	−92.0
							51.5	−227.6
$[PtL_2(\mu\text{-PHMes})]_2^{2+}$ (**3a**)[c]	7	293	2180	58	−182	1636	55.2	−273.9
$[PtL_2(\mu\text{-PHMes})]_2^{2+}$ (**3b**)[c]	5	287	2236	50	−165	1632	51.6	−243.3
$[PtL_2\{\mu\text{-P(Me)Mes}\}]_2^{2+}$ (**4**)	7	292	2090	52	−140	1770	53.3	−194.3
$[PtL_2\{\mu\text{-P(BH}_3\text{)Mes}\}]_2$ (**5**)	10	248	2216	160	−60	1482	45.2	−162.3
$[PtL_2\{\mu\text{-P(O)Mes}\}]_2$ (**6**)	25	290	1459	180	−220	2052	48.4	−88.6

[a] External reference 85% H_3PO_4; coupling constants (in Hz) were obtained from simulation of spectra recorded at ambient temperature. For the sign convention used for coupling constants, see ref 5. Note: $J_{14} = 0$. Solvents: CD_2Cl_2 for **2**, **3**, and **6**, C_6D_6 for **1**, CD_3NO_2 for **4**, THF for **5**. L_2 = dppe. [b] Labeling: $P_3 = \mu$-PMes (δ −92.0), $P_4 = \mu$-PHMes (δ −227.6). $J_{2,4} = 297$, $J_{4,5} = 1898$, $J_{5,6} = 2644$, $J_{5,7} = 5$, $J_{6,7} = 6$. [c] Syn and anti isomers; see ref 5.

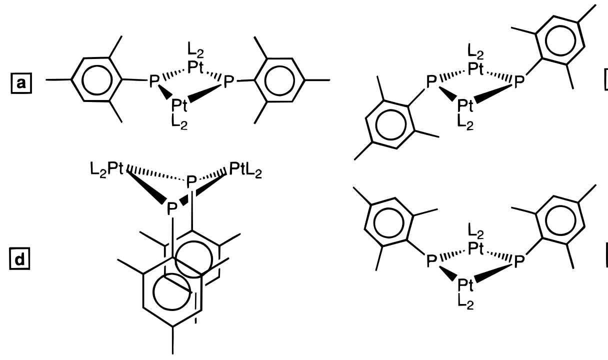


Figure 1. Possible geometries for **1** (L_2 = dppe).

We have not been able to obtain crystals of **1** suitable for X-ray crystallography, but ^{31}P and ^{1}H NMR data, especially in comparison to the results for precursor **3**, provide information about its structure and bonding. As previously reported,[5] dication **3** exists in solution as a mixture of syn and anti isomers analogous to **1b**−**1c**; the crystallographically characterized anti isomer contains a planar Pt_2P_2 core. The ^{1}H NMR spectra of both isomers at room temperature show restricted rotation about the P−C(Mes) bonds.

In contrast, neutral **1** shows only one set of signals in the ^{1}H and ^{31}P NMR spectra from room temperature to −70 °C in toluene-d_8. Further, room-temperature C_6D_6 solutions of **1** display sets of equivalent Mes aryl and *o*-Me signals at 5.85 and 2.74 ppm, respectively. At −70 °C in toluene-d_8, the different sides of the Mes groups are inequivalent and give rise to two Ar (δ 6.12 and 5.33) and two *o*-Me (δ 2.78 and 2.57) signals. The ^{31}P{^{1}H} NMR spectrum of **1** in C_6D_6 shows two multiplets at δ 45.8 and −56.8 assigned to dppe and PMes, respectively. ^{31}P−^{31}P and ^{195}Pt−^{31}P coupling constants obtained from spectral simulation for **1** and its derivatives (see below) are listed in Table 1.

These spectroscopic data suggest that **1** contains pyramidal μ-PMes ligands and probably adopts structure **1b** or **1c**. It is convenient to consider the ^{31}P NMR data first. A large positive ^{31}P NMR chemical shift is characteristic of μ-phosphinidene ligands with M−P multiple bonding.[14] For example, the signal due to the mesitylphosphinidene ligand in $C_5R_5W(CO)_2(\mu$-PMes)$C_5R_5W(CO)_2(PH_2Mes)$ appears at δ 313.9 (R = H) and 397.4 (R = Me), while for $[Cp^*W(CO)_2]_2(\mu$-PMes) this resonance is observed at δ 589.4.[15] The chemical shift of the μ-phosphinidene ligand in **1**, δ −56.8, is more similar to that of $Li_2[NiCp(\mu\text{-PMes})]_2$ (δ 13.8),[13] consistent with a lack of multiple bonding in these cases and disfavoring structure **1a**.

The trans P−P (50 Hz) and Pt−P (805 Hz) coupling constants observed for the μ-phosphinidene ligand in **1** are unusually small for square planar Pt(II) complexes[16] and are consistent with low s-character in the Pt−PMes bond, which is presumably a result of rehybridization at P to increase s-character in the lone pair and p-character in the Pt−P bonds. Similar observations have been made for terminal phosphido complexes with Pt−PR_2 groups.[17] Moreover, Bertrand and co-workers recently prepared a series of pyramidal μ_2-phosphinidene complexes $[\{Pd(PR_3)_2\}_2\text{-}\{\mu_2\text{-}P_2C{=}N(i\text{-}Pr)_2\}]^+$, one of which was structurally characterized by X-ray crystallography and all of which exhibited very small P−P couplings (∼15−20 Hz) similar to those in **1**.[18]

The ^{31}P NMR data for **1** also provide information about the trans influence of the phosphinidene ligand in comparison to isoelectronic species. Deprotonation of a series of hydroxide-bridged phosphine complexes $[PtL_2(\mu\text{-OH})]_2^{2+}$ led to a decrease in J_{Pt-P}, which was rationalized by greater trans influence of oxo with respect to hydroxide.[3c] The similar decrease in the $J_{Pt-P(dppe)}$ observed here (from 2180 and 2236 Hz in **3** to 2151 Hz in **1**) suggests that the trans influence of μ-PMes is slightly larger than that of μ-PHMes. Comparison of this J_{Pt-P} to that for $[Pt(dppe)(\mu\text{-O})]_2{\cdot}2LiBF_4$ (3120 Hz)[3c] suggests that the μ-phosphinidene ligand has a greater trans influence than the μ-oxo one. To our knowledge, the ^{31}P NMR spectra of related μ-sulfido complexes have not been reported, presumably due to their low solubility.

The ^{31}P NMR results are consistent with the variable-temperature ^{1}H NMR data, which provide additional structural

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information. Neither the trigonal planar (**1a**) nor the syn (**1d**) structures are consistent with the low-temperature ^{1}H NMR spectrum of **1**, since these geometries could not give rise to inequivalent *o*-Me and Ar *m* protons. Both anti and syn isomers **1b**,**c**, if static, would give the observed low-temperature spectrum. The Mes group equivalence observed at room temperature could be the result of free rotation about the P−C(Mes) bonds or rapid inversion at phosphorus on the NMR time scale. The latter is more likely, since steric effects in **1** should be similar to those in **3**, in which restricted rotation is observed in both syn and anti isomers at room temperature.[5] The proposed inversion, which is not possible in **3** or the other four-coordinate phosphorus compounds described below, is consistent with the anomalous NMR behavior of **1**. Low inversion barriers in metallophosphines M−PRR′ have been observed,[19] so it is plausible that dimetallophosphines like **1** show similar behavior.

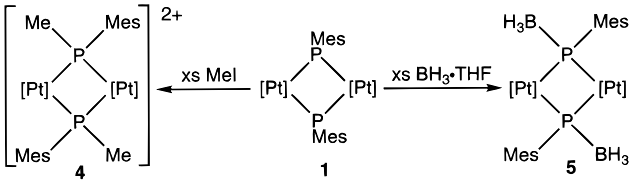
The simplest explanation of the NMR observations is that only one of the isomeric structures **1b**,**c** is adopted throughout the temperature range studied, but from the data, we cannot tell which one or rule out rapid interconversion between these isomers. On steric grounds, the anti isomer **1b** is likely to be energetically favored.

The related monocationic complex [{Pt(dppe)}$_2$(μ-PHMes)(μ-PMes)][BF$_4$] (**2**) can be prepared by deprotonation of precursor **3** with 1 equiv of base or by protonation of neutral **1** with HBF$_4$·Me$_2$O (Scheme 1).[20] Cation **2** shows a complicated ^{31}P NMR spectrum, with resonances assigned to μ-phosphido (δ −227.6), μ-phosphinidene (δ −92.0), and dppe (δ 54.4, 51.5) ligands. Coupling constants obtained by spectral simulation are listed in Table 1. The spectra allow *direct* comparison of phosphido and phosphinidene ligands on Pt(II), which complements the results from comparison of neutral **1** and dicationic **3**. Pt−P coupling in the dppe ligands (1874 Hz trans to PMes and 2644 Hz trans to PHMes) is consistent with the trans influence results from **1** and **3**, although greater in magnitude. The Pt−P couplings to the bridging ligands in **2** (744 Hz, PMes; 1898 Hz, PHMes) also compare well to those in **1** (805 Hz) and **3** (1636, 1632 Hz), as do the trans P−P couplings, 108 Hz (PMes; compare 50 in **1**) and 297 Hz (PHMes; vs 293, 287 Hz in **3**).

As in **3**, Mes rotation in **2** is restricted at room temperature. In CD$_2$Cl$_2$ there are four Ar (Mes) signals in the ^{1}H NMR spectrum (δ 6.06, 5.80, 5.71, 5.51), each of which integrates as one hydrogen, while the corresponding *o*-Me signals appear at δ 2.65, 2.21, 2.13, and 2.08. Two different signals are also observed for the *p*-Me groups at 1.96 and 1.36 ppm. Similarly, in the ^{13}C NMR spectrum, six Me resonances are observed, from 28.8 to 20.8 ppm. We could not identify resonances due to the P−H group in either the ^{1}H NMR or IR spectra, as previously observed for the related complex **3**.[5] As in **1**, only one species was observed by NMR at room temperature; we assume it adopts the anti geometry.

Treatment of neutral **1**, generated by deprotonation of **3**, with an excess of methyl iodide at room temperature leads to alkylation at both phosphorus centers and the precipitation of the analytically pure dication [Pt(dppe){μ-P(Me)Mes}]$_2^{2+}$ as the BF$_4$ salt (**4**; Scheme 2). Interestingly, the related alkylation of [Pt(PPh$_3$)$_2$(μ-S)]$_2$ with MeI affords only a monocation,[21] suggesting that the μ-phosphinidene ligand is more nucleophilic than the μ-sulfide.

Scheme 2



[Pt] = Pt(dppe)

Dication **4** was further characterized by ^{31}P NMR (Table 1), ^{1}H and ^{13}C NMR, and IR. The coupling constants in Table 1 show the expected similarity to those in dication **3**. Comparison of the Pt−P couplings to those of the dppe ligand in dimers **3** and **4** shows that the trans influence of the μ-PMeMes group ($J_{\text{Pt-P(dppe)}}$ = 2090 Hz) is slightly larger than that for the μ-PHMes ligand ($J_{\text{Pt-P(dppe)}}$ = 2180, 2236 Hz) as expected. Only one isomer of **4** is observed, as in [NiCp{μ-P(Me)Mes}]$_2$.[13] As in **3**, there is restricted rotation of the Mes groups: the Ar signals appear at δ 6.42 and 4.81 in CD$_3$NO$_2$. One signal due to a *o*-Me group is observed at δ 3.11, and the other is obscured by overlapping P−Me and CH$_2$ resonances from δ 2.33 to δ 2.00. Similarly, the ^{13}C NMR spectrum (CD$_3$NO$_2$) shows resonances due to methyl groups at δ 24.8 and 20.5 and two overlapping signals at δ 16.6−16.4.

Treatment of **1** with an excess of BH$_3$·THF gives the adduct [Pt(dppe){μ-P(BH$_3$)Mes}]$_2$ (**5**; Scheme 2), which was characterized spectroscopically (Table 1). Since this borane adduct decomposed on attempted recrystallization, satisfactory elemental analyses could not be obtained, but the high-resolution mass spectrum is consistent with this formula, as is the symmetry evidenced in the ^{31}P and ^{1}H NMR spectra. Although no ^{11}B−^{31}P coupling is observed, the ^{31}P NMR spectrum shows some line broadening, and the PMes chemical shift changes appreciably (from −56.8 to −162.3 ppm) on complexation. The trans P−P (50 to 248 Hz) and Pt−P (805 to 1482 Hz) couplings increase, consistent with rehybridization at phosphorus, as in the dications **3** and **4**. For comparison, on formation of the adduct PH$_2$Mes·BH$_3$ from mesitylphosphine, the ^{31}P NMR chemical shift moves from δ −153 to −68.8, while $J_{\text{P-H}}$ increases from 204 to 370 Hz.[22]

As with the other compounds, only one isomer is observed, and there is restricted rotation about the P−C(Mes) bonds. Two mesityl Ar signals are observed in CD$_2$Cl$_2$ (δ 6.09 and 5.39), in addition to two *o*-Me resonances (δ 2.66 and 2.04). The ^{13}C spectrum shows three methyl signals (δ 29.4, 23.7, and 23.6). Signals due to the BH$_3$ protons could not be confidently assigned in the ^{1}H NMR spectrum, but the IR spectrum showed a characteristic absorption due to BH$_3$ at 2416 cm^{-1}.[23]

Oxidation of **1** with air or O$_2$ yielded [Pt(dppe){μ-P(O)Mes}]$_2$ (**6**) (Scheme 3). Like borane adduct **5**, complex **6** decomposed on attempted recrystallization, but its high-resolution mass spectrum confirms the formulation. As in **5**, only one isomer is observed by NMR. Mes rotation is again restricted; in CD$_2$Cl$_2$ the Ar protons resonate at δ 6.01 and 5.01, and there are two different *o*-Me signals (δ 2.74 and 2.15). The ^{13}C NMR

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(19) See: Rogers, J. R.; Wagner, T. P. S.; Marynick, D. S. *Inorg. Chem.* **1994**, *33*, 3104−3110 and references therein.

(20) Related proton transfers (and in some cases alkylations; see complex **4** below) have been reported to interconvert μ-phosphido and μ-phosphinidene complexes of Ni,[13] Zr, and heterobimetallic Zr−Mo complexes. See: (a) Ho, J.; Hou, Z.; Drake, R. J.; Stephan, D. W. *Organometallics* **1993**, *12*, 3145−3157. (b) Ho, J.; Drake, R. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1993**, *115*, 3792−3793. (c) Bazhenova, T. A.; Kulikov, A. V.; Shestakov, A. F.; Shilov, A. E.; Antipin, M. Y.; Lyssenko, K. A.; Struchkov, Y. T.; Makhaev, V. D. *J. Am. Chem. Soc.* **1995**, *117*, 12176−12180.

(21) (a) Reference 7. (b) See ref 12b for discussion of the nucleophilicity of μ-sulfido dimers.

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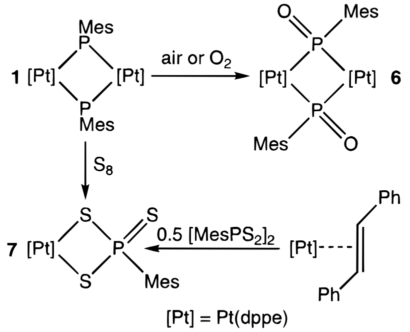
(23) Verkade, J. G. *Coord. Chem. Rev.* **1972/1973**, *9*, 1−106. Due to limitations of the available spectrometer, we did not attempt to record a ^{11}B NMR spectrum of **5**.

Scheme 3



spectrum shows three Me signals at δ 23.2, 22.6, and 20.6. The change in phosphorus oxidation state makes direct comparison of the ^{31}P NMR data (Table 1) to those of **1**−**5** difficult.

The known monomeric RPO complexes Cr(CO)$_5$[PN(i-Pr)$_2$-(O)]^{24} and [ReCl(dppe)$_2${P(O)CH$_2$-t-Bu}]^{25} have been characterized by IR spectroscopy ($\nu_{\mathrm{P=O}}$ = 1198 and 1097 cm^{-1}, respectively). Trimetallic μ_3-PO complexes, probably better models for the four-coordinate P in **6**, show P=O IR bands in the range from 1075 to 1266 cm^{-1}.^{26} The similarity of the IR spectra of **1** and **6** made assignment of $\nu_{\mathrm{P=O}}$ difficult, but a sample of **6** prepared from labeled oxygen (50% ^{18}O) exhibited a new set of peaks, centered at ~1055 cm^{-1}, consistent with its formulation as a phosphinidene oxide complex (calculated $\nu_{\mathrm{P=^{16}O}}$ = 1081 cm^{-1}).

A related phosphinidene sulfide complex^{27} was the expected product of the reaction of **1** with sulfur, but instead the trithioxophosphorane complex Pt(dppe)(S$_3$PMes) (**7**) was formed (Scheme 3). An unidentified Pt(dppe) complex [δ (^{31}P) 51.8, $J_{\mathrm{Pt-P}}$ = 2806 Hz] is a side product in this reaction, but it could be separated from **7** by recrystallization. The formula of **7** was established by elemental analysis and mass spectroscopy, and its NMR and IR spectra closely match those of the related complexes PtL$_2$(S$_3$PR) (L = tertiary phosphine) prepared by Woollins and co-workers from Lawesson's reagent^{28} and its ferrocenyl analog.^{29} For example, the S$_3$PAr ^{31}P NMR resonance appears at δ 108.9 in **7** (CD$_2$Cl$_2$) and at δ 99.8 (CH$_2$Cl$_2$/CDCl$_3$) in Pt(dppe)[S$_3$P(p-MeOC$_6$H$_4$)] (**8**),^{28b} with $^2J_{\mathrm{Pt-P}}$ values of 224 and 212 Hz, respectively. The dppe signals in these complexes are found at δ 43.4 and 42.2, with $^1J_{\mathrm{Pt-P}}$ values of 3093 and 3110 Hz. The IR spectrum (KBr) of **7** shows a characteristic P=S absorption at 691 cm^{-1}, as previously observed for **8** (673 cm^{-1}). Finally, the structural formulation of **7** was confirmed by independent synthesis (Scheme 3) from Pt(dppe)($trans$-stilbene) and [MesPS$_2$]$_2$,^{30} which proceeds like Woollins' reported synthesis of Pt(PPh$_3$)$_2$[S$_3$P(p-MeOC$_6$H$_4$)] from Pt(PPh$_3$)$_2$(C$_2$H$_4$) and Lawesson's reagent.^{28a} We assume that the reaction of **1** with sulfur first yields [Pt(dppe)(μ-PSMes)]$_2$ in analogy to **6**, followed by dimer cleavage and further oxidation to afford **7**. A related reaction with excess elemental Se gave several products; although one shows a ^{31}P NMR signal at δ 0.9 ($J_{\mathrm{Pt-P}}$ = 220 Hz) and is presumably analogous to **7**, we could not separate it from the mixture.

We briefly examined the chemistry of **1** with unsaturated substrates, which might be expected to react with the monomer Pt(dppe)(PMes), if it was formed in low concentration by reversible cracking of the dimer.^{31} No reaction was observed with CO$_2$, CS$_2$, PhCCPh, Mes*PCO (Mes* = 2,4,6-t-Bu$_3$C$_6$H$_2$),^{32} or Mes*PCNPh.^{33} In contrast, the azides Me$_3$SiN$_3$ and MeSO$_2$N$_3$ reacted smoothly with **1**, but we were not able to purify or identify the products.

Conclusion

We have prepared the dimeric platinum phosphinidene complex **1** by straightforward deprotonation of a cationic precursor. Spectroscopic studies suggest that **1** contains pyramidal μ-phosphinidene ligands which have a larger trans influence than isoelectronic oxo groups. Complex **1** undergoes nucleophilic reactions typical of a phosphine, including protonation, alkylation, oxidation, and Lewis acid complexation, and appears to be more nucleophilic than μ-sulfido ligands in related diplatinum systems. The isolation of dimeric **1** suggests that it may be possible to prepare a terminal phosphinidene complex PtL$_2$(=PR), whose reactivity should be quite different, by proper choice of substituents, and we are currently examining this possibility.

Experimental Section

General Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or by using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, and benzene were dried over and distilled from Na/benzophenone before use; CH$_2$Cl$_2$ was distilled from CaH$_2$.

NMR spectra were recorded on a Varian 300 MHz spectrometer. ^{1}H or ^{13}C NMR chemical shifts are reported vs Me$_4$Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H$_3$PO$_4$ (85%) used as an external reference. Coupling constants are reported in Hz. Unless otherwise noted, peaks in NMR spectra are singlets. IR (KBr) 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, Woodside, NY. Mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois.

Unless otherwise noted, reagents, including 1.6 M n-BuLi in hexanes and 1 M BH$_3$·THF, were from commercial suppliers. The complex Pt(dppe)($trans$-stilbene) was prepared by LiBEt$_3$H reduction of Pt(dppe)Cl$_2$ in THF in the presence of $trans$-stilbene; details will be described elsewhere.

[Pt(dppe)(*μ*-PMes)]$_2$·2LiBF$_4$·2THF (1-BF$_4$) and [Pt(dppe)(*μ*-PMes)]$_2$ (1). To a slurry of [Pt(dppe)(μ-PHMes)]$_2$[BF$_4$]$_2$ (**3**; 400 mg, 0.24 mmol) in THF (6 mL) was added n-BuLi (0.32 mL, 0.51 mmol) to give a red solution, which was concentrated. Layering of petroleum ether over the solution and cooling to −25 °C afforded a red solid, which was dried in vacuo to afford 180 mg (41% yield) of the title complex, which cocrystallized with LiBF$_4$ and THF, according to

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elemental analysis, ^{1}H NMR, and IR. The spectroscopically pure salt-free (as judged by IR and ^{19}F NMR) [Pt(dppe)(μ-PMes)]$_2$ (**1**) was obtained by extraction with benzene. The IR and ^{1}H, ^{31}P, and ^{13}C NMR spectra of **1** and **1-BF$_4$** were identical except for IR absorptions assigned to BF$_4$.

Anal. Calcd for **1-BF$_4$**, $C_{70}H_{70}P_6Pt_2\cdot 2LiBF_4\cdot 2THF$: C, 51.50; H, 4.77. Found: C, 51.34; H, 5.02. Anal. Calcd for **1**, $C_{70}H_{70}P_6Pt_2$: C, 56.52; H, 4.75. Found: C, 55.96; H, 5.16. IR (for **1**): 3051, 2919, 2851, 1483, 1435 (vs), 1406, 1384, 1262, 1103 (vs), 1027 (vs), 878, 844, 820, 746 (s), 693 (vs). ^{1}H NMR (C_6D_6): δ 7.56 (12H, broad, Ar), 6.97 (28H, Ar), 5.85 (4H, Mes), 2.74 (12H, *o*-Me), 2.03 (6H, *p*-Me), 1.69 (8H, m, CH$_2$). ^{1}H NMR (C_7D_8, −70 °C): δ 8.22 (12H, Ar), 6.78 (28H, Ar), 6.12 (2H, Mes), 5.33 (2H, Mes), 2.78 (6H, Me), 2.57 (6H, Me), 1.99 (6H, Me), 1.76 (8H, broad, CH$_2$). ^{13}C NMR (C_6D_6): δ 142.6 (m, Ar), 138.2 (Ar), 135.0 (m, Ar), 134.1 (broad, Ar), 133.4 (Ar), 126.0 (Ar), 34.8 (m, CH$_2$), 21.8 (Me), 21.4 (Me). Fewer than expected Ar peaks are observed because of the unfavorable overlap. ^{31}P{^{1}H} NMR (C_6D_6): δ 45.8 (m), −56.8 (m). ^{31}P{^{1}H} NMR (203K) (C_7H_8): δ 45.5 (m), −57.7 (m).

[{Pt(dppe)}$_2$(μ-PMes)(μ-PHMes)]BF$_4$ (2). To a slurry of [Pt(dppe)(μ-PHMes)]$_2$[BF$_4$]$_2$ (**3**, 200 mg, 0.12 mmol) in THF (4 mL) was added *n*-BuLi (0.07 mL, 0.11 mmol) to afford a red-orange solution, which was filtered through Celite to remove unreacted **3**. The filtrate was concentrated, layered with petroleum ether, and cooled to −25 °C to afford an orange solid, which analysis and ^{1}H NMR showed to be a THF hemisolvate (120 mg, 62% yield).

Anal. Calcd for $C_{70}H_{71}BF_4P_6Pt_2\cdot 0.5THF$: C, 53.67; H, 4.70. Found: C, 53.75; H, 5.02. IR: 3050, 2915, 1586, 1572, 1484, 1436 (vs), 1410, 1375, 1308, 1187, 1101 (vs), 1084 (vs), 1060 (broad, vs), 998, 879, 846, 819, 748, 692 (vs), 677 (s), 616, 553, 530 (vs). ^{1}H NMR (CD_2Cl_2): δ 7.76 (4H, m, Ar), 7.53−7.41 (10H, m, Ar), 7.29 (10H, m, Ar), 7.21 (8H, m, Ar), 6.98 (4H, m, Ar), 6.76 (4H, m, Ar), 6.06 (1H, Mes), 5.80 (1H, Mes), 5.71 (1H, Mes), 5.51 (1H, Mes), 2.65 (3H, Me), 2.25−1.6 (8H, broad, CH$_2$), 2.21 (3H, Me), 2.13 (3H, Me), 2.08 (3H, Me), 1.96 (3H, Me), 1.36 (3H, Me). ^{13}C NMR (CD_2Cl_2): δ 141.3 (m, Ar), 138.2 (Ar), 135.6 (Ar), 134.4 (d, J = 12, Ar), 133.7 (d, J = 11, Ar), 133.2 (d, J = 11, Ar), 131.9 (Ar), 131.4 (d, J = 11, Ar), 130.8 (Ar), 130.7 (Ar), 130.5 (Ar), 130.1 (Ar), 129.8 (Ar), 129.3 (d, J = 10, Ar), 128.8 (d, J = 10, Ar), 128.6 (d, J = 10, Ar), 127.9 (Ar), 127.4 (Ar), 32.6 (m, CH$_2$), 30.8 (m, CH$_2$), 28.8 (Me), 28.6 (Me), 26.3 (Me), 26.1 (Me), 22.5 (Me), 20.8 (d, J = 8, Me). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 54.4 (m), 51.5 (m), −92.0 (m), −227.6 (m).

[Pt(dppe){μ-P(Me)Mes}]$_2$[BF$_4$]$_2$ (4). To a slurry of **3** (100 mg, 0.06 mmol) in THF (4 mL) was added a solution of LiN(SiMe$_3$)$_2$ (30 mg, 0.18 mmol) in THF (2 mL). To the resulting red solution of **1-BF$_4$** was added MeI (30 mg, 0.21 mmol) to give a yellow solution, from which a yellow solid precipitated overnight. The solution was decanted, and the solid was dried in vacuo to afford 95 mg (93% yield) of **4**.

Anal. Calcd for $C_{72}H_{76}B_2F_8P_6Pt_2$: C, 51.13; H, 4.54. Found: C, 50.70; H, 4.59. IR: 3047, 2920, 1475, 1456, 1434 (vs), 1378, 1309, 1291, 1186, 1158, 1124, 1101 (vs), 1084 (s), 1026, 998, 876 (s), 822, 748 (s), 693 (vs), 677 (s), 654, 602, 553, 530, 486 (s). ^{1}H NMR (CD_3NO_2): δ 7.71−7.20 (40H, m, Ar), 6.42 (2H, broad, Mes), 5.81 (2H, broad, Mes), 3.11 (6H, broad, Me), 2.33−2.00 (20H, broad, Me + CH$_2$), 1.36 (6H, broad, Me). ^{13}C NMR (CD_3NO_2): δ 143.9 (m, Ar), 142.3 (m, Ar), 141.5 (Ar), 135.0 (d, J = 11, Ar), 133.7 (d, J = 15, Ar), 132.8 (Ar), 132.2 (Ar), 130.9 (d, J = 11, Ar), 130.1 (d, J = 11, Ar), 128.0 (d, J = 53, Ar), 127.3 (d, J = 49, Ar), 124.0 (broad, Ar), 31.0 (m, CH$_2$), 24.8 (Me), 20.5 (Me), 16.6−16.4 (Me + PMe). ^{31}P{^{1}H} NMR (CD_3NO_2): δ 53.3 (m), −194.3 (m).

[Pt(dppe){μ-P(BH$_3$)Mes}]$_2$ (5). To **1-BF$_4$** (100 mg, 0.055 mmol) was added a solution of $BH_3\cdot THF$ in THF (3 mL, 0.3 mmol) to give a red mixture. The solvent was removed, and the residue was washed with petroleum ether (5 × 5 mL) to afford 85 mg (91% yield) of a yellow solid, which IR and elemental analysis showed contains LiBF$_4$. The complex decomposed on recrystallization from THF/petroleum ether or CH$_2$Cl$_2$/Et$_2$O over hours.

Anal. Calcd for $C_{70}H_{76}B_2P_6Pt_2\cdot 2LiBF_4$: C, 49.38; H, 4.51. Found: C, 47.25; H, 5.27. IR: 3051, 2916, 2416 (broad, vs), 2200 (broad, s), 1484, 1434 (vs), 1310, 1100 (vs), 1063 (s), 998 (s), 911, 880, 820, 745 (vs), 691 (vs), 677 (vs), 615, 552, 520 (vs). Low-resolution FAB MS (Magic Bullet): *m/z* 1515.5 (MH$^+$), 1487.5 [(MH − 2BH$_3$)$^+$], 1369.0 [(MH − 2BH$_3$ − Mes)$^+$]. For high-resolution FAB MS (Magic Bullet) a peak on the left-hand side of the envelope of peaks was selected to reduce complications from the presence of different isotopes: *m/z* found 1511.3671. This could be due to $C_{70}H_{75}{}^{11}B_2P_6{}^{194}Pt_2$ (calcd 1511.3734) and/or $C_{70}H_{74}{}^{11}B_2P_6{}^{194}Pt^{195}Pt$ (calcd *m/z* 1511.3677) and/or $C_{70}H_{73}{}^{11}B_2P_6{}^{195}Pt_2$ (calcd *m/z* 1511.3620). ^{1}H NMR (CD_2Cl_2): δ 7.47−7.05 (40H, m, Ar), 6.09 (2H, broad, Mes), 5.39 (2H, broad, Mes), 2.66 (6H, Me), 2.04 (6H, Me), 1.83 (8H, broad, CH$_2$), 1.55 (6H, Me). The BH$_3$ protons were not observed. ^{13}C NMR (CD_2Cl_2): δ 141.8 (m, Ar), 141.2 (m, Ar), 138.0 (Ar), 134.2 (m, Ar), 132.5 (m, Ar), 131.6 (Ar), 130.7 (Ar), 129.7 (m, Ar), 129.2 (Ar), 128.8 (d, J = 5, Ar), 128.7 (d, J = 4, Ar), 128.2 (Ar), 30.7 (m, CH$_2$), 29.4 (broad, Me), 23.7 (Me), 23.6 (Me). ^{31}P{^{1}H} NMR (THF): δ 45.2 (m), −162.3 (m).

[Pt(dppe){μ-P(O)Mes}]$_2$ (6). A red solution of **1-BF$_4$** (100 mg, 0.055 mmol) in THF was exposed to air or oxygen to quickly afford a yellow solution. The solvent was removed, and the yellow residue was washed with petroleum ether (4 × 4 mL) and dried in vacuo to afford 86 mg (92% yield) of the spectroscopically pure product, which decomposed on attempted recrystallization or chromatography. Alternatively, a THF solution of BF$_4$-free **1** (100 mg, 0.067 mmol) was exposed to air to give a yellow solution. The solvent was removed in vacuum to give a yellow solid, which was washed with 2 × 3 mL of petroleum ether and dried in vacuo to afford 93 mg (91%) yield of the yellow product, which was used for elemental analysis.

Anal. Calcd for $C_{70}H_{70}O_2P_6Pt_2$: 55.33; H, 4.65. Found: C, 46.01; H, 4.70. IR: 3052 (s), 2924 (vs), 2868 (vs), 1483 (s), 1436 (vs), 1379 (m), 1080 (broad, vs, BF$_4$), 745 (s), 696 (vs). IR (BF$_4$ free): 3052 (s), 2924 (vs), 2868 (vs), 1483 (s), 1436 (vs), 1379 (m), 1101 (m), 1061 (m), 1026 (m), 998 (m), 742 (s), 690 (vs), 558 (s), 527 (vs). Low-resolution FAB MS (Magic Bullet): *m/z* 1535.6 [(MH + O)$^+$], 1519.6 (MH$^+$), 1487.5 [(MH − 2O)$^+$], 1369.0 [(MH − 2O − Mes)$^+$]. High-resolution FAB MS (Magic Bullet): *m/z* 1519.3180 (found), 1519.3176 (calcd for $C_{70}H_{71}O_2P_6{}^{195}Pt_2$). ^{1}H NMR ($CD_2Cl_2$): δ 8.04 (8H, m, Ar), 7.45 (12H, m, Ar), 7.23 (4H, m, Ar), 7.02 (8H, m, Ar), 6.74 (8H, m, Ar), 6.01 (2H, Mes), 5.01 (2H, Mes), 2.74 (6H, Me) 2.15 (6H, Me), 2.00 (6H, Me), 1.99 (8H, m, CH$_2$). ^{13}C NMR (CD_2Cl_2): δ 142.8 (Ar), 139.8 (Ar), 137.8 (d, J = 15, Ar), 135.0 (Ar), 132.2 (d, J = 11, Ar), 132.4 (Ar), 132.0 (Ar), 131.0 (Ar), 129.5 (m, Ar), 128.4 (d, J = 60, Ar), 31.5 (broad, *C*H$_2$), 23.2 (Me), 22.6 (Me), 20.6 (Me). ^{31} P{^{1}H} NMR (CD_2Cl_2): δ 48.4 (m), −88.6 (m).

Pt(dppe)(S$_3$PMes) (7). To a red solution of **1-BF$_4$** in THF (4 mL), prepared in situ from [Pt(dppe)(μ-PHMes)]$_2$[BF$_4$]$_2$ (200 mg, 0.12 mmol) and *n*-BuLi (0.2 mL, 0.32 mmol), was added S$_8$ (20 mg, 0.6 mmol) to afford a yellow solution. The solvent was removed to give 160 mg (79% yield) of a mixture of **7** and an unidentified impurity [^{31}P{^{1}H} NMR: δ 51.8 ($J_{\mathrm{Pt-P}}$ = 2806 Hz)]. Two recrystallizations from CH$_2$Cl$_2$/Et$_2$O at −25 °C gave pure white crystals of **7** for elemental analysis (∼80 mg, 39%). This material was BF$_4$-free according to the IR and ^{19}F NMR spectra.

Alternatively, to a solution of Pt(dppe)(*trans*-stilbene) (60 mg, 0.08 mmol) in THF (3 mL) was added (MesPS$_2$)$_2$ (17 mg, 0.038 mmol), and the resulting mixture was stirred overnight, during which a white solid precipitated. The solid was recrystallized twice from CH$_2$Cl$_2$/Et$_2$O to give spectroscopically pure **7** (30 mg, 45% yield).

Anal Calcd for $C_{35}H_{35}P_3PtS_3$: C, 50.05; H, 4.21; S, 11.45. Found: C, 49.89; H, 4.82; S, 12.32. IR: 3049, 2916, 1482, 1434 (vs), 1307, 1186, 1103 (vs), 1026, 997, 878, 849, 820, 747, 691 (vs), 655 (vs), 614, 531 (vs), 473. Low-resolution FAB-MS (Magic Bullet): *m/z* 840.0 (M)$^+$, 807.1 (M − S)$^+$, 775.1 (M − 2S)$^+$, 688.0 [(M − S − Mes)$^+$]. ^{1}H NMR (CD_2Cl_2): δ 7.76 (4H, m, Ar), 7.72 (4H, m, Ar), 7.62−7.41 (12H, m, Ar), 6.77 (2H, d, J = 3, Mes), 2.71 (6H, Me), 2.40 (4H, m, CH$_2$), 2.26 (3H, Me). ^{13}C NMR (CD_2Cl_2): δ 143.5 (d, J = 70, Ar), 138.7 (d, J = 3, Ar), 138.6 (d, J =11, Ar), 133.3 (m, Ar), 132.1 (d, J = 11, Ar), 130.7 (d, J = 11), 129.4 (m, Ar), 128.7 (d, J = 58, Ar), 28.4 (m, *C*H$_2$), 24.4 (d, J = 6, *o*-Me), 20.8 (*p*-Me). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 108.9 ($^2J_{\mathrm{Pt-P}}$ = 224), 43.4 ($^1J_{\mathrm{Pt-P}}$ = 3093).

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