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The Interaction of Hexaphenylcarbodiphosphorane with the Trimethylplatinum(IV) Cation

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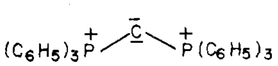
Treatment of $Me_3Pt^+X^-$ ($X^- = PF_6^-$, $OSO_2CF_3^-$, or I^-) with $Ph_3P{=}C{=}PPh_3$, a bis(ylide), gives $[HC(PPh_3)_2]X$, an ortho-metalated ylide–platinum(II) species, and methane. ^{13}C- and ^{2}H-labeling studies show that methane is formed by the combination of platinum methyl groups and ortho aromatic ylide hydrogen atoms. Methyl group transfer to an aromatic ring of an ylide ligand is also observed. This reaction is an example of ortho metalation in a high-valent transition-metal complex, which continues until all the platinum methyl groups are eliminated.

Introduction

There is considerable physical and chemical interest in bis(phosphoranylidene)methane molecules, such as **1** and **2**,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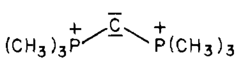
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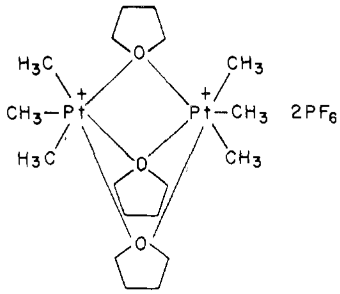
with low coordination numbers about the central carbon atom.[2,3] These double ylides have given new insights to the phosphorus–carbon bond with their unusual bent structures.[4] Besides having two different types of molecules in the unit cell with PCP valence angles of 143.8 and 130.1°, **1** shows the phenomenon of triboluminescence (i.e., pressure-induced emission of light from crystals[5]). Chemical reactions of **1** and **2** show a variety of complex ligand species[2] and reactions with organometallic compounds.[6,7] This paper describes yet another facet of **1** in its interaction with the trimethylplatinum cation.

Results

Although bis(triphenylphosphoranylidene)methane (or hexaphenylcarbodiphosphorane), $C(PPh_3)_2$, does interact directly with trimethyliodoplatinum(IV) tetramer, $[(CH_3)_3PtI]_4$, the reaction is sluggish and incomplete. Consequently, the iodoplatinum complex is first metathesized by treatment with silver hexafluorophosphate, $AgPF_6$, or silver trifluoromethanesulfonate, $AgOSO_2CF_3$ (AgOTf), in tetrahydrofuran (THF). This makes the platinum atom more accessible and allows ready substitution of the noncoordinating PF_6^- or weakly coordinating OTf^- anions.

Colorless trimethylplatinum hexafluorophosphate coordinates 1.5 THF molecules per trimethylplatinum unit as evidenced by ^1H NMR integration and thus may possibly exist as a dicationic dimer, **3**, to achieve the characteristic Pt(IV) hexacoordination.[8] The white trifluoromethanesulfonate (triflate) complex, however, does not coordinate solvent and thus probably exists as a tetramer, $[(CH_3)_3PtOTf]_4$, with μ_3-bridging OSO_2CF_3 groups similar to $[(CH_3)_3PtClO_4]_4$.[9]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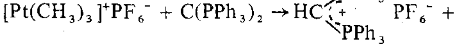
The trimethylplatinum moiety remains intact after metathesis under the conditions employed in this work since the solvated PF_6^- complex is readily converted to $\{(CH_3)_3[(CH_3)_3P]_3Pt\}PF_6$[10] in high yield by addition of trimethylphosphine. The triflate complex is similarly converted to trimethyltris(pyridine)platinum(IV) triflate, $[(CH_3)_3(py)_3Pt]OTf$, by the dissolution of $[(CH_3)_3PtOTf]_4$ in pyridine.[11]

Trimethylplatinum(IV) and Hexaphenylcarbodiphosphorane. Colorless solutions of solvated $[(CH_3)_3Pt]^+PF_6^-$ in THF are treated with 1, 2, 3, or 4 equiv of $C(PPh_3)_2$ in THF under an inert atmosphere at ambient temperatures. As shown in eq 1, the products of the reaction are methane, $[HC(PPh_3)_2]PF_6$,



$$[\mathrm{Pt(CH_3)_3}]^+\mathrm{PF_6}^- + \mathrm{C(PPh_3)_2} \rightarrow \mathrm{HC}\begin{matrix}\mathrm{PPh_3}\\ +\\ \mathrm{PPh_3}\end{matrix}\ \mathrm{PF_6}^- + \text{red solution} + \mathrm{CH_4} \qquad (1)$$

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and a red solution which contains platinum.

The white, crystalline $[HC(PPh_3)_2]PF_6$, which precipitates from the reaction mixture, is identified by its IR and ^1H NMR spectra and melting point in comparison with an authentic sample.[7] If 1 equiv each of $[Pt(CH_3)_3]^+PF_6^-$ and $C(PPh_3)_2$ are mixed, then only 0.5 equiv of $[HC(PPh_3)_2]PF_6$ is consistently isolated. However, treatment of 1 equiv of $[Pt(CH_3)_3]^+PF_6^-$ with 2 or 3 equiv of $C(PPh_3)_2$ gives 1 equiv of $[HC(PPh_3)_2]PF_6$; the remaining equivalents of $C(PPh_3)_2$ coordinate to the platinum moiety. When 4 equiv of $C(PPh_3)_2$ is added, 1 equiv of $[HC(PPh_3)_2]PF_6$ is again precipitated, and 1 equiv of unreacted $C(PPh_3)_2$ can be isolated from the filtrate. $[Me_3PtOTf]_4$ gives the same reaction stoichiometry.

The source of the proton in $[HC(PPh_3)_2]PF_6$ is of great interest and can be limited to the methyl groups in $[Pt(CH_3)_3]^+PF_6^-$, the solvent, or the ortho hydrogen atoms in $C(PPh_3)_2$. Unfortunately, the hydrogen atom in $HC(PPh_3)_2^+$ is readily exchangeable, and a ^2H label in this position is easily lost.[12] However, the white solid isolated from treating 1 equiv of $[(CD_3)_3Pt]^+PF_6^-$ with 2 equiv of $C(PPh_3)_2$ in THF-d^8 in D_2O-washed, baked-out, vacuum-dried glassware was not deuterated. The only remaining proton source is the aromatic hydrogen atoms of the ylide moiety.

Solvents. The solvent of choice for this reaction is THF, which allows the reaction to be completed quickly and facilitates product separation in both metathesis and ylide reactions. The metathesis of $[(CH_3)_3PtI]_4$ proceeds in either THF or CH_2Cl_2, but not in C_6H_6 or dioxane. Treatment of $[Me_3Pt]^+PF_6^-$ or $[Me_3PtOTf]_4$ with $C(PPh_3)_2$ proceeds well in dioxane, which avoids obscuring THF resonances in ^1H NMR spectra. The same products are observed when CH_2Cl_2 or C_6H_6 are used as solvents although yields of $[HC(PPh_3)_2]PF_6$ are lower. No evidence for reaction with any of these solvents is observed other than simple coordination to the platinum-containing products.

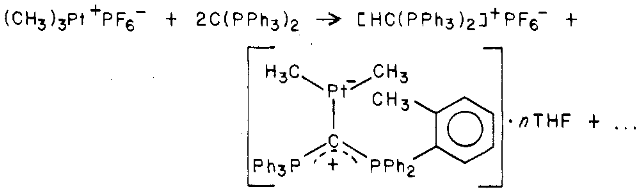
Methane Formation. When 1 equiv of $[(CH_3)_3PtOTf]_4$ is treated with 2 equiv of $C(PPh_3)_2$ in a sealed NMR tube (dioxane-d_8), a singlet appears at $\delta(Me_4Si)$ +0.20 ppm in addition to the resonances for the nonvolatile products. This is very close to the literature value for CH_4.[13,14] If an appreciable amount of CH_3D had formed (through reaction with solvent), ^2H coupling to the remaining protons should have been observed ($^2J_{HCD} = 1.9$ Hz).[15] The spectrum is measured on a 100-MHz pulsed Fourier transform instrument to greatly enhance the signal-to-noise ratio, and no evidence for ^2H coupling is observed. Furthermore, treatment of 3 equiv of $C(PPh_3)_2$ with $[Me_3PtI]_4$ in THF-d_8 in a sealed NMR tube shows a singlet at $\delta(Me_4Si)$ +0.18 ppm.

When $[(^{13}CH_3)(CH_3)_2PtI]_4$ is treated with $C(PPh_3)_2$ in THF-d_8 in a sealed NMR tube with the same reaction stoichiometry, a 1:4:1 triplet is observed and is centered at $\delta(^1H, Me_4Si)$ +0.18 ppm, $^1J_{CH} = 125.6$ Hz;[14] this corresponds to the same 33 atom % ^{13}C enrichment as in the $(CH_3)_3Pt^{IV}$ moiety. The ^1H-decoupled ^{13}C NMR spectrum of this sample includes a singlet at $\delta(^{13}C, Me_4Si)$ −4.8 ppm which gradually increases with time along with the product lines. The −4.8 ppm singlet attributed to $^{13}CH_4$ becomes a quintet, $^1J_{CH} = 125$ Hz, when a gated decoupling experiment gives the fully ^1H-*coupled* spectrum.

Mass spectroscopic analysis further confirms the ^1H NMR data that methane is the only gas evolved in the reaction. Treatment of 1 equiv of $[(CH_3)_3PtOTf]_4$ with 2 equiv of $C(PPh_3)_2$ in THF produces only CH_4. When the reaction is repeated with $C(PPh_3)_2$ in which 50% of the ortho aromatic protons are replaced with deuterium, a 50:50 mixture of CH_4 and CH_3D is observed.[16] Thus, not only is the product gas methane, but the hydrogen source for methane formation appears to be the ortho hydrogen atoms of the ylide.

Platinum-Containing Solutions. Platinum-containing solutions obtained from treatment of $[(CH_3)_3Pt]PF_6$ or $[(CH_3)_3PtOTf]_4$ with 1 equiv of $C(PPh_3)_2$ appear to be a mixture of $[(CH_3)_3Pt^{IV}]^+$ and ylide-substituted products. When treated with 2 equiv of ylide, the $(CH_3)_3Pt^{IV}$ moiety disappears, and a residual methyl group is present (δ 1.00, $^2J_{PtH} = 78.6$ Hz) along with the resonance for the 3:1 $C(PPh_3)_2$–$(CH_3)_3Pt^{IV}$ product (see below). The best ^1H NMR spectrum is provided by a sample obtained from 1 equiv of $[Me_3PtOTf]_4$ and 2 equiv of $C(PPh_3)_2$ in *p*-dioxane. An interesting feature of this ^1H NMR spectrum (C_6D_6) is a very small triplet at δ −0.78 ($J_{PtH} = 11.2$ Hz) which decouples upon irradiation of the platinum atom. At the same {Pt} frequency the triplet at 1.00 ppm also decouples. A very strong ν(PtH) band (2005 cm^{-1}) is seen in the infrared spectrum of this sample. The same hydride triplet, again very small, is observed in the ^1H NMR of a sample from the reaction of $[(CH_3)_3PtOTf]_4$ with 2 equiv of $C(PPh_3)_2$ in THF in addition to another small triplet at δ 8.54 ($^3J_{PtH?} = 16$ Hz). The hydride line is not too surprising when one considers the metalation process (see below); the low-field triplet may correspond to an aromatic hydrogen ortho to Pt. Alternatively, the low-field triplet may indicate that carbene (methylene) formation could have a role in the reaction, produced by hydride migration to the metal. The chemical shift of δ 8.54 is not far different from that reported for $Ta{=}CH_2$ by Schrock[17] (δ 10.2) when considering that the platinum(IV) atom (d^6) is much more electron rich than the d^0 Ta(V) species. This observation must be treated with caution, however, since no deuterium scrambling was observed in the methane produced from the 50% ortho-^2H-labeled ylide reaction previously described in this paper. If hydrogen atoms are allowed to freely migrate from the methyl groups to the metal and back under the reaction conditions, one would expect to see some CH_2D_2 and CHD_3 in the methane produced. Recall that *only* CH_4 and CH_3D are produced at the same ratio as the degree of ^2H enrichment in the ylide.

Product from Reaction with 2 Equiv of $C(PPh_3)_2$. After filtration of the $HC(PPh_3)_2^+PF_6^-$, a red-orange solution of the platinum moiety is obtained from treating $[(CH_3)_3Pt]PF_6$ or $[(CH_3)_3PtOTf]_4$ with 2 equiv of $C(PPh_3)_2$.



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When the filtrate is concentrated, the addition of ether or benzene gives an orange-yellow solid, **4**. A solution of this material in CD_2Cl_2 shows a singlet in the $^{31}P\{^1H\}$ NMR at 19.3 ppm. Its ^1H NMR spectrum has a 1:4:1 triplet at 0.80 ppm, $^2J_{PtH} = 79$ Hz, and another resonance at 2.10 ppm, which is not coupled to platinum, in a 2:1 integral ratio. The aromatic resonances are phosphonium salt like and occur in one multiplet at δ 7.0; THF resonances are also present in varying amounts. The material appears to coordinate THF initially but tends to lose the molecule upon prolonged vacuum drying. The analysis gives an empirical formula correct for **4** without THF.

In the infrared spectrum of **4**, three bands appear in the 1500–1600 cm^{-1} region at 1590, 1560, and 1550 cm^{-1}, whereas $HC(PPh_3)_2^+$ has only two (1590 and 1580 cm^{-1}). The presence of the third band provides evidence for ring substitution.

The mass spectrum of the product obtained by treating 1 equiv of $[(CD_3)_3Pt]PF_6$ with 2 equiv of $C(PPh_3)_2$ does not show the molecular ion or mass peaks higher than 270 amu because of the nonvolatility of the material. However, at the decomposition point of the sample the product fragmentation pattern reveals peaks which correspond to the presence of $(CD_3C_6H_4)(C_6H_5)_2P$ groups

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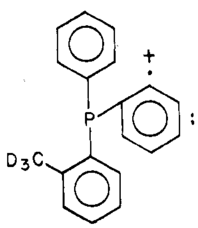

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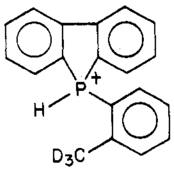

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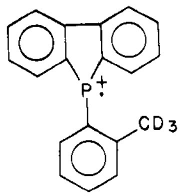

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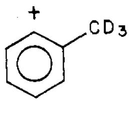
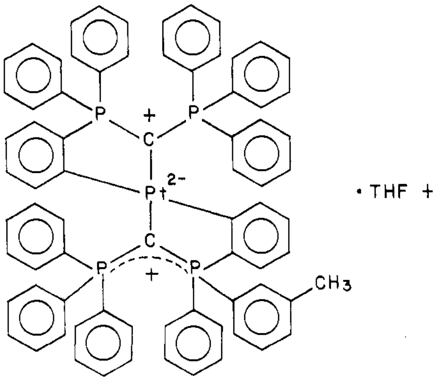


as well as peaks corresponding to fragmentation of the PPh_3 moiety.[18] A solid mixture of $[(CD_3)_3PtI]_4$ and $C(PPh_3)_2$ introduced into the mass spectrometer under the same conditions did not produce these fragments. This observation coupled with the relatively low chemical shift (δ 2.1)[19] of the methyl group strongly suggests that the methyl group has been transferred to an aromatic ring.

Product from Reaction with 3 Equiv of $C(PPh_3)_2$. A blood red solution of the platinum moiety **5** is obtained upon treatment of 1 equiv of $[(CH_3)_3Pt]PF_6$, or $[(CH_3)_3PtOTf]_4$, with 3 equiv of $C(PPh_3)_2$ and removal of precipitated $[HC(PPh_3)_2]PF_6$. The solution in THF is very stable to decomposition under an inert atmosphere, but dark red polymeric-appearing material slowly precipitates from CH_2Cl_2 or C_6H_6.

$[(CH_3)_3Pt]PF_6 + 3C(PPh_3)_2 \longrightarrow$



· THF +

5

$[HC(PPh_3)_2]PF_6 + 2CH_4$

The dark red solid **5** obtained from vacuum evaporation of the THF solution is moderately stable in air; the color slowly fades after some hours. If the red solid is dissolved in benzene, filtered, and recovered by vacuum evaporation, the bright red color often changes to orange. Solid samples stored in the drybox over long periods of time, e.g., 5–6 months, may also fade toward orange. The ^1H NMR spectra (C_6D_6) remain essentially the same, however, with the exception that in place of one set of THF resonances at δ 1.76 and 3.38, two then appear at δ 1.48 and 3.62 and δ 1.76 and 3.38. The THF multiplets all have the characteristic THF pattern and the δ 1.48 and 3.62 set are very close to the chemical shifts for free THF in C_6H_6 (δ 1.48 and 3.56). Integration of the THF multiplets against the aromatic resonances from the ylide moiety are consistent with 1 mol of THF/2 mol of ylide.

The striking feature of the ^1H NMR spectra (C_6D_6, THF-d_8, dioxane-d_8 is the very low intensity of any resonance, other than those due to solvent, in the upfield region. With the aid of pulsed FTNMR techniques, however, several small resonances usually appear at δ 2.2–2.4, a δ 2.33 (C_6D_6) peak generally being the largest and most consistent.

If the resonances are considered to be due to methyl groups (see below), integration against the ylide aromatic resonances indicates that one CH_3 group/*two* ylide moieties is present. The reaction product obtained from $[(CH_3)_3PtOTf]_4$ seems to be consistently a bit cleaner in this region, especially when dioxane is used as the reaction solvent. The δ 2.33 peak is clearly the major line in these spectra; it occurs as a broadish singlet, which does not have ^{195}Pt satellites or involve ^{31}P coupling since no change is observed during $\{^{195}Pt\}$ or broad-band $\{^{31}P\}$ decoupling experiments.

The evidence that the δ 2.33 line is indeed a methyl resonance (and the only apparent methyl resonance) is provided by ^{13}C-labeling experiments. ^1H NMR samples obtained from reactions of the $(^{13}CH_3)(CH_3)_2Pt^{IV}$ moiety show a reduced δ 2.33 peak relative to nearby lines, in particular with respect to a small triplet at δ 1.96 (see below). The ^{13}C satellites could not be located. The natural-abundance $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) shows aromatic and THF carbon resonances and a very small resonance at δ 23.1 (^{13}C). When the 33 atom %, ^{13}C-enriched $(CH_3)_3Pt$ moiety is used in the reaction, the δ 23.1 (^{13}C) peak alone becomes greatly intensified; it appears as a narrow, complex multiplet with a width at half-height of about 20 Hz. The fully ^1H-*coupled* spectrum, obtained by a gated decoupling technique, produces a 1:3:3:1 quartet from the ^{13}C-enriched resonance, $^1J_{CH}$ = 125.5 Hz. This identifies the band as a methyl resonance.

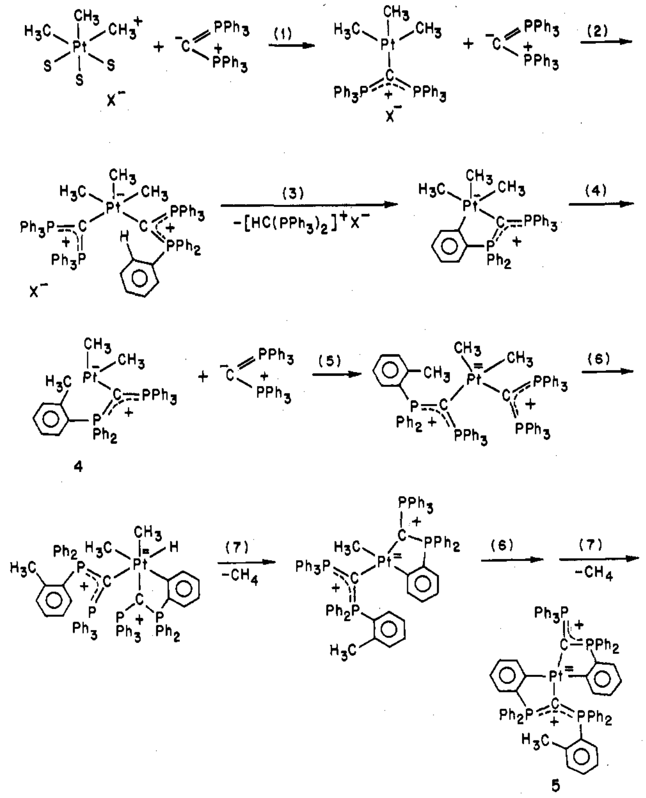
The remaining common feature in the upfield ^1H NMR spectra of the red solid is a 1:3:1 triplet that appears at δ 1.96, J_{PH} = 1.2 Hz. It also has no ^{195}Pt satellites and decouples when irradiated in the ^{31}P region. It is present in about the same intensity and integral ratio as the δ 2.33 resonance. We believe that this peak represents an impurity in the material with similar solubility properties; it was fortuitously isolated from a related reaction system and was identified as $Ph_2P(=O)CHPPh_3$, a hydrolysis product of $Ph_3P=C=PPh_3$.[33]

The aromatic resonances in the ^1H NMR spectrum of the red solid **5** always show pronounced deshielding of the ortho protons which is indicative of ylide character.[20] The meta and para protons absorb at δ 7.06 (C_6D_6) and the ortho protons at δ 7.91 with a roughly 3:2 integral ratio. Both resonances are complex multiplets. In the $^{13}C\{^1H\}$ NMR spectrum, the aromatic carbons appear at δ 128.9 and 133.7 (^{13}C) as complex multiplets of equal size and shape which are much more complicated than those of $[HC(PPh_3)_2]Br$ or $C(PPh_3)_2$. This indicates that the symmetry in the $C(PPh_3)_2$ moiety has been lowered. In addition, small lines can be observed at 98, 118, 140, and 172 ppm which are presumably the result of ortho-metalated rings,[21] though no ^{195}Pt satellites could be located.

The $^{31}P\{^1H\}$ NMR spectrum of **5** consists of a broad singlet (width at half-height = 19 Hz at 40.5 MHz) at +19.3 ppm. No platinum–phosphorus coupling is observed. The broadness of this line is believed to be due to unresolved $^2J_{PP}$ and $^4J_{PP}$ coupling. A hydrolysis product of $C(PPh_3)_2$, $Ph_2P(=O)CHPPh_3$, has a small doublet of doublets at 20.6 and 25.6 ppm, $^2J_{PP}$ = 18 Hz.

The 750–650-cm^{-1} region in the infrared spectra is quite complex for these compounds and, therefore, not very useful to confirm the presence of ortho-metalated systems. The 1500–1600-cm^{-1} region, however, appears to be more helpful. Hexaphenylcarbodiphosphorane has ν(C=C) bands at 1567 and 1568 cm^{-1}, the former being more intense. The red solid

Scheme I



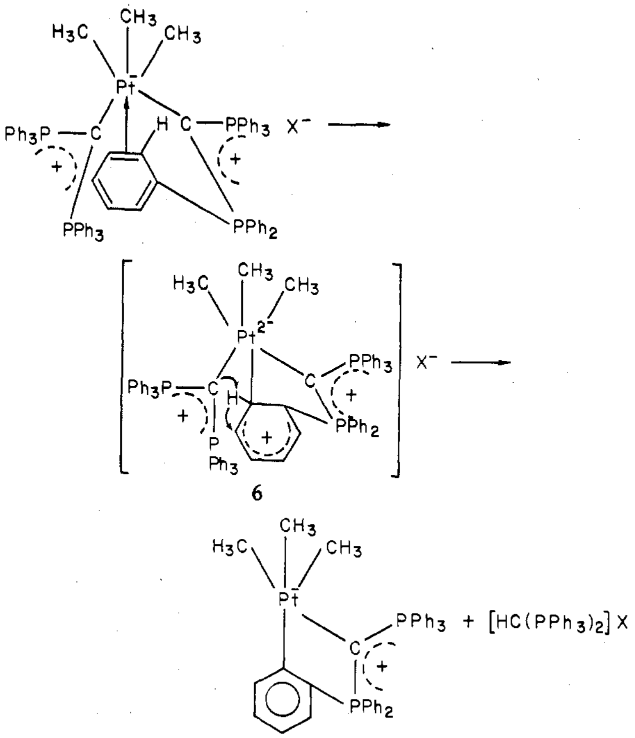
obtained from the 3:1 $C(PPh_3)_2$–Me_3Pt^{IV} reaction has bands at 1584, 1568 (sh), 1557, and 1538 cm^{-1}, the 1557-cm^{-1} band being more intense. The phosphonium salt $[HC(PPh_3)_2]PF_6$, on the other hand, has $\nu(C{=}C)$ bands at 1590 (most intense) and 1580 cm^{-1}. The product obtained from the 2:1 $C(PPh_3)_2$–Me_3Pt^{IV} reaction (see above) has only three bands in the 1500–1600-cm^{-1} region. Other Ph_3P moieties with only monosubstituted aromatic rings, such as Ph_3P and Ph_3PO, have $\nu(C{=}C)$ bands similar to those of $[HC(PPh_3)_2]PF_6$. The presence of additional bands in the 1500–1600-cm^{-1} region, as observed in the platinum-containing products, is indicative of more than monosubstitution of the aromatic rings. Bennett[22] observed for the $IrCl(PPh_3)_3$ system that two bands in this region became three upon ortho metalation. We submit that the observation of four bands in **5** shows the effects of a methyl substituent as well as ortho metalation.

A cryoscopic molecular weight determination (C_6H_6) on the red solid (**5**) from the 3:1 $C(PPh_3)_2$–Me_3Pt^{IV} reaction gives a value lower than the expected molecular weight. If the solid is recovered by evaporation and the procedure repeated, the apparent molecular weight increases to half of the theoretical value. We believe that the low results are due to disassociated, weakly coordinated THF which is always present in the ^1H NMR (see above). The elemental analysis (C, H, P) is consistent with the formulation of two $C(PPh_3)_2$ moieties and one THF per platinum atom.

Discussion

A probable reaction pathway for the interaction of the $[Me_3Pt^{IV}]^+$ moiety with hexaphenylcarbodiphosphorane is summarized in Scheme I, in which coordinated solvent molecules (usually THF) are neglected for clarity. One, however, would expect six-coordinate Pt(IV) species and four-coordinate Pt(II) species with solvent taking up the coordinately unsaturated sites.[8a] In spite of the steric bulk of $C(PPh_3)_2$, the molecule is in a fact a reasonably good nucleophile and will coordinate to transition metals. Treatment of $(Ph_3P)_3Pt^0$ or $(C_2H_4)(Ph_3P)_2Pt^0$ with $C(PPh_3)_2$ gives $(Ph_3P)_2PtC(PPh_3)_2$.[23] When $C(PPh_3)_2$ is added to $[Me_3Pt(PMe_3)_2]PF_6$ in THF, a complex reaction occurs which involves displacement of PMe_3 rather than simply the formation of $[Me_3(PMe_3)_2PtC(PPh_3)_2]PF_6$. However, $C(PPh_3)_2$ will not displace PMe_3 from the coordinatively saturated $[Me_3Pt(PMe_3)_3]PF_6$.[24] The $[Me_3Pt^{IV}]^+$ moiety is highly coordinately unsaturated, and coordination of two ylide moieties is likely as shown in step (2).

Scheme II



In step (3) a proton is transferred from an aromatic ortho position on one of the ylide moieties to the other ylide, forming $[HC(PPh_3)_2]X$ as a white precipitate. This step, or steps, is typical of a number of cyclo-metalation processes where there is no net change in the metal oxidation number.[25] One may envision the process as a two-step oxidative addition–reductive elimination cycle going through a Pt(VI) intermediate as proposed in the Pt(II)-catalyzed H–D exchange in benzene.[26]

An alternate possibility for the process involved in step (3) is electrophilic attack by the metal on one of the aromatic rings of an ylide moiety (Scheme II). Although the metal receives a great deal of electron density from the ylide moieties, it is still in a high oxidation state and, therefore, quite electrophilic. The oxidation state of the intermediate **6** would remain at the +4 oxidation level similar to $[(CH_3)_6Pt^{IV}]^{2-}$.[27] An example of electrophilic attack in a cyclo-metalation process is found in the palladation of para-substituted azobenzenes and similar reactions.[28] Electrophilic attack was also postulated in the metalation of a phenyl group of a Pt(IV) carbene complex.[29]

Once ortho metalation occurs, reductive elimination from the Pt(IV) species may occur to transfer a methyl group to an aromatic ring (Scheme I, step (4)). This gives the species **4**, which may be isolated with coordinated THF. If additional ylide is present, the reaction proceeds, possibly via step (5), to give a four-coordinate Pt(II) species similar to the known $[(CH_3)_4Pt]^{2-}$.[27]

The metal is now at the 2+ oxidation level and may undergo oxidative addition–reductive elimination cycles, steps (6) and (7), leading to loss of the methyl groups as methane and eventually to the isolated red solid **5**. This pathway is consistent with the previously mentioned deuterium-labeling study in which $[(CH_3)_3Pt^{IV}]PF_6$ was treated with ortho-deuterated ylide. D/H scrambling is not observed; the methane evolved contains the same level of deuterium as originally present in the ylide and consists of only CH_4 and CH_3D.

Experimental Section

Reactions are performed under dry, oxygen-free nitrogen or argon in modified Schlenk-type glassware. Reagents and products are manipulated in an argon-filled drybox[30] under conditions where a sodium–potassium alloy mirror persists for at least 2 min. THF, Et_2O, and C_6H_6 are distilled from sodium benzophenone ketyl under argon; diphenyl ether is added to the C_6H_6 to permit generation of the ketyl. C_6D_6, CD_2Cl_2, and *p*-dioxane-d^8 are used as purchased from the Aldrich Chemical Co. THF-d_8 is distilled from $LiAlH_4$ before use. Methyl iodide (90 atom %, ^{13}C enriched) is obtained from Merck Sharp and Dohme and used without further purification. $[(CH_3)_3PtI]_4$[31] and $C(PPh_3)_2$[5] are prepared as reported previously. $[HC(PPh_3)_2$-$d_6]Br$, 50% ortho-^2H labeled, is prepared from 50% ortho-^2H-labeled PPh_3[32] and CH_2Br_2 in two steps by previously published methods.[33] The 50% ortho-^2H-labeled bis(ylide) $C(PPh_3)_2$-d_6 is prepared analogously to $C(PPh_3)_2$.[5] (COD)$PtMe_2$ is prepared according to the procedure of Clark and Manzer.[34] $AgPF_6$ and $AgOSO_2CF_3$ are purchased from Ozark Mahoning and purified prior to use by dissolution in CH_2Cl_2, filtration, and vacuum evaporation.

NMR spectra are obtained from samples made up in the drybox and sealed off under vacuum. ^1H NMR spectra are obtained on a Varian T-60 spectrometer and a Varian XL-100 instrument with Nicolet TT-100 PFT equipment; chemical shifts are reported in ppm downfield from Me_4Si. ^{13}C NMR spectra are obtained on a Varian CFT-20 instrument; chemical shifts are reported in ppm downfield from Me_4Si. ^{31}P NMR spectra are obtained on the XL-100/Nicolet TT-100 combination; chemical shifts are reported in ppm downfield positive from H_3PO_4.

Infrared spectra are obtained on Perkin-Elmer PE-337 and PE-283 grating spectrophotometers. Cryoscopic molecular weight determinations are carried out in an apparatus described by D. H. Shriver.[35] Elemental analyses are performed by Chemalytics, Inc.[36] Mass spectra are obtained on an AEI MS-902 double-focussing mass spectrometer.

Preparation of $[(^{13}CH_3)(CH_3)_2PtI]_4$.[34,37] ($\eta^4$-1,5-Cyclooctadiene)dimethylplatinum(II), (COD)$PtMe_2$ (1.00 g, 3.00 mmol), is placed in a small flask and connected to a break-seal ampule of $^{13}CH_3I$ (1 g, 7 mmol) via ground-glass joints. The system is evacuated and refilled with dry N_2 several times, and the break-seal is broken with a glass rod. The system is resealed and the $^{13}CH_3I$ distilled into the (COD)$PtMe_2$ to produce a faintly brownish white slush. The mixture is stirred under a slight positive N_2 pressure at room temperature for 3 days. The volatiles are then distilled off to recover unreacted $^{13}CH_3I$. The white solid remaining is dissolved in reagent grade $CHCl_3$ and reduced to about 10 mL on the hot plate. The colorless solution turns slightly yellow. When acetone (10 mL) is added, a white solid crystallizes. The mixture is chilled in ice; the white crystals are then filtered, washed twice with ice-cold acetone, and air-dried (0.83 g (75%), dec pt >195 °C). Another 0.09 g was obtained as a second crop. ^1H NMR (C_6H_6): δ 1.83 (triplet of triplets, $^1J_{CH} = 138$ Hz, $^2J_{PtH} = 77$ Hz).

The integral ratio of the ^{13}C satellites to the main peak is 1:2, showing a 33% ^{13}C enrichment. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.7 (t, $^2J_{PtC} = 686$ Hz).

The coupled spectrum (decoupler power off) is a 1:4:1 triplet of quartets ($^1J_{CH} = 138$ Hz). The spin–spin splitting patterns of the ^1H and ^{13}C NMR spectra are consistent with the presence of one ^{13}C atom per trimethylplatinum moiety.

Metathesis of Trimethylplatinum Iodide. Prior to reaction with either ylide, the iodide anion bonded to platinum was metathesized to hexafluorophosphate or trifluoromethanesulfonate by the following procedure.

Me_3PtI (0.070 g, 0.19 mmol) is dried overnight at 100 °C (10^{-2} torr). In the drybox $AgPF_6$ (0.050 g, 0.20 mmol) is placed into a small dropping funnel and attached to the Me_3PtI flask. The system is sealed, removed from the box, and the $AgPF_6$ dissolved in 7–8 mL of dry, oxygen-free THF. Dropwise addition of the $AgPF_6$ solution to the Me_3PtI dissolved in 2–3 mL of THF produces a flocculent, light yellow AgI precipitate. The mixture is stirred for another 15 min and then decanted through a medium frit. The precipitate is washed once by distilling 3–4 mL of THF back under reduced pressure and redecanting the washing back through the frit. The clear, colorless filtrate thus obtained is either used directly or evaporated to give a white solid, containing solvated THF, which can be redissolved in another solvent (^1H NMR data are given in Table I).

Table I

solvent	δ	$^2J_{PtH}$, Hz		
C_6D_6	1.13 t	78	9 H	Me_3Pt
	1.50 m		6 H	THF
	3.53 m		6 H	THF
$CDCl_3$	1.18 t	80	9 H	Me_3Pt
	1.83 m		6 H	THF
	3.79 m		6 H	THF

The peak integrals indicate that the white solid is $Me_3PtPF_6\cdot 1.5THF$. The trifluoromethanesulfonate is prepared by the same procedure; it does not coordinate solvent when prepared in CH_2Cl_2 and is probably a μ_3-bridging anion, at least in the solid state.[8,9] ^1H NMR ($CDCl_3$): 1.42 ppm (t, $^2J_{PtH} = 82$ Hz).

The infrared spectrum (KBr pellet) of $[Me_3Pt(OSO_2CF_3)]_4$, a white solid, consists of bands due only to platinum methyl and $OSO_2CF_3^-$ groups. Its reaction with excess pyridine in acetone gives the tris(pyridine) complex $[Me_3Pt(py)_3][OSO_2CF_3]$.[11] ^1H NMR ($CDCl_3$): δ 1.16 (t, $^1J_{PtH} = 67$ Hz, 9 H, ($PtMe_3$)); 7.62 (m), 7.72 (m), 7.90 (m), 8.02 (m), 8.38 (m), 8.45 (m) (15.5 H (py)).

Reaction of the Me_3Pt^{IV} Cation with 2 Equiv of $Ph_3P{=}C{=}PPh_3$. To the colorless filtrate prepared from Me_3PtI (0.070 g, 0.19 mmol) and $AgPF_6$ (0.05 g, 0.20 mmol) in 10–15 mL of THF as described above is added $Ph_3P{=}C{=}PPh_3$ (0.20 g, 0.37 mmol) dissolved in 10 mL of THF dropwise over 30 min. The color of the reaction mixture gradually becomes orange; then a white precipitate of phosphonium salt separates. The mixture becomes deep orange as the remaining ylide is added. The mixture is stirred overnight at ambient temperature and then filtered. The white precipitate is washed twice by distilling back solvent under reduced pressure and vacuum-dried (0.13 g (1.0 equiv as $[HC(PPh_3)_2]PF_6$), mp 255–265 °C dec). The KBr pellet infrared spectrum matches that of a bona fide sample of $[HC(PPh_3)_2]PF_6^-$.[7] ^1H NMR ($CDCl_3$): δ 1.85 (t, $^2J_{PH} = 5.5$ Hz, 1 H (P_2CH)), 7.48 (mult, 30 H (aromatic hydrogen)).

The clear, orange filtrate is reduced to about 5 mL by vacuum evaporation; then about 25 mL dry ether is added to produce a yellow-orange precipitate. The supernatant THF–Et_2O is decanted off and the solid washed twice by distillation and then vacuum-dried (0.011 g (61%), mp 203–204 °C dec (foams; sinters at 178 °C)). Anal. Calcd for $C_{40}H_{38}P_2Pt$: C, 61.93; H, 4.94; P, 7.98. Found: C, 62.20; H, 4.33; P, 9.33. ^1H NMR (CD_2Cl_2): δ 0.89 (t, $^2J_{PCH} = 79$ Hz (one satellite), 6 H ($PtMe_2$)), 1.58 (m (THF)), 1.78 (m (THF, minor)), 2.10 (s, br, 3 H (tolyl methyl)), 3.38 (m (THF)), 3.64 (m (THF, minor)), 7.0–7.5 (m, >30 H (aromatic hydrogen)).

The material reacts slowly with $CDCl_3$ and immediately with dry HCl gas to produce a color change from intense red-orange to light orange. A 1:4:1 triplet (δ 1.30, $^2J_{PtH} = 81$ Hz) can then be observed in the ^1H NMR corresponding to the formation of an as yet unidentified methylplatinum species.

Mass Spectral Analysis of Evolved Gases. $[Me_3PtOSO_2CF_3]_4$ (0.100 g, 0.0642 mmol) is prepared as described above and dissolved in 5 mL of THF in the drybox. The solution is transferred to one leg of a two-legged ampule fitted with a ground-glass joint and a break-seal. $C(PPh_3)_2$-d_6, containing a 50% ortho-^2H label (0.279 g, 0.514 mmol, 2 mol/mol of Pt), is dissolved in 10 mL of THF and transferred to the other leg without allowing the solutions to mix. The ampule is sealed under vacuum, and the ylide solution is added to the $[Me_3PtOTf]_4$ solution in small portions with shaking at −80 to −90 °C. The solution gradually becomes orange and then turbid as the white precipitate of phosphonium salt comes out. The mixture is stirred at −78 °C for 18 h and then allowed to warm to room temperature. The yellow-orange mixture quickly becomes orange (white solid, red supernatant). The mixture is stirred another 25 h and then attached to the mass spectrometer. The connecting tube is evacuated, and the gas over the partly frozen reaction mixture is sampled through the break-seal.

Mass spectrum at 70 eV [*m*/*e* (ion, relative intensity)]: 12 (C^+, 1.2), 13 (CH^+, 3.4), 14 (CH_2^+, CD^+, 6.4), 15 (CH_3^+, CD_2^+, 55), 16 (CH_4^+, CDH_2^+, 100), 17 (CDH_3^+, 46), 18 ($^{13}CDH_3^+$, 0.48).

Reaction of the Me_3Pt^{IV} Cation with 3 Equiv of $Ph_3P{=}C{=}PPh_3$. A clear, colorless solution of $[Me_3Pt\cdot nTHF]PF_6$ is prepared as described above from Me_3PtI (0.250 g, 0.681 mmol) and $AgPF_6$ (0.172 g, 0.680 mmol) in 30 mL of THF. The solution is evaporated to about

15 mL and cooled to 0 °C. A solution of $(Ph_3P)_2C$ (1.096 g, 2.042 mmol) dissolved in 50–55 mL of THF is then added dropwise to the cold, stirring Me_3Pt^{IV} solution over 65 min. The reaction mixture rapidly turns orange and then turbid as the phosphonium salt begins to precipitate. As the rest of the ylide is added, the suspension gradually deepens to red-orange. After the solution has stirred at 0 °C for 9 h, the white solid is filtered out and washed once with THF by back-distillation under reduced pressure. The vacuum-dried solid weighs 0.497 g (108% as $[HC(PPh_3)_2][PF_6]$; 97% as $[HC(PPh_3)_2][PF_6]\cdot THF$). The compound is identified by its KBr pellet infrared spectrum (identical with that of known samples). The phosphonium salt crystallizes with 1 mol of solvent as evidenced by ^1H NMR; the higher field THF multiplet obscures the triplet produced by the proton on the α-carbon atom of the phosphonium salt.

The blood red filtrate is vacuum-evaporated, and the residue kept under vacuum for 15 min at room temperature. Dry C_6H_6 (100 mL) is then added; most of the residue dissolves to give a dark red solution. The mixture is stirred for 20 min and filtered through a medium frit, the gummy-looking residue being washed twice with benzene by distillation. The filtrate is vacuum-evaporated to give a dark red solid which slowly fades to orange under vacuum (15 min, 20 °C, 10^{-2} torr) (0.908 g (98%)), mp 122–124 °C dec (foams, sealed tube). Anal. Calcd for $C_{79}H_{68}OP_4Pt$: C, 70.16; H, 5.07; P, 9.16. Found: C, 69.86; H, 5.27; P, 10.41.[38] ^1H NMR (C_6D_6): δ 1.49 (m (THF)), 1.69–1.93 (small peaks (THF + impurity)), 2.32 (m, broadish (tolyl methyl)), 3.39 (s, small (THF)), 3.62 (m (THF)), 7.06 (m, major (meta and para aromatics)), 7.48 (m, minor (ortho aromatics of impurity)), 7.89 (m, major (ortho aromatics)). Molecular weight: calcd, 1352.41; found, 577 (43%), 763 (56%). For further details, see text.

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Registry No. 3, 68843-05-0; 4, 68843-06-1; 5, 68843-07-2; $[(^{13}CH_3)(CH_3)_2PtI]_4$, 68843-08-3; (COD)$PtMe_2$, 12266-92-1; $[Me_3Pt(OSO_2CF_3)]_4$, 68950-86-7; $[HC(PPh_3)_2]PF_6$, 54807-61-3; $Ph_3P{=}C{=}PPh_3$, 7533-52-0; $[Me_3Pt(py)_3][OSO_2CF_3]$, 68833-46-5.

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Complex Halides of the Transition Metals. 27.[1] Reactions of Nitric Oxide with Molybdenum(II) Dimers Containing Metal–Metal Quadruple Bonds. A New Route to Monomeric Dinitrosyl Derivatives of Molybdenum

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Nitric oxide reacts with the metal–metal bonded dimers $Mo_2X_4L_4$, where X = Cl or Br and L = $PEtPh_2$, PEt_3, or P-*n*-Bu_3, and $Mo_2X_4(LL)_2$, where X = Cl or NCS and LL = 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm) in dichloromethane to afford the dinitrosyls of molybdenum, $Mo(NO)_2X_2L_2$ and $Mo(NO)_2X_2(LL)$. The cleavage of the Mo–Mo quadruple bond of the starting materials is contrasted with the reaction of carbon monoxide with the rhenium(II) dimers $Re_2X_4(PR_3)_4$ to produce *trans*-$Re(CO)_2X_2(PR_3)_2$ and the lack of reactivity of $Mo_2X_4(PR_3)_4$ toward this same ligand.

Introduction

We have recently investigated the reactivity of the metal–metal bonded dimers $Re_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Pr, toward carbon monoxide.[2,3] One of the most significant results of these studies was the synthesis of a new class of carbonyl derivatives of rhenium(II), the paramagnetic 17-electron monomers *trans*-$ReX_2(CO)_2(PR_3)_2$. In contrast, complexes of the types $Re_2Cl_6(PR_3)_2$ and

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