Table IV. Approximate Nickel–Olefin Bond Strengths (kcal/mol)

olefin	ligand P(O-*o*-tolyl)$_3$	 P(O-*p*-tolyl)$_3$	 P(O-*p*-C$_6$H$_4$Cl)$_3$
cyclohexene	32	26	*b*
1-hexene	36	37	34
acn	42[a]	42	42
ma	48	48	45

[a] Calculated assuming that $\Delta S_2 = 0$, using $\Delta H_2 = -RT \ln K_2$ with $K_2 = 4.0 \times 10^4$ from ref 4c. [b] Not determined.

character of L. The smaller values of 23 and 13 kcal/mol,[6] respectively, for ΔH_d for dissociation of the first ligands of Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*o*-tolyl)$_3$]$_4$ are a consequence of steric strain, which is greater for the more bulky ligand. If we break eq 4 into steps, with eq 9 and 10 being hypothetical,[21] we have

$$\mathrm{NiL_4 = NiL_3 + L} \qquad (1)$$

$$\mathrm{NiL_3 = NiL_2 + L} \qquad (9)$$

$$\mathrm{NiL_2 + olefin = (olefin)NiL_2} \qquad (10)$$

$$\text{Net} \quad \mathrm{NiL_4 + olefin = (olefin)NiL_2 + 2L} \qquad (4)$$

The strength of the Ni–olefin bond given by $-\Delta H_{10}$ can then be determined from the data in Table III if we take ΔH_d = 23 kcal/mol for L = P(O-*p*-tolyl)$_3$ or P(O-*p*-C$_6$H$_4$Cl)$_3$[22] and ΔH_9 = 37 for all L. The results are given in Table IV.

It can be seen that the Ni–olefin bond strengths are equal within experimental error for L = P(O-*o*-tolyl)$_3$ and P(O-*p*-tolyl)$_3$ but are slightly less on average for the more electronegative P(O-*p*-C$_6$H$_4$Cl)$_3$. The values shown can be compared with the average Ni–olefin bond of 25 kcal/mol in Ni(COD)$_2$.[20] With ΔH_9 = 37 from the calorimetric work in place of the 30 assumed earlier,[4c] we estimate a Ni–ethylene bond strength of 40 kcal/mol in the tritolyl phosphite systems. The great strength of these Ni–olefin bonds explains why we do not observe the dissociation of (olefin)NiL$_2$ complexes in solution and why (C$_2$H$_4$)Ni[P(O-*o*-tolyl)$_3$]$_2$ can be recovered after pumping its solutions to dryness.[4a]

All known (C$_2$H$_4$)NiL$_2$ complexes of nickel have phosphorus ligands with cone angles of 130° or more. The reason why is now clear. Larger ligands cause sufficient strain energy[20] (>20 kcal/mol) in their NiL$_4$ complexes that ethylene can be effective in replacing two phosphorus ligands. With smaller ligands ethylene cannot compete, and NiL$_4$ complexes are preferentially formed.

Registry No. (acn)$_2$NiPBu$_3$, 86901-49-7; (acn)$_2$Ni(PBu$_3$)$_2$, 86901-50-0; (acn)$_2$Ni(PMe$_3$)$_2$, 86901-51-1; (acn)$_2$Ni[P(OMe)$_3$]$_2$, 86901-52-2; (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$, 31666-48-5; (acn)Ni[P(O-*p*-tolyl)$_3$]$_2$, 86901-53-3; (acn)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-54-4; (ma)Ni[P(O-*o*-tolyl)$_3$]$_2$, 41813-01-8; (ma)Ni[P(O-*p*-tolyl)$_3$]$_2$, 56558-10-2; (ma)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-55-5; P(O-*p*-tolyl)$_3$, 620-42-8; P(O-*p*-C$_6$H$_4$Cl)$_3$, 5679-61-8; P(O-*o*-tolyl)$_3$, 2622-08-4; P(O-*p*-Cl-*o*-tolyl)$_3$, 86901-48-6; ma, 108-31-6; acn, 107-13-1; (acn)$_2$Ni, 12266-58-9; Ni[P(OPh)$_3$]$_4$, 14221-00-2; (acn)Ni[P(OPh)$_3$]$_2$, 86901-64-6; Ni[PMe$_3$]$_4$, 28069-69-4; Ni[P(O-*o*-tolyl)$_3$]$_3$, 28829-00-7; (cyclohexene)Ni[P(O-*p*-tolyl)$_3$]$_2$, 86901-56-6; (1-hexene)Ni[P(O-*p*-tolyl)$_3$]$_2$, 86901-57-7; (cyclohexene)Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-58-8; (1-hexene)Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-59-9; (acn)-Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-60-2; (ma)Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-61-3; (cyclohexene)Ni[P(O-*o*-tolyl)$_3$]$_2$, 53323-39-0; (1-hexene)Ni[P(O-*o*-tolyl)$_3$]$_2$, 53323-45-8; (cyclohexene)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-62-4; (1-hexene)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-63-5.

Supplementary Material Available: Tables of (1) steric and electronic parameters of the phosphorus ligands used, (2) kinetics of reaction of Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_4$ with maleic anhydride, and (3) electronic spectral data for the (olefin)NiL$_2$ complexes in benzene (5 pages). Ordering information is given an any current masthead page.

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(21) All of the compounds for which we have any evidence in solution obey the 16- and 18-electron rule: Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337. Ni(acn)$_2$ appears superficially to be a 14-electron complex. Its insolubility in CH$_2$Cl$_2$ in the absence of added phosphorus ligands suggests however that it is polymeric. Attempts to grow single crystals suitable for X-ray structure analysis were unsuccessful.

(22) Equal values of ΔH_d are not unreasonable since both Ni[P(O-*o*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_4$ were found to have ΔH_d = 13 kcal/mol.

A Hydrido(μ-hydrido)methyldiplatinum(II) Complex. Reductive Elimination of Methane Induced by Reaction with an Alkyne

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Received February 8, 1983

Reaction of [Pt$_2$Cl$_2$(μ-CH$_2$)(μ-dppm)$_2$] with H[SbF$_6$] gives [Pt$_2$Cl(μ-Cl)Me(μ-dppm)$_2$][SbF$_6$] (II) and reduction of II with NaBH$_4$ gives [Pt$_2$H(μ-H)Me(μ-dppm)$_2$][SbF$_6$] (III), characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Complex III undergoes "A-frame inversion" on the NMR time scale, and it is proposed that a transition state with a linear MePtHPtH unit is involved; the activation energy at −60 °C is $\Delta G^* = 41$ kJ mol^{-1}. Complex III reacts with CF$_3$C≡CCF$_3$ in MeCN solution to give 90% [Pt$_2$H(MeCN)(μ-CF$_3$C=CCF$_3$)(μ-dppm)$_2$][SbF$_6$] and methane and 10% [Pt$_2$Me(MeCN)(μ-CF$_3$C=CCF$_3$)(μ-dppm)$_2$][SbF$_6$] (VIII) and hydrogen. Pure VIII was prepared by the similar reaction of CF$_3$C≡CCF$_3$ with [Pt$_2$(μ-H)Me$_2$(μ-dppm)$_2$][SbF$_6$], with elimination of methane. The alkyne has ability to induce reductive elimination of methane from III or VIII, whereas phosphines induce loss of H$_2$ from III and react only slowly with VIII.

Introduction

There has been considerable interest in the chemistry of alkylhydridotransition-metal derivatives. Such complexes may be formed in the activation of alkanes by C–H oxidative addition,[1,2] and studies of the reductive elimination of alkanes, RH, from alkyl hydrido complexes [L$_n$MHR] may give insight into the mechanism and en-

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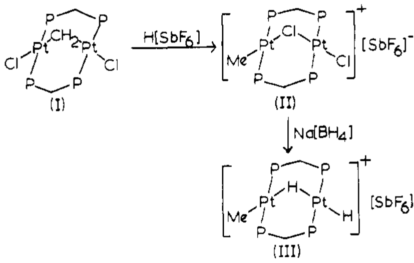
(1) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3722.

ergetics of the reverse oxidative addition.[3,4] Most of the work in this area has been carried out with mononuclear complexes, but there is also interest in binuclear systems that may be better models for activation of alkanes on metal surfaces.[5]

In earlier papers, we have reported the binuclear complex cation $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$, dppm = $Ph_2PCH_2PPh_2$, containing terminal methyl and bridging hydrido ligands,[6] as well as related hydrides $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ and $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$[7] and the methyl complex $[Pt_2Me_3(\mu\text{-}dppm)_2]^+$.[8] In this article, the new derivative $[Pt_2H(\mu\text{-}H)Me(\mu\text{-}dppm)_2]^+$ is reported. The complex is of particular interest because reductive elimination could give methane or hydrogen, and the selectivity can be studied. Reductive elimination from $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ is slow thermally, even when induced by tertiary phosphine ligands, and gives methane[6] while intramolecular elimination, induced by tertiary phosphine ligands, from $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ is fast and yields hydrogen.[9]

Results and Discussion

Synthesis and Fluxional Behavior of $[Pt_2H(\mu\text{-}H)Me(\mu\text{-}dppm)_2][SbF_6]$. The synthesis was achieved in two steps from the known (μ-methylene)diplatinum complex I,[10] as shown in eq 1.



(1)

The protonation of a μ-methylene group to give a methyl group is now a standard reaction.[11-13] Since the methyl group is a very poor bridging ligand in diplatinum complexes, the presumed μ-methyl intermediate rearranges to complex II having the methyl group in the terminal position. The methyl group in II reacts only very slowly with excess acid. A very close analogy to this reaction is seen in the protonation of $[Pd_2I_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ to give $[Pd_2I(\mu\text{-}I)Me(\mu\text{-}dppm)_2]^+$ (IV). Complex IV is fluxional due to the exchange of terminal and bridging I$^-$ ligands, which leads to inversion of the A-frame structure (eq 2).[13]

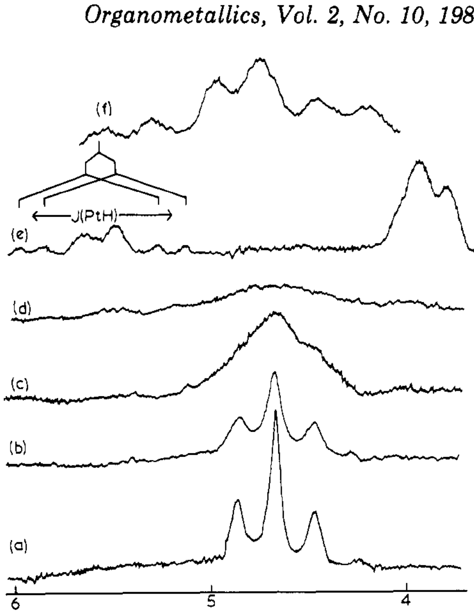
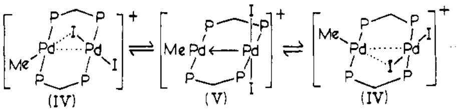


Figure 1. $^1H\{^{31}P\}$ NMR spectra (100 MHz) of complex III showing only the CH_2P_2 resonances. Spectra were recorded at (a) −30 °C, (b) −40 °C, (c) −60 °C, (d) −70 °C, (e) −80 °C, and (f) −80 °C (low-field resonance recorded at higher sensitivity).



(2)

In the platinum complex II, this A-frame inversion is slow on the NMR time scale. Thus the $CH^aH^bP_2$ protons of the dppm ligands give two resonances at δ 3.99 and 4.07, showing that there is no effective plane of symmetry containing the $Pt_2(\mu\text{-}dppm)_2$ unit. Complex II is further characterized by the ^1H NMR spectrum that gives a triplet due to the methylplatinum group [δ(MePt) 0.74 (^3J(PH) = 6.5 Hz)] with one-fourth intensity satellites due to coupling with ^{195}Pt [^2J(PtH) = 91 Hz)], clearly showing that the methyl group is in a terminal position. The $^{31}P\{^1H\}$ NMR spectrum gave an [AA′BB′] multiplet with $\delta(P^A)$ −1.23 ($^1J(PtP^A)$ = 2430 Hz) and $\delta(P^B)$ 8.09 (^1J(PtP) = 2990 Hz). Analysis of the fine structure gave $^2J(P^AP^B)$ = 30 Hz and $^3J(P^AP^{B'})$ unresolved and certainly less than 10 Hz. These couplings are typical of complexes having little or no PtPt bonding,[14] as expected for structure II. However, we cannot eliminate the possibility of weak PtPt interaction of the kind found in the palladium complex IV.[13] Certainly, an asymmetric $Pt_2(\mu\text{-}Cl)$ linkage is expected in view of the difference in trans influence between the terminal methyl and chloro ligands in II.

Reduction of II with $Na[BH_4]$ occurred smoothly to give the desired complex III in 96% yield. In one experiment with a long reaction time, the product was contaminated with $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][SbF_6]$ (VI), as shown by the ^1H NMR spectrum, but this was not a problem in most syntheses. Complex III is a colorless crystalline solid, which has good thermal stability in the solid state or in solution in dichloromethane but which is very photosen-

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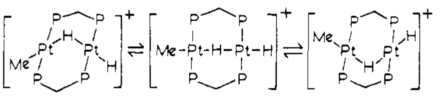
sitive. The infrared spectrum gave a band at 2096 cm^{-1} due to the terminal Pt–H stretching vibration, but no band was seen due to the bridging hydride.

In the ^{1}H NMR spectrum, the hydride signals were seen at δ −6.57 (bridging hydride, ^1J(PtH) = 540 Hz, ^2J(PH) = 9 Hz) and at δ −6.75 (terminal hydride, ^1J(PtH) = 1135 Hz, ^2J(PH) = 9.5 Hz). For comparison, $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ gives δ −5.86 (bridging hydride, ^1J(PtH) = 540 Hz) and δ −6.86 (terminal hydrides, ^1J(PtH) = 1138 Hz),[7] and the close similarity in coupling constants suggests very similar bonding and structure for the two complexes. The methyl group gave a triplet resonance [δ 0.22 (^3J(PH) = 6 Hz, ^2J(PtH) = 68 Hz)] with satellites due to coupling to ^{195}Pt of one-fourth intensity, showing that it occupies a terminal position.

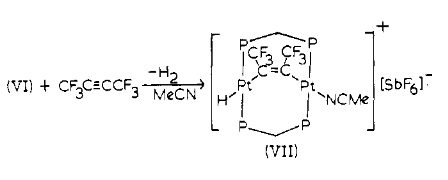
The ^{31}P NMR spectrum gave a closely spaced [AA′BB′] pattern with $\delta(P^A)$ 15.75 (^1J(PtH) = 2820 Hz) and $\delta(P^B)$ 15.30 (^1J(PtH) = 2850 Hz) and with $^2J(P^AP^B)$ = 37 Hz, fully consistent with the proposed formulation.

The above ^{1}H and ^{31}P NMR resonances were essentially unchanged over the temperature range −80 to +70 °C. In particular, the absence of exchange between bridging and terminal hydride ligands up to 70 °C, indicates that the activation energy for such exchange must be $\Delta G^{\ddagger} > 72$ kJ mol^{-1}. However, significant changes in the resonance due to the CH_2P_2 protons were observed at low temperature (Figure 1), indicating the presence of fluxionality. At room temperature the ^{1}H{^{31}P} NMR spectrum gives a 1:8:18:8:1 multiplet [δ 4.71 (^3J(PtH) = 34.5 Hz)], indicating that these protons are equivalent and that the coupling constants to the two nonequivalent ^{195}Pt atoms are approximately equal. However, at −80 °C the signal is split into two as the inequivalence of the $CH^aH^bP_2$ protons, expected for the A-frame structure,[13] is frozen out. Analysis gives $\delta(H^a)$ 3.98 ($^2J(H^aH^b)$ = 13 Hz) and $\delta(H^b)$ 5.54 ($^2J(H^aH^b)$ = 13 Hz, ^3J(PtH) = 66.5 Hz). At the coalescence temperature of approximately −65 °C (Figure 1), the activation energy for the fluxional process is ΔG = ~41 kJ mol^{-1}. The coalescence temperature was unchanged for solutions of concentration 0.01 and 0.02 M, indicating that an intermolecular mechanism of exchange is not operative. Since the NMR data clearly demonstrate that the fluxional process, which involves inversion of the A frame,[13-15] does not give exchange between bridging and terminal hydride ligands nor reversible loss of hydride from platinum, we are led to suggest that direct inversion of the A frame through an intermediate with a linear MePtHPtH unit is responsible (eq 3). In the complex $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$, the corresponding activation energy for A-frame inversion[15] is given by $\Delta G^{\ddagger}$ (253 K) = 46.5 kJ mol^{-1}.



(3)

Reactions with Hexafluorobut-2-yne. $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ (VI) reacts with hexafluorobut-2-yne in acetonitrile solution with reductive elimination of hydrogen as in eq 4.[16]



(4)

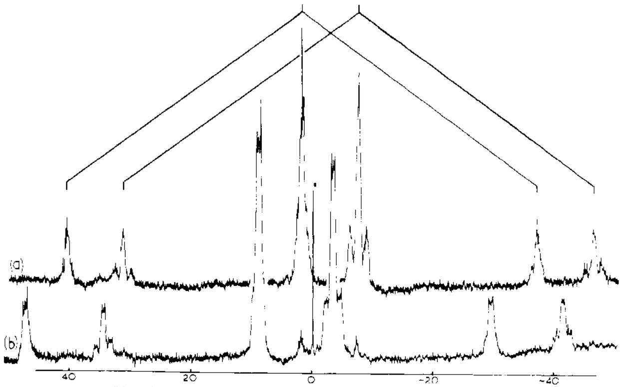
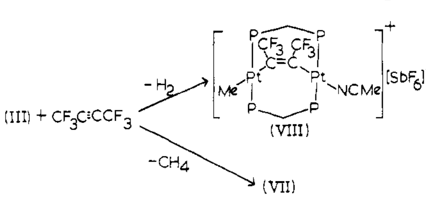


Figure 2. ^{31}P{^{1}H} NMR spectra (40.5 MHz) of (a) complex VIII with ^{195}PtP couplings indicated above and (b) 9:1 mixture of VII and VIII formed by reaction of eq 5. The peak marked asterisk is due to the reference trimethyl phosphate.

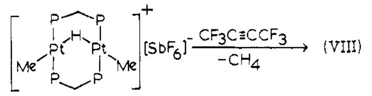
Similar reaction of III with hexafluorobut-2-yne gave a mixture of the complexes VII and VIII (eq 5).



(5)

The gas evolved was mostly methane with only a trace of hydrogen detected, and the product was a mixture of VII, (90 ± 2%) and VIII (10 ± 2%), as determined by integration of both ^{1}H and ^{31}P{^{1}H} NMR spectra of the product mixture.

It was not possible to isolate VIII in pure form from the above reaction mixture, but pure VIII was prepared by the ready reaction of hexafluorobut-2-yne with $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2][SbF_6]$ (IX) according to eq 6.



(6)

In this case the gas evolved was pure methane. The spectroscopic properties of VIII (Experimental Section) are very similar to those for VII, which has been characterized previously.[16] The chief difference is the presence of the methylplatinum group, which gives a characteristic triplet in the ^{1}H NMR spectrum [δ(MePt) 0.36 (^3J(PH) = 6.4 Hz, ^2J(PtH) = 56.4 Hz)], and no hydridoplatinum resonance in the high-field region of the ^{1}H NMR spectrum. The low coupling constant ^2J(PtMe) = 56.4 Hz is expected for a methyl group trans to a σ-bonded carbon donor ligand. The ^{31}P{^{1}H} NMR spectra of pure VIII and of the reaction mixture of eq 5 are shown in Figure 2 and illustrate clearly the presence of VIII in low abundance in the latter case.

Conclusions

The successful synthesis of complex III completes the series of complex cations $[Pt_2H_nMe_{3-n}(\mu\text{-}dppm)_2]^+$, where n = 0–3, and allows some general conclusions to be reached. It is clear that hydride is a good bridging ligand in these diplatinum complexes but that methyl is not.[6-8] Hence in the mixed methyl hydrido derivatives hydride always occupies the bridging position. The thermal stability of the methyl hydrido derivatives III and IX is almost cer-

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tainly a result of the mutually trans stereochemistry that prevents reductive elimination of methane (or hydrogen in III) by a concerted mechanism.

The selectivity in reductive elimination of methane or hydrogen from III is of considerable interest. Tertiary phosphine ligands, L, induce primarily reductive elimination of hydrogen and give the methyldiplatinum I complexes $[Pt_2MeL(\mu\text{-dppm})_2][SbF_6]$,[17] but hexafluorobut-2-yne induces primarily reductive elimination of methane to give VII. The ability of hexafluorobut-2-yne to induce reductive elimination of methane is also seen in the facile reaction with IX, whereas tertiary phosphines react only very slowly with IX to give reductive elimination of methane.[6] It is known that these reactions are associative, with an intermediate formed by addition of the reagent to the platinum complex, and the different reactivity and selectivity in reactions of the alkyne and of phosphines with $[Pt_2H_nMe_{3-n}(\mu\text{-dppm})_2]^+$ suggests that the intermediates have different structures in the two cases. Similar phenomena may have relevance in interpreting selectivity in catalysis, and a more detailed study of the mechanisms of these reactions is planned. We note that the overall sequence of reactions of I to give VII converts a μ-methylene group to methane by formal addition of H^+ followed by H^-, a sequence which may be involved in the methanation of carbon monoxide on heterogenous catalysts.

The low-temperature ^1H NMR spectra for complex III give particularly clear evidence for the direct inversion of the A-frame molecule[15] through an intermediate with a linear MePtHPtH unit. This process leads to an effective plane of symmetry containing the $Pt_2P_4C_2$ framework of the dppm ligands and hence to equivalence of the $CH^aH^bP_2$ protons in the ambient temperature ^1H NMR spectra,[13,15] without leading to equivalence of the bridging and termainal hydride ligands or of the nonequivalent dppm phosphorus atoms. The activation energy for the inversion appears to increase in the series[15] $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+ < [Pt_2MeH(\mu\text{-}H)(\mu\text{-dppm})_2]^+ < [Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$, indicating that terminal methyl ligands are more effective than terminal hydride ligands in facilitating the A-frame inversion.

Experimental Section

The synthesis of $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ was carried out as described previously.[10] ^1H, ^{19}F, and ^{31}P NMR spectra were recorded by using a Varian XL100 spectrometer, and chemical shifts are quoted with respect to Me_4Si, $CFCl_3$, and $PO(OMe)_3$, respectively. Spectra were recorded in CH_2Cl_2 (^{31}P) or $CD_2Cl_2/CDCl_3$ (^1H).

$[Pt_2Cl(\mu\text{-}Cl)CH_3(\mu\text{-dppm})_2][SbF_6]$. A yellow suspension of $[Pt_2Cl_2(\mu\text{-}CH_2)dppm_2]$ (0.1 g, 0.08 mmol) in CH_2Cl_2 (20 mL) was added to a flask containing $H[SbF_6]\cdot 6H_2O$ (0.03 g, 0.08 mmol). The suspension was stirred at room temperature under N_2 for 2.25 h to give a yellow solution. The volume was reduced, and diethyl ether was added when crystals of $[Pt_2Cl(\mu\text{-}Cl)CH_3(\mu\text{-dppm})_2][SbF_6]$ formed (0.11 g, 92% based on Pt). The compound was also obtained (85% yield) when the reaction was repeated with 2 molar proportions of $H[SbF_6]\cdot 6H_2O$: mp 210–215 °C dec; IR $\nu(SbF_6)$ 278, 653 cm^{-1}. Anal. Calcd. for $[Pt_2Cl_2Me(dppm)_2][SbF_6]$: C, 41.4; H, 3.2; Cl, 4.8. Found: C, 41.3; H, 3.25; Cl, 4.8.

$[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2][SbF_6]$. A solution $NaBH_4$ (0.49) in methanol (10 mL) was added dropwise to a yellow solution of $[Pt_2Cl(\mu\text{-}Cl)Me(\mu\text{-dppm})_2][SbF_6]$ (0.9124 g, 0.62 mmol) in CH_2Cl_2 (20 mL). The yellow solution, which was stirred in the absence of light, under N_2 at room temperature became almost colorless within a few minutes. After 0.5 h the solvent was removed and the residue was vacuum dried. The product was extracted with CH_2Cl_2, the solution was reduced in volume, and a white product was obtained by adding diethyl ether: yield 0.83 g (96% based on Pt); mp 190–200 °C dec; IR ν(Pt–H) 2096 cm^{-1}, $\nu(SbF_6^-)$ 658, 282 cm^{-1}. Anal. Calcd. for $[Pt_2H_2Me(dppm)_2][SbF_6]$: C, 43.4; H, 3.5.

$[Pt_2Me\{\mu\text{-}\eta^2\text{-}C(CF_3){=}C(CF)_3\}(MeCN)(\mu\text{-dppm})_2][PF_6]$. Hexafluorobut-2-yne (0.7 mmol) was condensed through the vacuum line into a thick-walled Pyrex tube containing a suspension of $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ (0.106 g, 0.08 mmol) in MeCN (3 mL), and the tube was sealed with a Teflon stopcock. The tube was allowed to stand in the dark at room temperature when the suspension slowly disappeared to give a yellow solution. After 3 days, the tube was opened and the gas phase was shown to contain CH_4 but no H_2(analysis by GC using porapak Q and molecular sieve 5A columns). The *product* was obtained from the MeCN solution by precipitation with pentane: yield 0.08 g (66%); mp 190–195 °C dec; h NMR in CD_3CN solution δ(MePt) 0.36 ($^3J(PH) = 6.4$ Hz, $^2J(PtH) = 56.4$ Hz), $\delta(CH^aH^bP_2)$ 3.63 ($^2J(H^aH^b) = 13.6$ Hz, $^2J(PH) = 13.5$ Hz), 4.19 ($^2J(PH) = 3.4$ Hz, $^3J(PtH) = 66$ Hz), δ (MeCN) 2.19, $\delta(CF_3)$ −48.8 ($^5J(FF) = 14.2$ Hz, $J(PtF) = 108$ Hz), −50.2 ($J(PtF) = 61.5$ Hz), $\delta(^{31}P)$ 1.88 ($^1J(PtP) = 3134$ Hz, $^2J(PP) = 23$ Hz), −7.41 ($^1J(PtP) = 3138$ Hz, $^2J(PtP) = 110$ Hz). Anal. Calcd for $[Pt_2Me(C_4F_6)(MeCN)(dppm)_2][PF_6]$: C, 45.0; H, 3.3; N, 0.9. Found: C, 45.0; H, 3.25; N, 1.0.

The corresponding complex with $[SbF_6]^-$ counterion was prepared in the same way from $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-dppm})_2][SbF_6]$ and gave identical NMR spectra.

The reaction of C_4F_6 with $[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2][SbF_6]$ (0.1 g) was carried out in the same way. Analysis of the gas phase now gave methane with a trace of hydrogen also detected. The product (0.104 g) was identified as a mixture of VII[16] (90%) and VIII (10%) by integration of the PtH signal of VII against the PtMe signal of VIII in the ^1H NMR spectrum and by integration of the signals due to dppm phosphorus atoms of VII[16] vs. VIII in the ^{31}P NMR spectrum of the crude product (Figure 2).

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