to that over $CoTPP/SiO_2$ and CoTPP, suggests a similar reaction scheme.

The adsorption of nitric oxide may be rather difficult as shown in the UV spectroscopy study of it in solution on CoTPP(Im); however, its activation will be more pronounced once it adsorbs. Such situations will be explained in terms of simple molecular orbitals as illustrated in Figure 7, where the orbitals interacting scarcely with nitric oxide are ignored. The orbitals composed of $d_{z^2} + p_\sigma + p_{\sigma'}$ and $\pi^* + d_\pi + p_\pi$ are related to the coordination and activation of nitric oxide, respectively. When the electronic density of these orbitals increases with the strong σ- and π-donating abilities of imidazole, the coordination of NO may be hindered but the activation is enhanced by a strenghthening of the anionic nature of adsorbed nitric oxide. The electronic configuration (Figure 7) after the electron transfer into the π MO ($\pi^* + d\pi + p\pi$, major contribution of π^* NO) from the σ-MO ($d_{z^2} + p\sigma + \sigma$) indicates a formal structure of $Co^{III}ImNO^-$.

An alternative route leading to nitrous oxide (Scheme II) may contribute to a certain extent. Such a reaction between the adsorbed NO and a gaseous NO may be probable because imidazole promotes the oxidation of a cobalt-nitrosyl complex by molecular oxygen.

Registry No. CoTPP, 14172-90-8; Co(Im)TPP, 79898-39-8; Co(NO)TPP, 42034-08-2; Co(Im)(NO)TPP, 79872-86-9; NO, 10102-43-9.

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Reactions of Binuclear Hydridoplatinum Complexes with Alkynes

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Reaction of the binuclear hydride $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$ (I) (dppm = $Ph_2PCH_2PPh_2$) with alkynes, RC≡CR, in dichloromethane solution gives $[Pt_2Cl(cis\text{-}CR{=}CHR)(\mu\text{-}RCCR)(\mu\text{-dppm})_2]$ (II), R = CF_3 or CO_2Me, and H_2. In donor solvents (S = MeCN, PhCN, or acetone) the reaction gives only $[Pt_2H(S)(\mu\text{-}RCCR)(\mu\text{-dppm})_2]PF_6$ (III), which can be converted to $[Pt_2HCl(\mu\text{-}RCCR)(\mu\text{-dppm})_2]$ (IV) or $[Pt_2Cl_2(\mu\text{-}RCCR)(\mu\text{-dppm})_2]$ (V) by reaction with NaCl or HCl, respectively, and to II by reaction with RCCR in CH_2Cl_2 solution (R = CF_3). 3,3,3-Trifluoropropyne reacts with I to give $[Pt_2(CCCF_3)_2(\mu\text{-}CF_3CCH)(\mu\text{-dppm})_2]$. The compounds are characterized by ^1H, ^{19}F, and ^{31}P NMR spectroscopy, and the sequence of reactions by which the compounds are formed is determined.

There has been great interest in the chemistry of binuclear and polynuclear platinum complexes, partly because there can be a resemblance between this chemistry and reactions that have been proposed to occur at a platinum surface in heterogeneous catalytic processes.[1-7] One of the best known catalytic reactions is the hydrogenation of alkenes and alkynes, and reactions of binuclear platinum hydrides with unsaturated reagents might be expected to give useful models for individual steps in the proposed catalytic cycles. For this reason we have studied reactions of the hydride[8] $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$, dppm = $Ph_2PCH_2PPh_2$, with alkenes and alkynes. This paper gives results for reactions with alkynes bearing electronegative substituents. There have been many studies of related reactions with mononuclear platinum hydrides, particularly by Clark and co-workers, and the mechanisms are understood in some detail.[9,10] However, we know of no previous studies of reactions of alkynes with binuclear platinum hydrides.[11] A preliminary account of parts of this work has been published.[12]

Results

Synthesis of New Compounds. A summary of many of the reactions studied is given in Scheme I. The characterization of the complexes will be discussed separately, and only the syntheses will be given here.

The first product to be isolated in pure form was IIa formed as very pale yellow crystals by reaction of excess hexafluorobut-2-yne, C_4F_6, with I in dichloromethane solution. Formally, this reaction involves loss of two hydrogen atoms from I, cis insertion of one alkyne into the remaining Pt-H bond, addition of a second alkyne between the two Pt atoms, and abstraction of Cl^- from the solvent. The presence of chloride in the product was unexpected but was clearly indicated by the mass spectrum and elemental analysis; the chloride was easily displaced by iodide to give IIe.

The sequence of reactions by which IIa is formed is clearly of interest, and we have investigated this problem.

Reactions with other alkynes show that electronegative substituents are necessary on the alkyne in order to observe any reaction. Thus acetylene, but-2-yne, and diphenylacetylene failed to react with I in dichloromethane at temperatures up to 70 °C. However, the dimethyl ester of acetylenedicarboxylic acid did react with I to give IIb in fair yield, along with ill-characterized oligomers of the alkyne, which could be separated from the desired IIb by column chromatography. In this reaction a gas was evolved immediately on mixing the reagents, and this was identified as H_2 by gas chromatography. Quantitative analysis gave yields of 60–80% of H_2; this is at least as high as the isolated yield of IIb but may indicate that a side reaction not involving H_2 elimination from I also occurs. Hydrogen was identified as a product (GC) in the reaction giving IIa, but quantitative analysis was not attempted in this case.

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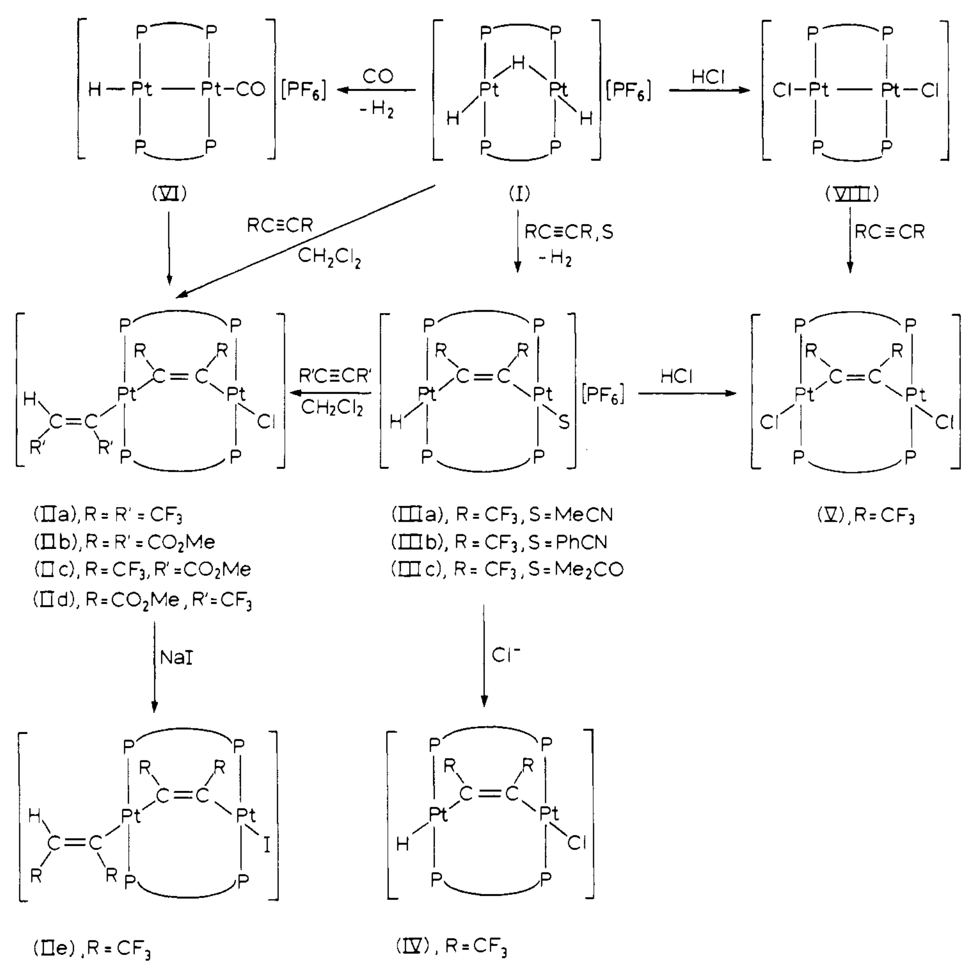
0020-1669/82/1321-0725$01.25/0

Scheme I[a]



[a] PP = dppm.

We have shown elsewhere that soft ligands such as tertiary phosphines and carbon monoxide induce binuclear reductive elimination of H_2 from I to give diplatinum(I) complexes $[Pt_2HL(\mu\text{-dppm})_2]PF_6$ (VIII).[13-15] From the above observations, it is reasonable to assume that the first step in the reaction of I with alkynes is this reaction to give VIII, L = alkyne. Some support is found in the observation that VI[14] reacts with C_4F_6 in dichloromethane to give IIa in very high yield. The carbonyl ligand in VI is labile and is presumably displaced by C_4F_6 to give VIII, L = C_4F_6, which then reacts further to give IIa.

Evidence on the next step in the sequence was obtained by reactions of I with C_4F_6 in donor solvents acetonitrile, benzonitrile, or acetone. Under these conditions, only one alkyne was incorporated to give yellow complexes III, with the alkyne bridging between platinum atoms and the Pt–H linkage intact. When they were dissolved in the donor solvent, these compounds were quite inert toward further reaction with C_4F_6, but, when it was dissolved in dichloromethane, IIIc reacted readily with C_4F_6 to give IIa.

At this point it is not clear if IIIc first reacts with a second molecule of C_4F_6 and then abstracts chloride from the solvent or if the reverse sequence prevails. The answer to this problem was found by reaction of IIIc with sodium chloride to give the neutral complex IV. When IV was reacted with C_4F_6 in dichloromethane, no reaction occurred and, under forcing conditions, only some decomposition to V was observed. Thus the acetylene insertion into the platinum–hydride bond must occur before the chloride abstraction from solvent occurs. Complex V was also formed by reaction of VII with hexafluorobut-2-yne.

It could be argued that the sequence deduced above need not be followed when IIa is formed from I in CH_2Cl_2 solution. To prove this directly, we have treated I with a stoichiometric amount of C_4F_6 in dichloromethane solution. Mixtures of products were formed, which could not be separated. However, from the characteristic ^{19}F and ^{31}P NMR spectra, mixtures of IIa, IV, and V were found to be present. Complex IV is presumably formed from a complex of structure III, R = CF_3, S = CH_2Cl_2, by chloride abstraction and strongly indicates that the reaction sequence discussed above is correct. The formation of V is unexpected since IV does not react rapidly with CH_2Cl_2 under the reaction conditions employed. It is presumably formed by reaction of the Pt–H linkage in an earlier intermediate with solvent, under conditions where the intermediate is not trapped rapidly by excess C_4F_6.

The final problem that we have attempted to solve is whether the incoming alkyne inserts into the Pt–H bond of IIIc or whether it takes up the bridging position, with the μ-alkyne group of IIIc inserting into the Pt–H bond.[16] In principle reaction of dimethyl acetylenedicarboxylate with IIIc should give IIc or IId, allowing these mechanisms to be distinguished. However, although IIIc does react with this alkyne, we were unable to separate the product from oligomers of the

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Table I. Analytical Data and Melting Points

complex	anal. calcd (found)				mp, °C
	% C	% H	% F	% other	
IIa	45.8 (46.2)	3.0 (3.1)	15.0 (16.0)	Cl, 2.3 (2.4)	>300
IIb	50.3 (50.4)	4.0 (4.0)		Cl, 2.4 (2.1)	160 dec
IIe	43.2 (43.0)	2.8 (3.5)	14.2 (14.5)	I, 7.9 (7.8)	>300
IIIa	44.6 (44.5)	3.2 (3.4)	15.1 (14.8)	N, 0.9 (0.9)	>200 dec
IIIb	46.6 (47.2)	3.2 (3.6)	14.5 (14.4)		>200 dec
IIIc	44.9 (45.1)	3.3 (3.2)	15.0 (15.0)		>200 dec
IV·CH_2Cl_2	45.8 (44.6)	3.3 (3.0)	7.9 (8.2)		224-227
V	46.6 (46.9)	3.2 (3.3)	8.2 (7.9)		>300
IX·$2CH_2Cl_2$	45.5 (45.6)	3.0 (3.0)	10.6 (10.0)		270 dec

Table II. ^1H NMR Spectra of the Complexes

complex	δ(CH_2P_2)[e]	δ(C=CH)[e]	δ(PtH)[e]	other[e]
IIa[a]	3.12 m (J(PtH) = 61, J(PH) = 8, J(HH) = 13), 3.90 m (J(PH) = 12)	6.30 m (J(PtH) = 56, J(PH) = 2, J(HF) = 10)		
IIb[a]	3.68 m	5.58 s (J(PtH) = 52)		δ(MeO) 2.42, 2.56, 3.22 s
IIe[a]	3.20 m (J(PtH) = 60, J(PH) = 6, J(HH) = 12), 3.85 m (J(PH) = 12)			
IIIa[b]	3.62 m (J(PH) = 12), 3.75 m (J(PtH) = 52, J(PH) = 6, J(HH) = 13)		−7.9 m (^1J(PtH) = 728, ^2J(PtH) = 30, ^4J(HF) = 4, ^2J(PH) = 14)	δ(CH_3CN) 1.97 s
IIIb[c]	3.88 m (J(PH) = 12), 4.60 m (J(PtH) = 58, J(PH) = 8, J(HH) = 12)		−7.7 m (^1J(PtH) = 730, ^2J(PH) = 14, ^4J(HF) = 5)	
IIIc[c]	3.84 m (J(PH) = 12), 4.52 m (J(PtH) = 55, J(PH) = 8, J(HH) = 13),		−7.6 m (^1J(PtH) = 738, ^2J(PtH) = 28, ^4J(HF) = 4, ^2J(PH) = 14)	δ(CH_3C) 2.00 s
IV[a]	3.24 m (J(PtH) = 70, J(PH) = 6, J(HH) = 12), 4.02 m (J(PH) = 12)		−8.55 m (^1J(PtH) = 734, ^2J(PtH) = 40, ^4J(HF) = 4, ^2J(PH) = 14)	
V[d]	3.12 m (J(PtH) = 60, J(PH) = 6, J(HH) = 13), 3.88 m (J(PH) = 12)			
IX[a]	3.24 m (J(PtH) = 72, J(PH) = 6, J(HH) = 13), 3.76 m (J(PH) = 13)	6.44 m		

[a] Solvent $CDCl_3$. [b] Solvent CD_3CN. [c] Solvent $(CD_3)_2CO$. [d] Solvent CD_2Cl_2. [e] s = singlet, m = multiplet; all J values in Hz.

Table III. ^{19}F and ^{31}P NMR Spectra of the Complexes

complex	δ(CF_3), assigt[a]	δ(^{31}P)[b]	^1J(PtP), Hz	^2J(PtP), Hz	^3J(PP),[d] Hz
IIa	−52.7, PtC(CF_3) (^5J(FF) = 12, ^3J(PtF) = 86)	−7.23	3110	100	
	−59.3, =CH(CF_3) (^5J(PF) = 2, ^3J(HF) = 10)	−9.63	2940	90	
	−50.2, μ-C_4F_6[c]				
IIb		−0.59	3160	...	20
		−1.10	3225	...	
IIe	−45.0, PtC(CF_3) (^5J(FF) = 12, ^3J(PtF) = 88)	−8.05	3010	80	
	−48.7, =CHCF_3 (^5J(PF) = 2, ^3J(HF) = 10)	−11.78	3116	80	
	−42.2, μ-C_4F_6[c]				
IIIa	−49.5, μ-C_4F_6 (^5J(FF) = 14, J(PtF) = 108)	8.95	3130	...	22
	−50.7, μ-C_4F_6 (J(PtF) = 60)	−3.62	3065		
IIIb	−49.4, μ-C_4F_6 (^5J(FF) = 13, J(PtF) = 102)	8.74	3125	...	20
	−50.2, μ-C_4F_6 (J(PtF) = 58)	−3.41	3068		
IIIc	−49.7, μ-C_4F_6 (^5J(FF) = 13, J(PtF) = 108)	8.88	3110	90	20
	−50.9, μ-C_4F_6 (J(PtF) = 58)	−3.15	3075	100	
IV	−50.6, μ-C_4F_6[c] (J(PtF) = 50)	8.30	3232	50	25
		−2.94	3193	70	
V	−50.9, μ-C_4F_6 (J(PtF) = 40)	−7.43	3132	82	18
IX	−46.4, PtCCCF_3 (^5J(PF) = 2, ^4J(PtF) = 26)	−2.10	3020	100	17
	−47.8, PtCCCF_3 (^5J(PF) = 3, ^4J(PtF) = 27)	−5.06	3250	100	
	−59.8, μ-CF_3CCH (^4J(PtF) = 62)				

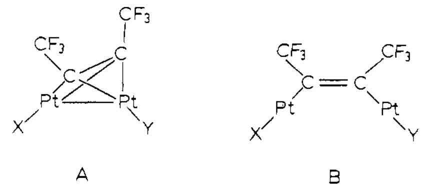
[a] $CFCl_3$ reference; all J values in Hz. [b] $(MeO)_3PO$ reference. [c] Complex A_3B_3 spectrum not resolved. [d] Long-range PP coupling was not observed.

alkyne and so have been unable to resolve this important mechanistic point.

Characterization of Complexes II–V. The complexes were characterized by elemental analysis, ^1H, ^{19}F, and ^{31}P NMR spectra, and infrared and mass spectra. Some data are given in Tables I–III.

One of the chief problems in characterizing the complexes is to determine the nature of the platinum–alkyne interaction. In principle, the alkyne can be η^2 bonded to a single platinum or η^2 (structure A, Chart I) or η^1 bonded (structure B, Chart I) to both platinum atoms in the dimers. The IR spectra of the C_4F_6 complexes contain bands in the region 1550–1600

Chart I. Possible Bonding Modes of the μ-C_4F_6 Group[a]



[a] The dppm ligands are omitted, and X and Y are one-electron ligands.

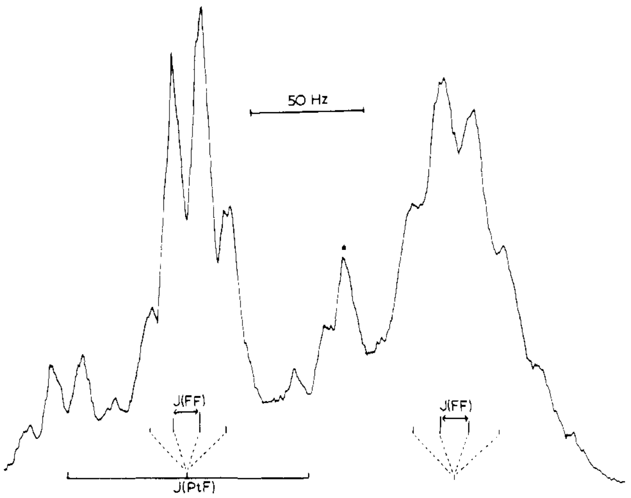


Figure 1. ^{19}F NMR spectrum (94.1 MHz) of complex IIIa. The peak marked with an asterisk is probably an impurity.

cm^{-1} due to the alkyne. This is consistent with either structure A or B but not with a terminal η^2-bonded alkyne.[2,17] Examples of diplatinum and triplatinum μ-alkyne complexes with structures in which the plane of the alkyne lies perpendicular or parallel to the Pt–Pt axis, as in structures A and B, respectively, are now known.[1,2,6,18] However, the presence or absence of a Pt–Pt bond depends on the particular complex, and, especially in triplatinum complexes, the situation is very complex.[2,6] For the present complexes it can be predicted, on the basis of theoretical studies[19] and by analogy with the structurally characterized complex $[Pd_2Cl_2(\mu\text{-}CF_3CCF_3)(\mu\text{-dppm})_2]$,[20] that structure B would not contain a metal–metal bond. Structure A is formulated with a Pt–Pt bond in order for each platinum to have a even-electron configuration, but the situation is less clear-cut since there are no directly analogous compounds. The diplatinum complexes known to have a bridging η^2-bonded alkyne do not contain a Pt–Pt bond.[2,6]

An unequivocal distinction between structures A and B can be made on the basis of the NMR spectra. According to structure A the CF_3 groups are equivalent whereas this will not be the case for structure B unless X = Y. Figure 1 shows the ^{19}F NMR spectrum for IIIa, and the observation of an A_3B_3 spectrum is only consistent with structure B; the value of $^5J(FF) = 14$ Hz (Table III) also proves that the CF_3 groups are mutually cis about the C=C bond as expected.[1] The peaks are broad due to unresolved PF and HF couplings. Complex V, which has partial structure B with X = Y = Cl, gives only one ^{19}F resonance (Table III); V is isoelectronic and isostructural with $[Pd_2Cl_2(\mu\text{-}C_4F_6)(\mu\text{-dppm})_2]$, whose structure has been proved by X-ray methods.[20]

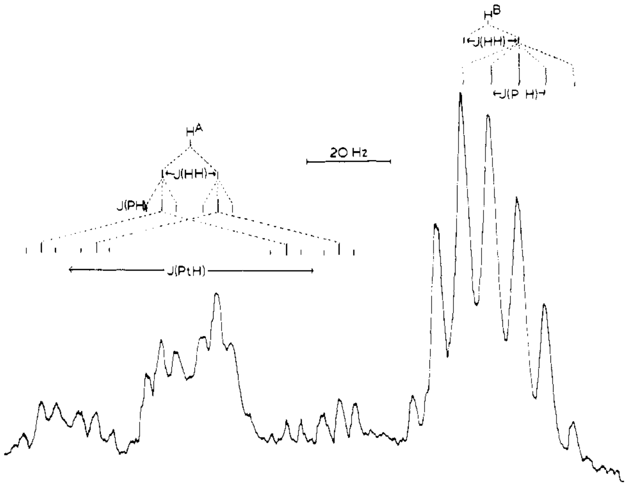


Figure 3. ^1H NMR spectrum (100.1 MHz) of complex IIIb showing only the $CH^AH^BP_2$ resonances. The coupling J(PH) is equal to $^2J(PH^B) + {}^4J(PH^B)$. The outer lines of the presumed quintet due to PH coupling are not resolved for the H^A resonance.

The Pt–H resonance for complex IIIa is shown in Figure 2 (supplementary material). The satellites due to coupling with ^{195}Pt are one-fourth intensity, showing that the hydride is in a terminal position.[8] This is confirmed by the Pt–H stretching frequency of 2047 cm^{-1}. The central resonance in the ^1H NMR spectrum appears as a triplet of quartets. The triplet is due to coupling with adjacent ^{31}P atoms, but the quartet is due to coupling with fluorine atoms of one of the CF_3 groups. Again this observation is only consistent with the complex having the partial structure B, with X = H. The couplings ^1J(PtH) of ~730 Hz for complexes III are at the low end of ^1J(PtH) couplings, consistent with the hydride being trans to a carbon donor with a high trans influence.[21]

The binuclear structures are most easily proved from the ^1H and ^{31}P NMR spectra due to the μ-dppm ligands. For the μ-alkyne complexes there is no plane of symmetry containing the Pt_2P_2C atoms of a $Pt_2(\mu\text{-dppm})$ grouping and hence the CH_2 protons of the dppm ligand are nonequivalent and give an AB coupling in the ^1H NMR spectrum (Figure 3).[22] The high-field signal, which has no resolved PtH coupling, shows a 1:4:6:4:1 quintet due to "virtual" coupling with all four phosphorus atoms in a closely coupled spin system. Since $^2J(H^AH^B) \approx {}^2J(PH^B) + {}^4J(PH^B)$, an apparent septet signal is observed as shown in Figure 3, and this was observed for all complexes II–V. The apparent septet collapsed to an AB doublet on phosphorus decoupling.[23] The bridging dppm ligands are also characterized by the ^{31}P NMR spectra (Figure 4 for complex IIIa, supplementary material). The nonequivalent phosphorus atoms give rise to an AA′BB′ spectrum with satellites due to coupling with ^{195}Pt. In related complexes with $Pt_2(\mu\text{-dppm})_2$ frameworks, the ^{31}P spectra are very rich due to significant long-range PP and PPt couplings[24] but for complexes II–V these long-range couplings are small (Table III) and hence the spectra are relatively simple. As discussed previously, the long-range PP and PtP couplings are very sensitive to the Pt–Pt separation.[24] In these complexes with

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(20) Balch, A. L.; Lee, C.-L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979**, *177*, C22.

(21) For example, *trans*-$\{PtH_2[P(cyclohexyl)_3]_2\}$ has ^1J(PtH) = 792 Hz: Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006.

(22) A similar effect has been observed in several other dppm "A-frame" complexes: Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733. Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Ibid.* **1979**, *18*, 2996.

(23) The extra coupling was previously thought due to ^{195}PtH coupling, but this is now disproved.

(24) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Organomet. Chem.* **1978**, *161*, C46.

a μ-alkyne linkage the platinum atoms will be forced apart and hence the long-range couplings are expected to be small. The analogous $[Pd_2Cl_2(\mu\text{-}C_4F_6)(\mu\text{-dppm})_2]$ has the longest metal–metal separation known for an $M_2(\mu\text{-dppm})_2$ species.[20] It should be noted that structure A may require a Pt–Pt bond to be present, and a short Pt–Pt distance and large long-range PP and PtP couplings would be expected in contradiction of the observed results.

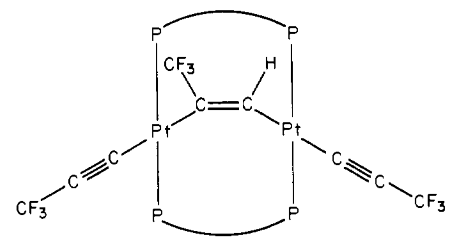
The complexes IIa and IIe are shown to have a terminal substituted vinyl group with cis stereochemistry about the C=C bond. This is characterized by an IR band at ~1610 cm^{-1} and by the characteristic value of the coupling ^4J(FF) (showing mutually cis CF_3 groups; Table III)[19] and ^3J(PtH) (showing mutually cis Pt and H substituents).[25] The vinyl proton peak occurred on the edge of the aryl resonances in the ^{1}H NMR spectrum but was positively identified by the large quartet coupling to a CF_3 group, which disappeared on decoupling at the fluorine frequency (Table II). The stereochemistry about the C=C bond for IIb is deduced only from the magnitude of the coupling constant ^3J(PtH), but this is quite characteristic.[25]

Reaction of I with 3,3,3-Trifluoropropyne. Complex I in dichloromethane solution reacted with $CF_3C{\equiv}CH$ to give a product $[Pt_2(CCCF_3)_2(CF_3CCH)(dppm)_2]\cdot 2CH_2Cl_2$. The presence of CH_2Cl_2 was confirmed by the NMR spectrum. The mass spectrum confirmed the empirical formula, giving a parent ion centered at m/e 1538 with the expected isotope pattern. The IR spectrum gave bands due to alkynyl groups at 2120 cm^{-1} and a weak C=C stretch at 1550 cm^{-1}. The ^{19}F NMR spectrum (Table III) contained three resonances of equal intensity. Two of these are easily assigned as due to $CF_3C{\equiv}C$—Pt groups[26,27] in terminal positions with well-resolved couplings to adjacent phosphorus atoms and platinum atoms, while the third peak appears as a broad singlet with resolved satellites due to coupling with ^{195}Pt. We assign this as due to a bridging trifluoropropyne with η^1 bonding to each platinum. The vinyl proton occurred as a complex unresolved multiplet at δ 6.44 and gave little structural information. The CH_2P_2 protons were nonequivalent, indicating the presence of a bridging group. The ^{31}P NMR spectrum (Table III) was very similar to those for complexes II–IV with very little long-range P–P or Pt–P coupling, indicating a similar μ-alkyne bonding mode. Thus we believe that the product has structure IX, PP = dppm.

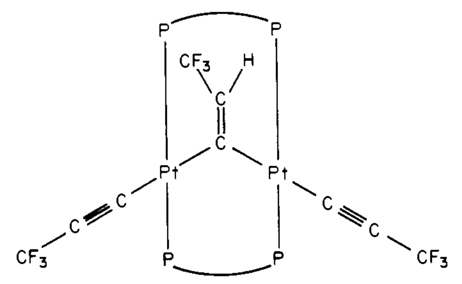
An alternative structure would be X, which would require a 1,2-H shift in the μ-alkyne unit. However, the PtPt separation would be smaller so that larger long-range PP couplings would be expected and a well-resolved coupling of ~8 Hz would be expected between the vinylic proton and the CF_3 group, by analogy with similar compounds. This structure is therefore considered very unlikely.

Conclusions

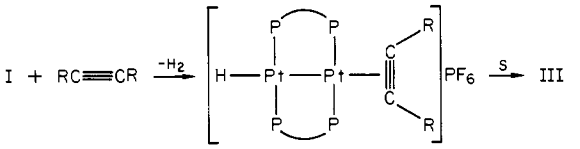
Although we are far away from having a complete description of the mechanism of reaction of alkynes with the binuclear hydride I, some of the principal features have been clarified, especially in the reactions with hexafluorobut-2-yne. The initial reaction involves reductive elimination of H_2 induced by the alkyne. Electronegative substituents on the alkyne are necessary to give this reaction. In the first isolated product of structure III the alkyne is already in the bridging position but, by analogy with binuclear reductive elimination of H_2 from I induced by other ligands,[13-15] it is probable that the alkyne first adopts a terminal position (eq 1).



IX

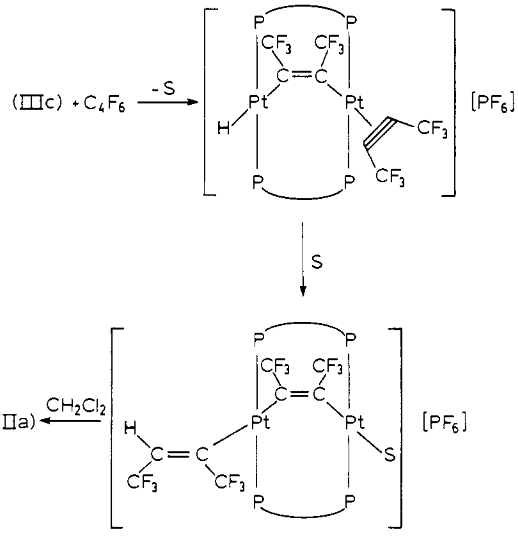


X



(1)

Since complexes III dissolved in the donor solvent, S, fail to react with C_4F_6 and since IV also fails to react with C_4F_6, it seems that the next step toward formation of IIa involves displacement of the weakly bound solvent S from III by C_4F_6 followed by rearrangement according to eq 2, PP = dppm.



(2)

Acetylenes with electronegative substituents are poor ligands for a cationic metal center and presumably cannot displace Cl$^-$ from IV or compete with coordination of donor solvent, S, when S is used as solvent and is in great excess. Since coordination of alkyne is necessary before rearrangement to II can occur, the observation that reaction of I with C_4F_6 in donor solvents stops at III is rationalized.

The mechanism by which the alkyne is inserted into the Pt–H bond is not known nor is the mechanism by which the cationic platinum center abstracts Cl$^-$ from dichloromethane.[29]

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It is probable that the reaction of I with $CF_3C{\equiv}CH$ to give IX proceeds in a similar way, but the reaction with the Pt–H group to give an alkynylplatinum group (and H_2) occurs instead of insertion. This also occurs in reactions of some alkynes with mononuclear platinum hydrides, although $CF_3C{\equiv}CH$ inserts into a Pt–H bond in one case.[30] Similarly, the cationic platinum center can presumably react with CF_3CCH to give a second alkynyl group more readily than it can abstract Cl^- from the dichloromethane solvent.

Experimental Section

The complexes $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$,[8] $[Pt_2H(CO)(\mu\text{-dppm})_2]PF_6$,[14] and $[Pt_2Cl_2(\mu\text{-dppm})_2]$[31] were prepared as described previously. ^1H, ^{19}F, and ^{31}P NMR spectra were recorded at 100.1, 94.1, and 40.5 MHz, respectively, with use of a Varian XL-100 spectrometer. References for ^{19}F and ^{31}P NMR spectra were $CFCl_3$ and $(MeO)_3PO$, respectively.

Reaction of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$ with $CF_3C{\equiv}CCF_3$. (i) In CH_2Cl_2 Solvent. Excess $CF_3C{\equiv}CCF_3$ (10 mmol) was condensed into a thick-walled Pyrex Carius tube containing $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$ (0.20 g, 0.15 mmol) in CH_2Cl_2 (2 mL). After 48 h, the tube was opened to the vacuum line and analysis of the gaseous phase by GC showed the presence of H_2. The solution was evaporated to give a yellow solid, which was purified by chromatography on a column of silica. The first product eluted was IIa, eluted with 1:3 hexane/CH_2Cl_2. This was recrystallized from CH_2Cl_2/pentane as pale yellow crystals (0.12 g, 52%). Mass spectrum: *m/e* 1518, parent ion, P; 1355, P – C_4F_6H; 1320, P – C_4F_6H – Cl; 1158, P – C_4F_6H – Cl – C_4F_6. IR (cm^{-1}): 1560 m, 1610 m (ν(C=C)).[32]

A yellow product (0.05 g) was eluted with 10:1 CH_2Cl_2/MeOH. This was shown to contain complex V in impure form by the ^{19}F and ^{31}P NMR spectra, but attempted recrystallizations were unsuccessful.

In another reaction, complex I (0.20 g, 0.15 mmol) was treated with C_4F_6 (0.2 mmol) under the above conditions. An intensely yellow solid was obtained and was shown to contain a mixture of complexes IV and V in approximately 2:1 mole ratio by the ^{19}F and ^{31}P NMR spectra. Attempts to separate the mixture were unsuccessful.

(ii) In Donor Solvents. In the same way, complex I (0.20 g) in MeCN (2 mL) was treated with C_4F_6 (0.2 mmol). After 48 h, the tube was opened and the solution was evaporated to give complex IIIa, which could be recrystallized from MeCN (0.17 g, 73%). Bright yellow crystals were obtained, which slowly lost solvent of crystallization to give a yellow powder. The same product was obtained in high yield when excess C_4F_6 was used. IR (cm^{-1}): 1575 m (ν(C=C)); 2047 m (ν(Pt—H)); 2310 w, 2290 w (ν(C≡N)).

Complexes IIIb (75%) and IIIc (77%) were prepared in the same way with use of PhCN or acetone as solvent. As with IIIa the bright yellow crystals slowly lost solvent of crystallization to give yellow powders. IR of IIIb (cm^{-1}): 1578 m, 1602 m (ν(C=C)); 2048 m (ν(PtH)); 2260 m, 2230 m (ν(C≡N)). IR of IIIc (cm^{-1}): 1575 m (ν(C=C)); 2060 m (ν(Pt—H)); 1670 ms, 1710 ms, (ν(C=O)).

Synthesis of $[Pt_2Cl_2(\mu\text{-}C_4F_6)(\mu\text{-dppm})_2]$ (V). (i) A solution of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (0.20 g) in CH_2Cl_2 (5 mL) was stirred under an atmosphere of C_4F_6 for 3 days. The volume was reduced, pentane was added, and the mixture was cooled when yellow crystals of complex V formed (0.15 g, 66%).

(ii) Complex IIIc (0.10 g) in benzene 5 mL was treated with concentrated HCl solution (0.5 mL), and the mixture was heated under reflux for 10 min. When the mixture was cooled, yellow crystals of complex V formed and were purified by recrystallization from CH_2Cl_2/pentane; yield 0.06 g, 66%. IR (cm^{-1}): 1560 m (ν(C=C)).

Synthesis of $[Pt_2HCl(\mu\text{-}C_4F_6)(\mu\text{-dppm})_2]$ (IV). Complex IIIc (0.10 g) in acetone (3 mL) was stirred with NaCl (0.1 g, excess) at room temperature for 18 h. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 (3 mL). The mixture was filtered to remove salts, and the filtrate was evaporated to yield the product, which was recrystallized from CH_2Cl_2/pentane; yield 0.06 g, 67%. IR (cm^{-1}): 1575 m (ν(C=C)); 2025 m (ν(PtH)).

Reaction of IIIc with $CF_3C{\equiv}CCF_3$. Hexafluorobut-2-yne (10 mmol, excess) was condensed into a Carius tube containing complex IIIc (0.15 g) in CH_2Cl_2 (2 mL). The tube was sealed and allowed to stand for 24 h at room temperature. The tube was opened, the solvent was evaporated, and the product, complex IIa, was recrystallized from CH_2Cl_2/pentane; yield 0.12 g, 80%.

Synthesis of the $[Pt_2I(C_4F_6H)(\mu\text{-}C_4F_6)(\mu\text{-dppm})_2]$ Complex (IIe). Complex IIa (0.10 g) was stirred with NaI (0.1 g, excess) in acetone (2 mL) for 2 h. The solution was evaporated, and the residue was extracted with CH_2Cl_2 (2 mL). The mixture was filtered to remove salts, and the filtrate was evaporated to give IIe, which was recrystallized from CH_2Cl_2/pentane; yield 0.08 g, 75%. IR (cm^{-1}): 1555 w, 1610 w (ν(C=C)).

Synthesis of $[Pt_2Cl(C(CO_2Me){=}CH(CO_2Me))(\mu\text{-}C_2Me)_2)(\mu\text{-dppm})_2]$ (IIb). A solution of complex I (0.2 g, 0.15 mmol) in CH_2Cl_2 (2 mL) was stirred with $MeO_2CC{\equiv}CCO_2Me$ (0.1 g). Effervescence was observed, and a yellow solution was obtained. After 24 h, the solvent was evaporated and the residue was washed with ether (10 mL) and then dried under vacuum. This solid, which was shown by NMR to be a mixture of products, was separated into components by chromatography on a column of silica gel by eluting with progressively more polar eluents. A pale yellow solid, IIb, was eluted with 3:1 CH_2Cl_2/methanol and was recrystallized from CH_2Cl_2/pentane; yield 0.13 g, 56%. IR (cm^{-1}): 1565 m, 1580 m (ν(C=C)); 1670–1730 s (ν(C=C)). Further products were eluted with 1:5 CH_2Cl_2/methanol but could not be unambiguously characterized.

In a separate experiment, a solution of I (0.020 g) in CH_2Cl_2 (0.5 mL) in a vial (5 mL) fitted with a serum cap was treated with $MeO_2CC{\equiv}CCO_2Me$ (0.05 g), added by syringe through the serum cap. After 10 min, a sample (1.0 mL) of the gas above the solution was removed with a gas syringe and injected into a GC column (6 ft × $^1/_8$ in., molecular sieve 5 Å). A calibration graph was drawn up by injecting known volumes of H_2 into the same vial containing CH_2Cl_2 (0.5 mL) and sampling in the same way. The graph was linear over the concentration range studied. A series of four experiments gave a mean yield of H_2 of 65% and a range from 61 to 80%.

Synthesis of $[Pt_2(CCCF_3)_2(\mu\text{-}CF_3CCH)(\mu\text{-dppm})_2]$ (IX). 3,3,3-Trifluoropropyne (10 mmol, excess) was condensed into a Carius tube containing complex I (0.20 g, 0.15 mmol) in CH_2Cl_2 (2 mL), and the tube was sealed. After 48 h, the tube was opened and the solution was filtered to remove the white polymer of CF_3CCH (0.06 g). Evaporation of the solvent gave a yellow oil, which was purified by chromatography on silica. The first fraction to be eluted with 1:1 hexane/CH_2Cl_2 was complex IX, which was recrystallized from CH_2Cl_2/pentane as pale yellow crystals (0.13 g, 53%). Further products were eluted in low yields but could not be purified or characterized.

Registry No. I, 63911-00-2; IIa, 80106-38-3; IIb, 80062-78-8; IIe, 80062-79-9; IIIa, 80062-81-3; IIIb, 80062-83-5; IIIc, 80062-85-7; IV, 80062-86-8; V, 80062-87-9; IX, 80062-88-0; $CF_3C{\equiv}CCF_3$, 692-50-2; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $[Pt_2Cl_2(\mu\text{-dppm})_2]$, 61250-65-5; 3,3,3-trifluoropropyne, 661-54-1.

Supplementary Material Available: Figures 2 and 4, NMR spectra of complex IIIa (2 pages). Ordering information is given on any current masthead page.

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(32) All compounds give weak bands due to dppm ligands at 1575 and 1590 cm^{-1}, in addition to ν(C=C) bands in this region.