determined by comparison of the mass spectrum to an authentic sample of C_6H_6 and C_6H_5D (prepared by addition of D_2O to PhMgBr). ^{2}H NMR spectroscopy showed resonances in the aromatic region (δ 6.9–7.9; 4 H), in the tolyl region (δ 2.35, 2.31, and 1.98; 3 H), and in the deuteride region (δ –7.75; 1 H), indicating formation of a mixture of tolyl hydride compounds. The resonances in the tolyl region were not well enough resolved to obtain accurate ratios of the three isomers, but the distribution was roughly 4:1:1.

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Models for Reactions of Acetylene on Platinum(111): Syntheses, Structures, and Properties of the First Triply Bridging Alkyne Complexes of Platinum

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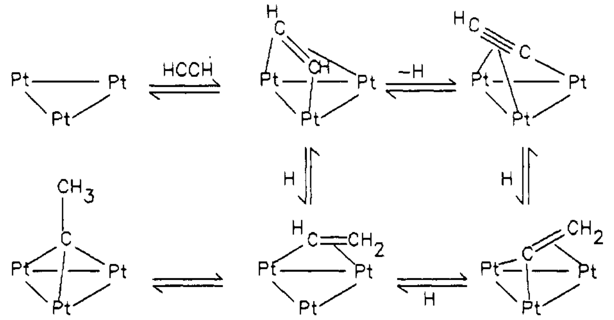
Reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**1**; dppm = $Ph_2PCH_2PPh_2$), as the PF_6^- salt, with acetylene gave $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)(CO)(\mu\text{-dppm})_3]^{2+}$ (**2**), which reacted with Cl^- to give $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)Cl(\mu\text{-dppm})_3]^+$ (**3**) or reversibly lost the CO ligand to give $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)(\mu\text{-dppm})_3]^{2+}$ (**4**). The acetylene ligand in **4** could be exchanged with DCCD or MeCCH and could be displaced by H_2S to give $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$. Details of the characterization of these complexes, including ^{1}H, ^{2}H, ^{13}C, ^{31}P, and ^{195}Pt NMR studies with isotopically substituted complexes (^{2}H, ^{13}C), are given. Complex **1** reacts with RCCH to give $[Pt_3(\mu_3\text{-}\eta^2\text{-}RCCH)(CO)(\mu\text{-dppm})_3]^{2+}$ (**7a**, R = Me; **7b**, R = EtO) and/or $[Pt_3(\mu_3\text{-}\eta^2\text{-}RCCH)(\mu\text{-dppm})_3]^{2+}$ (**6a**, R = Me; **6b**, R = CH_2CH_2OH; **6c**, R = *t*-Bu), and the relative stabilities of **6** and **7** are shown to depend primarily on the steric bulk of the substituent R. The complexes **4** and **6** exhibit fluxionality of the coordinated alkyne ligand, and the mechanism is discussed. The complex $[Pt_3(\mu_3\text{-}\eta^2\text{-}HCCOEt)(CO)(\mu\text{-dppm})_3][PF_6]_2$ [**7b**$(PF_6)_2$] has been characterized by X-ray diffraction and is shown to contain a distorted $\mu_3\text{-}\eta^2\text{-}\|$-bound alkyne ligand and just one Pt–Pt bond [**7b**$(PF_6)_2$ is triclinic, space group $P\bar{1}$, a = 13.615 (3) Å, b = 13.898 (2) Å, c = 22.668 (3) Å, α = 84.49 (1)°, β = 77.65 (2)°, γ = 80.07 (1)°, R = 0.043, for 412 parameters refined from 9028 reflections]. These complexes are the first examples of ($\mu_3\text{-}\eta^2$-alkyne)triplatinum complexes, and they can be considered to mimic the binding of acetylene at a 3-fold site on a Pt(111) surface.

Introduction

The chemisorption of acetylene on the Pt(111) surface has been studied in great detail.[2] At low temperature, an acetylene complex is formed, probably with the $\mu_3\text{-}\eta^2\text{-}\|$ geometry, but this decomposes on warming to give the ethylidyne species $Pt_3(\mu_3\text{-}CCH_3)$. Intermediates that have been suggested to be formed during this reaction include the units vinyl, $CH{=}CH_2$, vinylidene, $C{=}CH_2$, and acetylide, $C{\equiv}CH$, all bound at 3-fold sites on the surface (Scheme I). Surface hydrogen is also a necessary intermediate. At lower symmetry platinum surfaces, vinylidene may be the dominant species. Theoretical studies of the binding of these various hydrocarbon fragments have been carried out.

Although much of the surface science of acetylene has been carried out with platinum, no examples of alkynes bridging three platinum atoms in coordination complexes had been reported when this work began. There are several $\mu_2\text{-}\eta^2$-alkyne complexes of platinum and many terminal alkyne complexes.[3,4] The complex $[Pt(HCCH)(PPh_3)_2]$ had been well characterized, but no bridging complexes of the parent ethyne, HCCH, were known.[3,4] Modeling of surface alkyne reactions with metal cluster complexes has

Scheme I



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(1) (a) University of Glasgow. (b) University of Western Ontario. (c) Shiraz University.

(2) (a) Bertolini, J. C.; Massardier, J. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1984; Vol. 3, Chapter 3. (b) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685. (c) Koestner, R. J.; Stöhr, J.; Gland, J. L.; Horsley, J. A. *Chem. Phys. Lett.* **1984**, *105*, 332. (d) Kesmodel, L. L.; Dubsois, L. H.; Somoijai, G. A. *J. Chem. Phys.* **1979**, *70*, 2180. (e) Wang, P.-K.; Slichter, C. P.; Sinfelt, J. H. *Phys. Rev. Lett.* **1984**, *53*, 82. (f) Ogle, K. M.; White, J. M. *Surf. Sci.* **1986**, *165*, 234. (g) Felter, T. E.; Weinberg, W. H. *Surf. Sci.* **1981**, *103*, 265. (h) Demuth, J. E. *Surf. Sci.* **1979**, *80*, 367.

(3) (a) Cook, C. D.; Wan, K. Y. *J. Am. Chem. Soc.* **1970**, *92*, 2595. (b) Roundhill, D. M. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987.

(4) (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfeild, R. F. D.; Thomas, M. D. O.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 2182. (c) Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 862.

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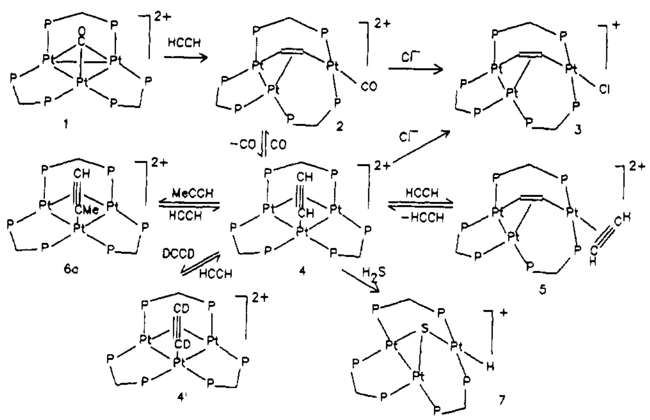
Scheme II



been of great interest, but most such research has been carried out with the iron group carbonyl clusters.[4a,5] Since coordinatively unsaturated 42-electron cluster $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (1; dppm = $Ph_2PCH_2PPh_2$) mimics many reactions of a Pt(111) surface, it was decided to examine its reactions with alkynes, and the results are described fully in this paper. A preliminary communication of parts of this work has been published,[6] and the related chemistry of the complex $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3]^+$ with alkynes has also appeared.[7]

Results

Reactions with HC≡CH. A summary of this chemistry is shown in Scheme II. Reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (1) with acetylene occurs rapidly, and the product is 2. However, the carbonyl ligand in 2 is labile and it reacts easily with sodium chloride to give 3, in a reaction that involves displacement of CO by Cl^-. Attempts to isolate 2 lead to partial dissociation of CO and formation of 4. Treatment of 4 with CO regenerates 2 very easily, and 4 also reacts easily with Cl^- to give 3. These reactions indicate that 4 is coordinatively unsaturated, and there is some evidence that, under high pressure of acetylene, the acetylene adduct 5 is formed. However, the equilibrium constant for formation of 5 is very small and hence 5 can only be generated in the presence of a large excess of acetylene, under which conditions it is difficult to characterize fully. If the terminal and bridging acetylene ligands in 5 could exchange, this would give a mechanism for alkyne for alkyne substitution in complex 4. Such exchange reactions do occur, as illustrated in Scheme II by the reactions with DCCD to give 4′ and with MeCCH to give 6a by displacement of HCCH from 4. Complex 4 also reacts with H_2S by displacement of acetylene, and the known complex 7 is formed.[8]

A spectroscopically pure sample of complex 2 was prepared by evaporation of a solution of 2 in CH_2Cl_2 in a stream of CO. A study of this complex by differential scanning calorimetry showed a broad endotherm over the range 60–150 °C, corresponding to loss of CO and formation of 4, as confirmed by the observed weight loss and by later identification of 4 by its ^{31}P NMR spectrum. Loss of CO is endothermic by about 60 kJ mol^{-1}, but because CO loss occurs over a wide temperature range, this value should be treated with caution.

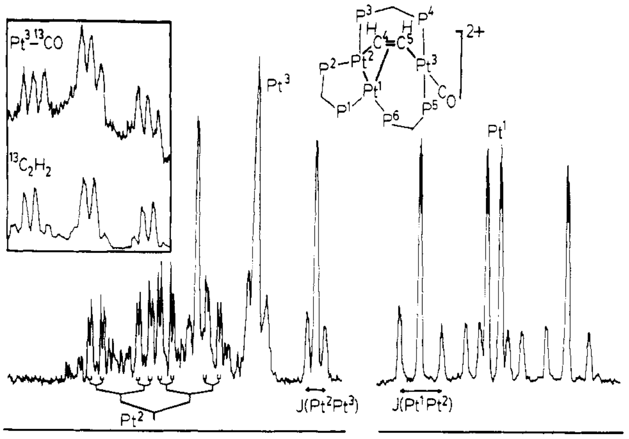


Figure 1. ^{195}Pt NMR spectrum (64 MHz) of $[Pt_3(HCCH)(CO)(\mu\text{-dppm})_3]^{2+}$. Some assignments are given, and complete data are in the Experimental Section. The inset shows the Pt^3 resonance of, above, the ^{13}CO- and, below, the $^{13}C_2H_2$-labeled derivatives, illustrating the extra doublet splitting due to $^1J(PtC)$.

The complexes shown in Scheme II are large ions with low symmetry, and their characterization is nontrivial. Fortunately, complex 3 formed X-ray-quality crystals, and its molecular structure was described in the preliminary communication;[6] furthermore, a substituted alkyne analogue of 2 has now been structurally characterized (see later). However, complexes 4 and 6, though they can be crystallized in analytically pure form, have failed to give X-ray-quality crystals and so their structures must be deduced from analytical and spectroscopic data. Spectroscopic study has been aided by the synthesis of isotopically labeled derivatives, using ^{13}CO, $H^{13}C^{13}CH$, and DCCD as reagents in place of CO and HCCH. Thus, although the structures are complex, the connectivities can be deduced from the ^1H, ^2H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra, with support in some cases from IR and MS methods. Complete data are in the Experimental Section, and only the examples 2 and 4 will be discussed in detail.

The low symmetry of 2 is clearly demonstrated by the ^{31}P NMR spectrum, which contains six resonances due to the six nonequivalent dppm phosphorus atoms. Similarly, the ^{195}Pt NMR spectrum (Figure 1) contains three resonances due to the three nonequivalent platinum atoms. Resonances can be assigned to individual platinum and phosphorus atoms by correlation of Pt–P coupling constants from both the ^{31}P and ^{195}Pt NMR spectra, assisted by correlation of PP couplings, so long as one ^{195}Pt resonance can be assigned independently. The complex 2*, enriched with ^{13}CO, gave the singlet ^{13}C NMR signal shown in Figure 2a, with satellites due to coupling to only one platinum atom. The only ^{195}Pt resonance that changed in 2* compared to 2 was that assigned as Pt^3 (Figure 1, inset), and hence the carbonyl is terminally bound to Pt^3. The carbonyl stretching frequency $\nu(CO)$ = 2090 cm^{-1} for 2 clearly confirms that this is a terminal carbonyl ligand. The complex 2**, prepared from $H^{13}C^{13}CH$, gave two ^{13}C resonances (Figure 2b,c), and comparison of the ^1H-coupled spectrum (Figure 2b) with the ^1H-decoupled spectrum (Figure 2c) clearly showed that a single hydrogen atom remained bonded to each carbon atom. Each carbon was strongly coupled to a single ^{195}Pt atom (Figure 2), and these were identified as Pt^2 and Pt^3 by correlation of the $^1J(PtC)$ couplings obtained from the ^{13}C and ^{195}Pt NMR spectra (Figures 1 and 2). The binding of the acetylene to Pt^1 was not clearly demonstrated by the NMR spectra but was proved crystallographically for 3 and is similarly required for 2. The remaining problem is to determine the nature

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(5) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (b) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(6) Douglas, G.; Manojlović-Muir, Lj.; Muir, K. W.; Rashidi, M.; Anderson, C. M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6527.

(7) (a) Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111. (b) Rashidi, M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 1636.

(8) Jennings, M. C.; Payne, N. C.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 3776.

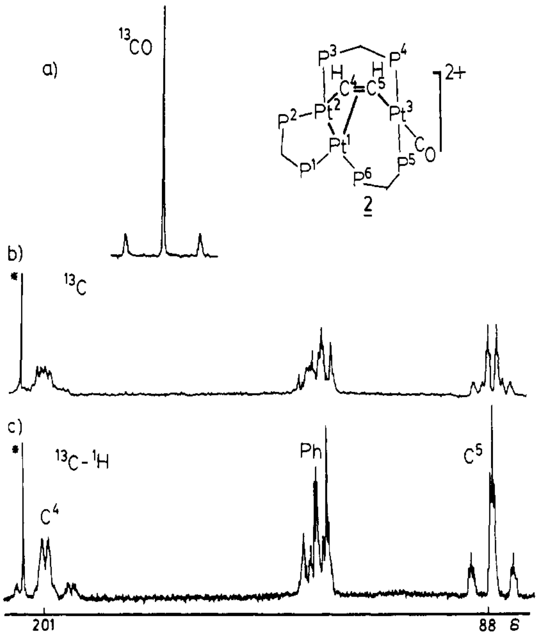

Figure 2. ^{13}C NMR spectra of $[Pt_3(HCCH)(CO)(\mu\text{-dppm})_3]^{2+}$: (a) ^{13}CO resonance of the *CO-labeled derivative; (b) ^{1}H-coupled spectrum of the $^{13}C_2H_2$-labeled derivative; (c) corresponding ^{1}H-decoupled spectrum. The extra doublet splittings in the C^4 and C^5 resonances in spectrum b are due to ^1J(CH) coupling. In (b) and (c), the resonance marked with an asterisk is due to solvent acetone-d_6.

of the Pt–Pt bonding. The largest Pt–Pt coupling constant is $^1J(Pt^1Pt^2)$ = 2100 Hz, clearly observed in both the Pt^1 and Pt^2 resonances (Figure 1), and this indicates the presence of a PtPt bond between these atoms. Although there is not a good general correlation between J(PtPt) and d(PtPt), within similar complexes there is a correlation[9] and so, from analogies with other $Pt_3(\mu\text{-dppm})_3$ complexes,[8,10] the Pt^{1}Pt^2 bond is clearly required. The coupling $^1J(Pt^2Pt^3)$ = 900 Hz is significant but too low for a direct Pt^{2}Pt^3 bond; it is assigned as a through-bond coupling $^3J(Pt^2C^4C^5Pt^5)$. Finally, the coupling $J(Pt^1Pt^3)$ was not resolved, and so there is no Pt^{1}Pt^3 bond. These conclusions are fully supported by the X-ray structure of 3, which gives Pt(1)–Pt(2) = 2.631 (2) Å, Pt(1)···Pt(3) = 3.232 (2) Å, and Pt(2)···Pt(3) = 3.277 (2) Å.[6] The ^{1}H NMR spectrum of 2 contained a resonance at δ = 11.80 ppm due to the acetylene proton C^{4}H, with clearly resolved satellites due to coupling to all three nonequivalent platinum atoms. The resonance due to C^{5}H was shown to be beneath more intense phenyl resonances by selective decoupling, and this was confirmed by recording the ^{2}H NMR spectrum of 2′, prepared from DCCD, which contained a resonance at δ = 7.85 ppm due to C^{5}D.

The complex 4 is fluxional at room temperature, and so the structure must be deduced from low-temperature NMR spectra. At −80 °C, the fluxionality is frozen out and well-resolved spectra are obtained. The fluxionality is easily demonstrated by the ^{31}P NMR spectra (Figure 3). At room temperature, a single broad ^{31}P resonance is observed with satellites due to coupling to ^{195}Pt, but at −80 °C, three resonances are observed. This indicates that the static structure has 2-fold (C_2) symmetry. This spectrum is consistent with structures containing a μ_3-η^2-$\perp$-HCCH ligand, as shown in 4, in which the acetylene lies in the plane of symmetry, or a μ_3-η^2-$\parallel$-HCCH ligand, in which the acetylene lies across the plane of symmetry. The latter

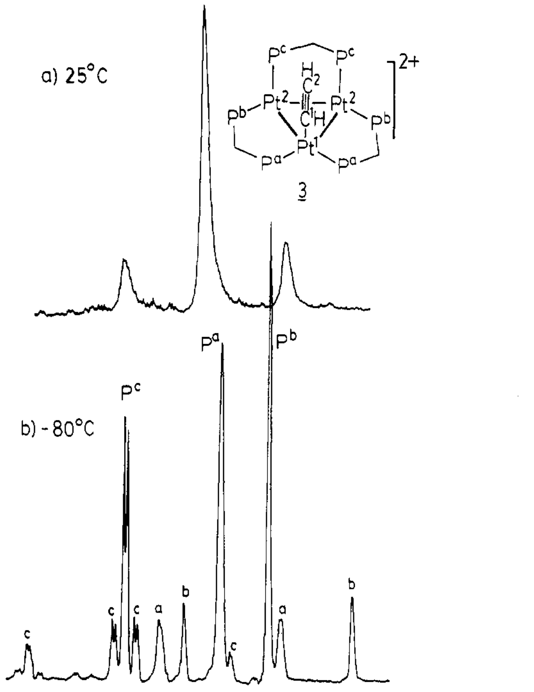

Figure 3. ^{31}P NMR spectra of $[Pt_3(HCCH)(\mu\text{-dppm})_3]^{2+}$ at (a) 25 °C and (b) −80 °C.

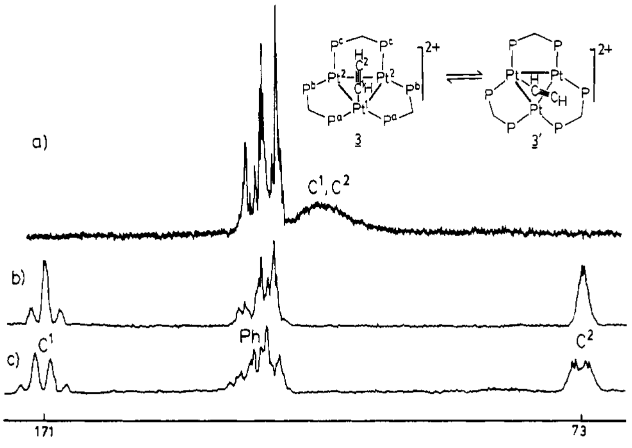

Figure 4. ^{13}C NMR spectra of $[Pt_3(HCCH)(\mu\text{-dppm})_3]^{2+}$ under the following conditions: (a) ^{1}H decoupled at 25 °C; (b) ^{1}H decoupled at −80 °C; (c) ^{1}H coupled at −80 °C.

structure, and structures having higher (e.g. C_{2v}) symmetry, can be eliminated by study of the ^{13}C NMR spectra (Figure 4) of the complex 4**, formed from H^{13}C^{13}CH. At room temperature (Figure 4a) there is a broad resonance due to the acetylene carbon atoms, but this splits at low temperature (Figure 4b) to give two resonances at δ = 73 and 171 ppm, both shown to be CH groups by the ^{1}H-coupled spectrum (Figure 4c). Only one ^{13}C resonance is expected for the μ_3-η^2-$\parallel$ structure, since the two carbon atoms would be equivalent, and hence the structure is deduced to have the μ_3-η^2-$\perp$-HCCH group shown in 4. A similar effect is observed in the ^{1}H NMR spectrum of 4. Thus at room temperature a broad resonance at δ = 9.91 ppm is observed for the acetylene protons but this splits into two resonances, one of which is observed at δ = 12.67 ppm (C^{1}H) and the other is obscured at δ = 7.15 ppm (C^{2}H) by more intense phenyl resonances. As expected, the ^{195}Pt NMR spectrum of 4 at low temperature contains two resonances, a triplet for Pt^1 and a doublet of doublets for Pt^2, due to ^1J(PtP) coupling. The coupling constant $^1J(Pt^1Pt^2)$ = 2010

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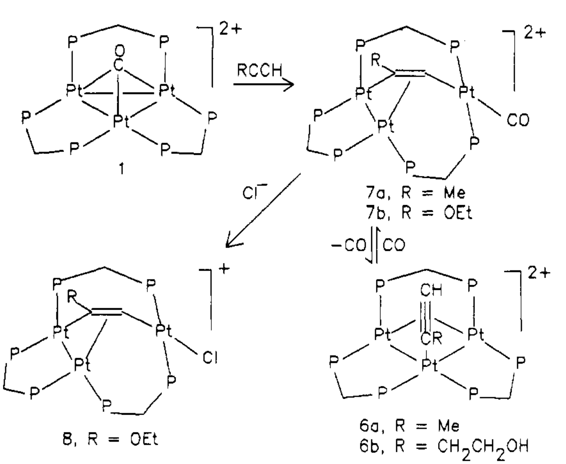
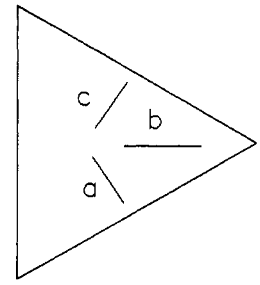
[9] Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.
[10] Hadj-Bagheri, N.; Puddephatt, R. J. *Inorg. Chem.* **1989**, *28*, 2384.

Scheme III

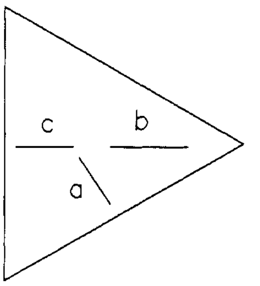


Hz clearly indicates that there are Pt^{1}Pt^2 bonds shown in 4, but there is no information about Pt^{2}Pt^2 bonding. When metal–metal bonds are present, it is usual to observe significant long-range couplings ^2J(Pt–Pt–P) or ^3J(P–Pt–Pt–P) operating through the metal–metal bond. Thus, for complex 4, significant couplings ^2J(Pt^{1}P^c) = 490 Hz and ^3J(P^{a}PtPtP^c) = 80 Hz are observed (Figure 3) but the analogous couplings ^2J(Pt^{2}Pt^{2}P^b) and ^3J(P^{b}Pt^{2}Pt^{2}P^b), which would be observable in the ^{195}Pt satellite spectra,[8] are not resolved, suggesting that there is no Pt^{2}Pt^2 bond. This conclusion is tentative, since major geometric distortions could lead to loss of long-range coupling even if a Pt^{2}Pt^2 bond were present.

It is significant that the fluxional process for 4 leads not only to equivalence of all the platinum and phosphorus atoms but also to equivalence of the two carbon atoms of the alkyne. On the basis of theory, Schilling and Hoffmann proposed two likely mechanisms for fluxionality of μ_3-η^2-⊥-acetylene complexes, as depicted in A (a → b → c) and B (a → b → c).[11]



A



B

Mechanism A does not lead to equivalence of the acetylenic carbon atoms whereas B does. The experimental evidence for complex 4 therefore supports mechanism B.

Reactions with RCCH. These reactions are shown in Scheme III. Propyne reacts with complex 1 in a way similar to that for acetylene to give [Pt$_3$(μ_3-MeCCH)(CO)(μ-dppm)$_3$]$^{2+}$ (**7a**), and further CO loss gives **6a**. The propyne was displaced from **6a** by excess acetylene, with formation of 4, and this reaction was reversed by treating 4 with excess propyne.

Ethoxyacetylene reacts with 1 to give **7b**, and this complex was sufficiently stable to be isolated. It has been characterized by an X-ray structure determination (see later) as well as by spectroscopic methods. Complex **7b** reacts with sodium chloride solution to give **8**.

Table I. Selected Distances and Angles in the Cation 7b

Distances (Å)			
Pt(1)–Pt(2)	2.623 (1)	Pt(1)–P(1)	2.257 (3)
Pt(1)–P(6)	2.278 (3)	Pt(1)–C(4)	2.249 (10)
Pt(1)–C(5)	2.206 (10)	Pt(2)–P(2)	2.304 (3)
Pt(2)–P(3)	2.268 (3)	Pt(2)–C(4)	2.020 (9)
Pt(3)–P(4)	2.344 (3)	Pt(3)–P(5)	2.329 (3)
Pt(3)–C(5)	2.084 (10)	Pt(3)–C(8)	1.917 (16)
P(1)–C(1)	1.817 (11)	P(2)–C(1)	1.847 (11)
P(3)–C(2)	1.849 (11)	P(4)–C(2)	1.827 (12)
P(5)–C(3)	1.811 (11)	P(6)–C(3)	1.831 (12)
O(1)–C(4)	1.352 (12)	O(1)–C(6)	1.449 (13)
O(2)–C(8)	1.10 (3)	C(4)–C(5)	1.377 (14)
C(6)–C(7)	1.51 (3)	Pt(1)···Pt(3)	3.205 (1)
P–C(methylene)	1.811 (11)–1.849 (11)	Pt(2)···Pt(3)	3.426 (1)
P–C(phenyl)	1.797 (14)–1.849 (8)		
Angles (deg)			
Pt(2)–Pt(1)–P(1)	85.1 (1)	Pt(2)–Pt(1)–P(6)	163.9 (1)
Pt(2)–Pt(1)–C(4)	48.2 (3)	Pt(2)–Pt(1)–C(5)	73.8 (3)
P(1)–Pt(1)–P(6)	111.0 (2)	P(1)–Pt(1)–C(4)	124.2 (3)
P(1)–Pt(1)–C(5)	158.6 (3)	P(6)–Pt(1)–C(4)	118.0 (3)
P(6)–Pt(1)–C(5)	90.1 (3)	C(4)–Pt(1)–C(5)	36.0 (4)
Pt(1)–Pt(2)–C(4)	56.2 (3)	P(2)–Pt(2)–P(3)	116.9 (1)
P(2)–Pt(2)–C(4)	153.3 (3)	P(3)–Pt(2)–C(4)	89.7 (3)
P(4)–Pt(3)–P(5)	156.4 (1)	P(4)–Pt(3)–C(5)	91.7 (3)
P(4)–Pt(3)–C(8)	91.3 (5)	P(5)–Pt(3)–C(5)	89.2 (3)
P(5)–Pt(3)–C(8)	88.3 (5)	C(5)–Pt(3)–C(8)	176.9 (6)
Pt(1)–P(1)–C(1)	110.5 (4)	Pt(2)–P(2)–C(1)	108.5 (4)
Pt(2)–P(3)–C(2)	105.0 (4)	Pt(3)–P(4)–C(2)	122.4 (4)
Pt(3)–P(5)–C(3)	116.5 (4)	Pt(1)–P(6)–C(3)	109.5 (4)
C(4)–O(1)–C(6)	118.4 (8)	P(1)–C(1)–P(2)	109.9 (6)
P(3)–C(2)–P(4)	113.8 (6)	P(5)–C(3)–P(6)	114.6 (6)
Pt(1)–C(4)–Pt(2)	75.6 (3)	Pt(1)–C(4)–O(1)	119.6 (7)
Pt(1)–C(4)–C(5)	70.3 (6)	Pt(2)–C(4)–O(1)	117.1 (7)
Pt(1)–C(5)–Pt(3)	96.6 (4)	Pt(1)–C(5)–C(4)	73.7 (6)
Pt(3)–C(5)–C(4)	119.2 (7)	O(1)–C(6)–C(7)	103.4 (10)
Pt(3)–C(8)–O(2)	171.4 (14)		

With bulkier substituents on the acetylene the reactions with 1 are slower and the intermediates 7 are not observable but only the products 6 are formed. The reaction with *t*-BuCCH was particularly slow. These observations are consistent with steric effects having a large effect on the rate of reaction and on the relative stabilities of complexes 6 and 7.

The characterization of complexes 6 and 7 by ^{31}P and ^{195}Pt NMR spectroscopy is essentially the same as for 4 and 2 and so will not be discussed in detail. The chief problem is to determine the position of the alkyne substituent, R, and, since ^{13}C-labeled alkynes are not readily accessible, this was determined initially by ^{1}H NMR spectroscopy. It was shown earlier that for complex 2 the C^{4}H and C^{5}H resonances occur at δ = 11.80 and 7.85 ppm, respectively, the former resonance being well separated from all others in the spectrum. For complexes 7 there was no observed resonance in this region, indicating the presence of the isomer RC^{4}C^{5}H rather than the alternative HC^{4}C^{5}R. It should be noted that the C^{5}H resonance was not directly observed either, since this region of the spectrum is obscured by phenyl resonances. For complex **7b**, the structure has been confirmed crystallographically. Similarly, complex 4 has well-separated alkyne CH resonances at δ = 12.67 and 7.15 and the resonance in the δ ~ 12 region was absent in complexes 6, thus defining the site of the alkyne substituent.

Structure of Complex 7b(PF$_6$)$_2$. The molecular structure of **7b**, determined as the hexafluorophosphate salt, is shown in Figure 5 and is characterized by the bond lengths and angles listed in Table I. The overall structure is similar to those of [Pt$_3$(HCCH)Cl(μ-dppm)$_3$]$^+$ (3) and [Pt$_3$(HCCH)(μ-dppm)$_2${μ_3-(Ph$_2$P)$_2$CHCH=CH}]$^+$ (9), which have been reported briefly elsewhere.[6,12] A com-

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[11] Schilling, B. E. R.; Hoffmann, R. *Acta Chem. Scand.* **1979**, *B33*, 231.

Table II. Comparison of Distances (Å) and Angles (deg) in Complexes 7b, 3, and 9

	7b	3	9
Pt(1)-Pt(2)	2.623 (1)	2.631 (2)	2.655 (2)
Pt(1)···Pt(3)	3.205 (1)	3.232 (2)	3.181 (2)
Pt(2)···Pt(3)	3.426 (1)	3.277 (2)	3.115 (2)
Pt(1)-C(4)	2.25 (1)	2.17 (3)	2.20 (2)
Pt(1)-C(5)	2.21 (1)	2.21 (3)	2.25 (2)
Pt(2)-C(4)	2.02 (1)	2.05 (3)	2.04 (2)
Pt(3)-C(5)	2.08 (1)	1.99 (3)	2.11 (2)
C(4)-C(5)	1.38 (2)	1.40 (4)	1.38 (3)
Pt(2)-C(4)-C(5)	117.3 (7)	119 (2)	122.1 (14)
Pt(3)-C(5)-C(4)	119.2 (7)	112 (2)	104.3 (12)
C(4)-Pt(2)-P(2)	153.3 (3)	152 (1)	148.3 (5)
C(5)-Pt(3)-X[a]	176.9 (6)	165 (1)	158.2 (7)
Pt(2)-C(4)-C(5)-Pt(3)	-27.4 (5)	-30 (1)	-26 (1)

[a] X = CO, Cl, and CH in complexes **7b**, **3**, and **9**, respectively. A common numbering system has been used for all three complexes.

parison of some important bond distances and angles for these compounds is given in Table II. The three platinum atoms in **7b** define an approximately isosceles triangle whose edges are bridged by the μ-dppm ligands. As for **3** and **9**, the Pt_3 triangle of **7b** contains only one Pt–Pt bond between Pt(1) and Pt(2) of 2.623 (1) Å; the Pt(1)···Pt(3) and Pt(2)···Pt(3) distances of 3.205 (1) and 3.426 (1) Å lie outside the range (2.6–2.8 Å)[13,14] for Pt–Pt bonds.

The EtOCCH ligand lies above the face of the Pt_3 triangle and is σ-bonded to Pt(2) and Pt(3) and π-bonded to Pt(1). The Pt(2)–C(4)–C(5)–Pt(3) unit is significantly distorted from planarity (torsion angle −27.4 (5)°) as a result of the requirement for π-bonding to Pt(1) and other factors discussed below, but the Pt_3(RCCH) unit can still be identified as an example of μ_3-η^2-∥ binding, which is the most common mode of attachment of alkynes to M_3 triangles.[4,5] However, the structures of complex **7b**, and its close analogues **3** and **9**, are unique in having only one metal–metal bond; all other known examples have two or three metal–metal bonds.[4,5]

The simplest view of the bonding in **7b** is to consider the alkyne as $RCCH^{2-}$, and the atoms Pt(1), Pt(2), and Pt(3) are then considered to be in oxidation states I, I, and II, respectively. Hence, including the PtPt bond, all metal atoms are expected to have square-planar stereochemistry. There are major distortions in **7b** as well as in **3** and **9**. For example, the ideal angle C(4)–Pt(2)–P(2) should be 180° but is 153.3 (3)° in **7b**. This distortion is caused by the π-bonding of C(4) to Pt(1). Similarly, the ideal angle P(4)–Pt(3)–P(5) is 180° but is actually 156.4 (1)° in **7b**.

The only other ethoxyethyne complex to have been studied crystallographically is $[Os_3H_2(CO)_9(HCCOEt)]$, and this also has the μ_3-η^2-∥ bonding form of the alkyne but with three metal–metal bonds [Os–Os = 2.770 (2)–3.006 (2) Å].[15] Ethoxyethyne complexes of ruthenium are known, but they have not been structurally characterized.[16]

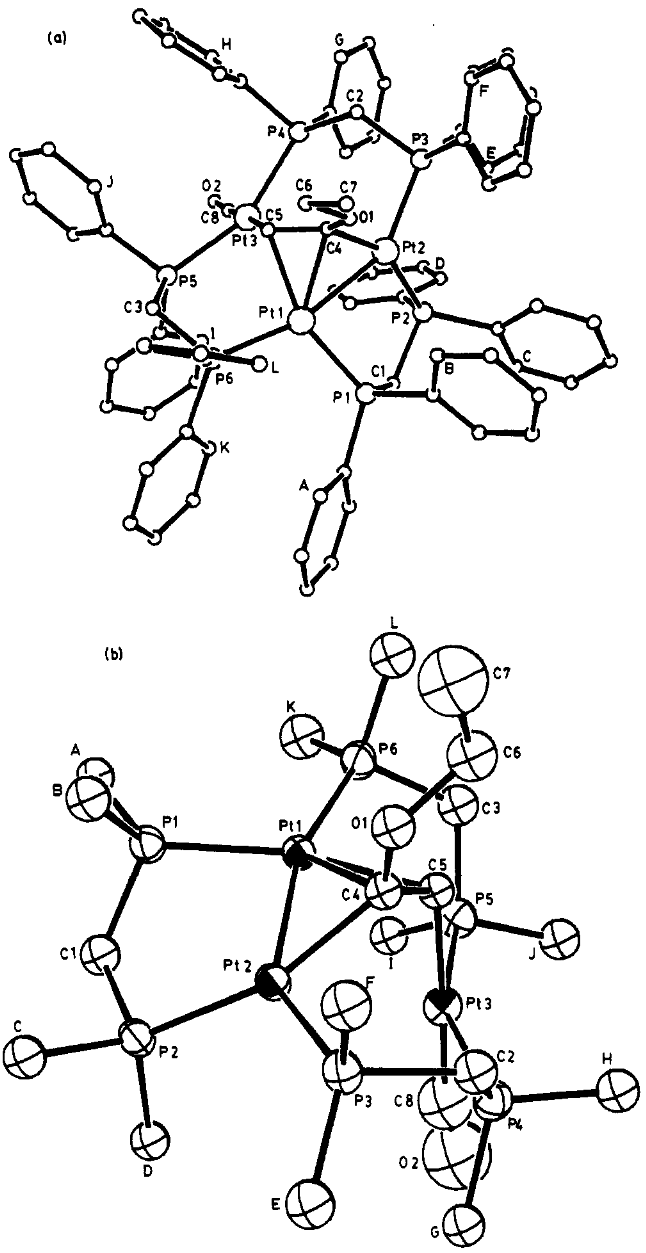

Figure 5. (a) View of the $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCOEt})(CO)(\mu\text{-dppm})_3]^{2+}$ cation **7b**, showing the numbering of the atoms. Hydrogen atoms are omitted, and other atoms are represented by spheres of arbitrary radius. The carbon atoms of rings A–L are numbered cyclically n = 1–6, starting with the atom attached to phosphorus. The ring label is placed adjacent to the n = 2 atom of each ring. (b) View of the metal coordination, showing 50% probability ellipsoids. Only the ipso carbon atom of each phenyl ring is displayed.

Discussion

Complex **1** is a 42-electron triplatinum cluster complex, and this is the most frequent electron count for such compounds, in which each platinum atom has a 16-electron configuration and one empty $6p_z$ orbital.[17] Addition of a 4-electron-donor alkyne ligand to give **2** or **7** (Schemes II and III) then gives a 46-electron count, while subsequent loss of the carbonyl ligand to give **4** or **6** gives a 44-electron count. The Wade–Mingos rules, adapted for platinum having a 16-electron count, would then predict the loss of two Pt–Pt bonds on formation of **2** or **7** and one Pt–Pt bond on formation of **4** or **6** from **1**. These predictions are certainly upheld for **2** and **7** and, on the basis of the spectroscopic data, are probably also valid for **4** and **6**. We note, however, that 44-electron and 46-electron clusters

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(12) Jennings, M. C.; Manojlović-Muir, Lj.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 745.

(13) Manojlović-Muir, Lj.; Muir, K. W.; Grossel, M. C.; Brown, M. P.; Nelson, C. D.; Yavari, A.; Kallas, E.; Moulding, R. P.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1986**, 1955.

(14) Puddephatt, R. J.; Manojlović-Muir, Lj.; Muir, K. W. *Polyhedron*, in press.

(15) Boyar, E.; Deeming, A. J.; Felix, M. S. B.; Kabir, S. E.; Adetia, T.; Bhusate, R.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1989**, 5.

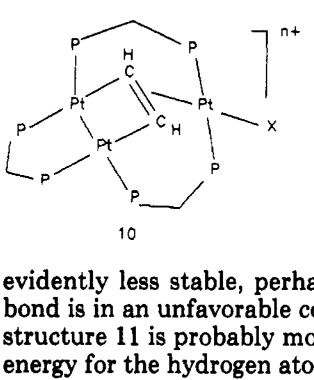
(16) Jensen, C. M.; Kaesz, H. D. *J. Organomet. Chem.* **1987**, *330*, 133.

(17) (a) Mealli, C. *J. Am. Chem. Soc.* **1990**, *9*, 1579. (b) Evans, D. G. *J. Organomet. Chem.*, **1988**, *352*, 397.

based on complex 1, such as $[Pt_3(\mu_3\text{-}CO)(PR_3)(\mu\text{-dppm})_3]^{2+}$ (44e) and $[Pt_3(\mu\text{-}CO)(\mu\text{-}S_2CNMe_2)(\mu\text{-dppm})_3]^+$ (46e), are known in which no Pt–Pt bond cleavage occurs.[18] From empirical observations, it would appear that bond cleavage occurs only when the addition reaction involves formal oxidation of the cluster. In formation of the 46-electron complex $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$ from 1, for example, oxidation occurs and two Pt–Pt bonds are broken whereas in formation of $[Pt_3(\mu\text{-}CO)(\mu\text{-}S_2CNMe_2)(\mu\text{-dppm})_3]^+$ from 1 no oxidation occurs and no Pt–Pt bonds are broken. The new acetylene clusters may be considered to be derived from $C_2H_2^{2-}$, and so their formation occurs with formal oxidation of the cluster 1. The observed structures are then expected.

The structures of 3 and 7b strongly support their formulation as dimetalated alkene derivatives, with Pt^2C^4 and Pt^3C^5 σ-bonds and the $C^4{=}C^5$ bond then π-bonded to Pt^1. Further support is obtained from the NMR parameters. Free acetylene has $^1J(CC) = 172$ Hz and $^1J(CH) = 262$ Hz whereas complex 2 has $^1J(CC) = 27$ Hz, $^1J(C^4H) = 152$ Hz, and $^1J(C^5H) = 163$ Hz. Ethylene has $^1J(CC) = 69$ Hz and ethane has $^1J(CC) = 35$ Hz, and so the observed data for 2 indicate hybridization at carbon close to sp³. In the simple acetylene complex $[Pt(C_2H_2)(PPh_3)_2]$, $^1J(CH) = 210$ Hz.[3] For complex 4 the values of $^1J(CC) = 41$ Hz, $^1J(C^1H) = 187$ Hz, and $^1J(C^2H) = 188$ Hz are higher than for 2 and suggest that hybridization at carbon is closer to ethylene (sp²). In general, the values of $^1J(CC)$ and $^1J(CH)$ decrease as acetylene binds to more metal atoms; for example, $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-HCCH})]$ has $^1J(CC) = 56$ Hz and $[Co_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-HCCH})]$ has $^1J(CC) = 21$ Hz.[3-5] The values for the μ_3-η^2-HCCH complexes 2 and 4 fall between the above values, as might be expected.

It has been noted earlier that the unsymmetrical structure of complexes 2 and 7 requires significant twisting of the alkyne ligand. There is a more symmetrical structure 10 that does not require the alkyne twist, but this is evidently less stable, perhaps because the alkyne–Pt π bond is in an unfavorable conformation. The vinylidene structure 11 is probably more stable,[7] but the activation energy for the hydrogen atom transfer needed to convert the HCCH ligand to $C{=}CH_2$ appears to be high. This is surprising, since, in a dicationic complex such as 2, proton transfer might be expected to be easy. Complexes 2 and 4 do not undergo deprotonation reactions with bases such as hydroxide, and it appears that the hydrogen atoms of the coordinated acetylene are not protonic and that isomerization of HCCH to $C{=}CH_2$ is therefore difficult.



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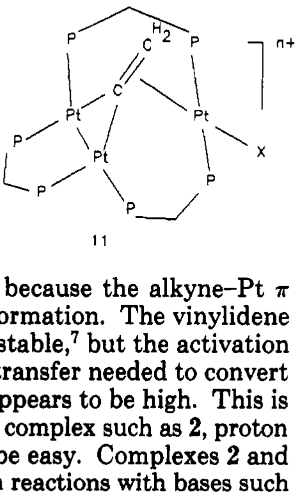

11

In terms of the cluster–surface analogy, the formation of the μ_3-η^2-∥-HCCH complex 2 (Scheme II) can be thought to mimic the low-temperature chemisorption of HCCH on the Pt(111) surface (Scheme I). Hoffmann has predicted that chemisorption of HCCH leads to platinum–carbon bonding at the expense of weaker Pt–Pt bonding,[19] and the complete loss of two Pt–Pt bonds on addition of HCCH to 1 to give 2 (Scheme II) can be considered an extreme illustration of this effect. The rearrangement of the HCCH ligand, which occurs easily on surfaces to give vinylidene and ethylidyne,[2] does not occur in the cluster complexes discussed here. However, there is a good analogy in terms of the relative affinities of different reagents for platinum. Both the cluster (Scheme II) and surface give the sequence $H_2S > HCCH > CO$.

Experimental Section

¹H NMR spectra were recorded by using a Varian XL-200 NMR spectrometer. ^{31}P, ^{195}Pt, ^{13}C, and ^2H NMR spectra were recorded by using a Varian XL-300 NMR spectrometer. Chemical shifts are quoted with respect to the references TMS (^1H, ^2H, ^{13}C), Me_3PO_4 (^{31}P), and aqueous $K_2[PtCl_4]$ (^{195}Pt). *J* values are given in hertz. The atom labeling for NMR assignments is defined in Figures 1–4, and where a coupling was observed in more than one spectrum, both values are given. The values obtained from the ^{195}Pt NMR spectra are least accurate because the line widths are greater than in ^1H, ^{13}C, or ^{31}P spectra. FAB mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer. C_2D_2 was prepared by reacting CaC_2 with D_2O and was dried by passing the evolved gas through a column of silica gel. C_2H_2 and $C_2H_2\text{-}^{13}C_2$ were commercial samples and were used without purification. $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ and the corresponding ^{13}C-labeled $[Pt_3(\mu_3\text{-}{}^*CO)(\mu\text{-dppm})_3][PF_6]_2$ were prepared by the literature methods.[7,20]

$[Pt_3(HCCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$. Acetylene was passed through a solution of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CD_2Cl_2 (0.3 mL) at −80 °C for 2 min, and the solution was then allowed to warm to room temperature. A similar reaction was carried out at room temperature, and a color change from red to orange was observed. The solution in both cases was shown by NMR spectroscopy to contain $[Pt_3(HCCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$ both at −80 °C and at room temperature.

The corresponding ^2H-labeled complex was prepared similarly by using C_2D_2 in CH_2Cl_2. The ^{13}C-labeled complexes were prepared similarly by using $[Pt_3(\mu_3\text{-}{}^{13}CO)(\mu\text{-dppm})_3][PF_6]_2$ in CH_2Cl_2 and C_2H_2 or by condensing excess acetylene-$^{13}C_2$ into a solution of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ in CH_2Cl_2 under vacuum. This solution was then allowed to warm to room temperature.

NMR data: ^1H in CD_2Cl_2, $\delta = 11.80$ [m, $^3J(H^4H^5) = 8.2$, $^1J(H^4C^4) = 152$, $^2J(H^4Pt^2) = 54$, $^3J(H^4Pt^3) = 66$, $^3J(H^4Pt^1) = 16$, 1 H^4], {4.87 [$^2J(PH) = 10$], 4.05 [$^2J(PH) = 9$], 4.00, CH_2 of dppm ligands, specific assignments were not made}; ^2D NMR in acetone, $\delta = 11.80$ (D^4), 7.85 (D^5); ^{13}C NMR in acetone-d_6, $\delta = 174$ [s, $^1J(Pt^3C) = 1000$, CO], 88 [m, $^1J(C^5H^5) = 163$, $^1J(C^5Pt^3) = 538$, $^1J(C^5C^4) = 27$, C^5], 201 [m, $^1J(C^4H^4) = 152$, $^1J(C^4Pt^2) = 662$, $^2J(C^4P^2) = 78$, C^4]; ^{31}P in acetone-d_6, $\delta = -10.24$ [m, $^1J(P^1Pt^1) = 4080$, $^2J(P^1P^2) = 40$, 1 P^1], −4.2 [m, $^1J(P^2Pt^2) = 2420$, $J(P^2C^4) = 78$, $^2J(P^2P^1) = 40$, 1 P^2], 11.55 [m, $^1J(P^3Pt^2) = 3440$, $^3J(P^3P^6) = 80$, 1 P^3], 12.67 [m, $^1J(P^4Pt^3) = 2800$, 1 P^4], 14.48 [m, $^1J(P^5Pt^3) = 3020$, $^2J(P^5Pt^2) = 170$, $J(P^5P^6) = 40$, 1 P^5], 5.00 [m, $^1J(P^6Pt^1) = 3360$, $^2J(P^6Pt^2) = 600$, $J(P^6P^5) = 40$, $J(P^6P^3) = 80$, 1 P^6]; ^{195}Pt in CD_2Cl_2, $\delta = -3300$ [m, $^1J(Pt^1Pt^2) = 2160$, $^1J(Pt^1P^1) = 4000$, $^1J(Pt^1P^6) = 3312$, 1 Pt^1], −2840 [m, $^1J(Pt^2Pt^1) = 2112$, $^1J(Pt^2Pt^3) = 900$, $^1J(Pt^2P^2) = 2355$, $^1J(Pt^2P^3) = 3450$, $^2J(Pt^2P^5) = 165$, $^2J(Pt^2P^6) = 600$, $^1J(Pt^2C^4) = 630$, 1 Pt^2], −2920 [m, $^1J(Pt^3Pt^2) = 900$, $^1J(Pt^3\text{–}^{13}CO) = 1000$, $^1J(Pt^3C^5) = 517$, $^1J(Pt^3P^5) = 2940$, $^1J(Pt^3P^4) = 2940$, 1 Pt^3]. IR in CH_2Cl_2: $\nu(CO) = 2090$ cm⁻¹.

$[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$. This complex was prepared by removing CO from the solution of $[Pt_3(HCCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CH_2Cl_2 (20 mL) either by flushing the solution with acetylene for several hours or by slowly evaporating the solvent and redissolving the residue in CH_2Cl_2 (20 mL) followed by further slow evaporation of the solvent. The red solid was dried under vacuum: yield 95%; mp 205–212 °C dec. Anal. Calcd for $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$: C, 44.98; H, 3.31. Found:

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(18) (a) Bradford, A. M.; Douglas, G.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 409. (b) Bradford, A. M.; Puddephatt, R. J.; Douglas, G.; Manojlović-Muir, Lj; Muir, K. W. *Organometallics* **1990**, *9*, 1579.

(19) Silvestre, J.; Hoffmann, R. *Langmuir* **1985**, *1*, 621.

(20) (a) Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344. (b) Lloyd, B. R.; Bradford, A.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 424.

C, 44.81; H, 3.65. The related ^{2}H- or ^{13}C-labeled complexes were prepared by using the corresponding precursors.

NMR data in acetone-d_6 at −80 °C: ^{1}H, $\delta = 12.67$ [m, $^{2}J(H^{1}Pt^{1}) = 128$, $^{2}J(H^{1}Pt^{2}) = 70$, 1 H^{1}], 3.70 and 4.46 (CH_2 of dppm ligands); ^{13}C, $\delta = 171.1$ [m, $^{1}J(C^{1}H^{1}) = 187$, $^{1}J(C^{1}Pt^{1}) = 440$, 1 C^{1}], 73.4 [m, $^{1}J(C^{2}H^{2}) = 188$, $^{1}J(C^{2}C^{1}) = 41$, $J(C^{2}Pt^{1})$ = not measurable, 1 C^{2}]; ^{31}P, $\delta = -7.43$ [m, $^{1}J(P^{a}Pt^{1}) = 2680$, $^{3}J(P^{a}P^{c}) = 80$, 2 P^{a}], −16.6 [s, $^{1}J(P^{b}Pt^{1}) = 3720$, 2 P^{b}], 9.70 [m, $^{1}J(P^{c}Pt^{2}) = 4240$, $^{2}J(P^{c}Pt^{1}) = 490$, $^{3}J(P^{c}P^{a}) = 80$, 2 P^{c}]; ^{195}Pt, $\delta = -2278$ [m, $^{1}J(Pt^{1}P^{a}) = 2684$, $^{2}J(Pt^{1}P^{c}) = 497$, $^{1}J(Pt^{1}Pt^{2}) = 2000$, $^{1}J(Pt^{1}C^{1}) = 446$, 1 Pt^{1}], −3471 [m, $^{1}J(Pt^{2}P^{b}) = 3800$, $^{1}J(Pt^{2}P^{c}) = 4250$, 2 Pt^{2}]. NMR data in acetone-d_6 (except for ^{2}D NMR in acetone) at 20 °C: ^{1}H, $\delta = 9.91$ [broad signal, $^{1}J(HC) = 193$, 2 H], 3.56 and 5.11 (CH_2 of dppm ligands); ^{13}C, $\delta = 120$ (broad signal, 2 C); ^{31}P, $\delta = -4.9$ [s, $^{1}J(Pt{-}P) = 3600$, 6 P]; ^{2}D, $\delta = 10.06$ (2 D).

Reaction of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ with CO. CO gas was bubbled through a solution of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CD_2Cl_2 (0.3 mL) in an NMR tube for 1 min. The solution was shown by NMR spectroscopy to contain $[Pt_3(HCCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$.

$[Pt_3(HCCH)(\mu\text{-dppm})_3Cl][PF_6]$. A solution of NaCl (0.5 g) in acetone (10 mL) was added to a solution of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ or $[Pt_3(HCCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in acetone (10 mL). This was stirred for 40 min. H_2O (20 mL) was added to the solution, and the resulting precipitate was filtered out, washed with H_2O (5 mL), and dried in vacuo. A sample was purified by slow diffusion of *n*-pentane into a solution of the product in acetone, after which yellow crystals were separated. The single crystals suitable for crystallography were grown similarly: yield 75%; mp 225–235 °C dec. Anal. Calcd for $[Pt_3(HCCH)(\mu\text{-dppm})_3Cl][PF_6]$: C, 47.51; H, 3.49. Found: C, 47.85; H, 3.70.

^{31}P NMR in acetone-d_6: $\delta = -7.22$ [m, $^{1}J(P^{1}Pt^{1}) = 4090$, $^{2}J(P^{1}P^{2}) = 37$, 1 P^{1}], −2.83 [m, $^{1}J(P^{2}Pt^{2}) = 2420$, $^{2}J(P^{1}P^{2}) = 37$, 1 P^{2}], 16.40 [m, $^{1}J(P^{3}Pt^{2}) = 3480$, 1 P^{3}], 17.52 [m, $^{1}J(P^{4}Pt^{3}) = 3440$, 1 P^{-4}], 14.71 [m, $^{1}J(P^{5}Pt^{3}) = 3340$, $^{2}J(P^{5}P^{6}) = 55$, $^{2}J(P^{5}Pt^{2}) = 72$, 1 P^{5}], 4.75 [m, $^{1}J(P^{6}Pt^{1}) = 3320$, $^{3}J(P^{6}P^{3}) = 95$, $^{2}J(P^{6}P^{5}) = 55$, 1 P^{6}].

$[Pt_3(CH_3CCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$. CH_3CCH gas was bubbled through a solution of $[Pt_3(\mu_3\text{-CO})(dppm)_3][PF_6]_2$ (0.1 g) in CD_2Cl_2 (0.3 mL) in an NMR tube for 20 s. This was followed by a color change to dark red. The solution was shown by NMR spectroscopy to contain the *product*.

NMR in CD_2Cl_2: ^{1}H, $\delta = 2.20$ [s, $^{3}J(Pt^{2}H) = 56$, $^{4}J(Pt^{3}H) = 32$, CH_3], 4.66, 3.97, 3.62 [CH_2 of dppm]; ^{31}P, $\delta = -5.5$ [s, $^{1}J(P^{1}Pt^{1}) = 3860$, 1 P^{1}], −6.1 [s, $^{1}J(P^{2}Pt^{2}) = 2350$, 1 P^{2}], 11.06 [m, $^{1}J(P^{3}Pt^{2}) = 3340$, $^{3}J(P^{3}P^{6}) = 100$, 1 P^{3}], 14.5 [m, $^{1}J(P^{4}Pt^{3}) = 2848$, 1 P^{4}], 15.1 [m, $^{1}J(P^{5}Pt^{3}) = 2940$, $^{3}J(P^{5}P^{6}) = 40$, 1 P^{5}], 3.6 [m, $^{1}J(P^{6}Pt^{1}) = 3120$, $^{2}J(P^{6}Pt^{2}) = 680$, $^{3}J(P^{6}P^{3}) = 100$, 1 P^{6}]; ^{195}Pt, $\delta = -3644$ [m, $^{1}J(Pt^{1}P^{1}) = 3858$, $^{1}J(Pt^{1}P^{6}) = 3100$, $^{1}J(Pt^{1}Pt^{2}) = 2100$, 1 Pt^{1}], −3228 [m, $^{1}J(Pt^{2}P^{2}) = 2350$, $^{1}J(Pt^{2}P^{3}) = 3325$, $^{1}J(Pt^{2}Pt^{1}) = 2100$, $^{2}J(Pt^{2}P^{6}) = 675$, 1 Pt^{2}], −3273 [m, $^{1}J(Pt^{3}P^{4}) = 2860$, $^{1}J(Pt^{3}P^{5}) = 2860$, $^{1}J(Pt^{3}{-}^{13}CO) = 1035$, 1 Pt^{3}]; ^{13}C, $\delta = 173.8$ [s, $^{1}J(CPt^{3}) = 1038$, ^{13}CO]. IR in CH_2Cl_2: $\nu(CO) = 2100$ cm^{-1}.

$[Pt_3(CH_3CCH)(\mu\text{-dppm})_3][PF_6]_2$. This compound was prepared by evaporation of the solvent from a solution of $[Pt_3(CH_3CCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CD_2Cl_2 (0.3 mL). The solid was again dissolved in CH_2Cl_2 (20 mL) and the solvent evaporated slowly. The residue was dried in vacuo, mp 225–230 °C. Anal. Calcd for $[Pt_3(CH_3CCH)(\mu\text{-dppm})_3][PF_6]_2$: C, 45.25; H, 3.38. Found: C, 45.13; H, 3.55.

NMR data in acetone-d_6 at −80 °C: ^{1}H, $\delta = 4.74$, 4.00 and 3.82 (CH_2 of dppm ligands); ^{31}P, $\delta = -8.6$ [m, $^{1}J(Pt^{1}P^{a}) = 2625$, $^{3}J(P^{a}P^{c}) = 82$, 2 P^{a}], −13.3 [s, $^{1}J(P^{6}Pt^{2}) = 3620$, 2 P^{6}], 10.2 [m, $^{1}J(P^{c}Pt^{2}) = 4150$, $^{3}J(P^{c}P^{a}) = 82$, $^{2}J(P^{c}Pt^{1}) = 512$, 2 P^{c}]; ^{195}Pt, $\delta = -2663$ [m, $^{1}J(Pt^{1}P^{a}) = 2600$, $^{2}J(Pt^{1}P^{c}) = 512$, $^{1}J(Pt^{1}Pt^{2}) = 2112$, 1 Pt^{1}], −3778 [m, $^{1}J(Pt^{2}P^{b})$, $^{1}J(Pt^{2}P^{c})$, and $^{1}J(Pt^{2}Pt^{1})$ = not measurable, 2 Pt^{2}]. NMR data in acetone-d_6 at 20 °C: ^{1}H, $\delta = 2.13$ [s, $^{3}J(Pt^{1}CH_3) = 60$, $J(Pt^{2}CH_3) = 36$, CH_3]; ^{31}P, $\delta = -10.8$ [broad s, $^{1}J(PtP)$ = not measurable, 6 P].

If CO gas is bubbled through a solution of $[Pt_3(CH_3CCH)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CD_2Cl_2 (0.3 mL) for 1 min, the product is spectroscopically shown to be $[Pt_3(CH_3CCH)(CO)(\mu\text{-dppm})_3][PF_6]_2$.

$[Pt_3(CH_3CCH)(\mu\text{-dppm})_3Cl][PF_6]$. This was prepared in a way similar to that for $[Pt_3(HCCH)(\mu\text{-dppm})_3Cl][PF_6]$ mentioned above by using $[Pt_3(CH_3CCH)(CO)(\mu\text{-dppm})_3][PF_6]$ or $[Pt_3(CH_3CCH)(\mu\text{-dppm})_3][PF_6]$: yield 70%; mp 224–232 °C dec. Anal. Calcd for $[Pt_3(CH_3CCH)(\mu\text{-dppm})_3Cl][PF_6]$: C, 47.78; H, 3.57. Found: C, 48.25; H, 3.93. ^{31}P NMR data in acetone-d_6: $\delta = -2.30$ [s, $^{1}J(P^{1}Pt^{1}) = 3800$, 1 P^{1}], −3.45 [s, $^{1}J(P^{2}Pt^{2}) = 2260$, 1 P^{2}], 15.18 [m, $^{1}J(P^{3}Pt^{2}) = 3400$, 1 P^{3}], 16.60 [m, $^{1}J(P^{4}Pt^{3}) = 3360$, $^{2}J(P^{4}P^{3}) = 59$, 1 P^{4}], 21.17 [m, $^{1}J(P^{5}Pt^{3}) = 3500$, $^{2}J(P^{5}Pt^{2}) = 148$, $^{2}J(P^{5}P^{6}) = 71$, 1 P^{5}], 3.95 [m, $^{1}J(P^{6}Pt^{1}) = 3200$, $^{2}J(P^{6}Pt^{5}) = 66$, $^{3}J(P^{6}P^{3}) = 104$, 1 P^{6}].

$[Pt_3(HCCOEt)(CO)(\mu\text{-dppm})_3][PF_6]_2$. HCCOEt (6 μL of 50% wt in hexane) was added to a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (60 mg) in acetone (2 mL) under nitrogen atmosphere. The color of the solution changed from orange to deep red. Diethyl ether was added to precipitate the product as a red powder, yield 95%. Anal. Calcd for $[Pt_3(HCCOEt)(CO)(\mu\text{-dppm})_3][PF_6]_2$: C, 45.15; H, 3.38. Found: C, 45.6; H, 3.7. NMR data in acetone-d_6: ^{1}H, $\delta = 0.92$ [t, $^{3}J(HH) = 7$, 3 H], 2.78 [dq, $^{2}J(H^{A}H^{B}) = 7$, $^{3}J(H^{A}H) = 7$, 1 H^{A} of $OCH^{A}H^{B}CH_3$], 3.00 [dq, $^{2}J(H^{B}H^{A}) = 7$, $^{3}J(H^{B}H) = 7$, 1 H^{B} of $OCH^{A}H^{B}CH_3$], 3.49–3.90 [broad signal, 4 H of P_2CH_2], 4.51 [dt, $^{2}J(H^{A'}H^{B'}) = 9$, $^{2}J(H^{A'}P) = 6$, 1 $H^{A'}$ of $PCH^{A'}H^{B'}P$], 4.83 [dt, $^{2}J(H^{B'}H^{A'}) = 9$, $^{2}J(H^{B'}P) = 6$, 1 $H^{B'}$ of $PCH^{A'}H^{B'}P$]; ^{31}P, $\delta = -12.0$ [s, $^{1}J(P^{1}Pt^{1}) = 2628$, P^{1}], −12.0 [s, $^{1}J(P^{2}Pt^{2}) = 2462$, P^{2}], −2.5 [dd, $^{1}J(P^{3}Pt^{2}) = 2500$, $^{2}J(P^{3}P^{4}) = 55$, $^{2}J(P^{3}P^{6}) = 113$, P^{3}], 10.6 [d, $^{1}J(P^{4}Pt^{3}) = 2792$, $^{2}J(P^{4}P^{3}) = 55$, P^{4}], 7.8 [d, $^{1}J(P^{5}Pt^{3}) = 2696$, $^{2}J(P^{5}P^{6}) = 43$, P^{5}], 5.0 [dd, $^{1}J(P^{6}Pt^{1}) = 2156$, $^{2}J(P^{6}P^{5}) = 43$, $^{2}J(P^{6}P^{3}) = 113$, P^{6}]. IR data: $\nu(CO) = 2087$ cm^{-1}. FAB MS: calcd, *m/e* 1838 (M); found, *m/e* 1808 (M − CO).

$[Pt_3(HCCOEt)(\mu\text{-dppm})_3(Cl)][PF_6]$. $[Pt_3(HCCOEt)(\mu\text{-dppm})_3(CO)][PF_6]_2$ (50 mg) in MeOH (10 mL) was reacted with an excess of NH_4Cl for 12 h. The solvent was then evaporated and the solid redissolved in CH_2Cl_2 and washed with water. Addition of ether to the solution produced a red precipitate. The red solid was separated and dried, yield 100%. Anal. Calcd for $[Pt_3(HCCOEt)(\mu\text{-dppm})_3(Cl)][PF_6]$: C, 47.67; H, 3.62. Found: C, 48.00; H, 3.80. NMR data in acetone-d_6: ^{1}H, $\delta = 0.9$ [t, $^{3}J(HH) = 7$, CH_3], 2.93 [dq, $^{2}J(H^{A}H^{B}) = 7$, $^{3}J(H^{A}H) = 7$, $OC\mathit{H}^{A}H^{B}CH_3$], 3.39 [dq, $^{2}J(H^{B}H^{A}) = 7$, $^{3}J(H^{B}H) = 7$, $OCH^{A}\mathit{H}^{B}CH_3$]; ^{31}P, $\delta = -6.8$ [s, $^{1}J(P^{1}Pt^{1}) = 3502$, P^{1}], −6.81 [s, $^{1}J(P^{2}Pt^{2}) = 2442$], 9.20 [dd, $^{1}J(P^{3}Pt^{2}) = 3536$, $^{2}J(P^{3}P^{4}) = 77$, $^{2}J(P^{3}P^{6}) = 116$, P^{3}], 19.98 [d, $^{1}J(P^{4}Pt^{2}) = 3286$, $^{2}J(P^{4}P^{3}) = 77$, P^{4}], 14.47 [d, $^{1}J(P^{5}Pt^{3}) = 3206$, $^{2}J(P^{5}P^{6}) = 57$, P^{5}], 1.21 (dd, $^{1}J(P^{6}Pt^{1}) = 3141$, $^{2}J(P^{6}P^{5}) = 57$, $^{2}J(P^{6}P^{3}) = 116$, P^{6}]. FAB MS: calcd, *m/e* 1844; (M) found, *m/e* 1844.

$[Pt_3(HCCCH_2CH_2OH)(\mu\text{-dppm})_3][PF_6]_2$. $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (0.007 g) was dissolved in acetone (15 mL). Excess $HC{\equiv}CCH_2CH_2OH$ (0.5 mL) was added to this solution, and the mixture was stirred for 2 h. The solvent was evaporated under vacuum. The excess 3-butyn-1-ol was removed with three washes with ethyl ether. The resulting product was further purified by acetone/*n*-pentane recrystallization. The resulting solid product was dried in vacuo. Anal. Calcd for $[Pt_3(HC{\equiv}CCH_2CH_2OH)(\mu\text{-dppm})_3][PF_6]_2$: C, 45.22; H, 3.46. Found: C, 46.16; H, 3.51. NMR data at −40 °C (except for ^{1}H at room temperature) in acetone-d_6: ^{31}P, $\delta = -11.2$ [d, $^{1}J(P^{a}Pt^{1}) = 2570$, $^{3}J(P^{a}P^{c}) = 80$, 2 P^{a}], −13.21 [s, $^{1}J(P^{b}Pt^{2}) = 3610$, 2 P^{b}], 9.8 [d, $^{1}J(P^{c}Pt^{2}) = 4080$, $^{2}J(P^{c}Pt^{1}) = 560$, $^{3}J(P^{c}P^{a}) = 80$, 2 P^{c}]; ^{195}Pt, $\delta = -3388$ [dd, $^{1}J(Pt^{2}P^{b}) = 3600$, $^{1}J(Pt^{2}P^{c}) = 4080$, 2 Pt^{2}], Pt^{1} was not observed; ^{1}H, $\delta = 3.5$ [m, 2 H^{b} of $CH_2{}^{a}CH_2{}^{b}OH^{c}$], 3.8 [m, 2 H^{a} of $CH_2{}^{a}CH_2{}^{b}OH^{c}$], 4.05 [m, 1 H^{c} of $CH_2{}^{a}CH_2{}^{b}OH^{c}$].

$[Pt_3(t\text{-BuCCH})(\mu\text{-dppm})_3][PF_6]_2$. *t*-BuCCH (0.15 mL) was added to a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CH_2Cl_2 (20 mL). The color changed to a dark red within about 20 min. This was stirred overnight, and then the solvent was removed. The red solid was dissolved in 10 mL of acetone, and the solution was layered with 40 mL of *n*-pentane. Brownish crystals formed. The crystals were separated and dried in vacuo: yield 90%; mp 245–250 °C dec. Anal. Calcd for $[Pt_3(t\text{-BuCCH})(\mu\text{-dppm})_3][PF_6]_2$: C, 46.06; H, 3.60. Found: C, 45.87; H, 3.89. NMR data in acetone-d_6: ^{1}H, $\delta = 1.79$ [s, 9 H of *t*-Bu group], 4.30 (broad signal, 2 H of one of the dppm ligands), 3.76 (broad signal, 2 H^{A} of two of the other dppm ligands), 5.8 [m, $^{2}J(H^{B}Pt) = 92$, 2 H^{B} of the above dppm ligands]; ^{31}P, $\delta = -9.80$ [m, $^{1}J(P^{a}Pt^{1}) = 2500$, $^{2}J(P^{a}P^{b}) = 24$, $^{3}J(P^{a}P^{c}) = 80$, 2 P^{a}], −11.98 [m, $^{1}J(P^{b}Pt^{2}) = 3600$, $^{2}J(P^{b}P^{a}) = 24$, 2 P^{b}], 10.69 [m, $^{1}J(P^{c}Pt^{2}) = 4140$, $^{3}J(P^{c}P^{a}) = 80$, $^{2}J(P^{c}Pt^{1}) = 550$, 2 P^{c}]; ^{195}Pt, $\delta = -2217$ [m,

Table III. Crystallographic Data for $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCOEt})(CO)(\mu\text{-dppm})_3][PF_6]_2$ (7b)

$C_{80}H_{72}F_{12}O_2P_8Pt_3$	space group: $P\bar{1}$
fw = 2126.49	T = 23 °C
a = 13.615 (3) Å	λ = 0.71069 Å
b = 13.898 (2) Å	ρ_{calcd} = 1.714 g cm^{-3}
c = 22.668 (3) Å	μ = 53.6 cm^{-1}
α = 84.49 (1)°	transm coeff: 0.81–1.25
β = 77.65 (2)°	$R(F_o)$ = 0.043
γ = 80.07 (1)°	$R_w(F_o)$ = 0.049
V = 4119.4 (11) Å^3	no. of refined params: 412
Z = 2	no. of obsd reflcns: 9028

$^1J(Pt^1P^a)$ = 2500, $^1J(Pt^1Pt^2)$ = 2200, $^2J(Pt^1P^c)$ = 550, 1 Pt^1], −3372 [m, $^1J(Pt^2P^b)$ = 3620, $^1J(Pt^2P^c)$ = 4115, $^1J(Pt^2Pt^1)$ = 2160, 2 Pt^2].

Note that CO gas was bubbled through a solution of $[Pt_3(t\text{-BuCCH})(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CD_2Cl_2 (0.3 mL) for 5 min and no change was observed spectroscopically.

Reaction of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ with C_2D_2 or CH_3CCH. C_2D_2 was bubbled through a solution of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ (0.07 g) in CH_2Cl_2 (10 mL) for 2 min. The product was identified as $[Pt_3(DCCD)(\mu\text{-dppm})_3][PF_6]_2$ by its ^1H and ^2D NMR spectra. A similar reaction of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ with MeCCH yielded $[Pt_3(CH_3CCH)(\mu\text{-dppm})_3][PF_6]_2$ identified by its NMR data. This reaction is found to be reversible, which could be driven either way depending on what was used in excess.

Reaction of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ with HCCH. Acetylene gas was bubbled through a solution of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ (0.2 g) in CD_2Cl_2 (0.4 mL) for 10 s at −80 °C. The solution was shown spectroscopically to contain starting cluster and $[Pt_3(HCCH)_2(\mu\text{-dppm})_3][PF_6]_2$. NMR data in CD_2Cl_2 at −80 °C: ^{31}P, δ = −10.10 [d, $^1J(P^1Pt^1)$ = 4060, $^2J(P^1P^2)$ = 36, 1 P^1], −4.92 [d, $^1J(P^2Pt^2)$ = 2480, $^2J(P^2P^1)$ = 36, 1 P^2], 12.5 [^1J(PPt)

Table IV. Fractional Coordinates[a] and Displacement Parameters[b] (Å^2) for $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCOEt})(CO)(\mu\text{-dppm})_3][PF_6]_2$ (7b)

	x/a	y/b	z/c	U		x/a	y/b	z/c	U
Pt(1)	0.18351 (3)	0.27747 (3)	0.23954 (2)	0.028	C(D5)	0.3142 (6)	−0.0405 (9)	0.0716 (5)	0.072 (4)
Pt(2)	0.04382 (3)	0.18135 (3)	0.22162 (2)	0.028	C(D6)	0.2577 (11)	0.0454 (9)	0.0939 (3)	0.063 (4)
Pt(3)	0.23965 (4)	0.05218 (3)	0.28320 (2)	0.034	C(E1)	−0.1186 (11)	−0.0036 (11)	0.2288 (3)	0.042 (3)
P(1)	0.1642 (2)	0.3607 (2)	0.1512 (1)	0.033	C(E2)	−0.0989 (6)	0.0042 (6)	0.1664 (3)	0.055 (3)
P(2)	0.0875 (2)	0.1878 (2)	0.1175 (1)	0.032	C(E3)	−0.1356 (8)	−0.0572 (8)	0.1349 (3)	0.071 (4)
P(3)	−0.0760 (2)	0.0878 (2)	0.2661 (1)	0.033	C(E4)	−0.1921 (9)	−0.1264 (9)	0.1659 (3)	0.073 (4)
P(4)	0.1040 (2)	−0.0368 (2)	0.3137 (1)	0.035	C(E5)	−0.2119 (4)	−0.1342 (4)	0.2283 (3)	0.078 (4)
P(5)	0.3852 (2)	0.1125 (2)	0.2914 (1)	0.037	C(E6)	−0.1752 (10)	−0.0728 (10)	0.2598 (3)	0.061 (4)
P(6)	0.3034 (2)	0.3316 (2)	0.2787 (1)	0.040	C(F1)	−0.1943 (10)	0.1590 (6)	0.3046 (7)	0.042 (3)
P(7)	0.1773 (4)	0.2178 (4)	0.5340 (2)	0.078	C(F2)	−0.2607 (8)	0.1177 (6)	0.3509 (6)	0.051 (3)
P(8)	0.6058 (4)	−0.2360 (3)	0.0791 (2)	0.080	C(F3)	−0.3490 (5)	0.1740 (5)	0.3789 (2)	0.066 (4)
F(1)	0.1784 (9)	0.1925 (9)	0.4682 (4)	0.138	C(F4)	−0.3710 (9)	0.2715 (5)	0.3605 (5)	0.072 (4)
F(2)	0.2336 (11)	0.1083 (8)	0.5453 (6)	0.185	C(F5)	−0.3046 (7)	0.3128 (6)	0.3142 (5)	0.068 (4)
F(3)	0.2825 (9)	0.2500 (10)	0.5170 (6)	0.161	C(F6)	−0.2163 (7)	0.2565 (5)	0.2863 (3)	0.052 (3)
F(4)	0.1759 (12)	0.2364 (13)	0.6004 (5)	0.215	C(G1)	0.0966 (11)	−0.1364 (9)	0.2693 (3)	0.036 (3)
F(5)	0.0735 (9)	0.1761 (12)	0.5540 (6)	0.194	C(G2)	0.0411 (10)	−0.2084 (8)	0.2970 (3)	0.051 (3)
F(6)	0.1200 (12)	0.3200 (9)	0.5227 (7)	0.213	C(G3)	0.0229 (4)	−0.2782 (4)	0.2630 (2)	0.058 (3)
F(7)	0.4897 (9)	−0.2407 (12)	0.1045 (7)	0.202	C(G4)	0.0601 (9)	−0.2760 (8)	0.2014 (3)	0.065 (4)
F(8)	0.5805 (14)	−0.1274 (9)	0.0882 (8)	0.239	C(G5)	0.1155 (8)	−0.2040 (7)	0.1737 (3)	0.063 (4)
F(9)	0.6316 (10)	−0.2549 (11)	0.1429 (4)	0.174	C(G6)	0.1338 (6)	−0.1341 (6)	0.2076 (3)	0.054 (3)
F(10)	0.7168 (9)	−0.2290 (15)	0.0524 (5)	0.234	C(H1)	0.1331 (8)	−0.0901 (11)	0.3861 (5)	0.039 (3)
F(11)	0.6194 (14)	−0.3479 (8)	0.0718 (6)	0.197	C(H2)	0.1880 (12)	−0.1829 (9)	0.3904 (4)	0.059 (4)
F(12)	0.5809 (11)	−0.2241 (10)	0.0128 (5)	0.177	C(H3)	0.2213 (9)	−0.2171 (6)	0.4430 (6)	0.076 (4)
O(1)	−0.0190 (6)	0.2716 (5)	0.3365 (3)	0.037 (2)	C(H4)	0.1998 (7)	−0.1585 (10)	0.4914 (4)	0.070 (4)
O(2)	0.3752 (11)	−0.1282 (10)	0.2323 (5)	0.124 (5)	C(H5)	0.1450 (11)	−0.0657 (7)	0.4871 (4)	0.068 (4)
C(1)	0.1769 (8)	0.2765 (8)	0.0924 (4)	0.036 (3)	C(H6)	0.1116 (9)	−0.0315 (8)	0.4345 (7)	0.054 (3)
C(2)	−0.0285 (8)	0.0224 (8)	0.3318 (4)	0.036 (3)	C(I1)	0.4843 (9)	0.1187 (5)	0.2241 (4)	0.039 (3)
C(3)	0.3654 (9)	0.2310 (8)	0.3228 (5)	0.042 (3)	C(I2)	0.4701 (6)	0.0932 (9)	0.1695 (4)	0.058 (3)
C(4)	0.0590 (8)	0.2122 (7)	0.3042 (4)	0.029 (2)	C(I3)	0.5465 (10)	0.0958 (10)	0.1187 (3)	0.079 (4)
C(5)	0.1510 (8)	0.1778 (7)	0.3206 (4)	0.027 (2)	C(I4)	0.6373 (8)	0.1240 (5)	0.1224 (4)	0.082 (5)
C(6)	−0.0087 (9)	0.2984 (9)	0.3948 (5)	0.048 (3)	C(I5)	0.6515 (7)	0.1495 (9)	0.1770 (4)	0.065 (4)
C(7)	−0.1000 (13)	0.3756 (12)	0.4123 (7)	0.087 (5)	C(I6)	0.5750 (11)	0.1468 (10)	0.2278 (2)	0.045 (3)
C(8)	0.3264 (12)	−0.0591 (11)	0.2465 (6)	0.075 (4)	C(J1)	0.4411 (6)	0.0305 (11)	0.3458 (6)	0.043 (3)
C(A1)	0.2471 (5)	0.4513 (5)	0.1155 (2)	0.035 (3)	C(J2)	0.3874 (10)	0.0282 (8)	0.4047 (7)	0.060 (4)
C(A2)	0.2526 (8)	0.5268 (6)	0.1493 (3)	0.042 (3)	C(J3)	0.4254 (10)	−0.0349 (6)	0.4482 (4)	0.072 (4)
C(A3)	0.3158 (9)	0.5946 (7)	0.1254 (3)	0.054 (3)	C(J4)	0.5172 (6)	−0.0957 (9)	0.4327 (5)	0.074 (4)
C(A4)	0.3736 (5)	0.5868 (5)	0.0676 (2)	0.051 (3)	C(J5)	0.5709 (9)	−0.0935 (6)	0.3737 (6)	0.080 (4)
C(A5)	0.3681 (8)	0.5113 (6)	0.0337 (3)	0.051 (3)	C(J6)	0.5328 (10)	−0.0304 (8)	0.3303 (3)	0.052 (3)
C(A6)	0.3049 (10)	0.4435 (7)	0.0576 (3)	0.043 (3)	C(K1)	0.4111 (7)	0.3817 (5)	0.2291 (5)	0.053 (3)
C(B1)	0.0368 (9)	0.4343 (9)	0.1548 (8)	0.041 (3)	C(K2)	0.4417 (10)	0.3490 (10)	0.1715 (3)	0.058 (3)
C(B2)	−0.0314 (7)	0.4431 (11)	0.2093 (6)	0.055 (3)	C(K3)	0.5213 (12)	0.3840 (10)	0.1317 (4)	0.082 (5)
C(B3)	−0.1266 (9)	0.4981 (7)	0.2118 (4)	0.084 (5)	C(K4)	0.5704 (7)	0.4518 (5)	0.1496 (4)	0.091 (5)
C(B4)	−0.1537 (8)	0.5444 (8)	0.1596 (6)	0.083 (5)	C(K5)	0.5398 (11)	0.4845 (10)	0.2073 (3)	0.125 (7)
C(B5)	−0.0855 (7)	0.5356 (10)	0.1051 (4)	0.069 (4)	C(K6)	0.4601 (13)	0.4495 (10)	0.2470 (5)	0.107 (6)
C(B6)	0.0097 (10)	0.4806 (6)	0.1026 (5)	0.058 (3)	C(L1)	0.2421 (15)	0.4200 (7)	0.3351 (7)	0.048 (3)
C(C1)	−0.0060 (6)	0.2314 (11)	0.0703 (6)	0.036 (3)	C(L2)	0.1522 (12)	0.4772 (13)	0.3267 (4)	0.065 (4)
C(C2)	0.0248 (8)	0.2404 (7)	0.0082 (6)	0.046 (3)	C(L3)	0.1002 (8)	0.5427 (10)	0.3690 (7)	0.084 (5)
C(C3)	−0.0443 (9)	0.2808 (7)	−0.0272 (3)	0.058 (3)	C(L4)	0.1382 (12)	0.5510 (7)	0.4197 (6)	0.102 (6)
C(C4)	−0.1444 (6)	0.3123 (9)	−0.0006 (5)	0.075 (4)	C(L5)	0.2281 (10)	0.4938 (12)	0.4282 (5)	0.112 (6)
C(C5)	−0.1752 (8)	0.3033 (5)	0.0614 (5)	0.075 (4)	C(L6)	0.2801 (10)	0.4283 (10)	0.3859 (8)	0.095 (5)
C(C6)	−0.1061 (9)	0.2628 (9)	0.0969 (3)	0.051 (3)	C(S1)	0.3646 (13)	0.3500 (11)	0.7012 (7)	0.082 (5)
C(D1)	0.1605 (11)	0.0751 (4)	0.0835 (6)	0.033 (2)	C(S2)	0.5687 (19)	0.3272 (16)	0.6833 (9)	0.148 (8)
C(D2)	0.1197 (7)	0.0190 (9)	0.0508 (6)	0.051 (3)	C(S3)	0.5180 (19)	0.3687 (17)	0.5117 (10)	0.163 (9)
C(D3)	0.1762 (9)	−0.0670 (9)	0.0284 (3)	0.061 (4)	C(S4)	0.612 (2)	0.515 (2)	0.436 (1)	0.22 (1)
C(D4)	0.2734 (9)	−0.0967 (4)	0.0389 (5)	0.070 (4)	C(S5)	0.406 (4)	0.392 (3)	0.636 (2)	0.36 (2)

[a] Phenyl rings were refined as rigid groups (see text). [b] For O and C atoms U is the isotropic displacement parameter. For Pt, P, and F atoms it is one-third of the trace of the orthogonalized U_{ij} tensor.

= not measurable, 1 P^3, 1 P^4, 1 P^5], 2.5 (broad signal, $1P^6$); ^{195}Pt, δ = −3305 [dd, $^1J(Pt^1P^1)$ = 4105, $^1J(Pt^1P^6)$ = 3242, $^1J(Pt^1Pt^2)$ = 2150, 1 Pt^1], −2893 (broad signal, 1 Pt^2), −2920 [t, $^1J(Pt^3P^4)$ = $^1J(Pt^3P^5)$ = 2872, 1 Pt^3]. If the solution is warmed up and the excess gas is allowed to escape, the starting material, $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$, is obtained. This was confirmed by the ^{31}P spectrum.

Reaction of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ with H_2S. H_2S gas was bubbled through a solution of $[Pt_3(HCCH)(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CH_2Cl_2 (10 mL) for 1 min. The product was identified as $[Pt_3H(\mu_3\text{-S})(\mu\text{-dppm})_3][PF_6]$ by its NMR spectra.

X-ray Analysis of $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCOEt})(CO)(\mu\text{-dppm})_3][PF_6]_2$ [7b$(PF_6)_2$]. The specimen was a transparent plate of dimensions 0.36 × 0.48 × 0.08 mm mounted in air. All crystallographic measurements were made on an Enraf-Nonius CAD4F diffractometer using Mo X-rays and a graphite monochromator. The dimensions of the reduced triclinic cell (Table III) are based on a least-squares fit to the setting angles of 22 reflections with $12 \le \theta \le 16°$. The intensities of 19 892 reflections with $15 \le h \le 15$, $15 \le k \le 15$, $25 \le l \le 25$, and $\theta < 24°$ were measured from $\omega/2\theta$ scans and corrected for Lp effects and absorption.[21] Merging equivalent intensities gave values for 14 362 unique reflections and R_{int} = 0.030. The analysis was carried out by using the 9028 unique intensities with $I > 2\sigma(I)$. During data collection, the intensities of two standard reflections showed only random fluctuations of ±3% about their mean values.

The structure was solved successfully in the space group $P\bar{1}$ by Patterson and Fourier methods and refined by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. In the final calculations, fixed contributions were added to the structure factors to account for the scattering of all 72 hydrogen atoms: they were assigned an isotropic displacement parameter 20% greater than that of the parent carbon atom and their positions were deduced geometrically, assuming C–H = 0.96 Å. For Pt, P, and F atoms, anisotropic displacement parameters were refined, whereas isotropic displacement parameters were adjusted for O and C atoms. The 12 phenyl rings were refined as planar rigid groups with C–C = 1.38 Å and ∠C–C–C = 120°. Because of program limitations, the parameters of the cation and those of the two anions were refined in alternate full-matrix least-squares cycles. In the later stages of refinement, five regions of electron density attributed to occluded solvent were observed; distinct molecules of the solvent, which is probably acetone, could not be identified crystallographically, and the five sites were therefore included as carbon atoms in the model, thereby reducing R and R_w from 0.045 and 0.054 to the final values of 0.043 and 0.049. The entries in Table III make no allowance for the unidentified solvent. Parameter shifts were <0.040 of the corresponding esd in the final refinement cycle. Function values in the final difference synthesis were between −1.3 and +1.6 e Å^{-3}. Mean $w\Delta^2$ showed no consistent variation with $|F_o|$ but increased at low $(\sin \theta)/\lambda$. Fractional coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms are presented in Table IV.

Neutral-atom scattering factors and complex anomalous dispersion corrections were taken from ref 22. Calculations were performed on a Gould 3227 32-bit minicomputer using the locally developed GX program package.[23]

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Supplementary Material Available: Listings of atomic coordinates and isotropic displacement parameters for hydrogen atoms (Table SV), anisotropic displacement parameters (Table SVI), and bond lengths and angles (Table SVII) (6 pages); a listing of observed and calculated structure factors (Table SVIII) (29 pages). Ordering information is given on any current masthead page.

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(21) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99 and 149.

(23) Mallinson, P. R.; Muir, K. W. *J. Applied Crystallogr.* **1985**, *18*, 51.

Complexation of Metal Cations by the Cryptand 1,1′-(1,4,10-Trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene

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Multinuclear NMR spectroscopy has been employed to study the configuration adopted in solution by the 3-fold nonsymmetrically bridged ferrocene-containing cryptand 1,1′-(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene when complexed with the range of metal cations Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}. The results show unambiguously that formation of complexes of 1:1 stoichiometry involves coordination of the cations with a cis configuration of the amide carbonyl groups. This results in the creation of a plane of symmetry in the complex, which is not present in the host. The guest cations are selectively coordinated on the short side of the host macrocycle.

Introduction

Cryptands are known to complex metal cations, often selectively.[1] Incorporation of a metallocene unit within the molecular framework of the cryptand yields ionophores capable of forming host–guest complexes within which metal–metal interaction is possible. Thus, ferrocene-containing cryptates have been shown to have useful electrochemical and chromogenic properties[2,3] and hence have potential as molecular sensors.[4] The ferrocene-containing cryptand 1,1′-(1,4,10-trioxa-7,13-diazacyclopentadecane-7,13-diyldicarbonyl)ferrocene (1) is 3-fold

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(1) Lehn, J. M. *Pure Appl. Chem.* **1978**, *50*, 871.

(2) Hall, C. D.; Sharpe, N. W.; Danks, I. P.; Sang, Y. P. *J. Chem. Soc., Chem. Commun.* **1989**, 419.

(3) Hall, C. D.; Danks, I. P.; Sharpe, N. W. *J. Organomet. Chem.* **1990**, *390*, 227.

(4) Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 409.

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