Reaction of 7b with CO. A slow stream of carbon monoxide was bubbled for ca. 1 min through a solution of **7b** (71 mg, 0.14 mmol) in 0.5 mL of C_6D_6. The solution turned yellow, and the carbonyl complex **13** as well as the unsaturated alkyne $HC{\equiv}C\text{-}C(CH_3){=}CH_2$ could be detected by IR and ^1H NMR spectroscopy.

Preparation of *trans*-[RhCl(=CCH=CMe$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (14). A solution of **7b** (97 mg, 0.19 mmol) in 10 mL of diethyl ether was treated at room temperature dropwise with 1 mL of a 0.2 M solution of HBF_4 in OEt_2. A violet solid precipitated, which was filtered off, repeatedly washed with ether, and dried in vacuo: yield 107 mg (95%); dec at 76 °C. Anal. Calcd for $C_{23}H_{49}BClF_4P_2Rh$: C, 45.01; H, 8.21. Found: C, 44.73; H, 8.40. ^1H NMR (CD_2Cl_2, 90 MHz, −60 °C): δ 3.93 (s, $-CH{=}$), 2.78 (m, $PCHCH_3$), 2.45 and 2.08 (both s, $=C(CH_3)_2$), 1.36 (dvt, $N = 14.6$, $J(HH) = 7.3$ Hz, $PCHCH_3$).

Reaction of 14 with NaH. A suspension of **14** (71 mg, 0.12 mmol) in 10 mL of ether was treated at room temperature with NaH (20 mg, 0.85 mmol). After being stirred for 10 min, a blue-green solution was obtained, which was filtered and concentrated in vacuo. The residue was washed with pentane (−30 °C) and shown by ^1H NMR spectroscopy to be **7b**, yield 50 mg (82%).

X-ray Structural Analysis of 7b. Single crystals were grown from pentane at 25 °C. Crystal data collection parameters are summarized in Table III. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 96.05%. The structure was solved by direct methods (SHELXS-86). There are two crystallographically independent molecules in the unit cell. Atomic coordinates (see Table IV) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H = 0.95 Å) and were refined by the riding method. For other details, see Table III.

X-ray Structural Analysis of 11b. Single crystals were grown from benzene/pentane with excess pyridine in 8 h at 25 °C. Crystal data collection parameters are summarized in Table III. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 95.9%. The structure was solved by direct methods (SHELXS-86). Atomic coordinates (see Table V) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of all hydrogen atoms except the metal-bound hydride were calculated according to ideal geometry (distance C–H = 0.95 Å) and were used for structure-factor calculations in the last full-matrix least-squares refinement. For other details, see Table III.

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Supplementary Material Available: SCHAKAL drawings of complexes **7b** and **11b**, showing the atom-numbering schemes, and tables of bond distances, bond angles, positional parameters, and general anisotropic displacement parameter expressions (23 pages). Ordering information is given on any current masthead page.

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Models for Chemisorption: Fluxional Cyanide Adducts of Trinuclear Platinum and Palladium Clusters

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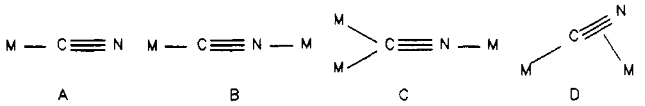
Reaction of the clusters $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$; **1a**, M = Pt; **1b**, M = Pd) with cyanide gave the adducts $[M_3(CN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ (**2a**, M = Pt; **2b**, M = Pd) in which the carbonyl is asymmetrically bridging and the cyanide is terminal. Solvated crystals of complex **2a**[PF$_6$] have been characterized by X-ray diffraction [crystal data for **2a**[PF$_6$]·Me$_2$CO·H$_2$O: $P\bar{1}$, $a = 11.3731$ (6) Å, $b = 15.4180$ (15), $c = 24.0242$ (29) Å, $\alpha = 79.839$ (9)°, $\beta = 82.117$ (7)°, $\gamma = 81.422$ (6)°, $V = 4073.5$ (7) Å^3, $Z = 2$, $R = 0.047$, $R_w = 0.066$]. Complexes **2** are fluxional in solution, with cyanide migrating rapidly around the M_3 triangle even at −90 °C. Thus, they provide good models for the structure and mobility of terminal cyanide on a metal surface. However, the binding mode of cyanide to the metal triangle appears to be different from that of CN on a Pd(111) or Pt(111) surface.

The binding of cyanide to metal surfaces has been of much recent interest, but the precise mode of attachment has been difficult to determine.[1] Because many ligands bind in similar ways to clusters and surfaces, a study of cyanide binding in clusters might aid assignments. Although cyanide is known to bond in transition metal complexes in the forms A–D (of which A and B are most



common), there are remarkably few cyanide cluster complexes and, to our knowledge, no coordinatively unsaturated clusters to act as models for chemisorbed cyanide.[2,3]

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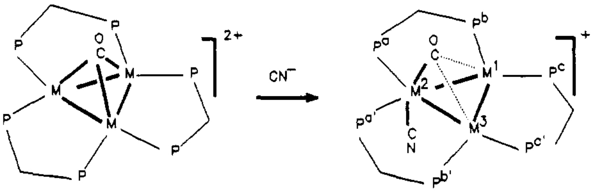
Table I. Cyanide and Carbonyl IR Data (cm^{-1}) for Complexes 2

complex	no.	ν(CO)	ν(^{13}CO)	ν(CN)	ν(^{13}CN)
$[Pt_3(\mu_3\text{-CO})]^{2+}$	**1a**	1765			
$[Pt_3(\mu_3\text{-CO})(CN)]^+$	**2a**	1807		2114	
$[Pt_3(\mu_3\text{-}^{13}CO)(CN)]^+$	**2a***		1769	2114	
$[Pt_3(\mu_3\text{-CO})(^{13}CN)]^+$	**2a****	1807			2066
$[Pd_3(\mu_3\text{-CO})]^{2+}$	**1b**	1860			
$[Pd_3(\mu_3\text{-CO})(CN)]^+$	**2b**	1823		2133	
$[Pd_3(\mu_3\text{-}^{13}CO)(CN)]^+$	**2b***		1784	2133	
$[Pd_3(\mu_3\text{-CO})(^{13}CN)]^+$	**2b****	1823			2095

Chemisorbed cyanide on Pd(111) and Pt(111) is thought to be bound parallel to the surface,[1a,1b] perhaps in bonding mode D,[3] but calculations for cyanide on Ni(111) strongly suggest that cyanide should be perpendicular to the surface and bound through the carbon atom only.[1c] This article reports the first cyanide adducts of coordinatively unsaturated clusters; the new complexes provide a good model for the proposed perpendicular surface bonding mode of cyanide, and it is shown that terminal cyanide can migrate rapidly between metal centers.

Reaction of the clusters $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$; **1a**, M = Pt; **1b**, M = Pd),[4] in acetone solution at −78 °C, with 1 equiv. of cyanide followed by warming to room temperature gave the corresponding adducts $[M_3(CN)(\mu_3\text{-CO})(\mu\text{-dppm})_3]^+$ (**2a**, M = Pt; **2b**, M = Pd)[5] according to eq 1.



(1)

1a, M = Pt
1b, M = Pd

2a, M = Pt
2b, M = Pd

The single-crystal X-ray structure determination of **2a** as the PF_6^- salt (Figure 1) defined the structure accurately but could not distinguish unequivocally between the cyanide and carbonyl group (vide infra). Therefore, selectively labeled derivatives **2*** (^{13}CO) and **2**** ($^{13}CN^-$) were also prepared and IR analysis (Table I) then clearly indicated the presence of *bridging* carbonyl and *terminal* cyanide groups in both **2a** and **2b**. The structure determination, taken together with the IR analysis, reveals that the cyanide ligand in **2a** is terminally bonded to Pt(2) [Pt(2)–CN = 2.07 (2) Å, Pt(2)–C–N = 177 (2)°] with the Pt(2)–C–N vector nearly parallel with the normal to the Pt_3 plane (intervector angle 10.1°) such that the Pt(1)–C(CN) and Pt(3)–C(CN) distances of 3.27 (2) and 3.56 (2) Å are clearly nonbonding. The carbonyl ligand bridges the Pt_3 triangle in a very asymmetric fashion: the Pt(2)–C(CO) distance of 1.94 (2) Å is very much shorter than the Pt(1)–C(CO) and Pt(3)–C(CO) distances of 2.44 (2) and 2.25 (2) Å.

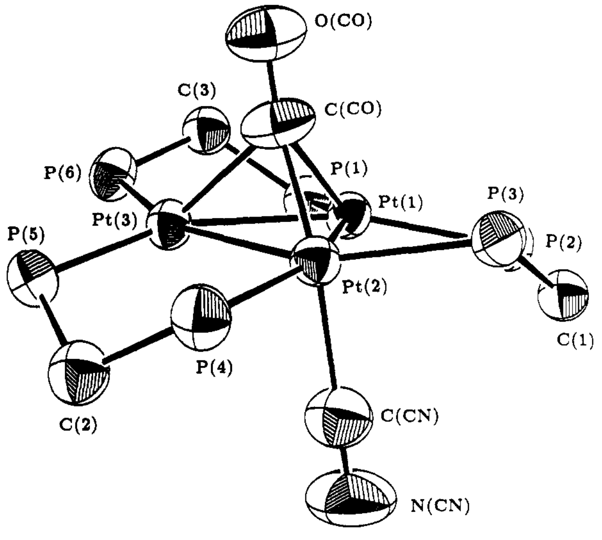
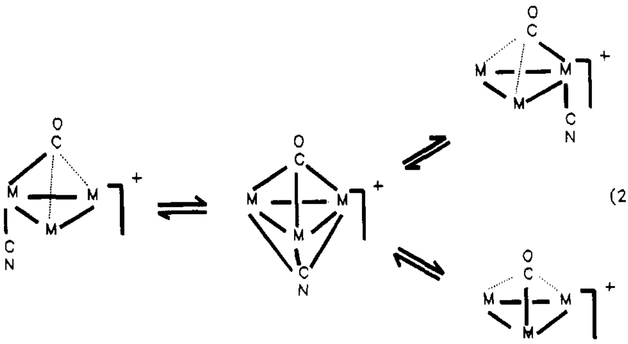


Figure 1. View of the cation **2a**, showing the coordination of the platinum atoms. Probability ellipsoids of 50% are displayed. Hydrogen atoms and phenyl rings are omitted for clarity.

The ground-state structure for **2** has only 2-fold symmetry, and the ^{31}P NMR spectrum is therefore expected to contain three resonances due to dppm phosphorus atoms. However, only a single resonance was observed for **2a** or **2b** at temperatures down to −90 °C, indicating that the cluster cations are fluxional.[5] The ^{13}C NMR spectra, at room temperature or −80 °C, of **2a*** or **2a**** each contained a 1:4:7:4:1 quintet due to coupling to ^{195}Pt, indicating the apparent presence of both triply bridging carbonyl [δ(CO) = 197 ppm, ^2J(PC) = 10, $^1J(^{195}PtC)$ = 636 Hz] and cyanide [δ(CN) = 126.8 ppm, $^1J(^{195}PtC)$ = 427 Hz] ligands, and the spectrum of **2a***** (^{13}CO, ^{13}CN labeled) showed the additional coupling $^2J(^{13}C^{13}C)$ = 32 Hz. These data establish that **2a** is fluxional, with the cyanide ligand migrating rapidly around the Pt_3 triangle as shown in eq 2. Further, the observation of the couplings ^1J(Pt–CO), ^1J(Pt–CN), and ^2J(CO–CN) in the fast fluxionality regime shows that the process occurs without dissociation of either the carbonyl or cyanide ligand from the cluster. It is not possible to distinguish between transition states having μ_2-CN or μ_3-CN groups for the cyanide migration, but eq



(2)

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(5) *Data for* **2a**$[PF_6]\cdot 2Me_2CO$ *are as follows.* Anal. Calcd for $[Pt_3(\mu_3\text{-CO})(CN)(dppm)_3][PF_6]\cdot$2(acetone): C, 45.95; H, 3.63; N, 0.65. Found: C, 45.3; H, 3.8; N, 0.8. FAB MS: *m/e* 1791 [calcd for $Pt_3(CO)(CN)(dppm)_3^+$, *m/e* 1791]. NMR data (multiplicities due to ^{195}Pt couplings omitted): $\delta(^1H)$ = 7.4–6.9 [m, 60 H, Ph]; 5.6 [br/s, 6H, ^3J(PtH) = 42 Hz, CH_2P_2]; $\delta(^{31}P)$ = −20.9 [s, ^1J(PtP) = 3223, ^2J(PtP) = 84, ^3J(PP′) = 182 Hz, dppm]; $\delta(^{195}Pt)$ = −2632 [br t, ^1J(PtP) = 3200 Hz]; $\delta(^{13}C)$ = 197 [dxsept, $^2J(C^aC^b)$ = 32.3, $^2J(C^aP)$ = 9.6, $^1J(C^aPt)$ = 636 Hz, C^aO], 126.8 [d, $^2J(C^aC^b)$ = 32.3, $^1J(C^bPt)$ = 427 Hz, C^bN]. Crystal data for **2a**-$[PF_6]\cdot Me_2CO\cdot H_2O$: $P\bar{1}$, a = 11.3731 (6) Å, b = 15.4180 (15) Å, c = 24.0242 (29) Å, α = 79.839 (9)°, β = 82.117 (7)°, γ = 81.422 (6)°, V = 4073.5 (7) Å^3, Z = 2, R = 0.047, R_w = 0.066. NMR for **2b** in CD_2Cl_2: $\delta(^{31}P)$ = −13.7 [s, dppm]; $\delta(^{13}C)$ = 200.1 [sept, ($^2J(C^aP)$ = 9.2-Hz coupling observed at −40 °C), μ_3-C^aO], 140.4 [sept, $^2J(C^bP)$ = 12 Hz, C^bN].

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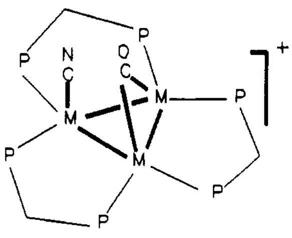
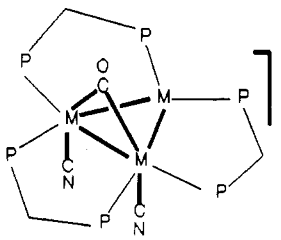
2 shows the simpler mechanism with a μ_3-CN intermediate.

While the complexes 2 have the same structure for M = Pd and Pt, intermediates in their formation from 1 and CN^- at low temperature were different and are characterized as $[Pt_3(CN)(\mu_2\text{-}CO)(\mu\text{-dppm})_3]^+$ (3) and $[Pd_3(CN)_2(\mu_2\text{-}CO)(\mu\text{-dppm})_3]$ (4), respectively, by their low-temperature NMR spectra.[6] These complexes were not fluxional at −40 °C, and for example, 3 gave a ^{13}C resonance for the cyanide ligand which appeared as a 1:4:1 triplet due to $^1J(^{195}PtC)$ = 984 Hz, as expected for a terminal cyanide.[2b,c]


3, M = Pt


4, M = Pd

The above data clearly establish that, in these model complexes, cyanide has a lower tendency than the isoelectronic carbonyl to act as a μ_2-C- or μ_3-C-bonded ligand (or a higher tendency to act as a terminal ligand) on the Pd_3 or Pt_3 triangle. No evidence for the bonding mode D, thought to be present on the Pd(111) or Pt(111) surface,[1] was found; this bonding mode, in which cyanide acts as a 4-electron ligand, is theoretically possible since the clusters 2 are still coordinatively unsaturated (44e clusters). Instead, the terminal cyanide bonding can be considered to model cyanide adsorbed on Ni(111) and several other metal surfaces.[1] The very easy mobility of terminal cyanide between metal centers, established here for the first time, suggests that a similar surface mobility can be expected and indicates that there is only a small energy difference between terminal and bridging cyanide bonding modes.

Acknowledgment. We thank the NSERC (Canada), NATO, and the SERC (U.K.) for financial support and the Kenyan High Commission for a studentship (to B.N.M.).

Supplementary Material Available: Text giving crystallographic details and tables of hydrogen atom parameters, anisotropic displacement parameters, and bond lengths and angles (8 pages). Ordering information is given on any current masthead page.

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[6] NMR for 3 in CD_2Cl_2 at −40 °C: $\delta(^{31}P) = -25.9$ [m, $^3J(P^aP^c) = 212$, $^2J(P^aP) = 19$, $^1J(PtP^a) = 3380$ Hz, P^a], −43.7 [m, $^3J(P^aP^c) = 212$, $^2J(P^bP^c) = 13$, $^1J(PtP^c) = 2240$ Hz, P^c], −61.1 [t, $^2J(P^bP^c) = 12.8$, $^1J(PtP^b) = 2920$, $^2J(PtP^b) = 412$, $^3J(P^bP^{b'}) = 228$ Hz, P^b]; $\delta(^{13}C) = 232.3$ [d, $^2J(C^aC^b) = 20$, $^1J(PtC^a) = 860$, $^2J(PtC^a) = 130$ Hz, μ-C^aO], 131.7 [d, $^2J(C^aC^b) = 20$, $^1J(PtC^b) = 984$ Hz, C^bN]. NMR for 4 in CD_2Cl_2 at −40 °C: $\delta(^{31}P) = 13.8$ [t, $^2J(P^aP^c) = 26.2$, $^2J(P^aC^a) = 29$ Hz, P^a], 11.8 [t, $^2J(P^bP^c) = 49.8$ Hz, P^b], −0.6 [tt, $^2J(P^bP^c) = 50$, $^2J(P^aP^c) = 26$ Hz, P^c]; $\delta(^{13}C) = 235.3$ [m, $^2J(P^aC^a) = 29$, μ-C^aO], 135.5 [td, $^2J(CP) = 17$, $^2J(C^bC^c) = 42$ Hz, C^bN], 131.7 [td, $^2J(CP) = 12$, $^2J(C^bC^c) = 42$ Hz, C^cN].

Kinetics and Mechanism of Photochemical Substitution Reactions of $Cp_2Fe_2(CO)_4$

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The photochemical reactions of $Cp_2Fe_2(CO)_4$ with various nucleophiles (L) in solution have been studied employing flash photolysis methods. The products of reactions were identified using IR spectroscopy, and formation of monsubstituted products $Cp_2Fe_2(CO)_3L$ were observed. It appears that the L = $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, $P(OBu)_3$, $P(OPh)_3$, PPh_3, $P(i\text{-}Pr)_3$, PCy_3, $PPh_2(C_6F_5)$, $PPh(C_6F_5)_2$, and CH_3CN derivatives occur as a mixture of cis and trans isomers in solution, whereas the PEt_3, PPr_3, PBu_3, $P(t\text{-}Bu)_3$, $P(o\text{-tolyl})_3$, $P(\text{mesityl})_3$, and 1-hexene derivatives are present as predominantly one isomer. The derivatives of L = $P(\text{mesityl})_3$, $PPh_2(C_6F_5)$, $PPh(C_6F_5)_2$, $P(C_6F_5)_3$, and 1-hexene are not stable at room temperature. For L = $P(OMe)_3$, both $Cp_2Fe_2(CO)_3P(OMe)_3$ and the disubstituted product $[CpFe(CO)P(OMe)_3]_2$ were observed at room temperature after a single flash photolysis of $Cp_2Fe_2(CO)_4$ with $P(OMe)_3$. An intermediate, possibly $Cp_2Fe_2(CO)(\mu\text{-}CO)_2(\eta^2\text{-}HC{\equiv}CBu)$, was observed as a precursor to the alkyne insertion product, $Cp_2Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}\sigma{:}\eta^3\text{-}HC{=}CBuCO)$, in the flash photolysis of $Cp_2Fe_2(CO)_4$ with 1-hexyne. The kinetics and mechanism of reactions of $Cp_2Fe_2(\mu\text{-}CO)_3$ with various ligands were investigated via studies of reaction rate law, determination of activation parameters, and analysis of kinetics data in terms of linear-free-energy relationships. Two possible reaction pathways, i.e., an associative bimolecular pathway and a nonassociative pathway involving an intramolecular bridge-cleavage step, are discussed. A consistent rate enhancement effect by an unsubstituted phenyl ring or oxygen atom in the ligand is evident in the data.

Introduction

The photochemical reactions of $Cp_2Fe_2(CO)_4$ ($Cp(CO)Fe(\mu\text{-}CO)_2Fe(CO)Cp$) continue to attract attention.[1-7] It has been established that photolysis of $Cp_2Fe_2(CO)_4$ generates 17-electron radicals, $Cp(CO)_2Fe^\bullet$, via homolysis of

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