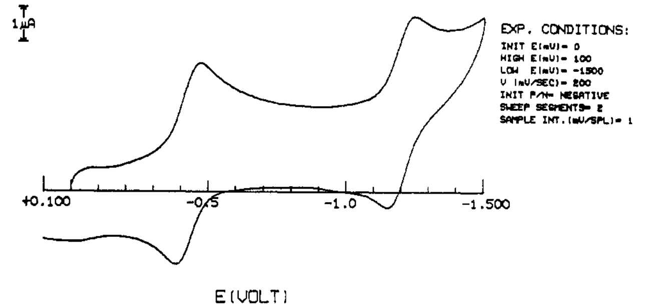

Figure 2. Cyclic voltammogram of complex **2b** measured in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate at a Pt working electrode using a scan rate of 200 mV s^{-1}. Reference is Ag/AgCl.

$C_5R_5)_2(CO)_2]$ (R = H, Me), which have terminal carbonyl groups.[2,9]

Treatment of ethereal solutions of 1 with either HBF_4 or CF_3SO_3H led to the precipitation of very dark metallic green microcrystals of $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^+X^-$ (**2a**, X = BF_4; **2b**, X = CF_3SO_3). Solutions of **2a** in nitromethane had conductivities associated with 1:1 electrolytes. Intense red solutions of 2 in dichloromethane exhibit a band at 1769 cm^{-1} in their IR spectra indicative of a triply bridging carbonyl group, and no metal hydride absorptions could be detected in the ^1H NMR spectrum.[10] This was an unexpected result since protonation of complexes of the type $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_{2n}]$ generally affords the hydrido-bridged cations $[M_2(\mu\text{-}H)(\eta^5\text{-}C_5R_5)_2(CO)_{2n}]^+$.[11]

An X-ray structure of **2b** (Figure 1) revealed it to consist of an approximately equilateral triangle of palladium atoms (mean Pd–Pd = 2.63 Å) with each face capped with a triply bridging carbonyl group and the three corners capped by $\eta^5\text{-}C_5Me_5$ ligands.[12] The molecule is bisected by a crystallographic mirror plane that lies perpendicular to the plane defined by the triangle of palladium atoms, passes through C3 and C6 of the pentamethylcyclopentadienyl group, and contains Pd1 and the two carbonyl groups. This mirror plane also orthogonally bisects the sulfur–carbon bond of the counterion which as a consequence has disorder between the CF_3 and SO_3 groups.

This Pd_3^+ cluster belongs to the family of the Fischer–Palm and related molecules $[Ni_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}CO)_2]$ (R = H, Me; charge = 1+, 0, 1−) studied extensively by Dahl.[13] It represents the first isolated and structurally characterized example of a 48-valence-electron cluster of this particular type, although it may be compared to other 48e clusters such as $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$.[14]

Cyclic voltammograms of 2 reveal two discrete redox processes (Figure 2). A reversible reduction is encountered at −0.43 V vs. Ag/AgCl and a second less reversible reduction at −1.22 V.

These data may imply facile electrochemical interconversions to the 49- and 50-valence-electron clusters. The partial reversibility of the second reduction wave could also indicate that the putative anion $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^-$ is less stable at room temperature than its nickel analogue. This is not an unexpected result since the poorer back-bonding ability of carbonyl groups on palladium compared to nickel would destabilize the electron-rich palladium cluster relative to its nickel counterpart.[15]

The isolation of 1 and its unusual reactivity with acids presage a rich and diverse chemistry for the (pentamethylcyclopentadienyl)palladium system. Preliminary studies of 1 indicate that carbonyl groups are readily lost from the palladium leading to unsaturation and cluster formation. We will describe these results in due course.

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Supplementary Material Available: Tables of experimental details, atomic coordinates, thermal parameters, and bond lengths and angles (12 pages); a listing of structure factors (32 pages). Ordering information is given on any current masthead page.

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Fluxionality of Phosphine and Phosphite Ligands on a Coordinatively Unsaturated Platinum Cluster Complex

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Summary: The complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$) adds phosphine or phosphite ligands (L) to give $[Pt_3(\mu_3\text{-}CO)L(\mu\text{-}dppm)_3]^{2+}$, which exhibit fluxional behavior involving migration of the ligand L around the triangular face of the cluster. This is the first time that such fluxionality involving phosphorus donor ligands has been observed, and the ease of reaction is attributed to the coordinative unsaturation of the clusters.

Phosphorus donor ligands are of major importance in metal cluster chemistry, but there are no known examples of easy migration of such ligands between metal centers; even phosphine ligand migration between coordination sites on the same metal atom is rare.[1-5] We are therefore

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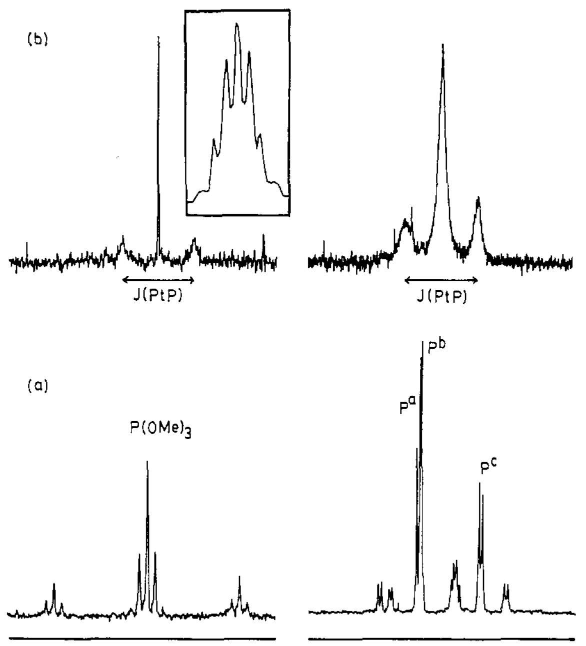


Figure 1. $^{31}P\{^1H\}$ NMR spectra (121.4 MHz) for **1a**: (a) at −43 °C and (b) at +59 °C (the inset shows an expansion of the central part of the $P(OMe)_3$ resonance, indicating the septet structure due to coupling to the six dppm phosphorus atoms).

prompted to report that several phosphine and phosphite ligands (L) add to the coordinatively unsaturated cluster cation $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$)[6] to give adducts $[Pt_3(\mu_3\text{-}CO)L(\mu\text{-dppm})_3]^{2+}$ (**1**) in which the added ligand L can migrate about the triangular face of the cluster.

The adducts **1** were stable compounds as the PF_6^- salts and could be isolated in analytically pure form when L = $P(OMe)_3$, (**1a**),[7] $P(OEt)_3$ (**1b**), $P(OPh)_3$ (**1c**), or PMe_2Ph (**1d**).[7] With the bulkier ligands L = $PMePh_2$ (**1e**), or PPh_3 (**1f**), adduct formation was reversible, and with L = PH_2Ph (**1g**),[7] the adduct could be studied in solution only at temperatures of −60 °C or lower, since loss of H_2 occurred on warming.

The nature of the fluxionality is shown in the equation, and some evidence is shown in Figures 1 and 2. The ^{31}P NMR spectra of **1a** at −43 and +59 °C are shown in Figure 1.[7] At low temperature, three resonances are observed for the dppm phosphorus atoms P^a, P^b, and P^c while the $P(OMe)_3$ resonance appears as a 1:4:1 triplet [due to $^1J(PtP)$ = 4910 Hz] of 1:8:18:8:1 quintets [due to $^2J(PtP)$ = 420 Hz]. At high temperature a single dppm resonance is observed and the $P(OMe)_3$ resonance appears as a sharp septet [$J(PP)$ = 10 Hz] with broad ^{195}Pt satellites [$J(PtP)$ ≈ 1900 Hz]. At higher temperature the satellites are sharper [for example in DMF solution at 100 °C $J(PtP)$ = 1910 Hz], but some decomposition occurs. The calculated value of $J(PtP^L)$ for rapid fluxionality according to eq 1 is $J_{obsd}(PtP^L) \approx {}^1/_3 \times 4910 + {}^2/_3 \times 420 = 1917$ Hz, in reasonable agreement with the observed value. When

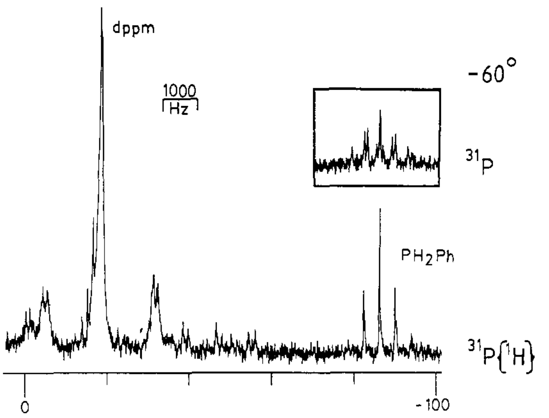
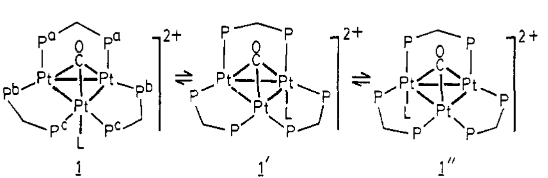


Figure 2. $^{31}P\{^1H\}$ NMR spectra (121.4 MHz) for **1g** at −60 °C. The inset shows the ^1H-coupled ^{31}P resonance of the PH_2Ph ligand, with extra triplet splitting due to $^1J(PH)$ = 370 Hz.

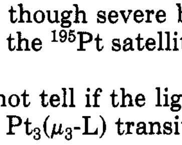


(1)

free $P(OMe)_3$ was present in solution, no exchange between free and complexed $P(OMe)_3$ occurred. This, and the observation of $J(PP)$ and $J(PtP)$ coupling for coordinated $P(OMe)_3$ in the fast exchange regime, proves that the fluxionality is an intramolecular process.

This ligand migration is remarkably easy in complex **1g**, and fluxionality is rapid even at −60 °C (Figure 2).[7] The PH_2Ph resonance in the ^{31}P NMR spectrum appears as a 1:4:7:4:1 quintet (a 1:12:49:84:49:12:1 septet is expected, but the weak outer lines are not observed[8]) with $J_{obsd}(PtP)$ = 936 Hz and fluxionality is not completely frozen out even at −90 °C, though severe broadening of the dppm resonance and the ^{195}Pt satellites of the PH_2Ph resonance is observed.

We cannot tell if the ligand migration involves a $Pt_2(\mu_2\text{-}L)$ or a $Pt_3(\mu_3\text{-}L)$ transition state, **2** or **3**, respectively,



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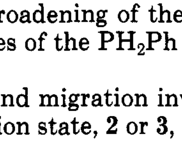

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but the low activation energy for fluxionality of **1g** opens up the possibility that stable complexes with such functional groups might be prepared. This first observation of phosphorus donor ligand fluxionality is almost certainly a result of the coordinative unsaturation of the clusters **1** and provides a good example of the high reactivity of such clusters.[8]

Acknowledgment. We thank NSERC (Canada) for financial support.

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[7] Typical spectroscopic data. **1a**: ^{31}P NMR [in $(CD_3)_2CO$ (referenced to H_3PO_4) at −43 °C, multiplicities are due to $J(PP)$ coupling only] δ −10.8 [d, $^3J(P^aP^c)$ = 170 Hz, $^1J(PtP)$ = 3930 Hz, P^a], −12.1 [s, $^1J(PtP)$ = 3080 Hz, $^3J(P^bP^{b\prime})$ = 150 Hz, P^b], −35.6 [d, $^3J(P^aP^c)$ = 170 Hz, $^1J(PtP)$ = 2500 Hz, P^c], 100.3 [s, $^1J(PtP)$ = 4910 Hz, $^2J(PtP)$ = 420 Hz, $P(OMe)_3$]; ^{31}P NMR (at 59 °C in CD_3OD) δ −20.1 [s, $^1J(PtP)$ ≈ 3250 Hz, P(dppm)], 98.6 [septet, $J(PtP)$ ≈ 1900 Hz, $J(PP)$ = 10 Hz, $P(OMe)_3$]; IR (Nujol) $\nu(CO)$ 1780 cm^{-1}. **1d**: ^{31}P NMR [at −43 °C in $(CD_3)_2CO$] δ −13.9 [d, $^3J(P^aP^c)$ = 170 Hz, $^1J(PtP)$ = 3800 Hz, P^a], −13.6 [s, $^1J(PtP)$ = 3070 Hz, $^3J(P^bP^{bl})$ = 150 Hz, P^b], −42.5 [d, $^3J(P^aP^c)$ = 170 Hz, $^1J(PtP)$ = 2640 Hz, P^c], −35.6 [s, $^1J(PtP)$ = 2800 Hz, $^2J(PtP)$ = 186 Hz, PMe_2Ph]; IR $\nu(CO)$ 1774 cm^{-1}. **1g**: ^{31}P NMR [at −60 °C in $(CD_3)_2CO$] δ −19.3 [s, $^1J(PtP)$ = 3293 Hz, $^3J(PP)$ = 167 Hz, P(dppm)], −88.4 [s, $J(PtP)$ = 936 Hz, $J(PC)$ = 85 Hz, $^1J(PH)$ = 370 Hz, PH_2Ph]; ^{13}C NMR δ 199 [d, $^2J(PC)$ = 85 Hz, $^1J(PtC)$ = 684 Hz, CO]. Note that the normal value of $^1J(PH)$ = 370 Hz for **1g** is evidence against any agostic PHPt interaction.

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