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Dynamical Skeletal Rearrangements in Transition-Metal Clusters. Evidence for Unusually Facile Metal–Metal Bond Reorganization in $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2$

Sir:

The types of molecules that exhibit stereochemically dynamical behavior range from the very simple to the most complex.[1] Recent studies have shown that even some high-nuclearity transition-metal-cluster compounds undergo facile skeletal rearrangements.[2] In our recent studies we have synthesized a series of phosphine-substituted platinum–osmium carbonyl cluster compounds. In this report we wish to describe a new member of this series that has been found to exhibit a very pronounced and unusually facile skeletal rearrangement.

The reaction of $Os_3(CO)_9(\mu_3\text{-}S)_2$[3] with $Pt(PMe_2Ph)_4$ in CH_2Cl_2 solvent at 25 °C under a CO atmosphere for 16 h gives a 18% yield of the compound $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**1**).[4] The molecular structure of **1** was established by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of the molecule is shown in Figure 1.[5] The structure is very similar to that of the related molecules $PtOs_3(CO)_{11-n}(PPh_3)_n(\mu_3\text{-}S)_2$ (n = 1, 2).[6] The cluster consists of an open triangular cluster of three osmium atoms with a $Pt(PMe_2Ph)_2$ moiety bridging one of the two osmium–osmium bonds. The Pt···Os(3) distance at 3.771 (1) Å is clearly nonbonding. The four bonding distances, Pt–Os(1) = 2.936 (1) Å, Pt–Os(2) = 2.789 (1) Å, Os(1)–Os(2) = 3.027 (1) Å, and Os(1)–Os(3) = 2.798 (1) Å, are similar to those found in the PPh_3 derivatives.[7] The principal difference between the PPh_3 derivatives and **1** is that in **1** both phosphine ligands are coordinated to the platinum atom, and since the molecule contains no symmetry they are inequivalent. The inequivalence was confirmed by the observation of two resonances, δ = 2.93 and −14.70 (vs. H_3PO_4), in the ^{31}P NMR spectrum that are appropriately coupled to each other and to the naturally abundant ^{195}Pt nucleus.[4] An additional consequence of the absence of symmetry is that all four methyl groups are inequivalent. However, the room-temperature ^1H NMR spectrum shows only two resonances, δ = 2.26 and 1.72, that are appropriately coupled to the ^{31}P and ^{195}Pt nuclei.[4] The absence of four separate methyl resonances suggested the possibility of a dynamical averaging process, and this was confirmed by measurements at low temperature. Spectra of the methyl region at several temperatures are shown in Figure 2. At the lowest

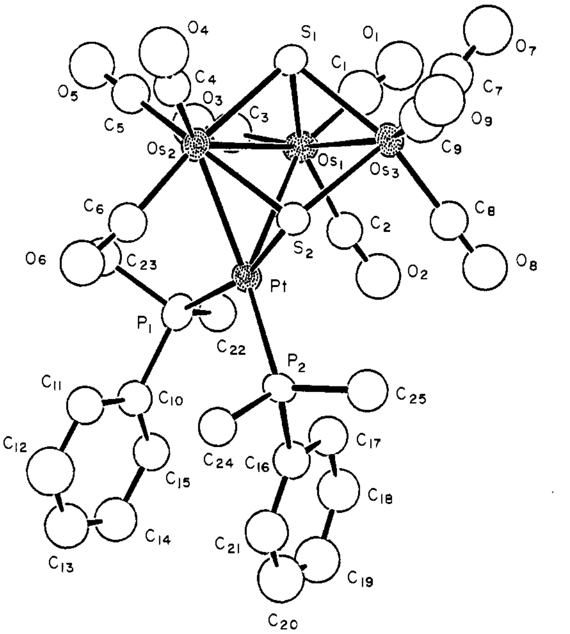

Figure 1. Perspective ORTEP drawing of $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**1**) showing 50% probability thermal motion.

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(4) Compound **1** was isolated by TLC on silica gel plates by eluting with a 20%/80% CH_2Cl_2/hexane solvent mixture. $Os_3(CO)_9(\mu_3\text{-}S)_2$ and its mono- and diphosphine substitution products elute ahead of the yellow-orange product **1**. For **1**, IR (ν(CO), cm^{-1}) in hexane solvent: 2075 m, 2056 vs, 2024 s, 1999 m, 1982 w, 1971 s, 1962 m, 1948 w, 1923 w. ^1H NMR (δ) in CD_2Cl_2 at 25 °C: 7.34–6.93 (m, C_6H_5); 2.26 (d, t, CH_3, J_{P-H} = 9.8 Hz, J_{Pt-H} = 29.9 Hz), 1.72 (d, t, CH_3, J_{P-H} = 9.9 Hz, J_{Pt-H} = 32.7 Hz. $^{31}P\{^1H\}$ NMR (δ) in $CDCl_3$: 2.93 (J_{P-P} = 27 Hz, J_{Pt-P} = 3547 Hz), −14.70 (J_{P-P} = 27 Hz, J_{Pt-P} = 3166 Hz). Compound **1** crystallizes with 0.5 mol of hexane solvent. Anal. Calcd: C, 23.98; H, 2.07. Found: C, 23.85; H, 1.96.

(5) Compound **1** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$, with a = 9.533 (4) Å, b = 15.580 (7) Å, c = 24.547 (8) Å, β = 99.87 (3)°, Z = 4, ρ_{calcd} = 2.59 g/cm^3. Intensity data were collected on an Enraf-Nonius CAD4 automatic diffractometer by using Mo Kα radiation and the ω-scan technique. The data were corrected for absorption by using the Gaussian integration method (μ = 147.8 cm^{-1}). The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques and refined by using 2527 reflections ($2\theta \leq 47°$) ($F^2 \geq 3.0\sigma(F^2)$) to the final residuals R_F = 0.034 and R_{wF} = 0.035. All calculations were performed on a Digital Equipment Corp. PDP 11/782 computer using the Enraf-Nonius SDP program library.

(6) Adams, R. D.; Hor, T. S. A.; Horvath, I. T. *Inorg. Chem.* **1984**, *23*, 4733.

(7) Selected interatomic distances (Å) and angles (deg) for **1** are as follows: Pt···Os(3) = 3.771 (1), Os(2)···Os(3) = 3.576 (1), Os(1)–Os(2) = 3.027 (1), Os(1)–Os(3) = 2.798 (1), Pt–Os(1) = 2.936 (1), Pt–Os(2) = 2.789 (1); Os(1)–Pt–Os(2) = 63.78 (3), Pt–Os(2)–Os(1) = 60.47 (3), Pt–Os(1)–Os(2) = 55.75 (2), Pt–Os(1)–Os(3) = 82.22 (3), Os(2)–Os(1)–Os(3) = 75.64 (3).

(8) Variable-temperature NMR spectra of **1** were recorded on a Bruker WH-400 NMR spectrometer operating at 400 MHz by using a 1/1 CH_2Cl_2/CF_2Cl_2 v/v solvent mixture.

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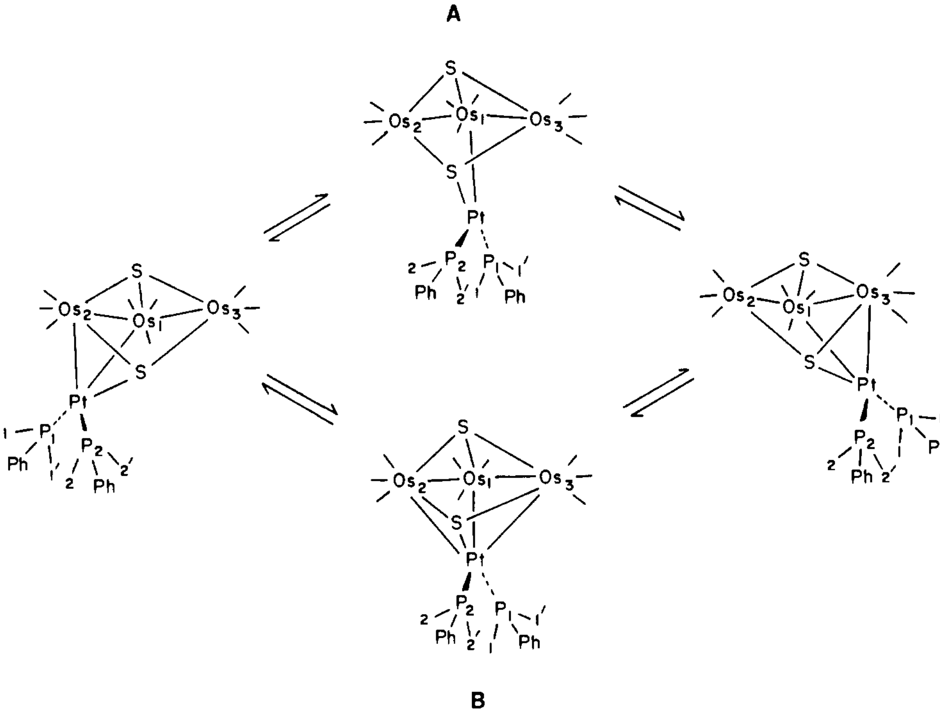
Scheme I



temperature attainable, 155 K, four broad resonances are observed at 2.36, 1.79, 1.70, and 1.47 ppm. As the temperature is raised, the resonances broaden and coalesce in pairs. The resonance at 2.36 ppm averages with the resonance at 1.79 ppm, and the resonance at 1.70 averages with the resonance at 1.47 ppm. The coalescence temperature for the former pair appears to be 167 K. Due to the smaller shift separation of the latter pair, their coalescence temperature occurs a few degrees lower. From the shift separation and coalescence temperature of the former pair, the rate of exchange and free energy of activation were estimated to be $R = 507\ \mathrm{s}^{-1}$ and $\Delta G^{*} = 7.5$ kcal/mol, respectively.[9] At higher temperatures, the averaged resonances sharpen, and at 199 K, coupling to the ^{31}P nuclei is observed in both resonances.

The NMR observations can be interpreted in the following way: (1) the separate resonances for the phosphorus nuclei at room temperature prove that the phosphine ligands do not interchange their environments; (2) the variable-temperature ^{1}H NMR spectra show that the four methyl environments are dynamically averaged in pairs; (3) the presence of coupling to ^{195}Pt in the fast exchange limit proves that the averaging process is an intramolecular one. The process shown in Scheme I generates a dynamically averaged plane of symmetry that does not allow the phosphine ligands to interchange their environments. Two symmetric intermediates, A and B, can be proposed. Intermediate A contains one less platinum–osmium bond than **1**. In A the platinum atom would have a 16-electron configuration. Intermediate B contains one more platinum–osmium bond than **1**. Although the structure of B violates the effective atomic number rule, it does adhere to the skeletal electron pair theory of bonding in clusters.[10,11] In fact, the isoelectronic clusters $Os_4(CO)_{11}L(\mu_3\text{-}S)_2$, L = CO,[12] $CNCH_3$,[13] and PMe_2Ph,[13] adopt this closed B-type structure as their ground state. The B-type structure for **1** might be only a few kilocalories in energy less stable than the observed structure, and this could explain the unusual facility of this rearrangement. It will be interesting to see if interconversions between structures that alternately conform to the EAN rule and the SEP theory produce a general pattern of facile stereochemical dynamics in metal-cluster compounds.

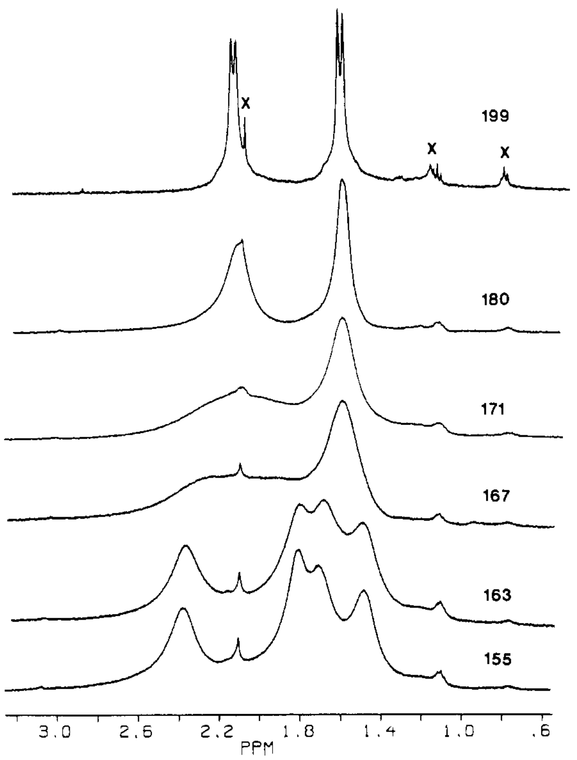


Figure 2. Variable-temperature ^{1}H NMR spectra of the compound $PtOs_3(CO)_9(PMe_2Ph)_2(\mu\text{-}S)_2$ (**1**) in the methyl region recorded at 400 MHz. The small peaks labeled X are due to unidentified trace impurities.

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[9] The resonance shifts of 2.36 and 1.79 ppm observed at 155 K were used in this calculation. Since the resonances are significantly broadened at this temperature and have thus begun to approach one another, a small error will be introduced that will result in the calculated exchange rate being slightly too slow and the free energy of activation being calculated slightly too high.

[10] Electron counting according to the skeletal electron pair theory shows that **1** contains eight pairs of cluster valence electrons. The $PtOs_3S_2$ cluster in structure B has the form of a nido pentagonal bipyramid, which is precisely the structure predicted for eight pairs of cluster valence electrons.

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Supplementary Material Available: Tables of positional and thermal parameters, bond distances and angles, anisotropic thermal parameters, and structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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(Carbonylbis((dialkylamino)phosphido))hexacarbonyldiiron Complexes: Migration of a Carbonyl Group from Iron to Phosphorus

Sir:

The chemistry of $Fe_2(CO)_6$ complexes includes derivatives in which a carbonyl group bridges two nitrogen atoms (e.g. $(RNCONR)Fe_2(CO)_6$, R = C_6H_5[1,2] and CH_3[3]) or two sulfur atoms (e.g. $S_2COFe_2(CO)_6$).[4] This communication describes the first $Fe_2(CO)_6$ complex in which a carbonyl group bridges two phosphorus atoms. Of particular interest is the apparent origin of this phosphorus-bridging carbonyl from a terminal carbonyl group bonded to iron. Such carbonyl migration from iron to phosphorus suggests that phosphido bridges might play an active role in metal carbonyl systems for the catalytic reduction of carbon monoxide.

A suspension of $Na_2Fe(CO)_4\cdot 1.5$(dioxane)[5] in diethyl ether was treated at −78 °C with a stoichiometric amount of (diisopropylamino)dichlorophosphine.[6] After the mixture was stirred for 3 days at room temperature, solvent was removed under reduced pressure. The residue was extracted with *n*-hexane in several portions until the extracts were no longer colored. Concentrating and cooling the filtered *n*-hexane extracts gave orange air-stable crystalline $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (Table I) in 35% yield. Analogous reactions of $Na_2Fe(CO)_4\cdot 1.5$(dioxane) with (dicyclohexylamino)dichlorophosphine[6] and (2,2,6,6-tetramethylpiperidino)dichlorophosphine[6] gave analogous $(R_2NP)_2COFe_2(CO)_6$ derivatives (Table I). However, analogous reactions of $Na_2Fe(CO)_4\cdot 1.5$(dioxane) with significantly less sterically hindered (dialkylamino)dichlorophosphines did *not* give analogous $(R_2NP)_2COFe_2(CO)_6$ compounds; the products from such reactions are still under investigation.

Bridging carbonyl groups in these $(R_2NP)_2COFe_2(CO)_6$ derivatives are indicated by single ν(CO) frequencies in the range 1715–1721 cm^{-1}. In order to determine the configuration of the carbonyl groups in these complexes as well as other important features of their structures, the structure of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ was determined by X-ray diffraction;[7] see Figure 1. The most significant feature of this structure is the carbonyl group (C1–O1 in Figure 1) bridging the two phosphorus atoms (P1–C1 = 1.884 (9) Å, P2–C1 = 1.895 (10) Å, P1–C1–P2 = 84.4 (4)°). The bonding Fe–Fe distance of 2.603 (2) Å is significantly longer than the Fe–Fe distance of 2.488 (1) Å reported[4] for the closely related $S_2COFe_2(CO)_6$ but is close to the 2.62–2.67 Å range found for bis(μ-phosphido)diiron hexacarbonyl complexes[8] (e.g. 2.623 (2) Å reported[9] for $(Ph_2P)_2Fe_2(CO)_6$).

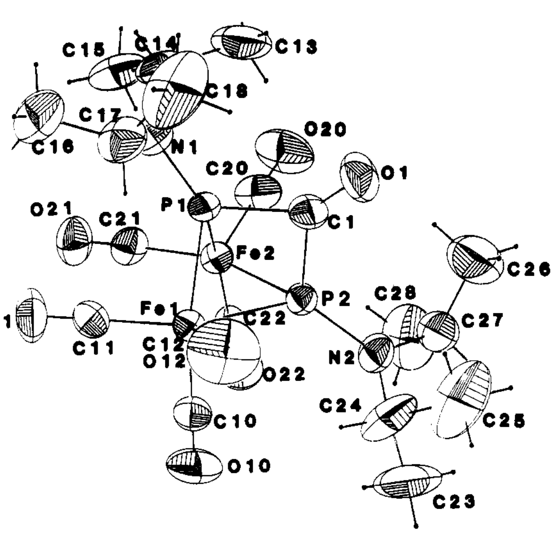
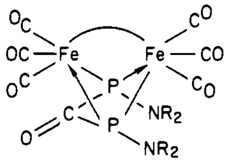
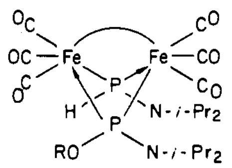


Figure 1. ORTEP diagram of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I, R = isopropyl).

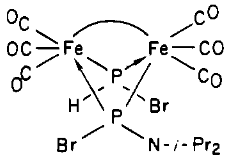
The carbon-13 NMR spectrum of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ exhibits a triplet resonance at δ 209.1 ($|^1J(P\text{–}C)|$ = 83 Hz) assigned to the phosphorus-bridging carbonyl in addition to a singlet terminal carbonyl resonance at δ 212.2.



I



II



III

Several reactions of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ have been investigated. Treatment with methanol or ethanol in boiling toluene for 16 h results in loss of the phosphorus-bridging carbonyl to give $(i\text{-}Pr_2NPOR)(i\text{-}Pr_2NPH)Fe_2(CO)_6$ (II, R = Me or Et). The proton-decoupled phosphorus-31 NMR spectra of these complexes (Table I) reveals a pair of doublets indicating coupled nonequivalent phosphorus atoms. Turning off the proton decoupling splits further the higher field doublet corresponding to the ^1J(P–H) coupling, indicating that one of the phosphorus atoms is directly bonded to hydrogen. Reaction of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ with

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(7) Crystal data for $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I): $Fe_2C_{19}H_{28}N_2O_7P_2$, M_r 570.08, monoclinic crystals, space group $P2_1/n$, a = 10.197 (3) Å, b = 31.403 (13) Å, c = 9.170 (3) Å, β = 112.18 (2)°, V = 2719.1 (17) Å^3, D_{calcd} = 1.392 g/cm^3, Z = 4, anisotropic least-squares refinement (Mo Kα radiation, μ(Mo Kα) = 12.18 cm^{-1}, F(000) = 1176, 3109 observed reflections, R = 0.075 R_w = 0.094).

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