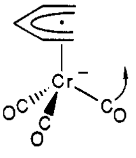
ligand by a pentadienyl anion (or alternatively, add H^- to the arene to generate a cyclohexadienyl anion) yielding VI,



VI

the symmetry has been broken by the formal removal of the sixth metal-bound carbon atom. Without the sixth carbon atom, the metal should have unused orbital density on its right side available for bonding which most likely leads to the upward tilts of the substituents under the pentadienyl edges (e.g., ca. 28° for Fe(2,4-C_7H_{11})$(CO)_2$I).[28] In the present case, the angles observed between the pentadienyl plane perpendicular and the Cl, P(1), and P(2) atoms are 137.6, 135.2, and 105.5°, respectively, corresponding to an upward tilt by P(2) of 30.9°.[31] As suggested earlier for Fe(2,4-C_7H_{11})$(CO)_2$I,[28] this difference is likely to lead to a preference of one ligand (thus far not being a σ-bound, one-electron donor such as Cl, I, or CH_3) for this site. As P(2), the upwardly tilted substituent, now is furthest from being opposite to a pentadienyl carbon atom (cf. ∠C(5)–Cr–Cl = 173.8 (2)°, ∠C(1)–Cr–P(1) = 166.7 (2)°, and ∠C(3)–Cr–P(2) = 150.2 (2)°) and presumably has better access to metal orbitals, its bond could well become stronger. Of course, other effects may also be involved (e.g., steric or σ- vs π-bonding considerations), and indeed, in Fe(2,4-C_7H_{11})$(CO)_2$I, no real difference in the Fe–CO bond distances was observed,[28] while in Fe(2,4-C_7H_{11})-$(PMe_3)_3^+$, a difference of ca. 0.042 (1) Å is present.[29e]

The hydrogen atom positions were refined successfully and yielded an average C–H bond distance of 0.925 (15) Å. As is normal, the endo and exo hydrogen atoms on C(1) and C(5) are bent significantly out of the pentadienyl plane. The bends for the exo hydrogen atoms average 8° toward the chromium atom, while the endo hydrogen atoms average 46° away from the chromium atom. The bonding parameters for the dmpe ligand are reasonable with average P–CH_3, P–CH_2, and C–C distances of 1.823 (4), 1.840 (5), and 1.525 (10) Å, respectively.

Acknowledgment. R.D.E. expresses his gratitude for support of this research from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank a reviewer for helpful crystallographic comments.

Registry No. Cr(2,4-C_7H_{11})$_2$, 80732-73-6; $Cr(dmpe)_3$, 75862-30-5; Cr(CN(t-C_4H_9))$_6$, 61817-78-5; *trans*-$CrCl_2(dmpe)_2$, 86747-55-9; Cr(2,4-C_7H_{11})(Cl)(dmpe), 110313-70-7; K(2,4-$(CH_3)_2C_5H_5$), 74205-98-4; Cr(η^5-2,4-$(CH_3)_2C_5H_5$), 110313-71-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and least-squares plane data for Cr(2,4-C_7H_{11})$_2$ and Cr(2,4-C_7H_{11})(Cl)(dmpe) and hydrogen atom parameters for Cr(2,4-C_7H_{11})$_2$ (5 pages); the structure factor tables (13 pages). Ordering information is given on any current masthead page.

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[30] (a) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2516. (b) Wang, Y.; Angermund, K.; Goddard, R.; Krüger, C. *J. Am. Chem. Soc.* **1987**, *109*, 587.

[31] The respective angles involving the Cr–center of mass vector are more similar, at 127.3, 133.1, and 123.0°, corresponding to a tilt of 7.2°. While this could be taken as an indication that there is actually only little distortion, we suspect the pentadienyl center of mass is not a good criterion for such comparisons. In particular, if one regards a (U) pentadienyl ligand as occupying five of six sites in a hexagon, it is clear that the pentadienyl center of mass is displaced from the equipoint (the center of mass of the hexagon, which would ideally be equidistant from all five or six carbon atoms).

Nonrigidity in $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–4)[1]

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The clusters $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–4) have been synthesized, from $Os_3(CO)_{12}$ and $P(OMe)_3$ at elevated temperatures, and their stereochemical nonrigidity studied by variable-temperature ^{13}C and ^{31}P NMR spectroscopy. All the clusters exhibit carbonyl exchange in toluene, and, furthermore, isomers are present for $Os_3(CO)_{10}[P(OMe)_3]_2$ and $Os_3(CO)_8[P(OMe)_3]_4$ which are in rapid, nondissociative equilibrium. The changes in the NMR spectra can be completely rationalized in terms of two mechanisms. The first, lower energy process is the well-known, pairwise terminal–bridge carbonyl exchange that involves six carbonyl groups rotating in a plane perpendicular to the Os_3 plane. This exchange appears to not occur in those vertical planes that contain a phosphite ligand: the phosphite is probably prevented from entering an axial site for steric reasons. The second, higher energy process involves the $P(OMe)_3$ ligand of an $Os(CO)_3[P(OMe)_3]$ unit in the cluster moving from one equatorial site to the other via a restricted trigonal-twist mechanism; this simultaneously involves axial–equatorial carbonyl exchange. Once again, it is believed the $P(OMe)_3$ ligand never enters an axial position.

Introduction

In 1982 we reported the preparation of $Ru(CO)_{5-n}[P(OMe)_3]_n$ (n = 1–5) by the ultraviolet irradiation of $Ru_3(CO)_{12}$ and excess $P(OMe)_3$ in hexane.[2] In an extension of this study the corresponding reaction of $Os_3(CO)_{12}$ with $P(OMe)_3$ was investigated. Rather than mononuclear products, the clusters $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–6) can be isolated. The clusters with x = 5 and 6 are the most highly substituted derivatives of $Os_3(CO)_{12}$ yet prepared.

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[1] Taken in part from: Alex, R. F. Ph.D. Thesis, Simon Fraser University, 1987.

[2] Alex, R. F.; Pomeroy, R. K. *Organometallics* **1982**, *1*, 453.

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We have reported the synthesis of these latter clusters along with the crystal structure of $Os_3(CO)_6[P(OMe)_3]_6$.[3,4]

During the characterization of $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1-5) by ^{13}C and ^{31}P NMR spectroscopy, it became apparent that the molecules were stereochemically nonrigid and that isomers were present for the cases with x = 2 and 4. At the start of this investigation the only systematic study of nonrigidity in phosphine-substituted derivatives of $Os_3(CO)_{12}$ was that of Johnson, Lewis, and co-workers on $Os_3(CO)_{12-x}[PEt_3]_x$ (x = 1-3).[5] Since the present series showed interesting differences to these molecules and because the more highly substituted derivatives were available, a detailed study of the nonrigid processes in the trimethyl phosphite complexes was carried out. Here we report the details of the investigation of $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1-4).

At the time of the publication of our study on the synthesis and fluxional properties of $Os_3(CO)_7[P(OMe)_3]_5$,[3] Deeming and co-workers published investigations of the nonrigid properties of some di- and trisubstituted phosphine derivatives of $Os_3(CO)_{12}$.[6,7] Some of their findings parallel the observations reported here.

Experimental Section

General Procedure. Unless otherwise stated, purification of solvents, reactions, and manipulation of compounds were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hydrocarbon solvents and THF were refluxed over potassium, distilled, and stored over type 4A molecular sieves before use. Dichloromethane was dried similarly except that P_2O_5 was used as the drying agent. Before use, trimethyl phosphite as obtained commercially was transferred under nitrogen to a 500-mL round-bottom flask (fitted with a Teflon valve); it was pure by $^{31}P\{^1H\}$ NMR spectroscopy. Dodecacarbonyltriosmium was prepared by a literature method.[8] The ^{13}CO-enriched $Os_3(CO)_{12}$ (~35% ^{13}C) was prepared by heating $Os_3(CO)_{12}$ in toluene at 125 °C under ~1.5 atm of ^{13}CO (99% ^{13}C) for 3 days. Column chromatography was performed with use of $P(OMe)_3$-deactivated Florisil. This was prepared by eluting the Florisil column with hexane/$P(OMe)_3$ (4:1 v/v) and then removing the excess $P(OMe)_3$ by washing the column with hexane.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. Electron-impact (70 eV) mass spectra were obtained on a Kratos-MS-50 instrument (University of British Columbia, regional facility) or on a Hewlett-Packard 5985 GC-MS system; the pattern of the envelope of the parent ions was matched with that simulated by computer for the species in question. Melting points were determined on samples sealed in capillaries under nitrogen by use of a Gallenkamp apparatus. Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University or by Canadian Microanalytical Service Ltd., New Westminster, B.C.

NMR Studies. NMR spectra were obtained with an extensively modified Varian XL-100 spectrometer (operating in the Fourier transform mode), a Bruker SY-100 spectrometer (operating frequencies: ^1H, 100.0 MHz; ^{13}C, 25.18 MHz; ^{31}P, 40.54 MHz), and a Bruker WM400 spectrometer (operating frequencies: ^1H, 400.13 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz). The ^{31}P NMR chemical shifts are given relative to internal $P(OMe)_3$ at δ 0 at 25 °C. A solution of ~1% of $P(OMe)_3$ in toluene/toluene-d_8 (5/1) at 31 °C was found to have a ^{31}P chemical shift of 140.2 ppm (downfield) relative to external 85% H_3PO_4. The ^{31}P chemical shifts and to a lesser extent the ^{13}C chemical shifts for the compounds reported here showed considerable temperature dependence. The temperature of the samples in the $^{31}P\{^1H\}$ NMR studies at an operating frequency of 40.54 MHz were obtained from the chemical shift difference between PPh_3 and $OPPh_3$ in toluene-d_8 contained in a coaxial capillary in contact with the sample solution.[9] The temperatures of the samples whose spectra were recorded on the WM400 spectrometer were obtained from the temperature controller of the spectrometer. The thermocouple of the temperature controller had been previously calibrated and shown to be accurate to ±2 °C in the temperature range concerned. The $^{13}C\{^1H\}$ NMR spectra were recorded on samples enriched with ~35% ^{13}CO. The NMR line-shape simulations were carried out with a computer program written by Professor R. E. D. McClung of the University of Alberta; the program is capable of simulating the spectra expected for the exchange of up to ten, uncoupled, spin $^1/_2$ nuclei. The free energies of activation were calculated in the normal way from the Eyring equation.

Preparation of $Os_3(CO)_{11}[P(OMe)_3]$ (1) and $Os_3(CO)_{10}[P(OMe)_3]_2$ (2). A Carius tube (fitted with a Teflon valve) was charged with $Os_3(CO)_{12}$ (0.50 g, 0.55 mmol), $P(OMe)_3$ (0.15 mL, 1.3 mmol), and hexane (15 mL). It was cooled to −196 °C and evacuated; the solution was degassed with three freeze-pump-thaw cycles. The tube was heated at 125 °C for 8 h. An infrared spectrum (carbonyl region) of the orange-yellow solution at this stage indicated the presence of **1** and **2** in an approximate 1:4 ratio, along with a trace amount of $Os_3(CO)_9[P(OMe)_3]_3$. The hexane and excess $P(OMe)_3$ were removed on the vacuum line. The orange oil that remained was dissolved in toluene (3 mL) and chromatographed on $P(OMe)_3$-deactivated Florisil (3.5 × 11 cm). Elution with hexane caused separation of a yellow band that was collected. Removal of the solvent on the vacuum line afforded $Os_3(CO)_{11}[P(OMe)_3]$ (0.05 g, 9%) as yellow crystals. Further elution with hexane/toluene (4/1 v/v) caused the development of a second yellow band that was also collected. Removal of the solvent on the vacuum line gave orange-yellow crystals of $Os_3(CO)_{10}[P(OMe)_3]_2$ (0.24 g, 40%). Both products may be recrystallized from hexane; they appeared to be air-stable.

The monosubstituted product was also prepared in reasonable yield by the reaction of $Os_3(CO)_{11}(CH_3CN)$ and $P(OMe)_3$.[10] $Os_3(CO)_{11}[P(OMe)_3]$: IR (hexane) ν(CO) 2111 (w), 2056 (s), 2040 (m), 2022 (s), 2003 (w), 1993 (m), 1983 (w), 1970 (w) cm^{-1} [lit.[10] 2111 (m), 2055 (s), 2039 (m), 2021 (s), 2002 (w), 1992 (m), 1981 (w), 1967 (w) cm^{-1}]; ^{13}C NMR ($C_6D_5CD_3$, −53 °C, 100.6 MHz) δ 189.8 (d, 2 C, J_{PC} = 12.3 Hz), 185.1 (s, 2 C) 184.2 (s, 2 C), 176.0 (s, 1 C), 174.5 (s, 1 C), 172.9 (s, 1 C), 171.8 (s, 1 C), 170.8 (s, 1 C); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3/C_6H_5Me$, 1/5, 25 °C, 162.0 MHz) δ −43.7 (s). $Os_3(CO)_{10}[P(OMe)_3]_2$: mp 96.5–97 °C; IR (hexane) ν(CO) 2094 (w), 2037 (m), 2020 (m), 2008 (s), 1987 (m), 1964 (w sh) cm^{-1}; ^1H NMR ($C_6D_5CD_3$, 25 °C, 100.13 MHz) δ 3.73 (d, J_{PH} = 12.2 Hz); ^1H NMR ($C_6D_5CD_3$, −47 °C, 400.13 MHz) δ 3.72 (d, J_{PH} = 12.4 Hz, relative intensity = 3), 3.69 (d, J_{PH} = 12.4 Hz, relative intensity = 3) 3.68 (d, J_{PH} = 12.3 Hz, relative intensity = 2); ^{13}C NMR ($C_6D_5CD_3$, −66 °C, 100.6 MHz) δ 192.5 (d, J_{PH} = 10.8 Hz, relative intensity = 32), 191.7 (d, J_{PC} = 11.7 Hz, relative intensity = 55), 187.5 (s, relative intensity = 11), 186.7 (s, relative intensity = 32), 179.6 (s, relative intensity = 16), 178.7 (s, relative intensity = 11), 177.1 (s, relative intensity = 16), 176.2 (s, relative intensity = 16), 175.0 (s, relative intensity = 11), 173.9 (s, relative intensity = 16); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3/C_6H_5Me$, 1/5, −59 °C, 40.5 MHz) δ −42.7 (d, J_{PP} = 1.8 Hz, relative intensity = 7), −40.8 (s, relative intensity = 5), −39.6 (d, J_{PP} = 1.9 Hz, relative intensity = 7); MS (EI), m/z 1100 (M^+) also ($M^+ - n$CO) (n = 1–5). Anal. Calcd for $C_{16}H_{18}O_{16}Os_3P_2$: C, 17.48; H, 1.65; P, 5.64. Found: C, 17.19; H, 1.61; P, 5.74.

Preparation of $Os_3(CO)_9[P(OMe)_3]_3$ (3). A Carius tube (fitted with a Teflon valve) charged with $Os_3(CO)_{12}$ (0.250 g, 0.276 mmol), $P(OMe)_3$ (0.10 mL, 0.85 mmol), and xylene (15 mL) was evacuated at −196 °C, and the solution was degassed with three freeze-pump-thaw cycles. The tube and contents were heated

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(3) Alex, R. F.; Pomeroy, R. K. *J. Organomet. Chem.* **1985**, *284*, 379.

(4) Alex, R. F.; Einstein, F. W. B.; Jones, R. H.; Pomeroy, R. K. *Inorg. Chem.*, in press.

(5) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.

(6) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E. *J. Organomet. Chem.* **1985**, *281*, C43. See also: Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(7) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Manning, P. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1037.

(8) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859.

(9) Dickert, F. L.; Hellmann, S. W. *Anal. Chem.* **1980**, *52*, 996.

(10) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* 1981, 407.

at 125 °C for 20 h. An infrared spectrum (carbonyl region) of the clear orange-yellow solution at this stage indicated a mixture of 2 and 3 in an approximate 1:2 ratio together with small amounts of 1 and $Os_3(CO)_8[P(OMe)_3]_4$. The tube was cooled, and the solvent and excess $P(OMe)_3$ were removed on the vacuum line. The resultant orange oil was dissolved in toluene (4 mL) and chromatographed on Florisil (11 × 3.5 cm) deactivated as described previously. The clusters 1 and 2 were removed from the column by elution with hexane/toluene (1/1 v/v). Subsequent elution with toluene caused the development of a yellow-orange band that was collected. Removal of the solvent on the vacuum line afforded the desired product **3** (0.11 g, 33%) as yellow-orange, air-stable crystals. The analytical sample was recrystallized from hexane: mp 158–159 °C dec; IR (hexane) ν(CO), 2072 (vw), 2010 (m), 1992 (s), 1954 (m br) cm^{-1}; IR (CH_2Cl_2) ν(CO) 2068 (vw), 2002 (m), 1985 (s), 1948 (m br) cm^{-1}; ^1H NMR ($(CD_3)_2CO$, 25 °C, 100.1 MHz) δ 3.67 (d, J_{PH} = 12.2 Hz); ^{13}C NMR ($C_6D_5CD_3/C_6H_5Me$, 1/4, –65 °C, 100.6 MHz) 193.3 (d, 2 C, J_{PC} = 10.3 Hz) 179.9 (s, 1 C); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3/C_6H_5Me$, 1/2, 31 °C, 40.5 MHz) δ –40.7 (s); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_5/C_6H_5Me$, 1/2, –91 °C, 40.5 MHz) δ –39.4 (s); MS (EI), m/z 1196 (M^+) also ($M^+ - n$CO) (n = 1–5). Anal. Calcd for $C_{18}H_{27}O_{18}Os_3P_3$: C, 18.09; H, 2.28; P, 7.78. Found: C, 18.18; H, 2.29; P, 7.97.

Preparation of $Os_3(CO)_8[P(OMe)_3]_4$ (4). A Carius tube (fitted with a Teflon valve) was charged with $Os_3(CO)_{12}$ (0.50 g, 0.55 mmol), $P(OMe)_3$ (4 mL, 34 mmol), and heptane (20 mL) and evacuated at –196 °C; the solution was degassed with three freeze–pump–thaw cycles. The tube and contents were heated at 140–145 °C for 24 h. An infrared spectrum (carbonyl region) of the orange solution at this stage contained strong absorptions due to 4 and $Os(CO)_3[P(OMe)_3]_2$ and weak absorptions due to other species. The solution was allowed to stand overnight at room temperature whereupon orange crystals formed. The yellow-orange mother liquor was removed from the crystals that were washed with hexane (4 × 10 mL) and dried on the vacuum line. The crystals (0.33 g, 46%) consisted mainly of the desired product **4** plus $Os_3(CO)_7[P(OMe)_3]_5$ (**5**). The crude product was dissolved in toluene (4 mL) and chromatographed on $P(OMe)_3$-deactivated Florisil (14 × 3.5 cm). Elution of the column with toluene or toluene/CH_2Cl_2 mixtures allowed collection of an orange band (**5** eluted only very slowly under these conditions). Removal of the solvent from the orange fractions gave orange, air-stable crystals of **4** that were analytically pure. The compound may be recrystallized from hexane/toluene or hexane/CH_2Cl_2 as pale/orange plates: mp 163–165 °C dec; IR (CH_2Cl_2) ν(CO) 2049 (vw), 1989 (m), 1969 (s), 1941 (m sh), 1909 (w sh) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C, 400.13 MHz) δ 3.62 (d, J_{PH} = 12.2 Hz, relative intensity = 1), 3.61 (d, J_{PH} = 11.8 Hz, relative intensity = 1); ^{13}C NMR ($C_6D_5CD_3$, –83 °C, 100.6 MHz) δ 200.2 (poorly resolved triplet, J_{PC} = 10.8 Hz, relative intensity = 4), 198.8 (poorly resolved triplet, J_{PC} = ~10 Hz, relative intensity = 3), 195.1 (br s, relative intensity = 10), 194.1 (d, J_{PC} = 6.4 Hz, relative intensity = 4), 181.9 (s, relative intensity = 2), 180.8 (s, relative intensity = 3), 178.7 (s, relative intensity = 2); at –70 °C and an operating frequency of 25.18 MHz the triplets were well-resolved, 200.4 (t, J_{PC} = 11.0 Hz), 198.9 (t, J_{PC} = 11.5 Hz); ^{13}C NMR ($C_6D_5CD_3$, 80 °C, 100.6 MHz) δ 198.4 (t, J_{PC} = 11.2 Hz, relative intensity = 1), 189.1 (s, relative intensity = 3); $^{31}P\{^1H\}$ ($C_6D_5CD_3/C_6H_5Me$, 1/5, –81 °C, 40.5 MHz) δ –33.4 (d, J_{PP} = 4.4 Hz), –33.6 (s), –35.0 (s), –36.4 (d, J_{PP} = 4.2 Hz), –36.7 (br s), –39.6 (d, J_{PP} = 3.9 Hz); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3/C_6H_5Me$, 1/5, 53 °C, 40.5 MHz) δ –38.5 (s, relative intensity = 1), –40.1 (s, relative intensity = 1); MS (EI), m/z 1292 (M^+) also ($M^+ - n$(CO)) (n = 1–5). Anal. Calcd for $C_{20}H_{36}O_{20}Os_3P_4$: C, 18.61; H, 2.82; P, 9.60. Found: C, 18.46; H, 2.67; P, 10.56.

Preparation of $Os(CO)_4[P(OMe)_3]$ and $Os(CO)_3[P(OMe)_3]_2$. A Carius tube was charged with $Os_3(CO)_{12}$ (0.60 g, 0.66 mmol), $P(OMe)_3$ (4 mL, 34 mmol), and heptane (15 mL) and evacuated at –196 °C; the solution was degassed with three freeze–pump–thaw cycles. The stirred solution was heated at 115 °C for 7 days. An infrared spectrum (carbonyl region) at this stage indicated the presence of $Os(CO)_4[P(OMe)_3]$ and $Os(CO)_3[P(OMe)_3]_2$ in addition to smaller amounts of the clusters 2–5. The solvent and excess $P(OMe)_3$ were removed at 0 °C on the vacuum line. The resultant orange oil was sublimed at 0 °C to a probe at –78 °C (<10^{-3} mm) for 24 h. An infrared spectrum (carbonyl region) of the white sublimate indicated the presence of a mixture of $Os(CO)_4[P(OMe)_3]$ and $Os(CO)_3[P(OMe)_3]_2$ in an approximate 10:1 ratio. An analytically pure sample of $Os(CO)_4[P(OMe)_3]$ was obtained by a second sublimation of this material under the same conditions. The complex may be recrystallized with considerable loss from hexane. It can be handled for short periods in air although it yellows on prolonged exposure. $Os(CO)_4[P(OMe)_3]$: mp 45.5–46.5 °C dec; IR (hexane) ν(CO), 2073 (s), 1997 (m), 1963 (vs), 1950 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (d, J_{PH} = 12.0 Hz); $^{31}P\{^1H\}$ NMR (hexane) δ –23.3 (s); MS (EI), m/z 428 (M^+). Anal. Calcd $C_7H_9O_7OsP$: C, 20.69; H, 3.47. Found: C, 20.89; H, 3.53.

The residue remaining from the sublimation described above was subjected to further sublimation at 35 °C (<10^{-3} mm) to a probe at –78 °C for 24 h. This afforded a white solid that consisted of $Os(CO)_3[P(OMe)_3]_2$ plus a small amount of $Os(CO)_4[P(OMe)_3]$. Recrystallization of the sublimate from hexane yielded analytically pure $Os(CO)_3[P(OMe)_3]_2$: mp 61.5–62.0 °C dec; IR (hexane) ν(CO) 1925 (s), 1915 (s) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 3.64 (virtual triplet, apparent J_{PH} = 6.5 Hz); $^{31}P\{^1H\}$ NMR (hexane) δ –16.5; MS (EI), m/z 524 (M^+). Anal. Calcd for $C_9H_{18}O_9OsP_2$: C, 19.72; H, 2.13. Found: C, 19.92; H, 1.99.

Results and Discussion

Synthesis and Characterization of $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–4). The clusters 1–4 were prepared by heating $Os_3(CO)_{12}$ and $P(OMe)_3$ above 125 °C in hydrocarbon solvents. (The temperature of 140–145 °C employed in the synthesis of 4 is crucial in order to obtain good yields of the cluster.) This method has been used repeatedly in the past for the preparation of phosphine-substituted derivatives of $Os_3(CO)_{12}$.[11] However, in most cases the maximum number of carbonyls that can be replaced is three.[12] As mentioned in the Introduction, further substitution by $P(OMe)_3$ of 4 can be achieved by ultraviolet irradiation methods to yield $Os_3(CO)_7[P(OMe)_3]_5$ (**5**)[3] and $Os_3(CO)_6[P(OMe)_3]_6$ (**6**).[4] The reasons why more extensive substitution of $Os_3(CO)_{12}$ by $P(OMe)_3$ can be achieved may be attributed to the small size and special electronic properties of the ligand.[4]

Another interesting aspect of the reaction of $Os_3(CO)_{12}$ with excess $P(OMe)_3$ is that when it was carried out at 115 °C for 7 days the mononuclear complexes $Os(CO)_4[P(OMe)_3]$ (**7**) and $Os(CO)_3[P(OMe)_3]_2$ (**8**)[14] were the major products. This unexpected result was not investigated further although it was found that 6 does not react with $P(OMe)_3$ under the same conditions.[1] Poë and co-workers have, however, observed similar behavior in the reaction of $Os_3(CO)_{12}$ with phosphorus-donor ligands and have carried out detailed kinetic studies of the system.[15] The properties of 7 and 8 are unremarkable and closely resemble their iron and ruthenium congeners.[13,16-18] For example, unlike most ax-$M(CO)_4L$ complexes[17,19] 7 exhibits

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[11] (a) Tripathi, S. C.; Srivastava, S. C.; Mani, R. P.; Shrimal, A. K. *Inorg. Chim. Acta* **1975**, *15*, 249. (b) Adams, R. D.; Selegue, J. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982, Vol. 4, p 1027 and references therein.

[12] A kinetic study of the reaction of $Os_3(CO)_{12}$ and L (L = PPh_3, PBu_3, $P(OPh)_3$, and $P(OMe)_3$) in hydrocarbon solution has been published.[13]

[13] Shojaie, A.; Atwood, J. D. *Organometallics* **1985**, *4*, 187.

[14] Bruce, M. I.; Cooke, M.; Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1969**, 987.

[15] Brodie, N.; Poë, A. J.; Sekhar, V. *J. Chem. Soc., Chem. Commun.* **1985**, 1090.

[16] (a) Conder, H. L.; Darensbourg, M. Y. *J. Organomet. Chem.* **1974**, *67*, 93 and references therein. (b) Ginderow, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2798. (c) Graff, J. L.; Sanner, R. D.; Wrighton, M. S. *Organometallics* **1982**, *1*, 837.

[17] Darensbourg, D. J.; Nelson, H. H.; Hyde, C. L. *Inorg. Chem.* **1974**, *13*, 2135.

[18] Cobbledick, R. E.; Einstein, F. W. B.; Pomeroy, R. K.; Spetch, E. R. *J. Organomet. Chem.* **1980**, *195*, 77.

[19] Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.

Table I. ^{13}C NMR Chemical Shifts (ppm) of the Carbonyl Ligands of $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 0–6; L = $P(OMe)_3$)^a

	eq-CO		ax-CO		
	$Os(CO)_4$ unit	$Os(CO)_3L$ unit	$Os(CO)_4$ unit	$Os(CO)_3L$ unit	$Os(CO)_2L_2$ unit
$Os_3(CO)_{12}$^{b}	170.4		182.3		
$Os_3(CO)_{11}[P(OMe)_3]$ (1)	170.8	176.0	184.2	189.8	
	171.8		185.1		
	172.9				
	174.5				
$Os_3(CO)_{10}[P(OMe)_3]_2$ (2)	173.9	177.1	186.7	191.7	
	175.0	178.7	187.5	192.5	
		179.6			
$Os_3(CO)_9[P(OMe)_3]_3$ (3)		179.9		193.3	
$Os_3(CO)_8[P(OMe)_3]_4$ (4)		178.7		194.1	198.8
		180.8		195.1	200.2
		181.9			
$Os_3(CO)_7[P(OMe)_3]_5$^{c} (5)				194.1	199.2
					199.7
$Os_3(CO)_6[P(OMe)_3]_6$^{d} (6)					203.4

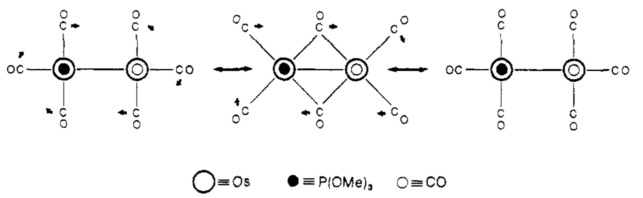
^{a} Slow-exchange region; toluene/toluene-d_8 solution. ^{b} From ref 31. ^{c} From ref 3. ^{d} From ref 4.

four rather than three carbonyl stretches in the infrared spectrum that may be attributed to the lack of threefold symmetry the phosphite ligand possesses.[18]

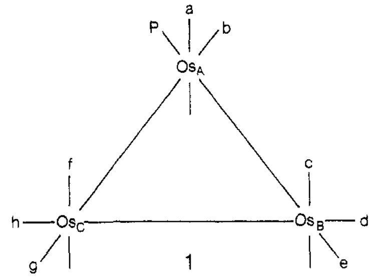
The clusters 1–4 are air-stable crystalline solids that change from yellow to orange with increasing phosphite substitution. As previously discussed for 6[4] (which is orange-red), we attribute this color change to a weakening of the Os–Os bonds in the cluster with increasing phosphite substitution. This in turn causes a shift to lower energies of the $\sigma \rightarrow \sigma^*$ electronic transitions of the metal–metal bonds and hence the color change. The structure of each cluster is discussed individually below along with the variable-temperature NMR spectra of each. An analysis based on signal intensities and phosphorus coupling[20] of the low-temperature limiting ^{13}C NMR spectrum of each member of the series $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 0–6) reveals that the resonances can be grouped according to whether the carbonyl giving rise to the resonance is in an axial or equatorial position and the extent of substitution at the osmium to which the carbonyl is bound. The analysis is shown in Table I. (There is also a shift to lower field of the chemical shifts of carbonyls of a given type as the number of phosphite ligands in the cluster increases.) Further assignment of the signals is possible given the exchanges that occur (see below).

Nonrigidity of $Os_3(CO)_{11}[P(OMe)_3]$ (1). The solid-state structure of 1 has been reported.[21] The trimethyl phosphite ligand adopts one of the less sterically hindered equatorial positions of the cluster. Furthermore, in 6 the $P(OMe)_3$ ligands occupy every equatorial site about the Os_3 triangle.[4] This is in agreement with other studies[21–24] that bulky ligands generally adopt equatorial positions in trinuclear clusters. (Small ligands such as H,[24–26] CH_3CN,[27] and CNR[26,28] normally are found in axial sites in such clusters.) In the molecules 1–6 there was no evidence for any stable cluster with an axial $P(OMe)_3$ substituent. Models show that if a bulky trimethyl phosphite grouping occupies an axial site in a triosmium cluster, then there are severe steric interactions of the methyl groups of this ligand with the two axial carbonyls on the same side of the osmium plane. (As we have pointed out previously,[3] this interaction has similarities to the well-known 1,3-diaxial interactions of cyclohexane derivatives.) We further believe, but cannot completely rule out, that intermediates with a $P(OMe)_3$ ligand in an axial position are not involved in any of the rearrangements proposed below.

Scheme I



The ^{13}C NMR spectrum of 1 at −53 °C in toluene-d_8 (Figure 1) is consistent with the structure found in the solid-state and shown diagramatically below. When the



1

sample is warmed to −24 °C, two axial and two equatorial signals (labeled a, f and b, g, respectively) broaden and are essentially collapsed to the base line in the spectrum at 20 °C. This behavior is similar to that observed for $Os_3(CO)_{11}(PEt_3)$[5] and $Os_3(CO)_{11}[Os(CO)_4(PMe_3)]$.[29] We agree with the explanation of Lewis and co-workers[5] that the most reasonable mechanism to account for this collapse is the familiar, pairwise terminal–bridge carbonyl exchange.[30,31] Since one of the signals that collapses is due

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(20) As previously observed in clusters of this type[5,7] there is coupling of the phosphorus atom to the axial carbon atoms but not to the equatorial carbon atoms. This is curious since the ^{13}C NMR spectra of the octahedral molecules *mer*-$Os(CO)_3(L)(SiCl_3)_2$ (L = $P(OCH_2)_3CMe$, PPh_3) the phosphorus–carbon coupling is approximately equal to the axial and equatorial carbonyls: Krentz, R.; Pomeroy, R. K., unpublished results.

(21) Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 666.

(22) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2375.

(23) For example: (a) Dahm, D. J.; Jacobson, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 5106. (b) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304. (c) Vënaläinen, T.; Pakkanen, T. *J. Organomet. Chem.* **1984**, *266*, 269.

(24) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 2397.

(25) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(26) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979**, *18*, 1909.

(27) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1982**, 233.

(28) Bruce, M. I.; Matisons, J. G.; Wallis, R. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2365.

(29) (a) Einstein, F. W. B.; Martin, L. R.; Pomeroy, R. K.; Rushman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 345. (b) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics*, in press.

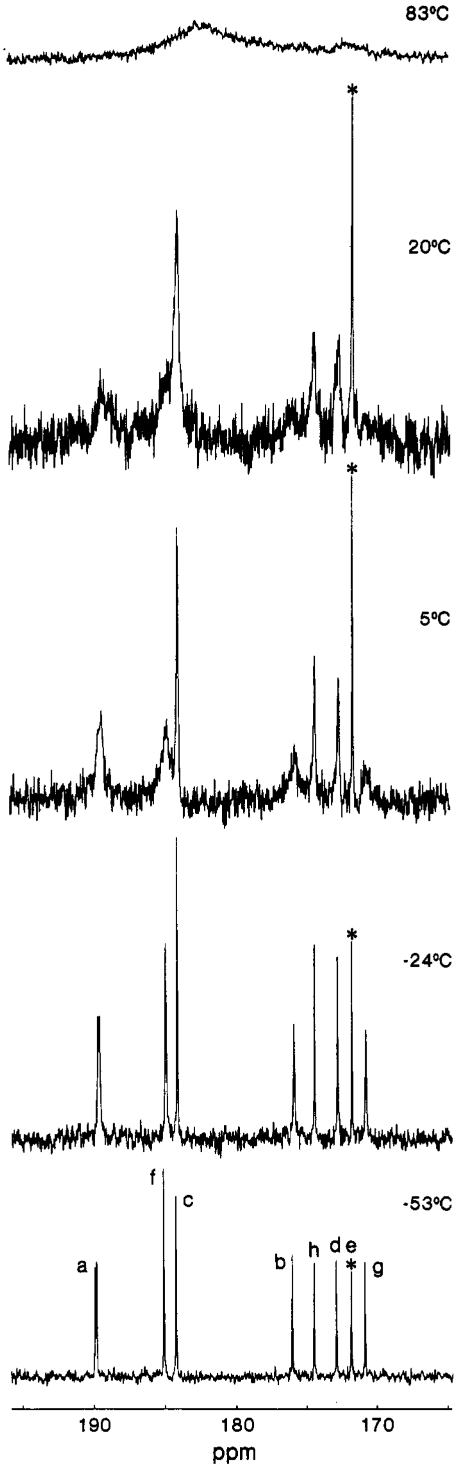
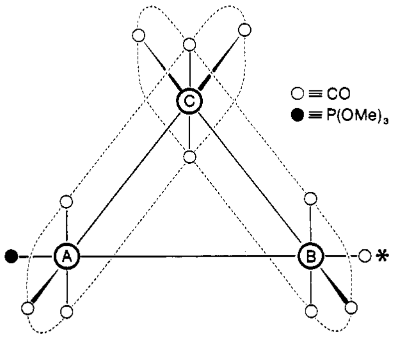
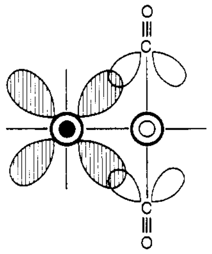


Figure 1. Variable-temperature ^{13}C NMR spectra of ^{13}CO-enriched $Os_3(CO)_{11}[P(OMe)_3]$ (1) in toluene/toluene-d_8.

to the axial carbonyls of the $Os(CO)_3[P(OMe)_3]$ unit, the plane in which the rearrangement occurs is thought to be the AC vertical plane. This is shown in Scheme I. In the scheme the exchange is viewed directly along one edge of the Os_3 triangle; this emphasizes the pseudo-fourfold nature of the rotations of the mechanism. As previously noted for $Os_3(CO)_{11}(PEt_3)$,[5] the phosphorus-donor ligand lowers the barrier to axial–equatorial exchange compared to the parent cluster $Os_3(CO)_{12}$.[32] (The barrier to the exchange in $Os_3(CO)_{12}$ is ca. 16.7 kcal mol^{-1}.) Substitution of a carbonyl by a phosphorus-donor ligand would be expected to cause an increase in the electron density at the osmium atom and cause expansion of the filled 5d orbitals. This in turn could result in better overlap with the π^* orbitals of the axial carbonyls on the adjacent osmium atom, as shown and thereby lower the activation energy for formation of the intermediate with bridging carbonyls. It is known that phosphorus-donor ligands can stabilize ground-state structures with bridging carbonyls. For example, $Ru_3(\mu\text{-}CO)_2(CO)_6[P(OMe)_2Ph]_4$[33] and $Ir_4(\mu\text{-}CO)_3(CO)_6[PPh_3]_3$[34] have bridging carbonyls, but the parent carbonyls $Ru_3(CO)_{12}$[35] and $Ir_4(CO)_{12}$[36] do not. Note that although $Ru_3(\mu\text{-}CO)_2(CO)_6[P(OMe)_2Ph]_4$[33] has bridging carbonyls in the solid-state, the less substituted derivative $Ru_3(CO)_{10}[P(OMe)_3]_2$[22] does not.

Scheme II





When the solution of 1 is warmed to 5 °C from −24 °C, three of the remaining four signals began to show the effects of exchange whereas one signal remained sharp (Figure 1). (This second exchange was not detected in $Os_3(CO)_{11}(PEt_3)$.[5]) This collapse may be rationalized by terminal–bridge carbonyl exchange in the second vertical plane that does not contain a phosphite ligand, i.e., the Os(B)–Os(C) vertical plane. The allowed planes in which this type of exchange can occur are illustrated in Scheme II. The sharp signal remaining in the spectrum of 1 at 20 °C may therefore be assigned to the carbonyl in the trans two-bond position to the phosphite ligand, namely, the carbonyl labeled e.

A simulation of the spectrum at 20 °C (Figure 2) confirmed that the proposed mechanism was consistent with the observed spectrum. The rate constant of 230 ± 5 s^{-1}

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(30) (a) Adams, R. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589. (b) Cotton, F. A.; Hunter, D. L. *Inorg. Chim. Acta* **1974**, *11*, L9. (c) Johnson, B. F. G.; Benfield, R. E. *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, England, 1980; p 471.

(31) Mann, B. E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 89 and references therein.

(32) (a) Foster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W.; Robinson, B. H.; Jackson, W. G. *J. Chem. Soc., Chem. Commun.* **1974**, 1042. (b) Aime, S.; Gambino, O.; Milone, L.; Sappa, E.; Rosenberg, E. *Inorg. Chim. Acta* **1975**, *15*, 53.

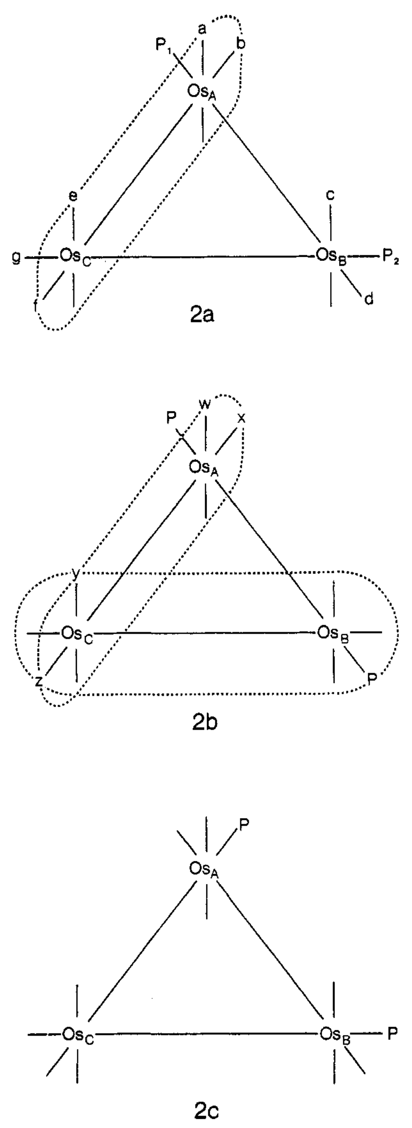
(33) Bruce, M. I.; Matisons, J. G.; Patrick, J. M.; White, A. H.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1985**, 1223.

(34) Albano, V.; Bellon, P. C.; Scatturin, V. *J. Chem. Soc., Chem. Commun.* **1967**, 730.

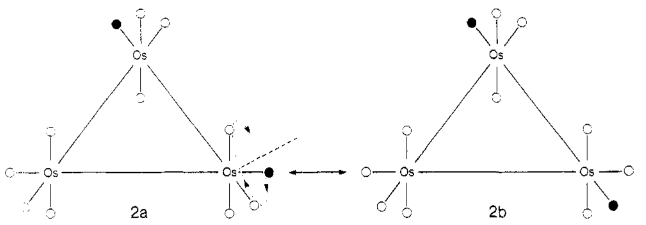
(35) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(36) Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

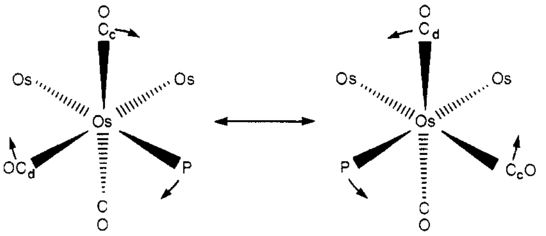
Scheme III



Scheme IV



Scheme V



at a temperature of 293 ± 2 K corresponds to a $\Delta G^{\ddagger}_{293}$ of 14.0 ± 0.4 kcal mol^{-1} for the exchange in the vertical AC plane. Similarly the rate constant of 50 ± 2 s^{-1} at the same temperature yields a $\Delta G^{\ddagger}_{293}$ value of 14.9 ± 0.4 kcal mol^{-1} for the exchange in the vertical BC plane. It is not surprising that the barrier in the latter plane is higher than that in the first plane given the position of the phosphite ligand. However, it is apparent that the effect of lowering the barrier by the phosphite group is transmitted across the cluster to the BC vertical plane since the exchange in this plane still occurs with a lower barrier than in $Os_3(CO)_{12}$.[32]

When the solution of 1 was warmed to above room temperature, the remaining signal collapsed (Figure 1). There are a number of mechanisms that could account for this collapse. However, from a consideration of the behavior of the other members of the series 2–5 (discussed in detail below) it is believed that the most likely process is a restricted trigonal twist at Os(A) that rotates the phosphite ligand from one equatorial position to the other. If this occurs, then terminal-bridged CO exchange can occur in the previously nonallowed AB vertical plane and cause complete equilibration of the carbonyls.

Nonrigidity of $Os_3(CO)_{10}[P(OMe)_3]_2$ (2). The $^{31}P\{^1H\}$ NMR spectrum of 2 at −59 °C in toluene/toluene-d_8 has three resonances: two are doublets with identical coupling constants and the other is a singlet. This indicates the presence of more than one isomer of **2**,[37] in contrast to $Os_3(CO)_{10}(PEt_3)_2$ where only one isomer was detected.[5] That one of the isomers of 2 has two phosphite ligands on the same osmium atom is rejected. Evidence will be presented that will show that the isomers of 2 are in rapid nondissociative equilibrium. An intermediate with a bridging $P(OMe)_3$ would therefore be required if such an isomer were present. As far as we are aware there is no firm evidence in the literature for the existence of an intermediate with a bridging phosphite ligand. Furthermore, Deeming and co-workers have shown that 1,1- and 1,2-$Os_3(CO)_{10}(PMe_2Ph)_2$ do not interconvert in solution even at 100 °C.[7] Therefore, the three most reasonable isomers of 2 are shown in Scheme III as **2a**, **2b**, and **2c**. The appearance of two doublets in the ^{31}P NMR spectrum of 2 is consistent with the presence of **2a**. Isomer **2c** is rejected from steric considerations since it has the bulky $P(OMe)_3$ ligands in a syn position in the cluster. In 6 there was evidence from the crystal structure of steric crowding between the adjacent phosphite ligands on different osmium atoms.[4] The ratio **2a**:**2b** was 2.8:1 from the $^{31}P\{^1H\}$ spectrum of 2 in toluene/toluene-d_8 at −59 °C.

It is interesting that the trans,cis three-bond coupling between the phosphorus atoms in **2a** was observed. This was not the case for 4 and 5[3] although trans,trans three-bond couplings were. It may be that for 4 and 5 the small trans,cis three-bond couplings were obscured by broadening due to still smaller cis,cis three-bond and cis one-bond phosphorus–phosphorus coupling.

When the solution of 2 is warmed to near 30 °C, the ^{31}P NMR signals coalesced. At 79 °C the spectrum consisted of a singlet. During this coalescence the signal due to the internal reference of $P(OMe)_3$ remained sharp which indicated the isomerization of 2 occurs without phosphite dissociation. (This was also the case for the other members of the series.)

The mechanism of the isomerization is believed to involve a restricted trigonal twist at one of the osmium atoms that has a phosphite substituent; this is shown in Schemes IV and V. A twist similar to this was proposed to account for the fluxional process in 5.[3] (In 5, terminal–bridge carbonyl exchange is blocked since each vertical plane contains at least one $P(OMe)_3$, ligand and yet exchange of some of the carbonyls occurs concurrently with exchange

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(37) It has been briefly mentioned in the literature that 2 exists as isomers in solution: Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* 1977, *124*, C19.

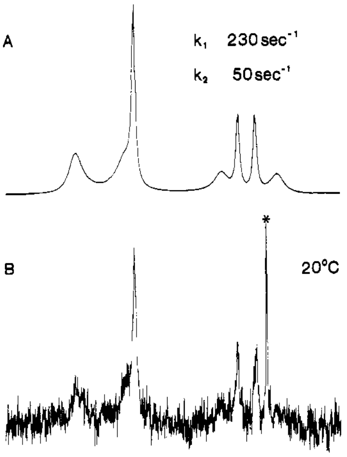


Figure 2. Calculated (A) and observed (B) ^{13}C NMR spectra for **1** in toluene/toluene-d_8 at 20 °C. The signal marked with an asterisk in the experimental spectrum has been omitted from the calculated pattern.

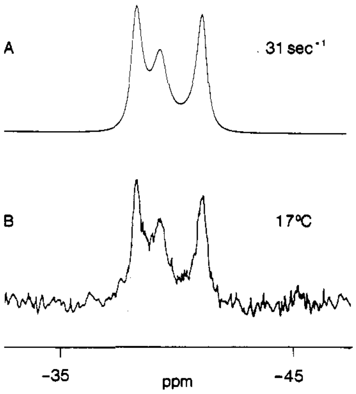


Figure 3. Calculated (A) and observed (B) $^{31}P\{^1H\}$ NMR spectra for $Os_3(CO)_{10}[P(OMe)_3]_2$ (**2**) in toluene/toluene-d_8 at 17 °C.

of some of the $P(OMe)_3$ ligands.) In the proposed twist (Scheme V) the trimethyl phosphite ligand for the steric reasons previously discussed never enters an axial site but rocks back and forth between the two equatorial positions.[38] This hindered rocking motion is therefore more correctly called a libration; it is also referred to as a turnstile or pinwheel mechanism in the literature. For **2b**, this motion can occur at either Os(A) or Os(B) since they are symmetry-related but not simultaneously at both since this would result in the isomer **2c** which is not observed.[39] For the same reason the reverse isomerization, from **2a** to **2b**, must occur at the osmium atom at which the original libration took place to convert **2b** to **2a**.

The $^{31}P\{^1H\}$ NMR spectrum of **2** at 17 °C (290 ± 2 K) was simulated based on this mechanism (Figure 3). The rate constant used for the simulated spectrum of 31 ± 1 s^{-1} yields a ΔG^{*}_{290} value of 15.0 ± 0.4 kcal mol^{-1}. This may be compared to a ΔG^{*} value of 13.4 ± 0.3 kcal mol^{-1} at 10 °C found for **5**.[3]

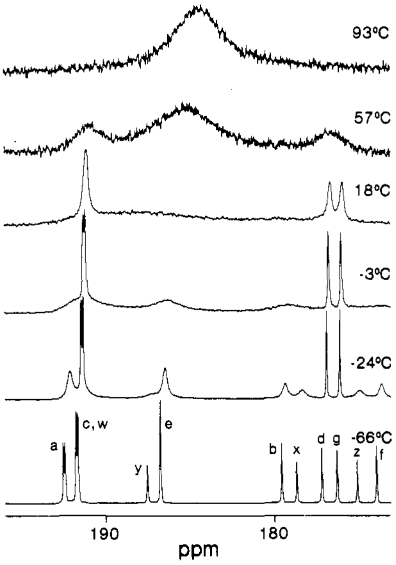
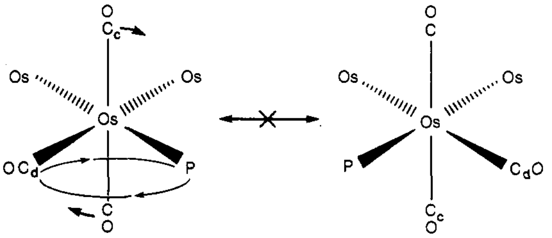


Figure 4. Variable-temperature ^{13}C NMR spectra of ^{13}CO-enriched **2** in toluene/toluene-d_8.

Scheme VI



There is no evidence for axial–equatorial carbonyl exchange in the $Os(CO)_4$ units of $Os_3(CO)_{12}$,[32] **1**, and **2** occurring at lower energies for the same exchange in the $Os(CO)_3[P(OMe)_3]$ units of **2**–**5**. It therefore appears that trimethyl phosphite also activates the molecule to this threefold twist as it does to terminal–bridge carbonyl exchange. In 1,1-$Os_3(CO)_{10}(PMe_2Ph)_2$ axial–equatorial carbonyl exchange at an $Os(CO)_4$ unit apparently takes place but at higher temperatures than the twists observed here.[7]

Variable-temperature ^{13}C NMR spectra (carbonyl region) of **2** in toluene-d_8 are shown in Figure 4. The assignment of the signals shown there and in Scheme III is based on the chemical ranges in which the axial and equatorial carbonyl resonances for $Os(CO)_{4-x}[P(OMe)_3]_x$ (x = 0–2) units occur (Table I), signal intensities, and the mode of collapse of the signals coupled with the mechanism proposed for the collapse. Note the degeneracies of the signal labeled c for **2a** and the signal labeled w for **2b**.

As can be seen from Figure 4 many of the signals show broadening due to chemical exchange below the temperature (approximately 5 °C) at which phosphite libration becomes rapid on the NMR time scale. Once again the results can be explained by terminal–bridge carbonyl exchanges that occur in those vertical planes that do not contain phosphite groups. For **2b**, the symmetry-related AC and BC vertical planes (Scheme III) are allowed, and this results in the exchange of all carbonyls in this isomer that is consistent with the observed collapse of all signals assigned as due to this molecule. For **2a**, there is only one allowed plane for terminal–bridge carbonyl exchange, namely, the AC vertical plane (Scheme III). The carbonyls labeled c, d, and g of **2a** remained unaffected by this exchange, and, indeed, three signals in the spectra remain sharp until the onset of phosphite libration whereupon complete exchange takes place as expected (Figure 4). As far as can be ascertained the last carbonyl exchange occurs concurrently with phosphite exchange. In $Os_3(CO)_{10}(PMe_2Ph)_2$ axial–equatorial carbonyl exchange apparently takes place before isomerization, and in order to account for this it was necessary to involve synchronous phosphorus-ligand rotation in the isomer equivalent to **2a**.[6]

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[38] The $^{31}P\{^1H\}$ NMR spectrum of **5** in solution at 82 °C shows that the phosphorus atoms of the $Os(CO)_2[P(OMe)_3]_2$ units in the molecule are not equivalent.[3] This indicates that even partial trigonal twists in these units do not readily occur.

[39] We cannot, of course, rule out the presence of undetectable amounts of **2c** in solution.

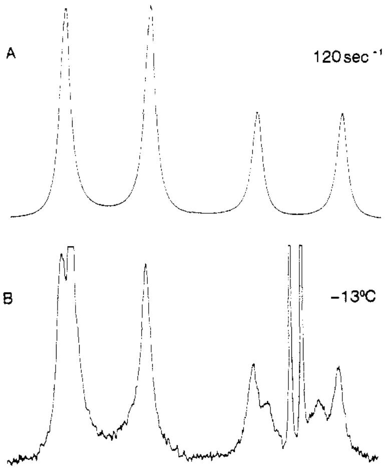
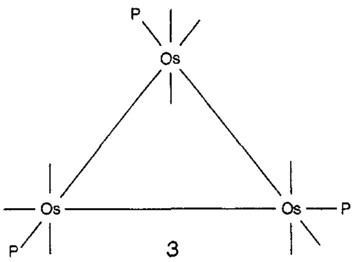


Figure 5. Calculated (A) and observed (B) ^{13}C NMR spectra for the terminal–bridge carbonyl exchange in **2a**. The signals due to carbonyls not taking part in the exchange or attributed to carbonyls of **2b** are omitted from the calculated spectrum.

The axial–equatorial carbonyl exchange takes place concurrently with isomerization rules out 180° rotations of the type shown in Scheme VI as the mechanism for isomerization.

A line-shape analysis of the part of the spectrum due to terminal–bridge exchange of the carbonyls in **2a** at −13 °C (260 ± 2 K) was carried out (Figure 5). The rate constant of 120 ± 4 s^{-1} used to simulate the spectrum yields a $\Delta G^{\ddagger}_{260}$ value of 12.7 ± 0.4 kcal mol^{-1}. A similar analysis was carried out for the exchange in **2b**. This rearrangement is a ten-site problem in which the carbonyl labeled y collapses at twice the rate of the other signals. Qualitatively this was observed in the spectra recorded at −45 and −34 °C (not shown) and in the spectrum at −24 °C (Figure 4). The analysis was made less accurate by the degeneracy of the signals due to carbonyls labeled c and w. The best fit for the spectrum at −13 °C (260 ± 2 K) was with a rate of 200 ± 15 s^{-1} which gives $\Delta G^{\ddagger}_{260}$ = 12.4 ± 0.5 kcal mol^{-1}. As can be seen from Figure 4, the collapse of the signals due to terminal–bridge carbonyl exchange occurs at about the same rate for the two isomers with the collapse in **2b** perhaps marginally faster than in **2a**. That the activation energies for these processes for **2** are significantly lower than in **1** (14.0 ± 0.4 and 14.9 ± 0.4 kcal mol^{-1}) is consistent with the view than an increase in phosphite substitution in these clusters causes a decrease in the barrier to terminal–bridge carbonyl exchange.

Nonrigidity of $Os_3(CO)_9[P(OMe)_3]_3$ (3). The $^{31}P\{^1H\}$ NMR spectrum of **3** in toluene/toluene-d_8 at −91 °C consists of a singlet. This is consistent with the presence of one isomer of **3** with the structure shown. The other possible isomer with one equatorial $P(OMe)_3$ group per metal atom would have a pair of phosphite ligands in a syn arrangement which, as discussed for **2**, appears to be unfavorable for steric reasons. The structure proposed for **3** is consistent with NMR studies on other trisubstituted triosmium clusters[5,7] and the solid-state structure of $Ru_3(CO)_9(PMe_3)_3$.[22]



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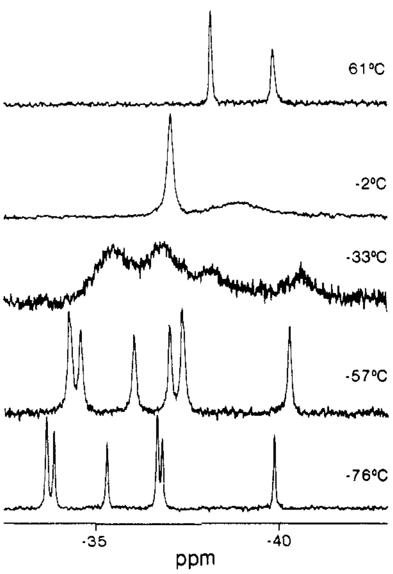


Figure 6. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $Os_3(CO)_8[P(OMe)_3]_4$ (**4**) in toluene/toluene-d_8.

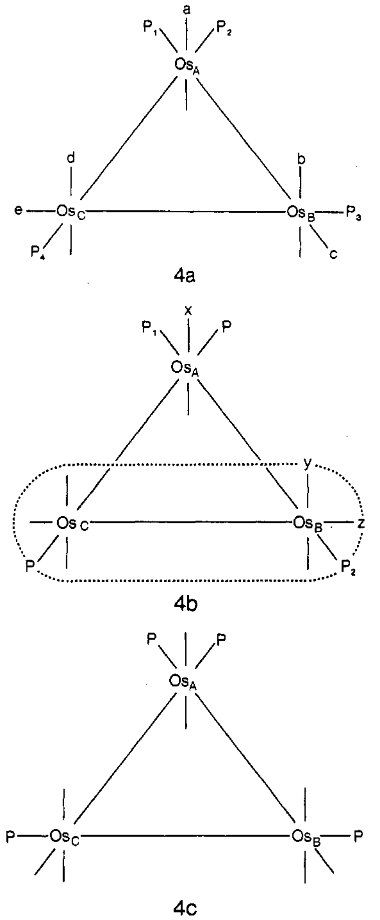
The ^{13}C NMR spectrum of **3**, in toluene/toluene-d_8, at −65 °C consists of a doublet (J_{PC} = 10.3 Hz) at 193.3 ppm and a singlet at 179.9 ppm with intensities in a ratio of 2:1. This is also consistent with the structure assigned to **3**, and the signals are attributed to the axial and equatorial carbonyls respectively. Once again, phosphorus coupling is observed to the axial but not to the equatorial carbon atoms.

When the solution of **3** is warmed, the signals began to broaden well below 0 °C, and by 60 °C there was complete collapse of the signals to the base line. A line-shape analysis of the spectrum at −2 °C (271 ± 2 K) gave a rate of 40 ± 2 s^{-1} and hence a $\Delta G^{\ddagger}_{271}$ value of 13.8 ± 0.4 kcal mol^{-1}.

Similar fluxional behavior has been observed before for $Os_3(CO)_9L_3$ (L = phosphorus-donor ligand),[5,7] but the details of the possible mechanism for the rearrangement were not discussed. However, turnstile rotations have been suggested to account for the nonrigidity in $Os_3(CO)_9[P(OMe)_3](PPh_3)_2$.[6] As previously mentioned, it appears that terminal–bridge carbonyl exchange only takes place with low activation energies in vertical planes through two osmium atoms that also do not contain a phosphite ligand. Cluster **3** does not possess such a plane, and we therefore believe that this type of exchange does not occur at low temperatures. Since **3** has three phosphite ligands, it might be expected that, were it not for this geometrical restriction, CO exchange would occur with a lower activation energy than in **2** ($\Delta G^{\ddagger}$ = 12.4 ± 0.5 and 12.7 ± 0.4 kcal mol^{-1}) given the activation effect of the phosphite ligands. From the studies on **2**, **4** (below), and **5**,[3] we believe axial–equatorial carbonyl exchange occurs via phosphite libration (Scheme V). If this occurs at a single osmium atom of **3**, a different isomer is produced which as stated previously was not detected. It, therefore, seems probable that synchronous phosphite libration occurs at the three osmium atoms of **3** to give rise to the observed collapse of the ^{13}C NMR signals. The presence of a low, undetectable concentration of the asymmetric isomer of **3** as a result of a restricted trigonal twist at a single osmium atom in the cluster cannot, however, be completely ruled out.

Nonrigidity of $Os_3(CO)_8[P(OMe)_3]_4$ (4). Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **4** are shown in Figure 6. The appearance of six resonances in the low-temperature-limiting spectrum signifies the presence of more than one isomer of **4**, a situation found for **2**. One of these

Scheme VII



isomers must be **4a** (Scheme VII) with its four chemically different phosphorus atoms. The other isomer is believed to be **4b** since like **4a** it has only one interaction arising from phosphite ligands cis to each other on adjacent osmium atoms whereas **4c** has two such interactions. As discussed for **2** and **3**, these interactions apparently dictate which isomers will be thermodynamically stable. The ratio **4a**:**4b** was judged to be about 1.3:1 in toluene at −86 °C from the $^{31}P\{^1H\}$ NMR spectrum.

The spectra shown in Figure 6 were recorded at an operating frequency of 162.0 MHz. In the corresponding low-temperature-limiting spectrum at an operating frequency of 40.5-MHz P–P coupling to three of the signals was clearly resolved. Similar behavior was observed for **5**,[3] and the broadening of the signals at the higher operating frequency was attributed to chemical shift anisotropy.[40]

Warming the solution of **4** caused collapse of the signals in a qualitatively similar manner to that observed for **2** and **5**.[3] Once again, we believe the isomerization of **4** is best explained in terms of phosphite libration at an $Os(CO)_3[P(OMe)_3]$ unit of one isomer of **4** so as to generate the second. Similar to **2**, it is thought that phosphite libration can only take place at one osmium atom in **4a** (Os(B)) but can occur at either of two osmium atoms in **4b** (Os(B) or Os(C)) but not simultaneously at both. (As before, a low concentration of **4c** cannot be completely ruled out.) In the region of fast exchange two $^{31}P\{^1H\}$ NMR signals are expected and observed. There was no evidence for a lower energy process that involved synchronous-restricted twists at osmiums A and B of **4a** so as to generate an equivalent form of **4a**. This would have caused collapse of the four signals of **4a** to two before coalescence with the signals due to **4b**.

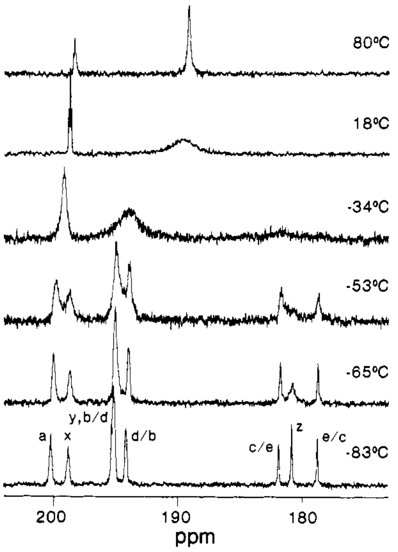


Figure 7. Variable-temperature ^{13}C NMR spectra of ^{13}CO-enriched **4** in toluene/toluene-d_8.

Variable-temperature ^{13}C NMR spectra of **4** are shown in Figure 7. The spectrum at −83 °C is consistent with the presence of isomers **4a** and **4b**, and the partial assignment of the signals shown (Figure 7, Scheme VII) is possible on the basis of arguments previously outlined. The high-temperature spectrum is consistent with the mechanism proposed. Note that the signal due to the axial carbonyls of the $Os(CO)_2[P(OMe)_3]_2$ unit maintain phosphorus coupling consistent with the nondissociative nature of the isomerization. Furthermore, the carbonyls of this unit show no evidence of exchange with the carbonyls of the $Os(CO)_3[P(OMe)_3]$ groupings, thereby ruling out rearrangements such as those that involve intermediates with triply bridging carbonyls and an all-axial merry-go-round CO exchange,[31] as having a low activation energy in this molecule.

The molecule **4b** possesses a vertical plane (BC) through which a lower energy terminal–bridge carbonyl exchange can occur (Scheme VII). As can be seen in the spectrum at −65 °C (Figure 7) the signal assigned to the carbonyls labeled z in **4b** does indeed broaden at a lower temperature than that expected from phosphite libration. The expected broadening of the signal assigned to the carbonyls labeled y was masked by other degenerate resonances. This broadening provides added support that **4b** and not **4c** is present: the latter isomer does not possess a plane for low-energy terminal–bridge carbonyl exchange.

A line-shape analysis of the signal due to the carbonyls labeled z yielded a rate of 60 ± 4 s^{-1} at 208 ± 2 K from which $\Delta G^{\ddagger}_{208} = 10.3$ kcal mol^{-1}. As expected this value is lower than the corresponding activation energies in **2** (12.4 ± 0.5 and 12.7 ± 0.4 kcal mol^{-1}). The phosphite libration that equilibrates **4a** and **4b** causes the signals due to the carbonyls of the $Os(CO)_2[P(OMe)_3]_2$ groupings for each isomer (i.e., the signals labeled a and x) to average. An approximate line-shape analysis for these signals was carried out for the spectrum at −45 °C (228 ± 2 K) (not shown). This yielded a rate constant of 300 ± 5 s^{-1} which corresponds to $\Delta G^{\ddagger}_{228} = 10.6 \pm 0.4$ kcal mol^{-1}.

Conclusion

The first five members of the series $Os_3(CO)_{12-x}[P(OMe)_3]_x$ ($x = 1-6$) exhibit stereochemical nonrigidity. (From our study of $Os_3(CO)_6[P(OMe)_3]_5[P(OEt)_3]$[41] it is

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[40] Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981; p 16.

probable that $Os_3(CO)_6[P(OMe)_3]_6$ is rigid on the ^{31}P NMR time scale.) The nonrigidity can be completely rationalized in terms of two mechanisms.[42] The lower energy process is the well-known terminal–bridge carbonyl exchange shown in Scheme I. This exchange is thought to occur only in those planes vertical to the Os_3 plane that do not contain a phosphite ligand. For exchange to occur in a plane that does contain a phosphite requires that the $P(OMe)_3$ group enters an axial site. It is thought this is prevented by steric interaction with the axial carbonyls on the same side of the Os_3 plane as the phosphite ligand. With this restriction in mind, however, increasing trimethyl phosphite substitution in $Os_3(CO)_{12}$ lowers the barrier to terminal–bridge carbonyl exchange.

Because of the symmetry of $Os_3(CO)_{12}$, definitive evidence as to the mechanism of axial–equatorial exchange in the parent cluster is lacking. However, given the solid-state structure of $Fe_3(CO)_{12}$,[43] that CO exchange occurs over all osmium atoms,[44] and the NMR results presented here and elsewhere,[5,7] it is probable that the lowest energy mechanism is the terminal–bridge carbonyl exchange analogous to that shown in Scheme I. This, of course, is consistent with the generally held view of the exchange.[30,31,44]

The second mechanism of carbonyl exchange in $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–5) is thought to be the restricted trigonal twist at an individual osmium atom in the cluster that rotates the trimethyl phosphite ligand from one equatorial position to the other (Scheme V) and simultaneously causes axial–equatorial carbonyl exchange. Once again the phosphite is thought not to enter an axial site for steric reasons. This phosphite libration also accounts for the isomerizations observed in **2** and **4**. The barriers to this rearrangement for **2**, **3**, **4**, and **5** were estimated to be 15.0, 13.8, 10.6, and 13.4 kcal mol^{-1}, respectively.

Trigonal twists have been implicated before as occurring in metal clusters.[45] We believe that the variable-temperature ^{13}C and ^{31}P NMR spectra of the present series of molecules provide some of the most convincing evidence for the process so far presented for metal clusters.

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Registry No. **1**, 66098-55-3; **2**, 61840-73-1; **3**, 93644-91-8; **4**, 109863-77-6; **7**, 107703-37-7; **8**, 22377-52-2; $Os_3(CO)_{12}$, 15696-40-9.

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[41] Prepared in poor yield by the UV irradiation of **5** and excess $P(OEt)_3$ in hexane.[1]

[42] It is pertinent to note here that there was no need to invoke the all equatorial merry-go-round CO exchange as occurring with low activation energies in these molecules even though this mechanism is thought to occur in other derivatives of $Os_3(CO)_{12}$.[31] For example, such a mechanism in **1** would cause the pairwise collapse of the ^{13}C NMR signals with the exception of those labeled a and e which (Figure 1) is not observed.

[43] (a) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. (b) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.

[44] Koridze, A. A.; Kizas, O. A.; Astakhova, N. M.; Petrovskii, P. V. Grishin, Y. K. *J. Chem. Soc., Chem. Commun.* **1981**, 853.

[45] For example: (a) Beringhelli, T.; D'Alfonso, G.; Molinari, H.; Mann, B. E.; Pickup, B. T.; Spencer, C. M. *J. Chem. Soc., Chem. Commun.* **1986**, 796. (b) Rosenberg, E.; Thorsen, C. B.; Milone, L.; Aime, S. *Inorg. Chem.* **1985**, *24*, 231. (c) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* **1976**, *162*, 389. (d) Tachikawa, M. Ph.D. Thesis, University of Illinois, 1977. See also: (a) Bryan, E. G.; Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1978**, 196. (b) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 144.

[46] **Note Added in Proof**: Farrar and Lunnis (*J. Chem. Soc., Dalton Trans.* **1987**, 1249) have recently described the fluxional behavior of $Fe_3(CO)_{10}[P(OMe)_3]_2$. Evidence was found to suggest that phosphite ligand mobility plays a role in the isomerization processes at higher temperatures.