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The Trimetaphosphate Ligand in Organometallic Chemistry. Isolation of Tricarbonylmanganese(I), Tricarbonylrhenium(I), (Pentamethylcyclopentadienyl)rhodium(III), and (Norbornadiene)rhodium(I) Adducts

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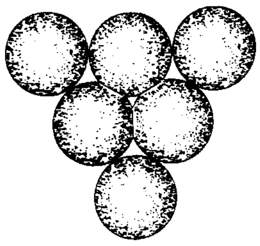
The trimetaphosphate ion $P_3O_9^{3-}$ as a tetrabutylammonium salt reacts with solvated $(OC)_3Mn^+$, $(OC)_3Re^+$, $[(CH_3)_5C_5]Rh^{2+}$, and $(C_7H_8)Rh^+$ as hexafluorophosphate salts in CH_3CN to form $[(OC)_3Mn(P_3O_9)]^{2-}$, $[(OC)_3Re(P_3O_9)]^{2-}$, $\{[(CH_3)_5C_5]Rh(P_3O_9)\}^-$, and $[(C_7H_8)Rh(P_3O_9)]^{2-}$, respectively, as tetrabutylammonium salts. According to spectroscopic and X-ray crystallographic data, these complexes all have a common structure derived from the tetrahedral P_4O_{10} structure by replacing one phosphorus atom and its terminal oxygen with an organometallic unit. The $P_3O_9^{3-}$ ligand coordinates in the same κ^3O fashion previously observed for the trimetaphosphimate ligand $[P_3(NH)_3O_6]^{3-}$ in a variety of coordination complexes.

Introduction

A key feature of the κ^3O-*cis*-$Nb_2W_4O_{19}^{4-}$ ligand is its steric bulk.[2,3] The η^5-$[(CH_3)_5C_5]$ ligand has similar dimensions,[2] and the methyl groups in this ligand are known to influence its steric properties dramatically relative to the smaller η^5-C_5H_5 ligand. The *cis*-$Nb_2W_4O_{19}^{4-}$ ligand's bulk arises from three peripheral oxygens which surround the three central, coordinating oxygen atoms (see **a**). The influence of this bulk might be probed through comparative studies involving an analogous κ^3O ligand, shown in **b**, that lacks these noncoordinating, peripheral oxygens. Precisely such a ligand is present in the P_4O_{10} cage,[4] **c**, in which each P^V center is bonded to one terminal oxo ligand plus a triangle of three oxygen atoms provided by the trimetaphosphate ($P_3O_9^{3-}$) ligand. We hoped therefore to prepare P_4O_{10} analogues **d** where a PO unit is replaced by an organometallic moiety ML_n. The preparations of tricarbonylmanganese(I) and tricarbonylrhenium(I) complexes have been described in a preliminary communication.[5] We provide here a complete report on these compounds plus two new trimetaphosphate complexes of (pentamethylcyclopentadienyl)rhodium(III) and (norbornadiene)rhodium(I).



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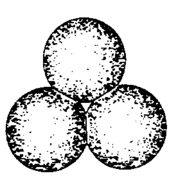

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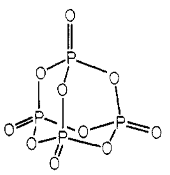

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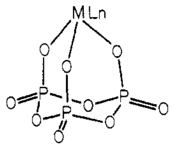

d

Experimental Section

Reagents, Solvents, and General Procedures. The follwing were purchased from commercial sources and used without further purification: $NaH_2PO_4\cdot H_2O$ and NaCl (Fisher); $RhCl_3\cdot xH_2O$, $AgPF_6$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ (Strem); bicyclo[2.2.1]hepta-2,5-diene, hexamethylbicyclo[2.2.0]hexadiene, CD_3CN, and $CDCl_3$ (Aldrich); 0.4 M aqueous $(n\text{-}C_4H_9)_4NOH$ (Eastman); and 50–100 mesh sulfonated 2% cross-linked polystyrene cation-exchange resin in hydrogen form (Bio-Rad).

$Mn(CO)_5Br$[6] and $Re(CO)_5Br$[6] were prepared according to literature procedures. $[(OC)_3M(NCCH_3)_3]PF_6$ (M = Mn, Re) were prepared according to the procedures described for the preparation of the analogous ClO_4^- salts[7] using $AgPF_6$ instead of $AgClO_4$. They were isolated and subsequently used in crude form. $Na_3P_3O_9\cdot 6H_2O$[8] and $\{[(CH_3)_5C_5]RhCl_2\}_2$[9] were prepared according to published procedures. $[(C_7H_8)RhCl]_2$ was prepared according to Schrock and Osborn's modification[10] of Abel's[11] original procedure. Cation-exchange resin was converted quantitatively from H^+ to $(n\text{-}C_4H_9)_4N^+$ form by stirring with 20% molar excess $(n\text{-}C_4H_9)NOH$ as a 0.1 M aqueous solution for 24 h. Resin capacity (mm/g) was determined from H^+ resin using standard procedures;[12] percentage cation exchange was determined by back titration of unreacted $(n\text{-}C_4H_9)_4NOH$.

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Anhydrous diethyl ether (Mallinckrodt) was used only from freshly opened cans. Acetonitrile (Aldrich, 99%) and dichloromethane (Fisher) were distilled under N_2 from P_4O_{10} onto activated 3 Å molecular sieves. Chloroform, 1,2-dichloroethane, and toluene (all Fisher) were stored over activated 4 Å molecular sieves. Tetrahydrofuran and acetone (both Fisher) were used only from freshly opened bottles. The acetonitrile used in the conductivity experiments required further purification. Prepurified acetonitrile was distilled under N_2 from CaH_2. The middle fraction was collected and stored over activated 3 Å molecular sieves. Molecular sieves were activated by drying at 350 °C for 24 h and storing under N_2 at room temperature.

Reactions involving organometallic reagents were routinely performed in an N_2 atmosphere.

Analytical Procedures. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Conductivity experiments[13,14] were performed by using acetonitrile solutions over an equivalent concentration range of ca. 10^{-2}–10^{-4} equiv/L at 25.0 ± 0.2 °C using a Beckman RC-18A conductivity bridge.

Infrared spectra were measured from mineral oil (Nujol) mulls between NaCl plates or as KBr pellets on a Perkin-Elmer 1330 spectrometer. The spectra were referenced to the 1028 cm^{-1} band of a 0.05-mm polystyrene film. Solution infrared spectra in the carbonyl stretching region were measured from CH_3CN solutions in Beckman F-05 solution cells (0.1-mm path length) equipped with CaF_2 windows. These spectra were referenced to the 1945 cm^{-1} band of a 0.05-mm polystyrene film.

^1H and ^{13}C NMR spectra were recorded, 360 and 90.5 MHz, respectively, on a Nicolet NTC-360 spectrometer equipped with a deuterium lock. Chemical shifts were internally referenced to $(CH_3)_4Si$. ^{31}P NMR spectra were measured at 40.5 MHz on a Varian XL-100 spectrometer equipped with a deuterium lock. These spectra were referenced to external 85% H_3PO_4 by the sample replacement method. Chemical shifts for all nuclei are reported as positive numbers for resonances which are observed at higher frequency (lower field) than the appropriate reference.

Preparation of $[(C_7H_8)Rh(NCCH_3)_2]PF_6$. This material was prepared following the procedures outlined in ref 15. Solid $AgPF_6$ (0.52 g, 2.1 mmol) was added to a solution of 0.47 g of $[(C_7H_8)RhCl]_2$ (1.0 mmol) in 13 mL of CH_2Cl_2 and 3 mL of CH_3CN with rapid stirring. An exothermic reaction occurred, yielding an off-white AgCl precipitate. After ca. 10 min of further stirring, the precipitate was removed by filtration and the clear, yellow filtrate was added to 65 mL of diethyl ether without stirring. Brilliant yellow microcrystals separated from the solution within an hour. These crystals were collected by filtration, washed with 3 × 5 mL of diethyl ether, and dried in vacuo over P_4O_{10} (0.72 g, 1.7 mmol, 85% yield).

Preparation of $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3$.[16] A solution prepared from 6.0 g (14.5 mmol) of $(P_3O_9)Na_3{\cdot}6H_2O$ and 300 mL of deionized water was passed at a flow rate of ca. 2 mL/min through a 2-cm diameter column containing 60 mmol of $(n\text{-}C_4H_9)_4N^+$ cation on the exchange resin described above which had been prewashed with 100 mL of deionized water. The initial 50 mL of effluent was discarded and the remainder combined with effluent generated by rinsing the column with 50 mL of deionized water after elution was completed. The effluent was evaporated to an oily solid under vacuum at 40–50 °C and washed with 3 × 50 mL of ether to yield a tacky, off-white solid which was dried overnight in vacuo over P_4O_{10}. The crude product was dissolved in 75 mL of 1,2-$C_2H_4Cl_2$ and gravity filtered under N_2 to remove insoluble impurities. Addition of excess ether (400 mL) to the filtrate caused separation of a tacky solid or oil which solidified to an off-white powder upon washing with 3 × 75 mL ether and scratching with a spatula. The solid was collected by suction filtration, washed with 3 × 50 mL of ether, and dried in vacuo over P_4O_{10} to yield 10.5 g product (10.4 mmol, 72% based on P). The resulting colorless, slightly hygroscopic powder was sufficiently pure to be utilized as the starting material for preparations described below. The reprecipitation procedure was repeated three times to obtain the analytical sample. The product decomposes slowly in the acidic environment of P_4O_{10} dessicant and should not be stored over P_4O_{10} for longer than a week.

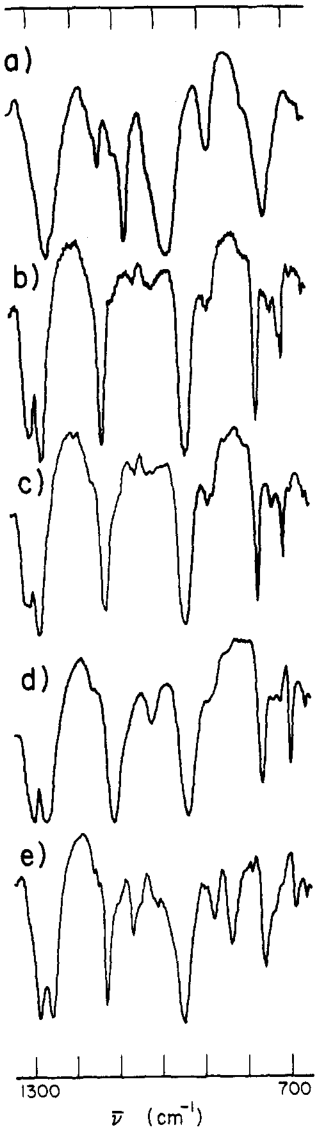

Figure 1. IR spectra of (a) $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3$, (b) $[(OC)_3Mn(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (1), (c) $[(OC)_3Re(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (2), (d) $\{[(CH_3)_5C_5]Rh(P_3O_9)\}[(n\text{-}C_4H_9)_4N]$ (3), and (e) $[(C_7H_8)Rh(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (4) measured from Nujol mulls. See Experimental section for numerical data.

Anal. Calcd for $C_{48}H_{108}N_3P_3O_9{\cdot}2.5H_2O$: C, 57.12; H, 11.28; N, 4.16; P, 9.21. Found: C, 57.15; H, 11.23; N, 4.11; P, 9.30.

IR (Nujol, 700–1325 cm^{-1}, see Figure 1a): 752 (s, br), 883 (m), 979 (s, br), 1076 (s), 1105 (m, sh), 1140 (m), 1151 (w, sh), 1247 (s, sh), 1261 (s, br); ^{31}P NMR (CD_3CN 25 °C, 0.033 M): δ −22.0.[17]

Preparation of $[(OC)_3Mn(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (1). The following procedure was performed in the dark because the product is very light sensitive in solution. The product in the solid state may be handled for short periods in ordinary room light but should be stored in foil wrapped containers. $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3{\cdot}2.5H_2O$ (2.64 g, 2.6 mmol) was added to a solution of 1.07 g of $[(OC)_3Mn(NCCH_3)_3]PF_6$ (2.6 mmol) in 14 mL of 1,2-$C_2H_4Cl_2$. The resulting clear yellow reaction solution was refluxed for 15 min. After the solution was cooled to room temperature, addition of excess ether (ca. 100 mL) caused a yellow, tacky solid to separate from solution which turned into a powdery yellow solid upon washing with ether (3 × 50 mL) and scratching

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with a spatula. The solid (2.8 g) was dried overnight in vacuo over P_4O_{10} and shown to contain PF_6^- by IR spectroscopy. Crystallization was accomplished by adding hot THF to a stirred suspension of the crude product in 4 mL of toluene. Initial addition of the THF caused the solid to turn into an orange oil. THF addition was continued while the suspension was stirred and heated at boiling temperature until the oil dissolved (final volume was ca. 60 mL). The resulting slightly cloudy, yellow solution was gravity filtered while hot and the filtrate was stored at −30 °C for ca. 6 h. After this time, the product usually separated from solution as feathery, yellow crystals. If crystals were not formed after this time period, the solution was shaken and stored for an additional 6 h at −30 °C to induce crystallization. The crystalline product was collected by filtration, washed with 3 × 20 mL of ether, and dried in vacuo over P_4O_{10} (1.50 g, 67%).

Anal. Calcd for $C_{35}H_{72}N_2P_3MnO_{12}$: C, 48.84; H, 8.43; N, 3.25; P, 10.79; Mn, 6.38. Found: C, 48.97; H, 8.47; N, 3.24; P, 10.87; Mn, 6.19.

Conductivity:[13,14] $\Lambda_0 = 163$, $A = 712$; $A_{\text{calcd}} = 711$ for 2:1 electrolyte, $A_{\text{calcd}} = 1516$ for 4:1 electrolyte.

IR (CH_3CN, 1850–2050 cm^{-1}): 1913 (s, br), 2034 (s). IR (Nujol, 700–1325 cm^{-1}, see Figure 1b): 714 (m), 722 (m, sh), 742 (w), 774 (s), 884 (w, br), 942 (s), 1136 (s), 1280 (s), 1308 (s). ^{31}P NMR (CD_3CN, 25 °C, 0.033 M): δ −9.9.

Preparation of [(OC)$_3$Re(P$_3$O$_9$)][(*n*-C$_4$H$_9$)$_4$N]$_2$ (2). The preparation of this compound closely resembles that of the Mn derivative. $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3\cdot 2.5H_2O$ (4.36 g, 4.3 mmol) was added to a solution of $[(OC_3)Re(NCCH_3)_3]PF_6$ (2.31 g, 4.3 mmol) in 15 mL of 1,2-$C_2H_4Cl_2$. A clear, pale yellow solution results. The reaction solution was refluxed for 5 h, during which time it became slightly cloudy. After the solution was cooled to room temperature, addition of excess ether (ca. 100 mL) caused a pale yellow oil to separate which turned into an off-white powder upon washing with 3 × 30 mL of ether and scratching with a spatula. The crude product was collected by suction filtration, washed with 4 × 20 mL of ether, and dried in vacuo over P_4O_{10} (5.4 g). Crystallization was accomplished by adding ca. 100 mL of hot THF to a stirred suspension of the crude product in 10 mL of toluene. Initial THF addition caused the product to turn into a pale yellow oil, and the addition was continued while the suspension was stirred and heated until all of the oil dissolved. The resulting slightly cloudy solution was gravity filtered while hot, and the pale yellow filtrate was cooled to −30 °C. After 12 h at this temperature, during which time the solution was occasionally shaken to induce crystallization, the colorless, featherlike crystals which separated were collected by suction filtration, washed with 3 × 20 mL of ether, and dried in vacuo (2.3 g, 54%).

Anal. Calcd for $C_{35}H_{72}N_2P_3ReO_{12}$: C, 42.37; H, 7.31; N, 2.82; P, 9.37; Re, 18.77. Found: C, 42.33; H, 7.41; N, 2.83; P, 9.36; Re, 18.90.

Conductivity:[13,14] $\Lambda_0 = 166$, $A = 700$; $A_{\text{calcd}} = 718$ for 2:1 electrolyte, $A_{\text{calcd}} = 1532$ for 4:1 electrolyte.

IR (CH_3CN, 1850–2050 cm^{-1}): 1885 (s, br), 2018 (s). IR (Nujol, 700–1325 cm^{-1}, see Figure 1c): 712 (m), 739 (w), 772 (s), 888 (w, br), 943 (s), 1130 (s), 1285 (s), 1314 (s, br). ^{31}P NMR (CD_3CN, 25 °C, 0.033 M): δ −11.5.

Preparation of {[(CH$_3$)$_5$C$_5$]Rh(P$_3$O$_9$)}[(*n*-C$_4$H$_9$)$_4$N] (3). The following procedure was performed in an anhydrous environment since $AgPF_6$ is hygroscopic. $AgPF_6$ (0.72 g, 6.8 mmol) was added to a stirred, partially dissolved slurry of 1.05 g (1.7 mmol) of $\{[(CH_3)_5C_5]RhCl_2\}_2$ in 20 mL of CH_3CN. This resulted in a rapid, exothermic reaction and immediate precipitation of AgCl and generation of $\{[(CH_3)_5C_5]Rh(NCCH_3)_3\}^{2+}$.[18] The AgCl was filtered off and washed with 3 × 5 mL of CH_3CN. These washes were added to the orange filtrate, and the combined solution was added with stirring to a solution of 3.42 g (3.4 mmol) of $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3\cdot 2.5H_2O$ in 10 mL of CH_3CN. Addition of excess ether (200 mL) caused the product to separate from solution as an orange microcrystalline solid or powder which was collected by suction filtration, washed with 3 × 20 mL of ether, and dried in vacuo (1.98 g, 81%). Recrystallization was accomplished by dissolving the crude product in 3 mL of hot $CHCl_3$ and cooling the clear red-orange solution to room temperature and then −30 °C. The irregularly shaped orange crystals which separated after 12 h were collected by filtration, washed with ether, and dried in vacuo (1.83 g, 93%).

Anal. Calcd for $C_{26}H_{51}NP_3RhO_9$: C, 43.52; H, 7.16; N, 1.95; P, 12.95; Rh, 14.34. Found: C, 43.34; H, 7.23; N, 1.88; P, 12.86; Rh, 14.21.

IR (Nujol, 700–1325 cm^{-1}, see Figure 1d); 701 (m), 713 (w), 740 (w), 766 (m), 891 (w, sh), 943 (s, br), 1024 (w) 1115 (s, br), 1274 (s, br), 1303 (s). ^{1}H NMR ($CDCl_3$, 25 °C): in addition to cation resonances at δ 0.95–1.05, 1.4–1.5, 1.55–1.65, and 3.15–3.25, the $(CH_3)_5C_5$ singlet is observed at δ 1.60. $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C): δ 92.1 (d, $^1J_{RhC} = 11$ Hz, $(CH_3)_5C_5$), 59.3 (t, NCH_2[19]), 24.4 (s, NCH_2CH_2[19]), 20.4 (s, CH_2CH_3[19]), 13.9 (s, CH_2CH_3[19]), 8.7 (s, $(CH_3)_5C_5$). ^{31}P NMR (CD_3CN, 25 °C, 0.033 M): δ −10.9 (d, $^2J_{RhP} = 2$ Hz).

Preparation of [(C$_7$H$_8$)Rh(P$_3$O$_9$)][(*n*-C$_4$H$_9$)$_4$N]$_2$ (4). The following procedure was carried out in an anhydrous environment because the product is extremely hygroscopic. A solution of 4.59 g (4.6 mmol) of $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3\cdot 2.5H_2O$ in 10 mL of CH_2Cl_2 was added dropwise over a 3–5-min period to a rapidly stirred solution of 1.92 g (4.6 mmol) of $[(C_7H_8)Rh(NCCH_3)_2]PF_6$ in 10 mL of CH_2Cl_2. Initial addition caused precipitation of a yellow powder which redissolved as more $(P_3O_9)[(n\text{-}C_4H_9)_4N]$ solution was added. A slightly cloudy, golden yellow solution was obtained after addition was complete. The reaction solution was filtered, and excess ether (ca. 60 mL) was added causing a gold oil to separate. The oil was solidified to a yellow powder by washing with ether and scratching with a spatula. The solid was collected by suction filtration, washed with 3 × 20 mL of ether, and dried in vacuo over P_4O_{10} (3.79 g, 4.1 mmol, 91%). Crystalline product was obtained by dissolving the crude product in ca. 7 mL of hot acetone and cooling the resulting golden yellow solution to room temperature and then −30 °C. Gold, rod-shaped, extremely hygroscopic crystals separated from solution within 12 h. The crystals were collected by filtration and washed with 3 × 10 mL of ether causing them to crumble to a yellow powder which was dried in vacuo over P_4O_{10} (2.2 g, 2.4 mmol, 58%).

Anal. Calcd for $C_{39}H_{80}N_2P_3RhO_9$: C, 51.09; H, 8.79; N, 3.06; P, 10.13; Rh, 11.22. Found: C, 51.14; H, 8.54; N, 3.05; P, 9.97; Rh, 11.16.

IR (Nujol, 700–1325 cm^{-1}, see Figure 1e): 764 (m), 842 (m), 884 (m), 954 (s, br), 1074 (m), 1135 (s), 1263 (s, br), 1292 (s). ^{1}H NMR ($CDCl_3$, 25 °C): in addition to cation resonances at δ 0.95–1.05, 1.4–1.5, 1.55–1.65, and 3.15–3.25, resonances for the C_7H_8 ligand are found at δ 3.60, 3.39, and 0.95. $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C): δ 59.2 (s, NCH_2[19]), 59.1 (d, $^3J_{Rh-C} = 8$ Hz, CH_2[20]), 49.6 (d, $^2J_{Rh-C} = 3$ Hz, aliphatic CH[20]), 43.0 (d, $^1J_{Rh-C} = 12$ Hz, olefinic CH[20]), 24.4 (s, NCH_2CH_2[19]), 20.3 (s, CH_2CH_3[19]), 13.9 (s, CH_3[19]). ^{31}P NMR ($CDCl_3$, 25 °C, 0.033 M): δ −13.6.

X-ray Crystallographic Study[21] of [(C$_7$H$_8$)Rh(P$_3$O$_9$)][(*n*-C$_4$H$_9$)$_4$N]$_2$ (4). Yellow single crystals of 4 suitable for X-ray diffraction studies were grown as described above from a hot acetone solution. They are, at 20 ± 1 °C, monoclinic with a = 11.339 (3) Å, b = 13.527 (3) Å, c = 32.739 (8) Å, β = 97.95 (2)°, V = 4973 (2) Å, and $Z = 4$ [$\mu_a(\text{MoK}\bar{\alpha})^{22a} = 0.48$ mm^{-1}; $d_{\text{calcd}} = 1.224$ g cm^{-3}]. The systematically absent reflections in the diffraction pattern were those uniquely required by the centrosymmetric space group $P2_1/n$ (an alternate setting of $P2_1/c$—C_{2h}^5, No. 14).[23]

Intensity measurements were made on a Nicolet P$\bar{1}$ autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation for a specimen having the shape of a rectangular parallelepiped with dimensions of 0.39 × 0.50 × 0.72 mm. This crystal was sealed under N_2 in a thin-walled glass capillary and mounted on a goniometer with its longest edge nearly parallel to the ϕ axis of the diffractometer. A total of 6835

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(21) See paragraph at end of paper regarding supplementary material.

(22) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 55–66; (b) pp 99–101; (c) pp 149–50.

(23) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

independent reflections having 2θ (Mo K$\bar{\alpha}$) <45.8° (the equivalent of 0.60 limiting Cu Kα spheres) were measured with scanning rates of 6°/min for those reflections having $3° < 2\theta < 43°$ and 4°/min for all others. The data collection and reduction procedures that were used are described elsewhere.[2] In the present study, the scan width and stepoff for background measurements were both 0.90° and the ratio of total background counting time to net scanning time was 0.50. The intensity data were corrected empirically for absorption effects using ψ scans for six intense reflections having 2θ between 7.9° and 30.4° (the relative transmission factors ranged from 0.823 to 1.000).

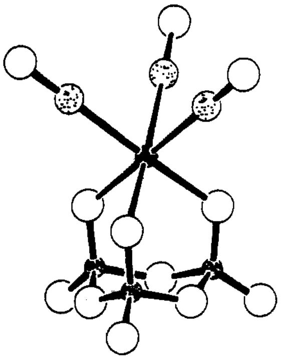
The structure was solved by using the "heavy-atom" technique. Isotropic full-matrix least-squares refinement of the structural parameters for the Rh atom converged to R_1 (unweighted, based on F)[24] = 0.505 and R_2 (weighted, based on F)[24] = 0.561 for 4042 independent absorption-corrected reflections having 2θ (Mo K$\bar{\alpha}$) < 45.8° and $I > 3\sigma(I)$. These and all subsequent refinement cycles employed weights derived from counting statistics.[24] Inclusion of the three phosphorus atoms, nine anionic oxygen atoms, and 33 cationic carbon and nitrogen atoms into the structural model with anisotropic thermal parameters gave $R_1 = 0.137$ and $R_2 = 0.208$ for 4042 reflections. A difference Fourier calculated at this point contained electron density maxima slightly above the noise level in the region near the Rh atom and opposite the three Rh-bonded $P_3O_9^{3-}$ oxygen atoms. Six of these peaks were nearly coplanar and equidistant from the Rh atom; they described an approximate hexagon which was oriented nearly parallel to the plane of the three Rh-bonded oxygen atoms. Such an arrangement would result from a statistical disordering of the norbornadiene (olefinic) bonds about the pseudo-C_3 axis passing through Rh and the center of gravity for the P_3O_9 ligand. These six peaks were included in the model as anisotropic carbon atoms with occupancies of 0.667 before calculating another difference Fourier map. Two of the top peaks in this map appeared to correspond to a (threefold disordered) bridgehead carbon (C_7) and the unique methylene carbon (C_8); these peaks were included in the model as anisotropic carbon atoms with occupancies of 0.333 and 1.000, respectively (Figure 2). Positions for the methylene hydrogen atoms of the $(n\text{-}C_4H_9)_4N^+$ cations were calculated at this point assuming idealized sp^3 hybridization for the carbon atom and a C–H bond length of 0.96 Å; each of these hydrogen atoms was included in the final structure factor calculations with an isotropic thermal parameter fixed at 1.2 times the value of the equivalent isotropic thermal parameter for the carbon atom to which it is covalently bonded.

The final cycles[21] of cascade block diagonal least-squares refinement which utilized anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all (fixed) cationic methylene hydrogen atoms gave $R_1 = 0.069$ and $R_2 = 0.072$ for 4042 absorption-corrected reflections having 2θ(Mo Kα) < 45.8° and $I > 3\ \sigma(I)$.

All structure factor calculations employed recent tabulations of atomic form factors[22b] and anomalous dispersion corrections[22c] to the scattering factors of the Rh and P atoms. All calculations were performed on a Data General Eclipse S-200 computer equipped with 128 K of 16-bit words, a floating point processor for 32- and 64- bit arithmetic, and versions of the EXTL and SHELXTL interactive crystallographic software package as modified at Crystalytics Co.

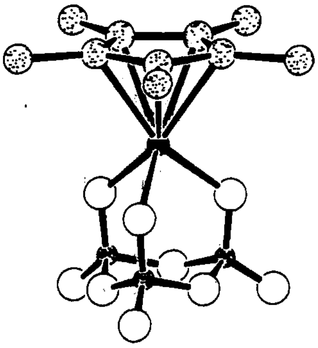
Results

$[(OC)_3M(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$, M = Mn (1) and Re (2). These complexes are easily prepared from $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3$ and $[(OC)_3M(NCCH_3)_3](PF_6)$ in CH_3CN. They are formulated on the basis of elemental analyses, and conductivity measurements clearly identify them as 2:1 electrolytes (see Experimental Section). The C_{3v} structure proposed in **e** is consistent with ^{31}P NMR spectra which show single resonances and with IR spectra in the carbonyl stretching region which show absorptions characteristic of facial tricarbonyl groups in octahedral complexes.[25]



e

$\{[(CH_3)_5C_5]Rh(P_3O_9)\}[(n\text{-}C_4H_9)_4N]$ (3). This complex is also prepared from $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3$ and a solvated organometallic cation, here $\{[(CH_3)_5C_5]Rh(NCCH_3)_3\}^{2+}$ as a PF_6^- salt, in CH_3CN. Comparison of its IR spectrum in the 700–1300 cm^{-1} region shown in Figure 1d with the spectra of compounds 1 and 2 in the same region (see Figure 1b,c) strongly suggests isostructural metal phosphate frameworks. The structure shown in **f** is supported by ^{1}H, ^{13}C{^{1}H}, and ^{31}P NMR data given in the Experimental Section.



f

$[(C_7H_8)Rh(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (4). Reaction of $(P_3O_9)[(n\text{-}C_4H_9)_4N]_3$ with $[(C_7H_8)Rh(NCCH_3)_2](PF_6)$ yields a product formulated as 4 from its elemental composition and NMR spectroscopic properties (see Experimental Section). The IR spectrum of 4 in the 700–1300 cm^{-1} region shown in Figure 1e displays the same principal absorptions present in spectra of 1–3 but differs significantly in detail. Since NMR data are consistent with either an 18-electron (norbornadiene)rhodium(I) complex containing a C_{3v}, tridentate trimetaphosphate ligand or a labile 16-electron complex containing a C_s, bidentate trimetaphosphate ligand which exchanges or rearranges rapidly on the NMR time scale, an X-ray diffraction study was undertaken to establish the $[(C_7H_8)Rh(P_3O_9)]^{2-}$ structure.

X-ray structural analysis revealed that single crystals of 4 are composed of discrete, disordered $[(C_7H_8)Rh(P_3O_9)]^{2-}$ anions (Figure 2) and $(n\text{-}C_4H_9)_4N^+$ cations (Figure 3).[21] Final atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms of 4 are given with estimated standard deviations in Tables I and II,[21] respectively. Idealized coordinates generated for the meth-

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[24] The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor. The weighting scheme uses $w = 1/\sigma_F^2$; for weights derived from counting statistics: $\sigma_F = \{[\sigma(F_o)]^2 + (0.01|F_o|)^2\}^{-1/2}$.

[25] Kraihanzel, C. S.; Maples, P. K. *J. Organomet. Chem.* **1976**, *117*, 159–170.

Table I. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[(C_7H_8)Rh(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (4)[a]

atom type[b]	10^4x	10^4y	10^4z	equiv isotropic thermal parameter,[c] Å^2
		Anion		
Rh	3164.4 (7)	3086.9 (5)	4025.1 (2)	8.32 (2)
P_1	1713 (2)	1542 (2)	3318 (1)	6.7 (1)
P_2	3962 (2)	893 (2)	3736 (1)	5.7 (1)
P_3	1913 (2)	916 (2)	4154 (1)	5.8 (1)
O_{1a}	1918 (5)	2598 (4)	3428 (2)	8.3 (2)
O_{2a}	4406 (4)	1894 (3)	3884 (1)	6.3 (2)
O_{3a}	2151 (5)	1939 (4)	4320 (2)	7.5 (2)
O_{12}	2982 (4)	1022 (4)	3334 (1)	6.0 (2)
O_{13}	1225 (3)	984 (4)	3691 (1)	5.9 (1)
O_{23}	3153 (4)	449 (3)	4061 (1)	5.4 (1)
O_{1b}	1015 (5)	1248 (5)	2931 (2)	10.2 (2)
O_{2b}	4813 (4)	128 (4)	3649 (2)	7.9 (2)
O_{3b}	1312 (4)	192 (4)	4381 (1)	7.5 (2)
C_1[d]	4335 (28)	3849 (17)	4459 (7)	12.0 (10)
C_2[d]	4608 (16)	4078 (16)	4146 (10)	11.2 (8)
C_3[d]	3790 (46)	4332 (20)	3814 (7)	19.5 (16)
C_4[d]	2451 (25)	4522 (19)	3961 (9)	13.4 (9)
C_5[d]	2496 (19)	4198 (14)	4384 (11)	11.8 (9)
C_6[d]	3476 (30)	4224 (28)	4580 (7)	15.7 (13)
C_7[d]	3674 (50)	5019 (20)	3999 (14)	13.1 (18)
C_8[d]	3814 (16)	5468 (10)	4363 (6)	17.3 (7)
		Cation 1		
N	2761 (4)	3941 (4)	−606 (2)	6.6 (2)
C_{1a}	1601 (5)	3821 (6)	−423 (2)	6.7 (3)
C_{2a}	2398 (6)	4099 (7)	−1069 (2)	7.6 (3)
C_{3a}	3470 (7)	4790 (6)	−415 (2)	7.1 (3)
C_{4a}	3593 (7)	3084 (7)	−516 (3)	8.7 (3)
C_{1b}	1702 (7)	3563 (6)	30 (2)	7.1 (3)
C_{2b}	3421 (8)	4252 (8)	−1305 (2)	10.9 (4)
C_{3b}	2854 (7)	5771 (7)	−479 (3)	9.1 (3)
C_{4b}	3135 (9)	2029 (9)	−679 (4)	13.6 (5)
C_{1g}	486 (7)	3494 (6)	175 (3)	9.2 (3)
C_{2g}	2925 (16)	4359 (15)	−1758 (5)	18.3 (10)
C_{3g}	3675 (8)	6621 (7)	−304 (3)	9.6 (4)
C_{4g}	3985 (11)	1146 (10)	−553 (5)	19.8 (8)
C_{1d}	472 (9)	3199 (6)	616 (3)	9.7 (4)
C_{2d}	2716 (27)	5184 (20)	−1855 (7)	26.3 (13)
C_{3d}	3119 (11)	7621 (8)	−354 (4)	12.5 (5)
C_{4d}	3571 (19)	227 (10)	−736 (7)	25.5 (11)
		Cation 2		
N	2194 (6)	3334 (5)	2175 (2)	7.1 (2)
C_{1a}	1304 (7)	2496 (6)	2114 (2)	8.2 (3)
C_{2a}	3149 (6)	2970 (6)	2514 (2)	7.9 (3)
C_{3a}	2724 (7)	3564 (6)	1776 (2)	7.8 (3)
C_{4a}	1618 (7)	4278 (5)	2296 (2)	7.3 (3)
C_{1b}	209 (8)	2657 (8)	1779 (3)	10.7 (4)
C_{2b}	4170 (8)	3677 (7)	2618 (3)	11.4 (4)
C_{3b}	3315 (9)	2703 (7)	1604 (3)	10.7 (4)
C_{4b}	950 (8)	4193 (7)	2657 (3)	8.9 (3)
C_{1g}	−636 (11)	1720 (9)	1767 (4)	14.8 (5)
C_{2g}	5175 (10)	3146 (9)	2922 (4)	14.0 (5)
C_{3g}	3889 (10)	2977 (7)	1229 (3)	12.4 (5)
C_{4g}	490 (10)	5133 (8)	2753 (3)	11.9 (5)
C_{1d}[e]	−1630 (20)	1815 (18)	1472 (8)	18.2 (12)
C_{1d}'[e]	−1387 (28)	1787 (21)	2109 (10)	19.0 (16)
C_{2d}	6282 (13)	3775 (12)	3033 (5)	18.6 (7)
C_{3d}	4414 (15)	2179 (10)	1028 (5)	21.3 (8)
C_{4d}	−493 (11)	5048 (11)	3095 (4)	16.8 (6)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figures 2 and 3. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor. [d] The C_7H_8 ligand is disordered in the lattice with three preferred orientations about a pseudo-C_3 axis passing through C_8 and Rh. $C_1 \rightarrow C_6$ therefore represent the statistically disordered positions for the four olefinic carbon atoms and were included in all structure factor calculations with occupancies of 0.67 each. Only one bridgehead carbon (C_7) could be located from the difference Fourier syntheses, and it was included in all structure factor calculations with an occupancy of 0.33; the bridging methylene carbon atom (C_8) was included with an occupancy of 1.00. [e] Methyl carbon atom C_{1d} of cation 2 is statistically disordered between two sites (C_{1d} and C_{1d}'); the occupancy factors for these two atoms refined to values of 0.55 (1) and 0.45 (1), respectively.

ylene hydrogens of the $(n\text{-}C_4H_9)_4N^+$ cations are given in Table III.[21] Bond lengths and angles for the $[(C_7H_8)Rh(P_3O_9)]^{2-}$ anion and two $(n\text{-}C_4H_9)_4N^+$ cations are given in Tables IV and V,[21] respectively.

Although the norbornadiene ligand in the anion is disordered, the Rh(I) atom clearly forms a formally five-co-

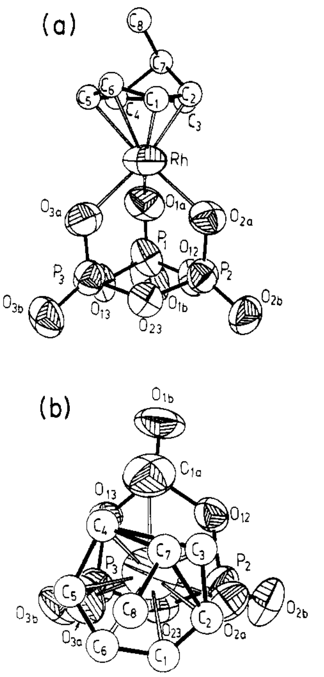
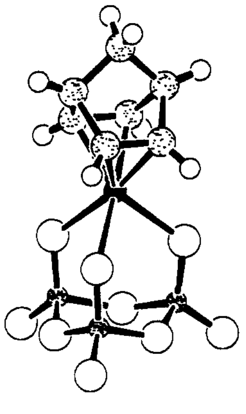


Figure 2. Perspective ORTEP drawings of the non-hydrogen atoms in the solid-state structure of $[(C_7H_8)Rh(P_3O_9)]^{2-}$ in 4. The rhodium, phosphorus, and oxygen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. The carbon atoms of the disordered norbornadiene ligand are represented by arbitrarily sized spheres for purposes of clarity. See footnote *d* of Table I regarding the norbornadiene disorder.

ordinated 18-electron complex by being σ bonded to three terminal oxygen atoms of the $P_3O_9^{3-}$ ligand (see **g**). Even though the norbornadiene ligand disorder prevents a precise characterization of the Rh(I) coordination geometry, the carbon atoms located by X-ray crystallography are in positions consistent with a threefold disordered norbornadiene ligand. Examination of Figure 2 and Table IV indicates the presence of only one (C_7) of the six bridgehead carbons anticipated for a threefold disordered η^4-norbornadiene ligand. This position (C_7) corresponds to a norbornadiene ligand where C_1–C_2 and C_4–C_5 are the π-bonded olefinic groups; the other two norbornadiene orientations would have C_2–C_3 and C_5–C_6 or C_3–C_4 and C_6–C_1 as the respective olefinic pairs. Clearly no choice can be made between square-pyramidal and trigonal-bipyramidal geometry at rhodium; the idealized square-pyramidal conformation chosen for **g** is arbitrary.



g

Table IV. Bond Lengths (Å) and Angles (deg) in the $[(C_7H_8)Rh(P_3O_9)]^{2-}$ Anion of Crystalline $[(C_7H_8)Rh(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (4)[a,b]

Lengths, Å			
Rh–O_{1a}	2.343 (5)	Rh–$C_{1,2}$[c,d]	2.01
Rh–O_{2a}	2.231 (5)	Rh–$C_{1,6}$[c,d]	2.15
Rh–O_{3a}	2.229 (5)	Rh–$C_{2,3}$[c,d]	1.93
Rh–C_1[c]	2.08 (2)	Rh–$C_{3,4}$[c,d]	1.87
Rh–C_2[c]	2.11 (2)	Rh–$C_{4,5}$[c,d]	1.98
Rh–C_3[c]	1.99 (3)	Rh–$C_{5,6}$[c,d]	2.16
Rh–C_4[c]	2.10 (3)	P_1–O_{1a}	1.484 (6)
Rh–C_5[c]	2.11 (3)	P_2–O_{2a}	1.502 (5)
Rh–C_6[c]	2.37 (3)	P_3–O_{3a}	1.497 (5)
C_1–C_2[c]	1.15 (4)	P_1–O_{1b}	1.455 (5)
C_1–C_6[c]	1.21 (5)	P_2–O_{2b}	1.469 (5)
C_2–C_3[c]	1.37 (4)	P_3–O_{3b}	1.455 (5)
C_3–C_4[c]	1.68 (6)	P_1–O_{12}	1.596 (5)
C_4–C_5[c]	1.45 (4)	P_1–O_{13}	1.597 (5)
C_5–C_6[c]	1.21 (4)	P_2–O_{12}	1.609 (4)
C_2–C_7[c]	1.68 (5)	P_2–O_{23}	1.614 (5)
C_3–C_7[c]	1.13 (4)	P_3–O_{13}	1.609 (4)
C_4–C_7[c]	1.53 (6)	P_3–O_{23}	1.608 (5)
C_7–C_8[c]	1.33 (5)		

Angles, deg			
$O_{1a}RhO_{2a}$	87.1 (2)	$O_{1a}P_1O_{12}$	107.8 (3)
$O_{1a}RhO_{3a}$	83.0 (2)	$O_{1a}P_1O_{13}$	109.2 (3)
$O_{2a}RhO_{3a}$	87.9 (2)	$O_{2a}P_2O_{12}$	109.2 (3)
$O_{1a}RhC_{1,2}$[c,d]	149.7	$O_{2a}P_2O_{23}$	108.5 (3)
$O_{1a}RhC_{4,5}$[c,d]	103.6	$O_{3a}P_3O_{13}$	109.2 (3)
$O_{2a}RhC_{1,2}$[c,d]	94.2	$O_{3a}P_3O_{23}$	108.3 (3)
$O_{2a}RhC_{4,5}$[c,d]	164.2	$O_{1b}P_1O_{12}$	106.7 (3)
$O_{3a}RhC_{1,2}$[c,d]	127.3	$O_{1b}P_1O_{13}$	109.5 (3)
$O_{3a}RhC_{4,5}$[c,d]	104.8	$O_{2b}P_2O_{12}$	108.4 (3)
$O_{1a}RhC_{2,3}$[c,d]	117.4	$O_{1a}P_1O_{1b}$	121.5 (4)
$O_{1a}RhC_{5,6}$[c,d]	132.2	$O_{2a}P_2O_{2b}$	119.9 (3)
$O_{2a}RhC_{2,3}$[c,d]	98.2	$O_{3a}P_3O_{3b}$	120.6 (3)
$O_{2a}RhC_{5,6}$[c,d]	140.7	$O_{2b}P_2O_{23}$	108.3 (3)
$O_{3a}RhC_{2,3}$[c,d]	158.9	$O_{3b}P_3O_{13}$	108.6 (3)
$O_{3a}RhC_{5,6}$[c,d]	95.0	$O_{3b}P_3O_{23}$	108.4 (3)
$O_{1a}RhC_{1,6}$[c,d]	157.9	$O_{13}P_1O_{12}$	99.9 (2)
$O_{1a}RhC_{3,4}$[c,d]	94.6	$O_{12}P_2O_{23}$	100.8 (2)
$O_{2a}RhC_{1,6}$[c,d]	113.3	$O_{13}P_3O_{23}$	99.6 (2)
$O_{2a}RhC_{3,4}$[c,d]	130.5	$C_6C_1C_2$[c]	120 (3)
$O_{3a}RhC_{1,6}$[c,d]	105.2	$C_1C_2C_3$[c]	122 (3)
$O_{3a}RhC_{3,4}$[c,d]	141.5	$C_2C_3C_4$[c]	111 (2)
$RhO_{1a}P_1$	122.0 (3)	$C_3C_4C_5$[c]	109 (2)
$RhO_{2a}P_2$	121.8 (2)	$C_4C_5C_6$[c]	114 (3)
$RhO_{3a}P_3$	124.3 (3)	$C_5C_6C_1$[c]	122 (3)
$P_1O_{12}P_2$	126.3 (3)	$C_1C_2C_7$[c]	103 (3)
$P_1O_{13}P_3$	124.9 (3)	$C_5C_4C_7$[c]	98 (3)
$P_2O_{23}P_3$	124.7 (3)	$C_2C_7C_8$[c]	96 (3)
		$C_4C_7C_8$[c]	106 (4)
		$C_2C_7C_4$[c]	103 (2)

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit. [b] Atoms are labeled in agreement with Figure 2 and Tables I and II. [c] See footnote *d* of Table I. [d] $C_{m,n}$ refers to the midpoint of the olefinic bond between the carbon atoms C_m and C_n.

The bond lengths and angles given in Table IV are unexceptional. The Rh–O and Rh–C distances are within the ranges expected for a (diene)RhL$_3$ complex,[26] with average bond lengths of 2.268 (5, 50, 75, 3) Å[27] and 2.13 (3, 18, 24, 6) Å,[27] respectively. The average P^V–O bond lengths in 4 clearly reflect the weakness of Rh^I–O bonds relative to P^V–O bonds. The P^V–O bonds for oxygens that bridge phosphorous and rhodium atoms [average length

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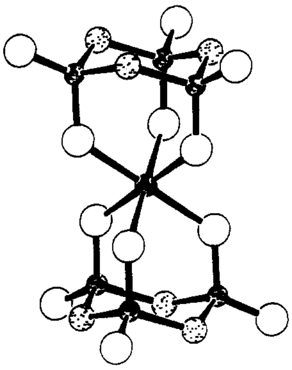
(26) Hughes, R. P.; Krishnamachari, N.; Lock, C. J. L.; Powell, J.; Turner, G. *Inorg. Chem.* **1977**, *16*, 314–319.

(27) The first number in parentheses following an averaged value of a bond length is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

= 1.494 (5, 7, 10, 3) Å[27]] are only 0.035 Å longer than the terminal P^V–O bonds [average length = 1.459 (5, 6, 10, 13) Å[27]] but are 0.112 Å shorter than the P^V–O bonds for oxygens that bridge two phosphorus atoms [average length = 1.606 (5, 6, 10, 6) Å[27]].

Discussion

The compounds reported here are believed to be the first metal trimetaphosphate complexes to be isolated. The coordination chemistry of the closely related trimetaphosphimate ligand $[P_3(NH)_3O_6]^{3-}$ has been investigated, however. In this cyclic ligand, PO_2 units are linked by bridging NH units, not O units as in the trimetaphosphate ligand $P_3O_9^{3-}$. The trimetaphosphimate ligand acts as a κ^3O ligand in several complexes.[28] The structure of $\{Ga[P_3(NH)_3O_6]_2\}Na_3$,[28a] **h**, is representative and illustrates the similarity between tridentate $P_3O_9^{3-}$ and $P_3(NH)_3O_6^{3-}$ ligand geometries. Other ligation modes are also possible. The $\{Cu[P_3(NH)_3O_6]_2(OH_2)_2\}^{4-}$ ion,[29] for example, contains two bidentate, κ^2O trimetaphosphimate ligands. By analogy, the trimetaphosphate ligand is potentially a flexidentate ligand.



h

Compounds 1–4 are probably only the first examples of a large family of polymetaphosphate organometallic complexes. The tetrametaphosphate anion, for example, can be isolated as an organic soluble tetrabutylammonium salt.[17] Its metaphosphimate analogue $[P_4(NH)_4O_8]^{4-}$ has been shown to act as a κ^4O ligand in the eight-coordinate sandwich compound $\{Tm[P_4(NH)_4O_8]_2\}^{4-}$.[30] The $P_4O_{12}^{4-}$ anion therefore may play a role in organoactinide chemistry similar to the role played by $P_3O_9^{3-}$ in organotransition-metal chemistry.

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Registry No. 1, 76791-29-2; 2, 76791-27-0; 3, 94518-32-8; 4, 94518-34-0; $[(C_7H_8)Rh(NCCH_3)_2]PF_6$, 83232-01-3; $\{[(CH_3)_5C_5]Rh(NCCH_3)_3\}(PF_6)_2$, 59738-28-2; $[(C_7H_8)RhCl]_2$, 12257-42-0; $[(OC)_3Mn(NCCH_3)_3]PF_6$, 54039-60-0; $[(OC)_3Re(NCCH_3)_3]PF_6$, 66610-18-2; $\{[(CH_3)_5C_5]RhCl_2\}_2$, 12354-85-7; $(P_3O_9)[n\text{-}C_4H_9)_4N]_3$, 57344-39-5; $(P_3O_9)Na_3$, 7785-84-4.

Supplementary Material Available: Crystal Structure Analysis Report, Table II (anisotropic thermal parameters for non-hydrogen atoms in 4), Table III (idealized positions for methylene hydrogen atoms in cations of 4), Table V (bond lengths and angles in cations of 4), Figure 3 (ORTEP drawings for cations of 4), and structure factor tables for the X-ray structural study of 4 (33 pages). Ordering information is given on any current masthead page.

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