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Articles

Multimetallic Complexes Containing Tris(dimethylphosphino)methane. Crystal and Molecular Structure of $[Ru_3(CO)_9(HC(P(CH_3)_2)_3)(\mu\text{-}AuP(C_6H_5)_3)]O_3SCF_3{\cdot}(CH_3)_2CO$[1]

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Tris(dimethylphosphino)methane (tmpm) forms the complexes $Ru_3(CO)_9(\eta^3\text{-tmpm})$, $Re_2(CO)_8(\eta^2\text{-tmpm})$, $MCl(CO)((\mu\text{-tmpm})Re_2(CO)_8)_2$ (M = Rh, Ir), $cp_2W_2(CO)_4(\eta^2\text{-tmpm})$, $cp_2W_2(CO)_4((\mu\text{-tmpm})IrCl(CO)(PPh_3))$, $Fe_2(CO)_7(\mu\text{-tmpm})$, and $M(CO)_4(\eta^2\text{-tmpm})$ (M = Cr, Mo). $Ru_3(CO)_9(\eta^3\text{-tmpm})$ reacts with $HPF_6{\cdot}Et_2O$ and $[(PPh_3)Au]O_3SCF_3$ to form $[Ru_3(CO)_9(\eta^3\text{-tmpm})(\mu\text{-}X)]Y$ (X = H, Y = PF_6; X = $AuPPh_3$, Y = O_3SCF_3), which are fluxional in solution at room temperature. $[Ru_3(CO)_9(\eta^3\text{-tmpm})(\mu\text{-}AuPPh_3)]O_3SCF_3$ crystallizes as an acetone solvate in the orthorhombic space group *Pnma* (No. 62) with $a = 26.387$ (2) Å, $b = 13.824$ (2) Å, $c = 13.247$ (4) Å, $V = 4832$ (2) Å^3, $Z = 4$, 2937 reflections ($I \geq 2\sigma(I)$), $R = 0.035$, and $R_w = 0.045$. The cation has crystallographically imposed mirror symmetry, a symmetrically capping tmpm ligand, all terminal carbonyl ligands and an edge-bridging $\{AuPPh_3\}$ moiety which is nearly coplanar with the Ru_3 triangle.

Introduction

Despite a growing feeling that small transition-metal clusters may not be as satisfactory models for metal surfaces as originally proposed by Muetterties,[2] considerable interest remains in the synthesis of such clusters, in their reactivity towards small molecules, and in the possibility of catalysis by intact clusters.[3] Since the presence of dissimilar metals in a cluster can lead to reactivities not seen in homometallic species, much effort continues toward the synthesis of heterometallic clusters. While a number of successful routes for the designed synthesis of such species have been developed, most depend upon the presence of bridging phosphide[4] or phosphinidene[5] moieties which often have proved to be "noninnocent" ligands. Noting the success with which the "short-bite" ligands $R_2PCH_2PR_2$ (R = Ph (DPPM), Me (dmpm)) enable the formation of homo- and heterometallic species containing two and three metal atoms,[6] we considered that $HC(PMe_2)_3$ (tmpm) would be a particularly suitable ligand for the synthesis of trimetallic clusters. We report here on initial results of these studies.

Experimental Section

All manipulations were carried out under an atmosphere of prepurified nitrogen using standard Schlenk techniques or a Vacuum Atmospheres Model DLX-001-S-P glovebox. Solvents were purified by standard methods and distilled under nitrogen just prior to use. Silver trifluoromethanesulfonate was obtained from Alfa Inorganics. $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $AuCl(PPh_3)$, and K_2PtCl_4 were purchased from Strem Chemicals. $Cr(CO)_6$, $Mo(CO)_6$, $[cpMo(CO)_3]_2$, and $[cpW(CO)_3]_2$ were supplied by Pressure Chemical Co., while hexafluorophosphoric acid etherate was obtained from COC. Carbon monoxide was Matheson CP grade, and all other reagents were of laboratory grade and were used as received unless otherwise specified.

Literature methods were used to prepare $[MCl(COD)]_2$ (M = Rh[7], Ir[8]; COD = cycloocta-1,5-diene), $HC(PMe_2)_3$ (tmpm),[9] $Cr(CO)_4(NBD)$ (NBD = bicyclo[2.2.1]heptadiene),[10] *cis*-$Mo(CO)_4(pip)_2$ (pip = piperidine)[11], $Re_2(\mu\text{-}H)(\mu\text{-}C_6H_{11})(CO)_8$,[12] $[cpM(CO)_2]_2$ (M = Mo, W),[13] *trans*-$IrCl(CO)(PPh_3)_2$,[14] and $Pt(C_2H_4)(PPh_3)_2$.[15] Infrared spectra were obtained on a Mattson Cygnus 100 Fourier transform spectrometer as Nujol mulls unless otherwise specified. Proton, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were obtained at ambient temperature (ca. 298 K) on an IBM/Bruker AC-200 spectrometer at 200.13, 81.02, and 50.32 MHz, respectively. Proton and carbon chemical shifts are referred to external tetramethylsilane (δ 0.0) while those for phosphorus are referred to external 85% phosphoric acid (δ 0.0). Positive shifts are downfield of the reference. NMR spectral simulations were performed with the PANIC program supplied as part of the AC-200 software. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

$Ru_3(CO)_9(HC(P(CH_3)_2)_3)$ (1). To a solution of 0.326 g (0.51 mmol) of $Ru_3(CO)_{12}$ in 30 mL of acetone was added 0.100 g (0.51 mmol) of tmpm dissolved in 2 mL of THF. After refluxing for 1 h, the mixture was cooled to room temperature and filtered to remove a small amount of finely divided solid. The orange brown

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[1] Taken in part from the Ph.D. Thesis of Charles L. Lloyd, Tulane University, May 1991.

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filtrate was taken to dryness in vacuo and washed with hexane to afford the product as a red orange powder in 70% yield. The analytical sample was recrystallized from acetone/diethyl ether. Anal. Calcd for $C_{16}H_{19}O_9P_3Ru_3$: C, 25.58; H, 2.53. Found: C, 25.2; H, 3.0. IR: 2031 (s), 1980 (vs), 1936 (vs), 1793 (s) cm^{-1} (ν_{CO}).[16] ^1H NMR ($(CD_3)_2CO$): δ 4.2 (q, $^2J_{P-H}$ = 7.7 Hz, 1 H, $P_3C\mathit{H}$)[17], 1.8 ("q", $|J_{P-H}|$ = 2.3 Hz, 18 H, $P\text{–}C\mathit{H}_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 19.7 (s).

$[Ru_3(\mu\text{-}H)(CO)_9(HC(P(CH_3)_2)_3)]PF_6$ (2). A slight excess of $HPF_6\cdot Et_2O$ was added dropwise to a dichloromethane (10 mL) solution of 1. The solution remained dark red orange, and monitoring the reaction by ^{31}P NMR spectroscopy showed it to be complete after ca. 2 h at room temperature. Evaporation of the solvent in vacuo followed by washing of the residue with diethyl ether and recrystallization from acetone/diethyl ether afforded the product as orange microcrystals in quantitative yield. Despite repeated attempts, elemental analyses were ca. 2% low in carbon. We have no adequate explanation for this result, but the formulation of the product is satisfactorily supported by the spectroscopic data. IR (acetone solution): 2093 (m), 2077 (w), 2062 (s), 2040 (vs) cm^{-1} (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): (298 K) δ 5.4 (q, $^2J_{P-H}$ = 8.3 Hz, 1 H, $P_3C\mathit{H}$), 2.2 ("q", $|J_{P-H}|$ = 2.6 Hz, 18 H, $P\text{–}C\mathit{H}_3$), –16.8 (q, $^2J_{P-H}$ = 9.8 Hz, 1 H, $Ru_3\mathit{H}$); (212 K) δ –16.8 (t, $^2J_{P-H}$ = 14.9 Hz, $Ru_3\mathit{H}$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): (298 K) δ 7.5 (s); (212 K) AB_2 $\delta(P_A)$ 5.5, $\delta(P_B)$ 9.2 ($J_{P(A)-P(B)}$ = 45.2 Hz).

$[Ru_3(CO)_9(HC(P(CH_3)_2)_3)(\mu\text{-}AuP(C_6H_5)_3)]O_3SCF_3\cdot C_6H_5CH_3$ (3). A mixture of 0.056 g (0.22 mmol) of AgO_3SCF_3 and 0.108 g (0.22 mmol) of $AuCl(PPh_3)$ in 15 mL of acetone was stirred for 0.5 h in the dark and filtered through a pad of diatomaceous earth to remove precipitated silver chloride. The filtrate was added dropwise to a solution of 0.164 g (0.22 mmol) of 1 in 15 mL of acetone. During the course of the addition the solution darkened somewhat, and after 1 h hexane was added to afford the product as dark red orange microcrystals in 60% yield. The analytical sample was recrystallized from toluene/hexane and obtained as toluene solvate. Anal. Calcd for $C_{42}H_{42}O_{12}P_4F_3SRu_3Au$: C, 34.75; H, 2.89. Found: C, 34.7; H, 2.9. IR: 2070 (m), 2054 (m), 2019 (s), 1992 (s), 1960 (s) cm^{-1} (ν_{CO}). ^1H NMR ($(CD_3)_2CO$, 298 K): δ 7.6 (m, 15 H, $PC_6\mathit{H}_5$), 7.2 (m, 5 H, $H_3CC_6\mathit{H}_5$), 6.1 (q, $^2J_{P-H}$ = 8.4 Hz, 1 H, $P_3C\mathit{H}$), 2.3 (s, 3 H, $\mathit{H}_3CC_6H_5$), 2.1 (m, 18 H, $P\text{–}C\mathit{H}_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): (298 K) δ(P–Au) 70.5 ("q", J_{P-P} = 5.4 Hz), δ(P–Ru) 7.5 (s, br); (202 K) ABB′M, $\delta(P_A\text{–}Ru)$ 6.8, $\delta(P_B\text{–}Ru)$ 7.7, $\delta(P_M\text{–}Au)$ 69.9 ($J_{P(A)-P(B)}$ = 45.3, $J_{P(A)-P(B')}$ = 48.3, $J_{P(B)-P(B')}$ = 90.0, $J_{P(A)-P(M)}$ = 1.1, $J_{P(B)-P(M)}$ = –12.1, $J_{P(B')-P(M)}$ = –4.1 Hz).

$Re_2(CO)_8(HC(P(CH_3)_2)_3)\cdot 0.5$(acetone) (4). A toluene solution (25 mL) containing 0.813 g (1.25 mmol) of $Re_2(CO)_{10}$ and excess hex-1-ene was photolyzed overnight to generate $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C_6H_{11})$ in situ.[12] To this was added 0.244 g (1.25 mmol) of tmpm in 2 mL of toluene. After stirring 2 days at room temperature, a light yellow solid had formed, which was filtered off, washed with hexane, and recrystallized from acetone/diethyl ether (yield 70%). Anal. Calcd for $C_{16.5}H_{22}O_{8.5}P_3Re_2$: C, 24.12; H, 2.70. Found: C, 23.7; H, 2.6. IR (acetone solution): 2067 (s), 2012 (s), 1969 (s, br), 1945 (w), 1935 (w), 1910 (s) cm^{-1} (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 2.2 ("t", $|J_{P-H}|$ = 3.3 Hz, 6 H, $ReP\text{–}C\mathit{H}_3$), 2.0 ("t", $|J_{P-H}|$ = 4.0 Hz, 6 H, $ReP\text{–}C\mathit{H}_3$), 1.6 (d, $^2J_{P-H}$ = 5.1 Hz, 6 H, $P_2CHP(C\mathit{H}_3)_2$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): (298 K) δ(P–Re) –19.7 (br), δ (P′) –25.1 (t, $^2J_{P-P'}$ = 25.1 Hz); (214 K) δ(P–Re) –19.6 (d), δ(P′) –21.9 (t) ($^2J_{P-P'}$ = 26.1 Hz).

***trans*-$[Re_2(CO)_8(HC(P(CH_3)_2)_3)]_2Rh(CO)Cl$ (5).** A solution of $[RhCl(COD)]_2$ (0.006 g, 0.013 mmol) in acetone (10 mL) was purged with carbon monoxide for 5 min and allowed to stir under a CO atmosphere for 20 min. Subsequent addition of 0.042 g (0.052 mmol) of 4 as a solid resulted in gas evolution and the formation of a clear orange solution. Removal of the solvent in vacuo followed by washing of the residue with diethyl ether and recrystallization from acetone/diethyl ether afforded the product as orange microcrystals (yield 80%). Anal. Calcd for $C_{31}H_{38}O_{17}P_6ClRe_4Ph$: C, 21.26; H, 2.17. Found: C, 20.9; H, 2.2. IR (acetone solution): 2068 (m), 2028 (sh), 2014 (m), 1971 (s, br), 1912 (m) cm^{-1} (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 3.7 (tt, $|J_{P'-H}|$ = 13.7 Hz, $^2J_{P-H}$ = 5.5 Hz, 2 H, $P_2P'C\mathit{H}$), 2.8 (d, $|J_{P'-H}|$ = 4.2 Hz, 12 H, $Rh\text{–}P'(C\mathit{H}_3)_2$), 2.6 ("t", $|J_{P-H}|$ = 3.4 Hz, 12 H, $Re\text{–}PC\mathit{H}_3$) 2.3 ("t", $|J_{P-H}|$ = 3.9 Hz, 12 H, $Re\text{–}PC\mathit{H}_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ(P–Rh) 19.3 (dquin, $^1J_{Rh-P'}$ = 118.4 Hz, $|J_{P-P'}|$ = 6.0 Hz), δ(P–Re) –22.5 (br).

***trans*-$[Re_2(CO)_8(HC(P(CH_3)_2)_3)]_2Ir(CO)Cl\cdot 1.5$(acetone) (6).** To a solution of $[IrCl(COD)]_2$ (0.024 g, 0.04 mmol) in 25 mL of acetone was added 0.110 g (0.14 mmol) of 4 as a solid, and the solution was purged with carbon monoxide for 10 min. The resulting orange solution was worked up as described for 5 to afford orange microcrystals in 85% yield. Anal. Calcd for $C_{35.5}H_{47}O_{18.5}P_6ClRe_4Ir$: C, 22.12; H, 2.44. Found: C, 22.5; H, 2.6. IR (acetone solution): 2068 (s), 2029 (sh), 1971 (vs, br), 1913 (s) cm^{-1} (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 3.4 (tt, $|J_{P'-H}|$ = 13.4 Hz, $^2J_{P-H}$ = 5.3 Hz, 2 H, $P_2P'C\mathit{H}$), 2.6 ("t", $|J_{P-H}|$ = 3.4 Hz, 12 H, $Re\text{–}PC\mathit{H}_3$), 2.3 ("t", $|J_{P-H}|$ = 3.9 Hz, 12 H, $Re\text{–}PC\mathit{H}_3$), 2.2 (d, $|J_{P'-H}|$ = 2.9 Hz, 12 H, $Ir\text{–}P(C\mathit{H}_3)_2$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ (Ir–P′) 10.2 (quin, $J_{P-P'}$ = 6.5 H), δ(Re–P) –22.9 (br).

$(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(HC(P(CH_3)_2)_3)$ (7). Addition of 0.157 g (0.80 mmol) of tmpm to 0.488 g (0.80 mmol) of $[cpW(CO)_2]_2$ dissolved in 25 mL of acetone caused the original dark orange solution to become a dark red orange. An in situ ^{31}P NMR spectrum showed the presence of two major tmpm-containing species. Attempts at chromatographic separation were unsuccessful, so the crude reaction mixture was taken to dryness in vacuo and extracted with diethyl ether. Repeated recrystallization from acetone/diethyl ether afforded the product as a red powder in low yield. Anal. Calcd for $C_{21}H_{29}O_4P_3W_2$: C, 31.27; H, 3.60. Found: C, 30.9; H, 3.7. IR: 1924 (w), 1917 (w), 1849 (s), 1788 (s), 1776 (s) cm^{-1} (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 5.3 (s, 10 H, $C_5\mathit{H}_5$), 2.3 (m, 1 H, $P_3C\mathit{H}$), 1.9 (d, J_{P-H} = 6.4 Hz, 3 H, $PC\mathit{H}_3$), 1.8 (m, 6 H, $PC\mathit{H}_3$), 1.7 ("t", $|J_{P-H}|$ = 5.0 Hz, 3 H, $PC\mathit{H}_3$), 1.4 ("t", $|J_{P-H}|$ = 5.7 Hz, 6 H, $PC\mathit{H}_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): ABM + ABMX + ABMY (X = Y = ^{183}W), $\delta(P_A\text{–}W)$ –9.3, $\delta(P_B\text{–}W)$ –10.7, $\delta(P_M)$ –31.0 ($J_{P(A)-P(B)}$ = 70.7, $J_{P(A)-P(M)}$ = 21.0, $J_{P(B)-P(M)}$ = 16.7, $^1J_{P(A)-W(X)}$ = 321.0, $J_{P(A)-W(Y)}$ = 4.5, $J_{P(B)-W(X)}$ = –5.4, $^1J_{P(B)-W(Y)}$ = 322.0 Hz).

$(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(\mu\text{-}HC(P(CH_3)_2)_3)Ir(CO)Cl(P(C_6H_5)_3)\cdot C_6H_5CH_3$ (8). To a solution of 0.025 g (0.03 mmol) of $IrCl(CO)(PPh_3)_2$ in 20 mL of toluene was added 0.026 g (0.03 mmol) of solid 7. After stirring for 12 h at room temperature, the solution had become orange. Removal of the solvent in vacuo followed by washing the residue with hexane and recrystallization from toluene/hexane afforded the product as an orange powder in 66% yield. Anal. Calcd for $C_{47}H_{52}O_5P_4ClW_2Ir$: C, 39.87; H, 3.67. Found: C, 39.7; H, 3.8. IR: 1954 (s), 1843 (s), 1807 (m), 1788 (m), 1773 (m) cm^{-1} (ν_{CO}). ^1H NMR (C_6D_6): δ 7.4–7.9 (m, 15 H, $C_6\mathit{H}_5$), 7.2 (m, 5 H, $C_6\mathit{H}_5CH_3$), 4.9 (s, 5 H, $C_5\mathit{H}_5$), 4.8 (s, 5 H, $C_5\mathit{H}_5$), 2.5 (d, J_{P-H} = 6.8 Hz, 3 H, $WPC\mathit{H}_3$), 2.3 (s, 3 H, $C\mathit{H}_3C_6H_5$), 2.2 (d, J_{P-H} = 7.2 Hz, 3 H, $WPC\mathit{H}_3$), 2.0 (dd, J_{P-H} = 8.5, 2.5 Hz, 3 H, $IrPC\mathit{H}_3$), 1.9 (d, J_{P-H} = 6.3 Hz, 3 H, $WPC\mathit{H}_3$), 1.8 (d, J_{P-H} = 8.5 Hz, 3 H, $WPC\mathit{H}_3$), 1.7 (dd, J_{P-H} = 9.2, 2.3 Hz, 3 H, $IrPC\mathit{H}_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta(P_1)$ 24.2 (dd), $\delta(P_2)$ 3.7 (ddd), $\delta(P_3)$ –7.3 (ddd), $\delta(P_4)$ –16.7 (dd) ($^2J_{P(1)-P(2)}$ = 359.2, $^4J_{P(1)-P(3)}$ = 6.2, $^2J_{P(2)-P(3)}$ = 26.7, $^2J_{P(2)-P(4)}$ = 9.4, $|J_{P(3)-P(4)}|$ = 72.6 Hz) (see Discussion for labeling of phosphorus atoms).

$Fe_2(CO)_7(HC(P(CH_3)_2)_3)$ (9). The addition of 0.091 g (0.46 mmol) of tmpm in 2 mL of toluene to a solution of 0.24 g (0.47 mmol) of freshly sublimed $Fe_3(CO)_{12}$ in 30 mL of toluene followed by stirring at room temperature for 1 h resulted in a dark orange brown solution. This was stirred for 3 days, concentrated to ca. 3 mL in vacuo, and placed on a 2 × 20 cm column of Brockman II alumina which had been made-up in hexane. Successive elutions with 9:1 hexane/toluene, 1:9 hexane/toluene, and 1:1 toluene/acetone removed three fractions (see Discussion). The middle fraction on concentration in vacuo yielded a red orange, air-sensitive oil whose ^{31}P NMR spectrum showed the presence of small amounts of impurities and which could not be induced to crystallize. Because of its air sensitivity and the presence of these impurities, satisfactory analyses could not be obtained but the spectroscopic data for the major component adequately support the proposed formulation. IR (acetone solution): 2048 (s), 2010 (m), 1979 (s), 1937 (vs), 1896 (s) cm^{-1} (ν_{CO}). ^1H NMR (C_6D_6): δ 3.5 (dt, $^2J_{P-H}$ = 10.0, $^2J_{P'-H}$ = 13.5 Hz, 1 H, $PP_2'C\mathit{H}$), 1.4 ("t", $|J_{P-H}|$

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(16) Key to infrared absorption band intensities: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

(17) Key to NMR peak multiplicities: s, singlet; d, doublet; t, triplet; "t", apparent triplet; q, quartet; "q", apparent quartet; quin, quintet; dd, doublet of doublets; dt, doublets of triplets; d"t", double of apparent triplets; dquin, doublet of quintets; tt, triplet of triplets; ddd, doublet of doublets of doublets; m, multiplet; br, broad.

= 4.8 Hz, 6 H, $P(CH_3)_2$), 1.3 ("t", $|J_{P-H}|$ = 5.1 Hz, 6 H, $P(CH_3)_2$), 1.0 (d, $^2J_{P'-H}$ = 9.4 Hz, 6 H, $P(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta(P)$ 47.5 (t), $\delta(P')$ 27.2 (d) ($J_{P-P'}$ = 18.5 Hz).

$Cr(CO)_4(HC(P(CH_3)_2)_3)$ (10). A solution of 0.149 g (0.83 mmol) of tmpm in 2 mL of acetone was added to 0.212 g (0.83 mmol) of $Cr(CO)_4(NBD)$ dissolved in 30 mL of hexane. After stirring 10 h at room temperature a yellow green precipitate had formed. This was filtered off, washed with cold hexane, and recrystallized from acetone/diethyl ether, affording a yellow microcrystalline product in 70% yield. Anal. Calcd for $C_{11}H_{19}O_4P_3Cr$: C, 36.7; H, 5.28. Found: C, 36.8; H, 5.5. IR: 2006 (m), 1929 (m), 1870 (s), 1853 (s) cm^{-1} (ν_{CO}). ^1H NMR (C_6D_6): δ 2.4 ($^2J_{P-H}$ = 10.1 Hz, 1 H, $P'P_2CH$), 1.2 (d"t", $|J_{P-H}|$ = 4.3, $^4J_{P'-H}$ = 2.1 Hz, 6 H, $CrPCH_3$), 1.0 ("t", $|J_{P-H}|$ = 4.0 Hz, 6 H, $CrPCH_3$), 0.3 (d, $^2J_{P'-H}$ = 4.0 Hz, 6 H, $CP'(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta(P)$ 16.4 (d), $\delta(P')$ −46.1 (t) ($J_{P-P'}$ = 4.0 Hz).

$Mo(CO)_4(HC(P(CH_3)_2)_3)$ (11). Addition of 0.072 g (0.37 mmol) of solid tmpm to a solution of 0.14 g (0.37 mmol) of $Mo(CO)_4(pip)_2$ in 20 mL of acetone resulted in a clear yellow solution after 3 h of stirring at room temperature. Concentration in vacuo followed by dilution with hexane afforded yellow microcrystals in 75% yield. Anal. Calcd for $C_{11}H_{19}O_4P_3Mo$: C, 32.71; H, 4.70. Found: C, 32.5; H, 4.6. IR: 2014 (m), 1903 (s), 1884 (s), 1864 (s) cm^{-1} (ν_{CO}). ^1H NMR (C_6D_6): δ 2.4 (t, $^2J_{P-H}$ = 9.2 Hz, 1 H, $P'P_2CH$), 1.2 (m, 6 H, $MoPCH_3$), 1.0 ("t", $|J_{P-H}|$ = 3.4 Hz, 6 H, $MoPCH_3$), 0.5 (d, $^2J_{P'-H}$ = 4.1 Hz, 6 H, $CP'CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta(P)$ −12.7 (d), $\delta(P')$ −47.8 (t) ($J_{P-P'}$ = 5.2 Hz).

Reaction of $Fe_2(CO)_9$ with tmpm. A mixture of 0.12 g (0.33 mmol) of $Fe_2(CO)_9$ and 0.044 g (0.22 mmol) of tmpm was heated at 60 °C in toluene for 3 days to give an orange solution which was filtered to remove a small quantity of black solid. In situ $^{31}P\{^1H\}$ NMR and infrared spectra of this solution showed a single phosphorus resonance at δ 43.1 (s) and carbonyl bands at 2045 (s), 1977 (s), 1930 (s), and 1880 (m) cm^{-1}, suggestive of the formation of $Fe_2(CO)_8(dmpm)$ (dmpm = bis(dimethylphosphino)methane). Subsequent reaction of this solution with trimethylamine *N*-oxide yielded a yellow solution from which yellow crystals were obtained on dilution with hexane. IR: 2036 (m), 1984 (m), 1955 (s), 1930 (s), 1907 (s), 1733 (m) cm^{-1} (ν_{CO}). ^1H NMR (C_6D_6): δ 1.2 (t, J_{P-H} = 13.9 Hz, 2 H, CH_2), 0.8 ("t", $|J_{P-H}|$ = 3.9 Hz, 12 H, PCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 42.0 (s). These data compare well with those reported previously for $Fe_2(CO)_6(\mu$-CO)(dmpm).[18]

Reaction of $cp_2Mo_2(CO)_4$ with tmpm. Addition of 0.190 g (0.97 mmol) of tmpm in 2 mL of acetone to 0.416 g (0.96 mmol) of $cp_2Mo_2(CO)_4$ in 25 mL of acetone caused an immediate color change from dark orange to red purple. The solution was concentrated to ca. 3 mL under reduced pressure and placed on a 2 × 20 cm column of Brockman II alumina which had been prepared in hexane. Successive elutions with 1:9 and 1:1 acetone/toluene mixtures afforded two reddish purple fractions. The $^{31}P\{^1H\}$ NMR spectrum of the first fraction ($(CD_3)_2CO$) showed resonances at δ 29.1 (d), 29.0 (d), and −29.6 (t) ($J_{P-P'} = J_{P-P''}$ = 18.2 Hz) which are similar to those found for **7** and a singlet at δ −24.6. Over time the last resonance grows at the expense of the others. The second fraction also contained the species responsible for the singlet resonance together with several other minor components which could not be readily identified.

Reaction of $cp_2Mo_2(CO)_6$ with tmpm. Reaction of 0.144 g (0.73 mmol) of tmpm with 0.360 g (0.73 mmol) of $cp_2Mo_2(CO)_6$ in 30 mL of toluene produced a pale yellow precipitate after 12 h at room temperature. This was filtered off and washed with diethyl ether. A 10^{-3} M solution in acetone had a conductivity of 79 Ω^{-1} M^{-1} indicating a 1:1 electrolyte behavior. IR: 1970 (s), 1981 (s), 1783 (s), 1748 (s) cm^{-1} (ν_{CO}). ^1H NMR $(CD_3)_2CO$): δ 5.6 (s, C_5H_5), 5.5 (s, C_5H_5), 5.1 (s, C_5H_5), 4.6 (m, $P_2P'CH$), 3.5 (m, $P_2P'CH$), 1.87 (m, $P'CH_3$), 1.23 (m, $P-CH_3$). ^1H NMR ($(CD_3)_2CO$): $\delta(P)$ −10.5 (d), $\delta(P')$ −41.6 (t) ($J_{P-P'}$ = 7.8 Hz); $\delta(P)$ −12.5 (d), $\delta(P')$ −41.2 (t) ($J_{P-P'}$ = 9.6 Hz).

Table I. Crystallographic Data for $[Ru_3(CO)_9(tmpm)(\mu\text{-}AuPPh_3)]O_3SCF_3 \bullet (CH_3)_2CO$ (3)

formula	$C_{38}H_{40}O_{13}P_4F_3SRu_3Au$
wt	1417.90
space group	*Pnma* (No. 62)
a, Å	26.387 (2)
b, Å	13.387 (2)
c, Å	13.247 (4)
V, Å^3	4832 (2)
Z	4
μ(Mo Kα), cm^{-1}	41.6
d_{calc}, g cm^{-3}	1.95
2θ range for unit cell detn, deg	19.8–29.8
range trans factors	0.8407–1.0000
λ(Mo Kα) radiation, graphite monochromated), Å	0.710 73
2θ range for data coll, deg	2–50
scan type	ω–2θ
scan width, deg	0.8 + 0.2 tan θ
scan speed, deg min^{-1}	4.1–0.6
no. of data measd	4758
no. of data used ($I \geq 2\sigma(I)$)	2937
no. of variables	310
largest shift/esd in final cycle	0.28
R^a	0.035
R^b	0.045
GOF^c	1.72
programs used	Enraf-Nonius MolEN^d

$^a R = \sum ||F_0| - |F_c|| / \sum F_0$. $^b R_w = [\sum w(F_0 - |F_c|)^2 / \sum w(F_0)^2]^{1/2}$ with $w = 1/(\sigma_F)^2$ where $\sigma_F = \sigma(F^2)/2F$ and $\sigma(F^2) = [(\sigma_I)^2 + (0.04F^2)^2]^{1/2}$. ^{c} GOF = $[\sum w(F_0 - |F_c|)^2/(N_0 - N_v)]^{1/2}$, where N_0 and N_v are, respectively, the number of observations and variables. ^{d} *MolEN, An Interactive Structure Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

X-ray Crystallography. A large red orange crystal of **3** was grown by slow evaporation of an acetone solution of the complex under nitrogen. Two pieces cut from it showed photographic evidence for twinning but a small fragment, 0.08 × 0.1 × 0.3 mm, dislodged during the cutting appeared single. It was mounted on a thin glass fiber and coated with epoxy to retard possible decomposition. General procedures for unit cell determination and data collection on the CAD-4 diffractometer as well as for data reduction have been published.[7] Table I provides details specific to this structure. The orthorhombic cell indicated by the CAD-4 software was confirmed by the observation of *mmm* diffraction symmetry, and the systematic absences observed in the final data set were consistent with nonstandard settings of the space groups $Pna2_1$ and *Pnma*. Insufficient material was available for a density measurement but a reasonable calculated value indicated *Z* = 4. As the intensity statistics did not provide a clear distinction between centric and acentric space groups, the latter was chosen since it would not require imposition of crystallographic symmetry on the molecule. Although all non-hydrogen atoms were readily located in $Pna2_1$, final refinement proved unsatisfactory so it was concluded that the correct space group is *Pnma*, a conclusion confirmed by the subsequent successful refinement. The original data were transformed to the standard setting of *Pnma* and corrected for a 3–4% linear decay in the intensity monitors and for absorption based on ψ scans for two reflections with χ near 90°. The location of the gold atom was determined from an origin-removed Patterson map and the remaining non-hydrogen atoms, including those of a molecule of solvent acetone, were located using successive cycles of full-matrix least-squares refinement followed by difference Fourier synthesis. A reasonable number of hydrogen atoms could be discerned in difference maps near the end of the refinement. These were placed in calculated positions as fixed contributions with isotropic thermal parameters 20% larger than those of the attached carbon atoms and updated periodically in the final refinement. There appears to be a degree of disorder of the anion about the mirror plane at $y = {}^1/_2$, which is primarily indicated by the pronounced elongation of the thermal ellipsoid for the sulfur atom perpendicular to this plane. However careful inspection of difference maps in this region did not indicate any resolution of alternate locations so refinement was completed using anisotropic thermal parameters. While perhaps not totally satisfactory this is the best model that could reasonably be used and in any event is unlikely to markedly affect the rest of the structure. The final difference map showed no features larger than ±0.5 e/Å^3. Final positional parameters are listed in Table II, while the remaining crystallo-

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[18] King, R. B.; Raghuveer, K. S. *Inorg. Chem.* **1984**, *23*, 2482.

Table II. Positional Parameters (Esd's) for $[Ru_3(CO)_9(tmpm)(\mu\text{-}AuPPh_3)]O_3SCF_3\bullet(CH_3)_2CO$

atom	x	y	z	B, Å$^{2\,a}$
Au	0.13523 (2)	0.250	0.07074 (4)	3.188 (9)
Ru(1)	0.18097 (2)	0.14023 (4)	0.21910 (5)	2.85 (1)
Ru(2)	0.23842 (4)	0.250	0.36798 (7)	3.06 (2)
P(1)	0.0841 (1)	0.250	-0.0705 (3)	3.17 (6)
P(2)	0.1684 (1)	0.250	0.4786 (3)	4.87 (9)
P(3)	0.1094 (1)	0.1435 (2)	0.3265 (2)	4.50 (6)
O(1)	0.2670 (3)	0.1333 (6)	0.0661 (6)	7.2 (2)
O(2)	0.3279 (4)	0.250	0.2226 (8)	6.7 (3)
O(3)	0.2867 (3)	0.0894 (6)	0.4908 (6)	8.5 (2)
O(4)	0.1167 (3)	0.0038 (5)	0.0920 (5)	6.3 (2)
O(5)	0.2278 (3)	-0.0248 (5)	0.3359 (7)	9.0 (2)
C(1)	0.2361 (4)	0.1410 (6)	0.1246 (7)	4.3 (2)
C(2)	0.2932 (5)	0.250	0.2725 (9)	4.2 (3)
C(3)	0.2679 (4)	0.1490 (8)	0.4440 (8)	5.8 (3)
C(4)	0.1417 (4)	0.0594 (6)	0.1346 (7)	4.2 (2)
C(5)	0.2109 (4)	0.0416 (7)	0.2948 (8)	5.3 (2)
C(10)	0.1086 (5)	0.250	0.4077 (9)	4.7 (3)
C(11)	0.1655 (5)	0.150 (1)	0.5675 (9)	12.8 (4)
C(12)	0.0490 (4)	0.136 (1)	0.263 (1)	11.2 (4)
C(13)	0.1023 (7)	0.0361 (9)	0.408 (1)	10.8 (4)
C(21)	0.0903 (3)	0.1457 (6)	-0.1530 (6)	3.2 (2)
C(22)	0.1316 (4)	0.0864 (6)	-0.1486 (7)	4.2 (2)
C(23)	0.1378 (4)	0.0097 (8)	-0.2095 (7)	5.8 (3)
C(24)	0.1010 (5)	-0.0121 (7)	-0.2768 (7)	6.1 (3)
C(25)	0.0586 (4)	0.0442 (7)	-0.2846 (7)	5.2 (2)
C(26)	0.0529 (4)	0.1214 (7)	-0.2227 (7)	4.4 (2)
C(31)	0.0185 (5)	0.250	-0.0252 (9)	4.2 (3)
C(32)	-0.0033 (4)	0.1639 (8)	-0.0004 (9)	5.4 (2)
C(33)	-0.0506 (5)	0.164 (1)	0.0498 (8)	8.3 (4)
C(34)	-0.0722 (6)	0.250	0.075 (1)	9.5 (7)
S	0.4733 (2)	0.250	0.9476 (4)	14.0 (3)
O(6)	0.4522 (5)	0.250	0.853 (1)	25 (1)
O(7)	0.4984 (4)	0.333 (1)	0.9799 (8)	25.5 (5)
C(17)	0.4184 (8)	0.250	1.023 (1)	6.7 (4)
F(1)	0.4333 (4)	0.250	1.1205 (7)	9.2 (3)
F(2)	0.3894 (3)	0.1770 (5)	1.0098 (7)	10.6 (2)
O(1S)	0.2727 (6)	0.250	0.669 (1)	15.7 (7)
C(1S)	0.3029 (9)	0.250	0.730 (1)	10.3 (6)
C(2S)	0.291 (1)	0.250	0.836 (2)	15 (1)
C(3S)	0.3555 (8)	0.250	0.694 (2)	12.8 (8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3\ [a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

graphic data are provided as supplementary material (Tables S1–S6).

Results and Discussion

Chemical Studies. The reaction of tmpm with $Ru_3(CO)_{12}$ in refluxing THF readily gives a significant yield of a product characterized as the ligand-capped cluster $Ru_3(CO)_6(\mu\text{-}CO)_3(\eta^3\text{-tmpm})$ (1) on the basis of analytical and spectroscopic data. Thus all three phosphorus atoms and all six ligand methyl groups are equivalent by NMR spectroscopy. Further, the carbonyl region of the infrared spectrum compares well with those reported previously[19] for analogous complexes with $HC(PPh_2)_3$ and $MeSi(PBu^n{}_2)_3$. The low-energy band at 1793 cm^{-1} indicates the presence of bridging carbonyls although it is not possible to determine from this alone whether they are symmetrically bridging or unsymmetrical, as found in the structural study on $Ru_3(CO)_6(\mu\text{-}CO)_3(MeSi(PBu^n{}_2)_3)$.[20] Of note is the relatively high yield of 1 and the absence of significant side products, which contrasts with what was found in the syntheses of the related complexes noted above. This is likely due, at least in part, to the nearly ideal "fit" of the ligand to the Ru_3 triangle (vide infra).

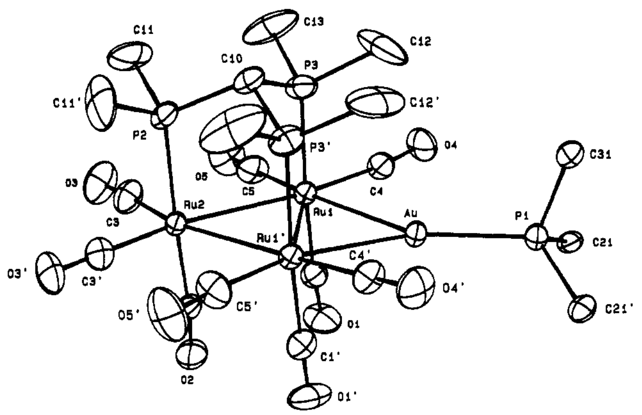

Figure 1. Perspective view of the $[Ru_3(CO)_9(tmpm)(\mu\text{-}AuPPh_3)]^+$ cation. Thermal ellipsoids are drawn at the 30% probability level. Only the ipso carbons of the phenyl rings on P(1) are shown. Primed atoms are related to their unprimed counterparts by the crystallographic mirror plane.

Disappointingly, 1 has proven quite unreactive. Attempts to promote substitution and/or addition reactions with phosphines, phosphites, olefins, isocyanides, and dihydrogen either thermally or photochemically failed as did the use of electron-transfer catalysis, a method which has proven successful with $Ru_3(CO)_{12}$.[21] Reaction does occur, however, with hexafluorophosphoric acid etherate, and $[Au(PPh_3)]O_3SCF_3$ to form the salts $[Ru_3(CO)_9(tmpm)(\mu\text{-}X)]Y$ (X = H, Y = PF_6 (2); X = $Au(PPh_3)$, Y = O_3SCF_3 (3)). The structure of 3 has been determined by X-ray crystallography (Figure 1), and that of 2 is presumed to be analogous based on spectroscopic data. In both complexes the infrared spectra show the presence of only terminal carbonyl ligands while the proton and phosphorus NMR spectra show that the complexes are fluxional in solution at room temperature. Thus a single phosphorus resonance is seen for the tmpm ligand as a singlet which is upfield of and somewhat broader than that for 1. The resonance for the triphenylphosphine ligand in 3 appears as an apparent quartet while in 2 a high-field resonance appears in the proton NMR spectrum which integrates for one proton and also appears as a quartet. In both instances, therefore, essentially equivalent coupling to all three tmpm phosphorus atoms occurs. On cooling, the tmpm phosphorus resonance broadens and eventually resolves into an AB_2 pattern for 2 and the ABB′ portion of an ABB′M pattern for 3. Concomitantly, the high-field proton resonance for 2 and the triphenylphosphine resonance for 3 become triplets. The low-temperature ^{31}P NMR spectrum for 3 is wholly consistent with the solid-state structure, while the low-temperature spectra for 2 indicate that its static structure contains an edge-bridging hydride ligand. While the data do not permit one to determine what the exact nature of the fluxional process is or if it is the same in both 2 and 3 at least in the latter, passage through a transition state in which the $\{AuPPh_3\}$ moiety is μ_3-coordinated opposite to the tmpm ligand would require the least motion of the carbonyl ligands.

Attempts to prepare alkyne derivatives of 1 were also unsuccessful. Dimethyl acetylenedicarboxylate failed to react while both methyl propiolate and phenylacetylene yielded cyclotrimers of the alkyne. Specifically with the former, a 3:1 mixture of 1,2,4- and 1,3,5-tris(methoxycarbonyl)benzene was formed, as determined by ^1H and

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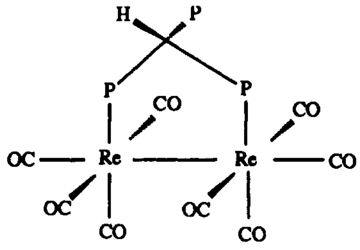
[19] Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Organomet. Chem.* **1982**, *226*, C17.

[20] de Boer, J. J.; van Doorn, J. A.; Masters, C. *J. Chem. Soc., Chem. Commun.* **1978**, 1005.

[21] Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321.

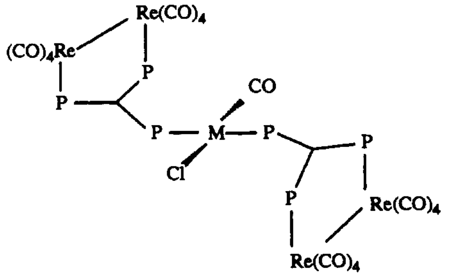
^{13}C NMR and a GC–mass spectrometric analysis. The same result was obtained on reaction of methyl propiolate with 2, and in both instances the starting tmpm complex, 1 and 2, respectively, was the only phosphorus-containing species detectable at the end. By contrast, in the same reaction with $Ru_3(CO)_{12}$, while substantial cyclotrimerized alkyne was also obtained, infrared evidence suggested that no intact $Ru_3(CO)_{12}$ remained. While this last reaction was not examined in detail, the absence of $Ru_3(CO)_{12}$ at the end is not surprising since the predominant mode of reaction of $Ru_3(CO)_{12}$ with terminal and internal alkynes is to form a variety of Ru_3 carbonyl clusters containing intact and/or modified alkyne moieties.[22] Cyclotrimerization of methyl propiolate and phenylacetylene could also be effected using catalytic quantities of 1. The relative ease of these reactions is somewhat surprising given the apparent lack of reactivity of 1 noted above, but as no alkyne adducts or other potential intermediates were detected, it is premature to speculate on possible mechanisms. While we cannot rule out the possibility of some decomposition of the tmpm complexes to generate the catalytically active species, we believe that recovery of unchanged 1 or 2 is essentially quantitative, suggesting that they may in fact be the active catalyst. Further studies are planned to explore this point.

A major focus of our study of tmpm as a ligand has been an exploration of its use in the directed synthesis of heterotrimetallic clusters. An attractive route appeared to be the coordination of tmpm to a bimetallic moiety in a bridging fashion while leaving one phosphorus atom uncoordinated. This could then be coordinated to a third metal in a subsequent step, and it was hoped that accompanying cluster formation might occur. Failing this, it was still anticipated that cluster formation could be induced following coordination of the third metal by generation of sufficient coordinative unsaturation in subsequent steps. In light of the fact that the readily available $Re_2(CO)_{10}(\mu\text{-}H)(\mu\text{-}C_6H_{10})$ had previously been shown to form DPPM-bridged derivatives,[23] its reaction with tmpm was undertaken. This affords a good yield of a pale yellow complex which analyzes for $Re_2(CO)_8(tmpm)$ (4). The ^{31}P NMR spectrum of 4 shows two resonances attributable to coordinated and uncoordinated phosphorus atoms in a 2:1 intensity ratio, respectively. That for the free phosphorus atom is a sharp triplet, while that for the coordinated phosphorus atoms appears as a broad singlet due to the presence of the quadrupolar rhenium nuclei. This broadening is considerably diminished at low temperatures so that this resonance is resolved into a doublet with a splitting matching the triplet splitting for the uncoordinated phosphorus atom. The infrared spectrum in the carbonyl region closely resembles that reported for $Re_2(CO)_8(DPPM)$,[23] and from these data the complex is proposed to have the structure shown.



4

With 4 in hand, introduction of a third metal into the complex was explored. Reaction of 4 with $[RhCl(CO)_2]_2$ (prepared in situ from $[RhCl(COD)]_2$) or with $[IrCl(COD)]_2$ and then carbon monoxide employing a 1:1 ratio of 4 to rhodium or iridium afforded high yields of orange crystalline materials characterized by elemental analysis and ^1H and ^{31}P NMR spectroscopy as *trans*-$MCl(CO)[(\mu\text{-}tmpm)Re_2(CO)_8]_2$ (M = Rh (5), Ir (6)). All attempts to add only one molecule of 4 to rhodium or iridium were unsuccessful, and as a result, the preferred stoichiometry for synthesis of 5 and 6 is 4 mol of 4 to 1 mol of rhodium or iridium dimer. The ^{31}P NMR spectrum of 5 consists of a doublet of quintets (intensity 1) downfield of a broad singlet (intensity 2) which can be assigned respectively to phosphorus atoms bound to rhodium and to rhenium. The doublet splitting compares well with values of $^1J_{Rh-P}$ in square-planar Rh(I) complexes,[24] while the quintet pattern indicates that each rhodium-bound phosphorus atom is effectively coupled to all four rhenium-bound phosphorus atoms. This can be explained if one assumes strong coupling between the phosphorus atoms on rhodium, which in turn supports the proposed trans disposition of tmpm ligands on rhodium. A similar situation was previously noted in the related complex $RhCl(CO)[(\mu\text{-}TPPM)Mo(CO)_4]_2$ (TPPM = tris(diphenylphosphino)methane).[25] While the infrared spectrum of 5 in the carbonyl region is little different from that of 4, the ^{13}C NMR spectrum of a sample of 5 prepared from $[RhCl(^{13}CO)_2]_2$ contains a prominent resonance at δ 187.2 (dt, $^1J_{Rh-C} = 76.8$, $^2J_{P-C} = 15.8$ Hz), clearly indicating the presence of a carbonyl ligand bound to rhodium. The ^{31}P NMR spectrum of 6 is essentially the same as that for 5 but without the doublet splitting of the lower field resonance, and an analogous structure is proposed.



5 (M = Rh)
6 (M = Ir)

Despite the fact that 5 and 6 were more complex than desired, several attempts were made to cause further reaction and the formation of new metal–metal bonds. Treatment with trimethylamine *N*-oxide did not lead to reaction, as determined by infrared and ^{31}P NMR spectroscopy. While photolysis in Pyrex flasks did not lead to any detectable change in the infrared spectrum (suggesting that the $\{Re_2(CO)_8\}$ moiety remained unchanged), the ^1H and ^{31}P NMR spectra of the resulting solutions were extremely complex and we were unsuccessful in obtaining any characterizable products from the apparent mixtures.

Attention was next directed toward reaction of 4 with $Pt(C_2H_4)(PPh_3)_2$. Employing a 1:1 ratio of reactants the

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[22] (a) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Chapter 32.5. (b) Deeming, A. J. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; John Wiley & Sons: New York, 1980; Chapter 6.

[23] Lee, K. W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *Organometallics* 1984, *3*, 404.

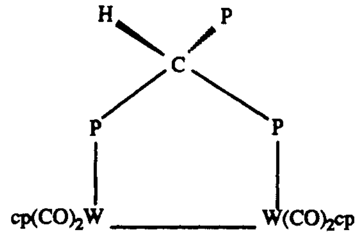
[24] Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer Verlag: Berlin, 1979; Table 16.

[25] Mague, J. T.; Dessens, S. E. *J. Organomet. Chem.* 1984, *262*, 347.

initial pale yellow solution became dark orange upon mixing but soon became yellow again. The ^{31}P NMR spectrum of the crude reaction mixture showed a considerable number of broad, ill-defined resonances together with two that appeared to be due to unreacted 4. Even when the reaction was run at -70 °C we were unable to obtain conclusive evidence for the formation of a platinum adduct of 4 and in no instance could well-characterized solid products be obtained. The initial color change observed indicates that some reaction has occurred and we suggest that possibly the desired Re$_2$(CO)$_8$(μ-tmpm)Pt(PPh$_3$)$_2$ had formed but is sufficiently labile that redistribution then occurs to reform 4 and platinum triphenylphosphine clusters. In the hope that an effective increase in the oxidation state of the platinum would slow down this apparent redistribution reaction, solutions of 4 and Pt(C$_2$H$_4$)(PPh$_3$)$_2$ were combined at -70 °C and dimethyl acetylenedicarboxylate (DMAD) then added to trap the desired adduct. All that was accomplished was to form Pt(DMAD)(PPh$_3$)$_2$, which appears totally unreactive toward 4 under a wide variety of conditions. Also explored was the reaction of 4 with Pt(C$_2$Ph$_2$)(PPh$_3$)$_2$, which afforded an orange solution after refluxing in THF for 2 h. An in situ ^{31}P NMR spectrum indicated the major species present to be unreacted starting materials, but in addition a set of minor resonances was observed at δ(P) 30.0 (d), δ(P′) 1.3 (dt), δ(P″) -19.5 (br) ($J_{\text{P-P}'}$ = 42.0, $J_{\text{P}'\text{-P}''}$ = 11.4 Hz) with relative intensities 1:1:2, respectively. The first two exhibited platinum satellites (^{195}Pt, I = $^1/_2$, 33.7% abundance; $^1J_{\text{P-Pt}}$ = 3508, $^1J_{\text{P}'\text{-Pt}}$ = 3303 Hz) indicating both are due to phosphorus bound to platinum while the chemical shift and breadth of the third is consistent with it being due to two tmpm phosphorus atoms bound to rhenium. The relative intensities and splitting patterns of the two platinum–phosphorus resonances indicate that only one triphenylphosphine ligand remains and on this basis we tentatively suggest that the species formed is Re$_2$(CO)$_8$(μ-tmpm)Pt(Ph$_2$C$_2$)(PPh$_3$) although it is puzzling that no resonance for free triphenylphosphine could be detected. Unfortunately, the yield of this species was so small that we were unable to isolate it.

Further attempts to attach other coordinately unsaturated metal species to 4 by reaction with Cr(CO)$_4$(NBD), (η^6-C$_7$H$_8$)Mo(CO)$_3$, M(THF)(CO)$_5$ (M = Cr, Mo, W) and Mo(CO)$_4$(pip)$_2$ did not yield any characterizable products.

Tris(dimethylphosphino)methane also reacts readily with [cpW(CO)$_2$]$_2$ to form a mixture of two products from which the major component was separated with some difficulty and shown by elemental analysis to have the composition cp$_2$W$_2$(CO)$_4$(tmpm) (7). The ^{31}P NMR spectrum of 7 is shown in Figure 2. The downfield resonance of relative intensity twice that of the upfield resonance clearly possesses tungsten satellites, while the latter does not, implying coordination of only two of the three phosphorus atoms. The observation of a single resonance for the cyclopentadienyl protons and the analysis of the ^{31}P NMR spectrum (vide infra) indicate that the tmpm is bound to the ditungsten moiety in a bridging fashion.



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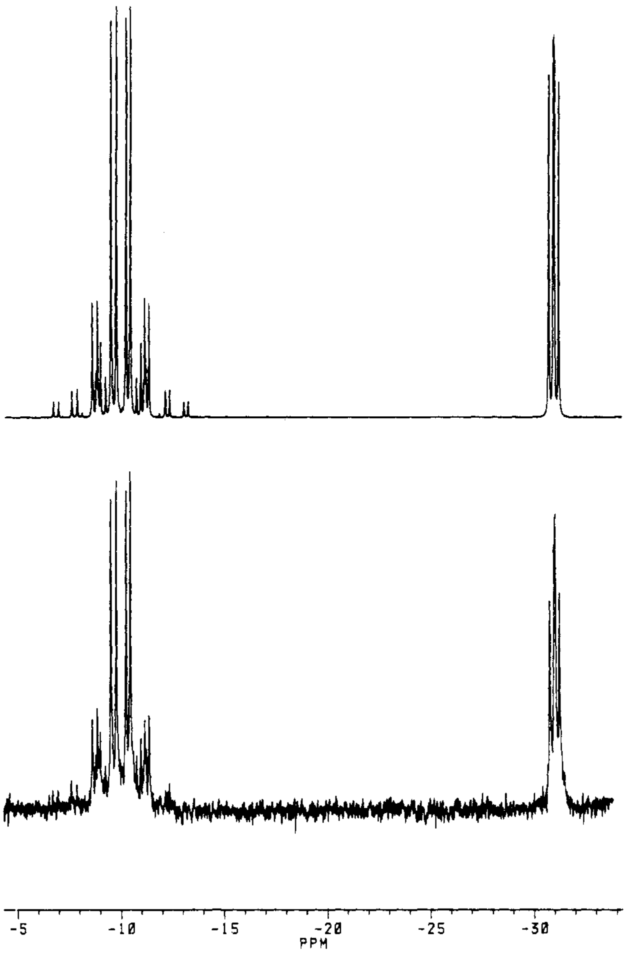
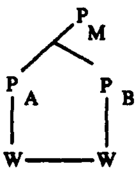
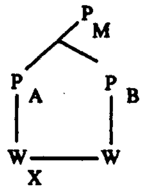
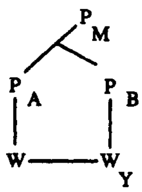


Figure 2. Observed (bottom) and simulated (top) ^{31}P{^{1}H} NMR spectra for cp$_2$W$_2$(CO)$_4$(η^2-tmpm) (7).

As shown in Figure 2, the ^{31}P NMR spectrum of 7 can be simulated as the superimposition of ABMX and ABMY satellite spectra upon the primary ABM pattern (X, Y = ^{183}W, I = 1/2, 14.4% abundance) using the following notation, resulting in the spectral parameters listed in the Experimental Section.







The satellite spectrum for the component containing two ^{183}W nuclei was not included because its abundance, 2.1%, was too low to be observed. The presence of carbonyl bands below 1800 cm^{-1} in the infrared spectrum suggests the presence of bridging or perhaps strongly semibridging carbonyl ligands. A semibridging carbonyl has been shown to exist in cp$_2$Mo$_2$(CO)$_4$(μ-L) (L = N$_2$CPh$_2$,[26] C$_2$Et$_2$[27]).

The second component of the product mixture formed initially in the above reaction could not be obtained pure. From the in situ ^{31}P NMR spectrum of the crude reaction mixture it appears to exhibit resonances at δ -34.2 (br, 2 P) and -44.5 (t, $J_{\text{P-P}}$ = 5.1 Hz, 1P). The former shows tungsten satellites with $^1J_{\text{W-P}}$ ~ 242 Hz, while the latter does not. Because the resonance for the two tungsten-

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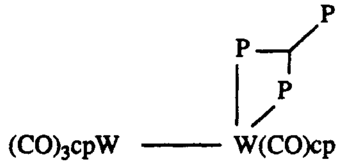
[26] Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789.

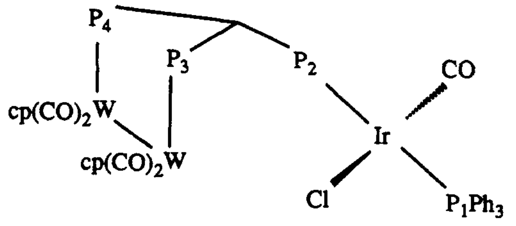
[27] Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

bound phosphorus atoms is considerably upfield of that for the corresponding atoms in 7, it seems likely that the tmpm ligand is bound to a single tungsten as a chelate.[28] A plausible structure is I, but a mononuclear species cannot be ruled out.



I

While the bulk of the cyclopentadienyl ligands on 7 would probably render it less likely than 4 to form a trimetallic cluster following coordination of a third metal to the free arm of the tmpm ligand, this chemistry was briefly explored. A slow reaction occurs between 7 and *trans*-$Ir(CO)Cl(PPh_3)_2$ at room temperature in toluene and a moderate yield of an orange powder having the composition $cp_2W_2Ir(CO)_5Cl(tmpm)(PPh_3)$ (8) resulted. The appearance of a new strong carbonyl band at 1954 cm^{-1}, characteristic of an Ir(I) carbonyl moiety, together with a low-field phosphorus resonance close to that for $Ir(CO)Cl(PPh_3)_2$, a significant downfield shift of the resonance attributed to the free arm of tmpm in 7, and the equal relative intensities of all four phosphorus resonances suggest the structure shown.



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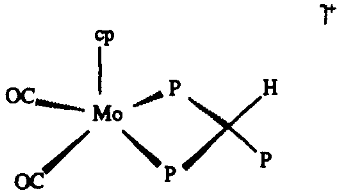
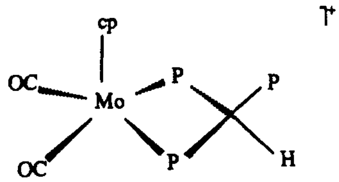
The trans disposition of P_1 and P_2 is indicated by the large value of their coupling constant while the chemical shift inequivalence of P_3 and P_4 and their unequal coupling to P_2 suggest that the $\{Ir(CO)Cl(P_1)(P_2)\}$ moiety is not symmetrically disposed with respect to the tungsten atoms. This is also indicated by the fact that the two sets of cyclopentadienyl protons have different chemical shifts and by the observation of coupling between P_1 and P_3 but not between P_1 and P_4.

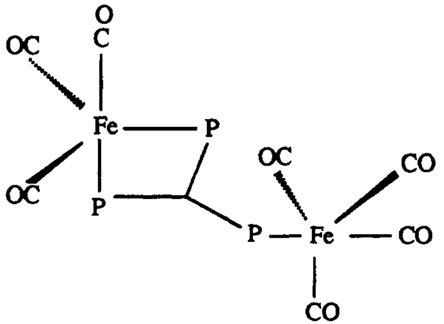
Reactions of tmpm with both $[cpMo(CO)_2]_2$ and $[cpMo(CO)_3]_2$ were briefly examined. With the former, an immediate color change from red orange to red purple occurred upon mixing acetone solutions of the reactants and monitoring by ^{31}P NMR spectroscopy indicated the formation of several species. Two fractions could be obtained by chromatography on Brockman II alumina. In the first fraction the major species present appeared from ^1H and ^{31}P NMR spectra to be the Mo analogue of 7 (see Experimental Section). However, after standing as a solid under nitrogen for 2 days, the ^{31}P NMR spectrum of this fraction showed only a singlet at δ −24.6. The species responsible for this resonance was present initially as a minor component of the first fraction and is the major component of the second fraction. Unfortunately, all attempts to purify the presumed analogue of 7 and the species responsible for the singlet at δ −24.6 afforded only ill-defined solids. By contrast, the reaction of tmpm with $[cpMo(CO)_3]_2$ proceeded slowly and yielded a yellow solid which showed a conductance in acetone solution characteristic of a 1:1 electrolyte. The ^{31}P NMR spectrum consists of two sets of doublet and triplet resonances, each having relative intensities of 2:1. The high-field triplet resonances clearly indicate the presence of an uncoordinated arm of tmpm, while the lower field doublets are consistent with the other two arms being bound to a single molybdenum atom. The ^1H NMR spectrum exhibits three cyclopentadienyl resonances, with the highest field one being sharper and having a relative intensity equal to the sum of those of the other two. In addition there are two multiplet resonances attributable to methine protons of tmpm ligands. These data together with the infrared spectrum are consistent with the formation of the ionic species $[cpMo(CO)_2(\eta^2\text{-tmpm})][cpMo(CO)_3]$ with the cation existing in two isomeric forms, viz.





An analogous unsymmetrical cleavage of $[cpMo(CO)_3]_2$ by chelating ditertiary phosphines has been reported.[29]

Unlike the clean reaction of tmpm with $Ru_3(CO)_{12}$, that with $Fe_3(CO)_{12}$ involves not only fragmentation of the cluster but also cleavage of the ligand resulting in iron carbonyl complexes of dmpm. The same behavior was previously noted for the reaction of TPPM with $Fe_3(CO)_{12}$.[25] A ^{31}P NMR spectrum of the crude reaction mixture showed the presence of four species, and upon separation by column chromatography three fractions were obtained. The middle fraction afforded an air-sensitive red orange oil whose ^{31}P NMR spectrum showed it to be a mixture of two of the species seen initially. Further attempts to separate these were unsuccessful. The major species (**9**) has a ^{31}P NMR spectrum consisting of a triplet and a doublet, in order of increasing field, having relative intensities of 1:2, respectively. The major bands in the carbonyl region of the infrared spectrum can reasonably be interpreted as a superimposition of the bands expected



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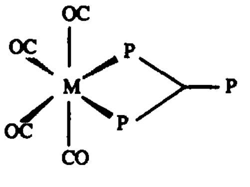
[28] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

[29] King, R. B.; Pannell, K. H.; Eggers, C. A.; Houk, L. W. *Inorg. Chem.* **1968**, *7*, 2353.

for $\{Fe(CO)_3\}$ and $\{Fe(CO)_4\}$ moieties, which together with the NMR spectra strongly suggests formulation of **9** as shown, which is analogous to one product previously reported from the reaction of TPPM with $Fe_3(CO)_{12}$.[25] The minor component of this fraction has a ^{31}P NMR spectrum consisting of multiplet resonances at δ 56.6 and 26.1 having relative intensities of 1:2, respectively. Although a complete analysis could not be performed because of insufficient resolution, the spectral pattern bears a striking resemblance to the AA′A″A‴XX′ spectrum reported for *fac-fac*-$W_2(CO)_6(MeN(\overline{POCH_2CH_2O})_2)_2(\mu\text{-}MeN\text{-}(\overline{POCH_2CH_2O})_2)$,[30] suggesting this species contains six phosphorus atoms. Because of the large proportion of **9** in the mixture and our lack of success in obtaining the minor component pure, the ^1H NMR spectrum of the mixture provides no useful information on the nature of the ligand(s) present; in particular whether it is tmpm or dmpm. As the chemical shifts are close to those for **9**, it is clear that two phosphorus atoms are coordinated in a monodentate fashion while the others are associated with four-membered chelate rings. On this basis, a possible formulation could be $Fe(CO)_3[(\mu\text{-tmpm})Fe(CO)_3]_2$, $Fe(CO)[(\mu\text{-tmpm})Fe(CO)_4]_2$, or $Fe_2(CO)_4(dmpm)_2(\mu\text{-dmpm})$.

The other fractions did not afford characterizable products, but the most prominent peaks in the ^{31}P NMR spectra of the crude materials were singlet resonances at δ 43.1 (fraction 1) and 42.2 (fraction 3) (C_6D_6). The reaction of tmpm with $Fe_2(CO)_9$ produces as the initial product a species also exhibiting a single resonance at δ 43.1 whose infrared spectrum in the carbonyl region is consistent with the presence of $\{Fe(CO)_4\}$ moieties. When this solution is treated with trimethylamine *N*-oxide, a new species is produced whose ^{31}P NMR spectrum consists of a singlet at δ 42.0 and whose ^1H NMR and infrared spectra are in good agreement with those reported previously for $Fe_2(CO)_6(\mu\text{-}CO)(dmpm)$.[18] A yellow crystal of this material was examined by X-ray crystallography, from which it was evident that a binuclear iron species containing only one phosphorus atom per iron was present, but severe disorder prevented a full solution. On the basis of the chemistry involved, we suggest that the initial species formed in the reaction of tmpm with $Fe_2(CO)_9$ is $Fe_2(CO)_8(\mu\text{-dmpm})$ and that this and $Fe_2(CO)_6(\mu\text{-}CO)(dmpm)$ are also produced in the reaction of tmpm with $Fe_3(CO)_{12}$.

Reaction of tmpm with $Cr(CO)_4(NBD)$ and $Mo(CO)_4(pip)_2$ forms yellow crystalline products analyzing as $M(CO)_4(tmpm)$ (M = Cr (**10**), Mo (**11**)). From the spectroscopic data, **10** and **11** can readily be formulated as



10 (M = Cr) **11** (M = Mo)

Table III. Selected Bond Distances (Å) and Interbond Angles (deg) for $[Ru_3(CO)_9(tmpm)(\mu\text{-}AuPPh_3)]O_3SCF_3\bullet(CH_3)_2CO$ (3)

Bond Distances			
Au–Ru(1)	2.7608 (6)	Ru(2)–C(2)	1.92 (1)
Ru(1)–Ru(2)	2.9138 (9)	Ru(2)–C(3)	1.889 (9)
Ru(1)–Ru(1)′	3.0348 (8)	P(2)–C(10)	1.84 (1)
Au–P(1)	2.306 (3)	P(3)–C(10)	1.824 (6)
Ru(1)–P(3)	2.364 (2)	C(1)–O(1)	1.130 (9)
Ru(2)–P(2)	2.359 (3)	C(2)–O(2)	1.13 (1)
Ru(1)–C(1)	1.920 (8)	C(3)–O(3)	1.144 (9)
Ru(1)–C(4)	1.891 (8)	C(4)–O(4)	1.160 (8)
Ru(1)–C(5)	1.868 (8)	C(5)–O(5)	1.156 (9)

Interbond Angles			
Ru(1)–Au–P(1)	146.42 (1)	C(1)–Ru(1)–C(4)	91.9 (3)
Ru(1)–Au–Ru(1)′	66.68 (1)	C(1)–Ru(1)–C(5)	91.9 (4)
Au–Ru(1)–Ru(2)	115.03 (2)	C(4)–Ru(1)–C(5)	96.8 (4)
Au–Ru(1)–Ru(1)′	56.66 (2)	Ru(1)–Ru(1)–P(3)	89.91 (6)
Ru(1)–Ru(2)–Ru(1)′	62.77 (3)	Ru(2)–Ru(1)–C(1)	92.5 (2)
Ru(2)–Ru(1)–Ru(1)′	58.62 (2)	Ru(2)–Ru(1)–C(4)	173.5 (2)
Au–Ru(1)–P(3)	93.94 (6)	Ru(2)–Ru(1)–C(5)	78.3 (2)
Au–Ru(1)–C(1)	82.2 (2)	Ru(1)–Ru(2)–P(2)	90.74 (7)
Au–Ru(1)–C(4)	70.3 (2)	Ru(1)–Ru(2)–C(2)	86.9 (3)
Au–Ru(1)–C(5)	165.5 (3)	Ru(1)–Ru(2)–C(3)	101.0 (3)
Ru(1)′–Ru(1)–P(3)	88.91 (7)	Ru(1)–Ru(2)–C(3)′	163.7 (3)
Ru(1)′–Ru(1)–C(1)	89.7 (3)	P(2)–Ru(2)–C(2)	177.2 (3)
Ru(1)′–Ru(1)–C(4)	126.2 (3)	P(2)–Ru(2)–C(3)	89.5 (3)
Ru(1)′–Ru(1)–C(5)	136.9 (3)	C(3)–Ru(3)–C(3)′	95.3 (3)
P(3)–Ru(1)–C(1)	176.0 (3)	Ru(1)–P(3)–C(10)	112.4 (3)
P(3)–Ru(1)–C(4)	86.0 (2)	Ru(2)–P(2)–C(10)	110.8 (4)
P(3)–Ru(1)–C(5)	91.6 (3)	P(2)–C(10)–P(3)	106.9 (4)
		P(3)–C(10)–P(3)′	107.7 (4)

Structure of 3. The crystal structure of **3** consists of well-separated $[Ru_3(CO)_9(tmpm)(\mu\text{-}AuPPh_3)]^+$ cations, trifluoromethanesulfonate anions, and solvent acetone molecules with no unusual intermolecular contacts. A perspective view of the cation is presented in Figure 1, while the relevant bond distances and interbond angles appear in Table III. The cation has crystallographic *m* symmetry with the mirror plane passing through Ru(2), Au, P(1), and P(2). Both the anion and the solvent molecule also lie on the mirror. The excellent "fit" of the tmpm ligand on the Ru_3 triangle is indicated by the fact that all Ru–Ru–P angles are essentially 90° in contrast to an average value of 96.52 (7)° found in $Ru_3(CO)_9(MeSi(PBu^n_2)_3)$.[20] The Ru(1)–Ru(1)′ distance of 3.0348 (8) Å is significantly longer than the 2.9138 (9) Å value for the unbridged Ru(1)–Ru(2) side of the triangle. Although there are no data for direct comparison—other structurally characterized complexes containing the $\{AuPR_3\}$ moiety bridging the edge of a Ru_3 triangle[31-36] are all *neutral* species containing formally anionic face-bridging ligands—in general some lengthening of the Ru–Ru bond accompanies the introduction of the $\{AuPR_3\}$ moiety. In the present case, the lengthening is 4%, which can be compared to a range from 1% in $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CBu^t)(\mu\text{-}AuPPh_3)$[32] to 7.2% in $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}S)(\mu\text{-}AuPPh_3)$,[34] with a very comparable lengthening of 4.6% seen in $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}PPh)(\mu\text{-}AuPMe_2Ph)$[33] (comparison with the one unbridged Ru–Ru bond in the last two complexes). Both Ru–Ru distances in **3** are longer than the values found previously[31-36] for R_3PAu-bridged (2.802 (1)–2.950 (1) Å) and unbridged (2.737 (1)–2.891 (1) Å) Ru–Ru distances in Ru_3Au clusters, which could be attributed to its cationic nature. However, as noted above, all of these other examples contain face-capping ligands

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(30) Mague, J. T.; Johnson, M. P. *Organometallics* **1990**, *9*, 1254.

(31) Bruce, M. I.; Williams, M. L.; Patrick, J. M.; Skelton, B. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 2557.

(32) Braunstein, P.; Predieri, G.; Tiripicchio, A.; Sappa, E. *Inorg. Chim. Acta* **1982**, *63*, 113.

(33) Mays, M. J.; Raithby, P. R.; Taylor, P. L.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 959.

(34) Bruce, M. I.; Shawkataley, O. B.; Nicholson, B. K. *J. Organomet. Chem.* **1985**, *286*, 427.

(35) Lavigne, G.; Papagorigou, F.; Bonnet, J.-J. *Inorg. Chem.* **1984**, *23*, 609.

(36) Bateman, L. W.; Green, M.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2599.

which are geometrically more constrictive than is tmpm and we note that the average Ru–Ru distance in $Ru_3(CO)_9(MeSi(PBu^n{}_2)_3)$ is 2.916 (1) Å[20] while in $Ru_3(CO)_9(Ph_2PCHP(Ph)C_6H_4PPh)$, the Ru–Ru distances are 2.903 (1) and 2.878 (1) Å;[37] so this conclusion, while plausible, is by no means firm. The Ru(1)–Au distance of 2.7608 (6) Å is well within the ranges of Ru–Au distances (2.727 (1)–2.786 (1) Å) observed in the examples cited above. All other bond distances and interbond angles are unexceptional and, in particular, all Ru–C–O angles are sufficiently close to 180° as to preclude any suggestion of semibridging character for the carbonyl ligands.

The most unusual feature of 3 is the near coplanarity of the gold atom with the Ru_3 triangle. Specifically, the dihedral angle between the Ru(2)Ru(1)Ru(1)′ and AuRu(1)Ru(1)′ planes is 174.0 (9)° with the gold atom bent slightly away from the tmpm ligand. Corresponding dihedral angles in the examples cited above vary widely but the largest previously found are 147.5° in $Ru_3(CO)_9(\mu_3\text{-}SBu^t)(\mu\text{-}AuPPh_3)$[34] and 144.2° in $Ru_3(CO)_9(\mu_3\text{-}Ph_2PCH_2PPh)(\mu\text{-}AuPPh_3)$.[31] It is unclear whether this feature is the result of steric or electronic factors or both. That butterfly complexes of this type are quite flexible is demonstrated by the fluxionality of 3 in solution and by the observation in the crystal structure of $Fe_3(CO)_9(\mu_3\text{-}HC{=}NBu^t)(\mu\text{-}AuPPh_3)$[38] that the two crystallographically independent molecules have dihedral angles of 110.9 and 132.1°, with the difference being attributed to packing forces. In 3 there are no obvious intermolecular packing constraints requiring a large dihedral angle, although in the crystal the orientation of the triphenylphosphine ligand is such that the phenyl rings built on C(21) and C(21)′ would contact the axial carbonyl groups C(1)O(1) and C(1)′O(1)′ were the dihedral angle to be significantly less than the observed value. The question of electronic factors is even less certain. Bruce et al.[34] have reported a dihedral angle of 147.5° in $Ru_3(CO)_9(\mu_3\text{-}SBu^t)(\mu\text{-}AuPPh_3)$, while in $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}S)(\mu\text{-}AuPPh_3)$ the angle is 119.4°, which is within the range observed for a number of other Ru_3Au clusters of similar type.[32,33,35,36] They attribute the increase in dihedral angle to an increased donor power of the *tert*-butyl thiolate ligand relative to sulfide on the basis of a proposal by Carty that an increase in the electron count in Ru_4 butterfly clusters from 62 to 64 leads to an increase in the dihedral angle and an increase in the Ru–Ru distance.[39] Complex 3 has a large dihedral angle, long Ru–Ru distances, and a capping ligand of considerable donor ability. However the cluster in 3 is also cationic and it is unclear what would be the effect of this feature. Even more problematical is the fact that 3 together with all the clusters cited by Bruce et al.[34] are 60-electron species, not 62-electron clusters as they state, and consequently, it is not certain that Carty's proposal is even relevant to these systems.

Conclusions

The tmpm ligand has been found to exhibit a variety of coordination modes. While moderately successful in permitting the directed stepwise synthesis of heterotrimetallic complexes, the formation of new metal–metal bonds in these complexes, and therefore tmpm-stabilized heterotrimetallic *clusters*, has yet to be accomplished. Studies to achieve this and to explore the ability of such species to activate small molecules are ongoing.

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Registry No. **1**, 137433-69-3; **2**, 137393-57-8; **3**, 137393-59-0; **3**·$(CH_3)_2CO$, 137393-68-1; **4**, 137393-60-3; **5**, 137393-61-4; **6**, 137393-62-5; **7**, 137393-63-6; **8**, 137393-64-7; **9**, 137393-65-8; **10**, 137393-66-9; **11**, 137393-67-0; I, 137433-70-6; $Fe_2(CO)_8(dmpm)$, 94529-45-0; $Fe_2(CO)_6(\mu\text{-}CO)(dmpm)$, 90624-22-9; $Ru_3(CO)_{12}$, 15243-33-1; AgO_3SCF_3, 2923-28-6; $AuCl(PPh_3)$, 14243-64-2; $Re_2(CO)_{10}$, 14285-68-8; $[RhCl(COD)]_2$, 12092-47-6; $[IrCl(COD)]_2$, 12112-67-3; $[CpW(CO)_2]_2$, 62853-03-6; *trans*-$IrCl(CO)(PPh_3)_2$, 15318-31-7; $Fe_3(CO)_{12}$, 17685-52-8; $Cr(CO)_4(NBD)$, 12146-36-0; *cis*-$Mo(CO)_4(pip)_2$, 65337-26-0; $Fe_2(CO)_9$, 15321-51-4; $Cp_2Mo_2(CO)_4$, 56200-27-2; $Cp_2Mo_2(CO)_6$, 12091-64-4; $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C_6H_{11})$, 88294-19-3; $Pt(C_2Ph_2)(PPh_3)_2$, 15308-61-9; $Re_2(CO)_8(\mu\text{-}tmpm)Pt(Ph_2C_2)(PPh_3)$, 137393-69-2; $Cp_2Mo_2(CO)_4(tmpm)$, 137393-70-5; $[CpMo(CO)_2(\eta^2\text{-}tmpm)][CpMo(CO)_3]$ (isomer 1), 137393-72-7; $[CpMo(CO)_2(\eta^2\text{-}tmpm)][CpMo(CO)_3]$ (isomer 2), 137491-69-1; Au, 7440-57-5; Ru, 7440-18-8.

Supplementary Material Available: For 3, complete listings of bond distances and interbond angles, anisotropic thermal parameters, calculated H atom positions, and rms amplitudes of anisotropic displacement (7 pages); a list of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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