checked by IR and the color, which should be golden yellow or orange-yellow.

When the above reaction is carried out on a larger scale (6 g of $RhCl_3 \cdot xH_2O$), the best reaction is found to occur by slow addition of the NaOH solution (over ca. 2 h); this avoids a fast reduction and formation of brown insoluble products. Recrystallization to obtain high-purity compounds or a large crystalline specimen is performed by slow diffusion of 2-propanol (saturated with CO) into THF or acetone solutions, under a CO atmosphere.

Anal. Found (calcd) for the $[N(C_2H_5)_4]_2[PtRh_4(CO)_{14}]$ salt: C, 28.58 (28.61); H, 3.25 (3.20); N, 2.22 (2.22); Pt, 14.70 (15.49); Rh, 34.26 (32.68).

5. Synthesis of $[PtRh_4(CO)_{12}]^{2-}$. In a typical preparation, $[PPN]_2[PtRh_4(CO)_{14}]$ (0.280 g, 0.135 mmol) was dissolved in THF (15 mL) under a nitrogen atmosphere. The solution was slowly evaporated under vacuum, and the reddish brown solid obtained was redissolved in THF (15 mL); and IR spectrum revealed complete conversion to $[PPN]_2[PtRh_4(CO)_{12}]$. Recovery was accomplished by addition of 2-propanol (30 mL); the microcrystalline precipitate was filtered, washed with 2-propanol (5 + 5 mL), vacuum-dried, and stored under nitrogen; yield 0.250 g (92%). The same procedure can be used to obtain any other salt using the corresponding salt of the parent compound. When larger amounts of products are worked up, more than one cycle of evaporation and redissolution may be necessary; in any case purity should be checked by IR. Recrystallization from acetone/2-propanol using the slow-diffusion technique gives good crystals of the product.

Gas Volumetric Analysis of Evolved CO. A sample of $[PPN]_2[PtRh_4(CO)_{14}]$ (0.8502 g, 0.4095 mmol) was dissolved under vacuum in THF. The evolved CO (reduced to STP conditions) was 0.7875 mL, corresponding to 1.923 mol/mol of starting material.

6. Reaction of $[PtRh_4(CO)_{12}]^{2-}$ with CO. A THF or acetone solution of any salt of $[PtRh_4(CO)_{12}]^{2-}$ prepared under nitrogen is briefly evacuated and submitted to 1 atm CO; within minutes the color turns yellow from the original reddish brown and the IR spectrum taken under CO shows complete conversion to $[PtRh_4(CO)_{14}]^{2-}$.

7. Reaction of $[PtRh_4(CO)_{14}]^{2-}$ with $[Rh(CO)_2(CH_3CN)_2]^+$. $[NEt_4]_2[PtRh_4(CO)_{14}]$ (0.0465 g, 0.037 mmol) was dissolved in acetonitrile under CO. Addition of $[Rh(CO)_2(CH_3CN)_2][BF_4]$ (2 mL of a 0.0185 M solution in acetonitrile) gave immediate reaction, yielding a brown solution of $[NEt_4][PtRh_5(CO)_{15}]$ (IR bands at 2035 s, 2004 m, and 1775 ms cm^{-1}).

8. Reaction of $[PtRh_4(CO)_{14}]^{2-}$ with $Rh_6(CO)_{16}$. Finely powdered $Rh_6(CO)_{16}$ (0.051 g, 0.048 mmol) was reacted under CO with $[PPN]_2[PtRh_4(CO)_{14}]$ (4.8 mL of a 0.01 M THF solution). After 1 h of stirring, a dark red solution was obtained, which showed the characteristic IR bands of $[Rh_5(CO)_{15}]^-$ (2038 s, 2004 vs, 1868 m, 1838 ms, and 1785 m cm^{-1}) superimposed on those of $[PtRh_5(CO)_{15}]^-$ (2035 s, 2004 m, and 1785 ms cm^{-1}).

Acknowledgment. We acknowledge the support of the National Research Council of Italy (CNR), SERC for a fellowship (to R.D.) and for high-field NMR facilities, and Prof. G. Longoni (Università di Milano) for the help in the identification of the platinum carbonyl species.

Registry No. $Na[PtRh_5(CO)_{15}]$, 67954-67-0; $[NEt_4][PtRh_5(CO)_{15}]$, 68034-57-1; $PPN[PtRh_5(CO)_{15}]$, 68034-56-0; $Na_2[PtRh_4(CO)_{14}]$, 91238-53-8; $[PPN]_2[PtRh_4(CO)_{14}]$, 78179-93-8; $[N\text{-}n\text{-}Bu_4]_2[PtRh_4(CO)_{14}]$, 91238-54-9; $[NEt_3\text{-}n\text{-}Pr]_2[PtRh_4(CO)_{14}]$, 91238-55-0; $[PPh_4]_2[PtRh_4(CO)_{14}]$, 91265-29-1; $[NEt_4]_2[PtRh_4(CO)_{14}]$, 91238-57-2; $[N\text{-}n\text{-}Bu_4]_2[PtRh_4(CO)_{12}]$, 91238-56-1; $[PPN]_2[PtRh_4(CO)_{12}]$, 77906-02-6; Na_2PtCl_6, 16923-58-3; $[N\text{-}n\text{-}Bu_4]_2[Rh_{12}(CO)_{30}]$, 12576-05-5; $[N\text{-}n\text{-}Bu_4]_2[Pt_{12}(CO)_{24}]$, 61084-51-3; $[Rh(CO)_2(CH_3CN)_2][BF_4]$, 53513-97-6; $Rh_6(CO)_{16}$, 28407-51-4; $[Rh_5(CO)_{15}]^-$, 72826-87-0; Rh, 7440-16-6; Pt, 7440-06-4.

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Synthesis of $M_2Pt(CO)_{12}$ (M = Re, Mn). Crystal Structure of $Re_2Pt(CO)_{12}$

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Received November 3, 1983

The heterobimetallic carbonyl compounds $M_2Pt(CO)_{12}$ (M = Re, Mn) have been synthesized in high yield from the reaction of $Me_2Pt(COD)$ (COD = 1,5-cyclooctadiene) with excess $HM(CO)_5$ (M = Re, Mn) in the presence of CO at room temperature. The concomitant formation of $M_2(CO)_{10}$ is suggested as evidence of a radical pathway for this reaction. The molecular structure of $Re_2Pt(CO)_{12}$ is reported and compared to the structure of $Re_2(CO)_{10}$. Crystals of $Re_2Pt(CO)_{12}$ form in the triclinic space group $P\bar{1}$ with $a = 7.225$ (2) Å, $b = 10.116$ (2) Å, $c = 6.503$ (2) Å, $\alpha = 94.57$ (2)°, $\beta = 91.86$ (2)°, $\gamma = 71.59$ (2)°, $V = 449.5$ (2) Å^3, and ρ(calcd) = 3.338 g cm^{-3}, for mol wt 903.61 and $Z = 1$. The structure can best be described as a platinum atom in a square-planar environment, bound to two carbonyl ligands and two $Re(CO)_5$ moieties in the trans configuration. Anisotropic refinement of all atoms has resulted in final discrepancy factors of $R = 0.030$ and $R_w = 0.038$ for 1094 observed reflections. The observed Pt-Re bond distance is 2.8309 (5) Å.

Introduction

As part of a program to evaluate oxide-supported heterobimetallic compounds as heterogeneous catalysts, we have sought high-yield pathways to new mixed-metal compounds that contain catalytically important metals.[1] One of the most important commercial bimetallic catalysts is alumina-supported platinum-rhenium, which is used in the catalytic reforming of petroleum naphthas.[2] To date, however, only a few bimetallic compounds of platinum-rhenium have been reported,[3] and all of them contain phosphine ligands. This is an undesirable feature for a catalyst precursor, in that supported metal particles generated from such compounds may be poisoned by phosphorus. The preparation of platinum-rhenium bimetallic compounds that contain easily removable ligands is therefore a desirable goal.

We have previously shown that mixed-metal clusters could be prepared by the addition of metal hydride complexes to

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reactive metal-cluster species.[4] More recently, the reaction of metal hydrides with metal alkyl compounds has been used to prepare mixed-metal species via "binuclear reductive elimination".[5] We have used the latter approach to prepare the heterobimetallic compounds $Re_2Pt(CO)_{12}$ and $Mn_2Pt(CO)_{12}$[6] by the reaction of $HM(CO)_5$ (M = Re, Mn) with $Me_2Pt(COD)$ (COD = 1,5-cyclooctadiene). We report here our results on the synthesis and characterization of these compounds together with a single-crystal X-ray diffraction study of $Re_2Pt(CO)_{12}$.

Experimental Section

Materials. $Me_2Pt(COD)$[7] and $Mn(CO)_5Br$[8] were prepared according to published procedures. In a variation of the literature procedure,[9] $Re(CO)_5Br$ was prepared by "titrating" a dichloromethane solution of $Re_2(CO)_{10}$ (Strem Chemicals) with liquid bromine at room temperature. After the solvent was removed in vacuo, the crude product was recrystallized from 1:2 acetone/methanol solution. $HM(CO)_5$ (M = Re, Mn) was prepared from the corresponding bromide in tetraglyme by reaction with H_3PO_4 in the presence of zinc dust.[10] Unlike $HRe(CO)_5$, $HMn(CO)_5$ is extremely air sensitive and was handled in a nitrogen-filled glovebox (Vacuum Atmospheres Corp.). All other manipulations were performed under nitrogen or carbon monoxide with the use of standard Schlenk and inert-atmosphere techniques unless otherwise noted. Hexanes and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone ketyl before use. Dichloromethane was dried by heating to reflux over phosphorus pentoxide and then distilled. Carbon monoxide (Air Products) was CP grade and was used without further purification. ^{13}C-enriched carbon monoxide (Mound Laboratory) contained 90 mol % ^{13}CO.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 281B spectrophotometer and calibrated with cyclohexane (2138 and 1776 cm^{-1}). Electron-impact (70 ev) mass spectra were obtained with a Varian MAT CH-5 mass spectrometer by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences. Simulated isotopic multiplets were calculated with the aid of the computer program MASPAN, written by Dr. M. A. Andrews in association with Professor H. D. Kaesz.[11] ^{13}C NMR spectra were recorded on a Nicolet NT-360 spectrometer operating at 90 MHz. The spectra were obtained on ca. 3 mg of a ^{13}CO-enriched sample dissolved in 0.5 mL of THF-d_8 in a 5-mm tube. Elemental analyses were performed in the Microanalytical Laboratory of the School of Chemical Sciences. Methane analyses were determined with a Packard Model 430 gas chromatograph equipped with a flame ionization detector and a $^1/_8$ in. × 7 ft Durapack *n*-octane/Porasil C column (100/120 mesh, Alltech Associates). The GC was calibrated by sampling ultrapure methane (Linde) with a gastight syringe (Precision Sampling). The calibration gas was contained in a manifold of precisely known volume to which a high-accuracy capacitance manometer (MKS) was attached. The pressure and volume of methane admitted to the syringe could therefore be accurately determined.

Preparation of $Re_2Pt(CO)_{12}$. To a 50-mL Schlenk tube containing a magnetic stir bar was added freshly distilled hexanes (10 mL) and $HRe(CO)_5$ (198 mg, 0.61 mmol). After several freeze–pump–thaw cycles the tube was charged with CO to a pressure of 1 atm. The stopper on the Schlenk tube was then removed, and $Me_2Pt(COD)$ (49.3 mg, 0.148 mmol) was quickly added against a carbon monoxide flow. The stopcock was closed, and the solution was stirred under CO. An immediate purple solution resulted, and a bright red precipitate gradually formed. The solution was stirred at ambient temperature for 24 h, after which the solvent, cyclooctadiene, and unreacted $HRe(CO)_5$ were removed in vacuo. The crude red solid that remained was washed in the air on a sintered glass frit with 10 mL of cold hexane to remove $Re_2(CO)_{10}$. The remaining red powder was dissolved in a minimum of *freshly* distilled THF (20 mL) and the resulting dark purple solution filtered through the frit. Acetone (40 mL) was then added to the filtrate, and bright red crystals formed upon cooling at −10 °C overnight. The product was collected by vacuum filtration, washed with cold hexanes (2 mL), and dried in vacuo. A second crop of crystals was obtained from the filtrate by removing the solvent in vacuo and recrystallizing the residue from THF/acetone as described above (total yield 113.1 mg, 0.125 mmol, 84% based on Pt). Mp: 157–159 °C dec. Anal. Calcd for $Re_2Pt(CO)_{12}$: C, 15.95; Pt, 21.59; Re, 41.21. Found: C, 15.97; Pt, 21.69; Re, 41.0. Mass spectrum (electron impact): *m/z* 905 (M^+, ^{187}Re, ^{195}Pt) as well as $M^+ - xCO$ (x = 1–12). The isotopic pattern for the molecular ion is shown in Figure S-1a, provided as supplementary information. IR (C_6H_{12}): ν_{CO} 2083 (m), 2026 (vs), 2006 (s), 1983 (s) cm^{-1} (Figure S-2a, supplementary material). IR (KBr): ν_{CO} 2084 (s), 2038 (s), 2020 (s), 1997 (sh), 1986 (vs), 1968 (vs) cm^{-1}. ^{13}C NMR (−60 °C, THF-d_8): δ 190.3 (~8 C), 183.7 (~2 C).

Preparation of $Mn_2Pt(CO)_{12}$. A 50-mL Schlenk tube containing a magnetic stir bar and $HMn(CO)_5$ (240 mg, 1.22 mmol) in 10 mL of hexanes was fitted with a solids-addition tube containing $Me_2Pt(COD)$ (100 mg, 0.30 mmol). After a freeze–pump–thaw cycle, the solution was frozen, the platinum compound was added, and the tube was charged with CO to a pressure of 1 atm. The tube was then warmed to room temperature and the stopcock closed. The solution developed a dark red color, and gradually a red solid precipitated out. The solution was stirred at ambient temperature for 24 h, after which the solvent, cyclooctadiene, and unreacted $HMn(CO)_5$ were removed in vacuo. The red solid that remained was washed by stirring with hexanes (10 mL) to remove $Mn_2(CO)_{10}$. The resulting suspension was cooled to −78 °C and the solution was removed by filter cannula. This wash procedure was repeated, and the residue was dissolved in dichloromethane (30 mL). The dark red solution was then filtered via cannula into another Schlenk tube and cooled to −78 °C to crystallize the product. After about 3 h the solution was filtered at −78 °C by filter cannula, leaving bright red microcrystals, which were then dried in vacuo (134.6 mg, 0.210 mmol, 70% based on Pt). Mp: 141–142 °C dec. Anal. Calcd for $Mn_2Pt(CO)_{12}$: C, 22.48; Mn, 17.41. Found: C, 22.19; Mn, 17.49. Mass spectrum (electron impact): *m/z* 641 (M^+, ^{55}Mn, ^{195}Pt) as well as $M^+ - xCO$ (x = 4–12). The isotope pattern for the molecular ion is shown in Figure S-1b, supplementary material. IR (C_6H_{12}): ν_{CO} 2059 (m), 2036 (vs), 2001 (s), 1988 (s) cm^{-1} (Figure S-2b, supplementary material). IR (KBr): ν_{CO} 2061 (s), 2039 (s), 2014 (s), 1996 (sh), 1984 (vs), 1966 (vs) cm^{-1}; lit.[6b] ν_{CO} 2066 (s), 2046 (s), 2022 (s), 1994 (sh), 1984 (vs), 1967 (vs) cm^{-1}. ^{13}C NMR (−40 °C, THF-d_8): δ 216.7 (broad).

^{13}CO-Enrichment of $M_2Pt(CO)_{12}$. The following procedure was that used for $Re_2Pt(CO)_{12}$. To a 50-mL Schlenk tube containing 10 mL of hexanes was added $HRe(CO)_5$ (75 mg, 0.23 mmol). This solution was degassed by several freeze–pump–thaw cycles, after which the tube was charged with ^{13}CO to a pressure of 1 atm in order to enrich the hydride.[12] After 12 h of stirring, $Me_2Pt(COD)$ was added, and the tube was sealed under ^{13}CO. The product (ca. 50% enriched) was isolated after 24 h of stirring as described above. The manganese analogue was enriched in a similar manner.

Structure Determination of $Re_2Pt(CO)_{12}$. The transparent, red, prismatic crystal used for data collection was obtained from a 1:1 THF/acetone solution. The interior of the crystal was clear and free of visible defects. The sample extinguished plane-polarized light.

The crystal was bound by faces with indices (0,0,−1), (0,1,−1), (0,−1,1), (010), (0,−1,0), (110), (−1,−1,0), (100), and (−1,0,0). The

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[6] $Mn_2Pt(CO)_{12}$ has previously been isolated in 3% yield from the reaction of *cis*-$PtCl_2(PPh_2Cl)_2$ with $Mn(CO)_5^-$ in THF. A trans geometry about the platinum was proposed on the basis of dipole moment measurements. See: (a) Braunstein, P.; Matt, D.; Bars, O.; Grandjean, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 797. (b) Braunstein, P.; Matt, D.; Bars, O.; Louer, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79.

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Table I. Experimental Data for the X-ray Diffraction Study of $Re_2Pt(CO)_{12}$

A. Crystal Parameters[a] at 24 °C

cryst syst: triclinic
$a = 7.225\ (2)$ Å
$b = 10.116\ (2)$ Å
$c = 6.503\ (2)$ Å
$\alpha = 94.57\ (2)°$
$\beta = 91.86\ (2)°$
$\gamma = 71.59\ (2)°$

space group: $P\bar{1}$
$V = 449.5\ (2)$ Å^3
mol wt = 903.61
ρ(calcd) = 3.338 g cm^{-3}
$Z = 1$
approx cryst size: 0.10 × 0.12 × 0.13 mm

B. Data Collection

radiation: Mo Kα ($\bar{\lambda}$ = 0.710 69 Å)
monochromator: graphite crystal
lin abs coeff: 215.2 cm^{-1}
trans coeff (abs cor): max = 0.390, min = 0.300
no. of unique reflcns collcd: 1594
no. of reflcns obsd: 1094
internal consistency $[I > 3\sigma(I)]$: 0.020

[a] Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections.

Table II. Positional Parameters for $Re_2Pt(CO)_{12}$

atom	x/a	y/b	z/c
Pt	0.0	0.0	0.0
Re	−0.11378 (8)	0.26834 (5)	0.21209 (8)
O1	−0.253 (2)	0.559 (1)	0.455 (2)
O2	0.242 (2)	0.322 (1)	0.020 (2)
O3	−0.457 (1)	0.180 (1)	0.378 (2)
O4	0.150 (2)	0.132 (1)	0.580 (2)
O5	−0.353 (2)	0.377 (1)	−0.182 (2)
O6	0.413 (2)	−0.060 (1)	0.171 (2)
C1	−0.198 (2)	0.451 (1)	0.360 (2)
C2	0.115 (2)	0.301 (1)	0.089 (2)
C3	−0.334 (2)	0.210 (1)	0.319 (2)
C4	0.057 (2)	0.181 (1)	0.446 (2)
C5	−0.269 (2)	0.338 (1)	−0.044 (2)
C6	0.256 (3)	−0.036 (1)	0.108 (2)

estimated distance from the (001) face to the center of the crystal was 0.04 mm. The four remaining centrosymmetric pairs of faces had interfacial separations of 0.10, 0.12, 0.13, and 0.13 mm, respectively. The sample was mounted on a glass fiber normal to the (0,−1,1) face and aligned on a Syntex P2$_1$ automated diffractometer equipped with a graphite-crystal monochromator. A set of intensity data (±*h*,±*k*,+l) was collected within the angular range 3° < 2θ < 50° by the 2θ/θ scan technique. A scan range from 0.8° 2θ below the calculated Kα_1 peak position to 0.9° 2θ above the calculated Kα_2 position was used with a variable scan rate from 1 to 15°/min. Three standard reflections monitored after every 97 reflections measured showed only normal variations in intensity. Data were corrected for Lorentz and polarization factors, secondary extinction, and absorption; scattering factors were corrected for anomalous dispersion.[13] X-ray and crystal data are shown in Table I.

Coordinates for the two metal atoms were deduced from a Patterson map. Least-squares refinement of the rhenium atom position (the platinum atom was constrained to the inversion center) and a subsequent difference Fourier synthesis gave positions for the remaining atoms. Full-matrix least-squares refinement of the structure with anisotropic thermal parameters for all the atoms led to final convergence $[(\Delta/\sigma_{\max} = 0.02]$ with discrepancy factors

$$R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.030$$

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.038$$

where w was the weighting factor, defined as $2.09/\{[\sigma(|F_o|)]^2 + (0.04|F_o|)^2\}$, and F_o and F_c are the observed and calculated structure factors. There were no recognizable fragments in the final difference Fourier and no apparent systematic errors between F_o and F_c. Final positional parameters of all atoms are given in Table II. Tables of the final thermal parameters and final observed and calculated

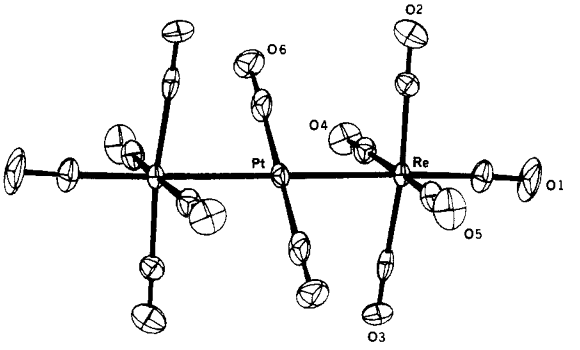

Figure 1. ORTEP diagram of the molecular structure of $Re_2Pt(CO)_{12}$. The platinum–rhenium bond length is 2.8309 (5) Å.

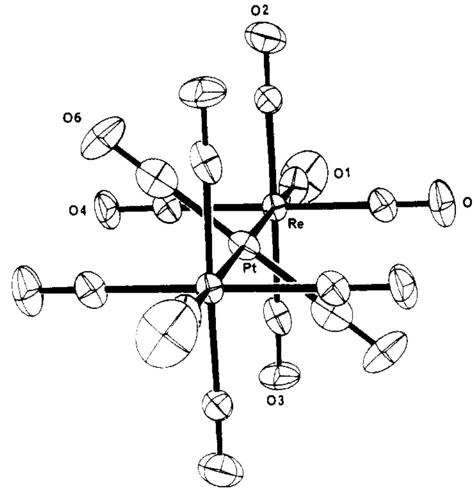

Figure 2. Perspective view of $Re_2Pt(CO)_{12}$ illustrating the eclipsed configuration of the equatorial carbonyl groups on rhenium.

Table III. Intramolecular Bond Angles (deg) for $Re_2Pt(CO)_{12}$

Re–Pt–Re 180.0

	M′–M–CO Angles		
Pt–Re–C1	178.4 (4)	Pt–Re–C4	87.3 (4)
Pt–Re–C2	88.1 (4)	Pt–Re–C5	86.9 (4)
Pt–Re–C3	84.6 (3)	Re–Pt–C6	89.7 (4)
	OC–M–CO Angles		
C1–Re–C2	93.5 (6)	C2–Re–C4	89.2 (6)
C1–Re–C3	93.8 (6)	C2–Re–C5	88.5 (6)
C1–Re–C4	92.7 (6)	C3–Re–C4	90.1 (5)
C1–Re–C5	93.2 (6)	C3–Re–C5	91.4 (5)
C2–Re–C3	172.7 (5)	C4–Re–C5	173.8 (5)
	M–C–O Angles		
Re–C1–O1	177 (1)	Re–C4–O4	179 (1)
Re–C2–O2	179 (1)	Re–C5–O5	180 (1)
Re–C3–O3	179 (1)	Pt–C6–O6	178 (1)

Table IV. Selected Distances (Å) for $Re_2Pt(CO)_{12}$

Pt–Re 2.8309 (5)

	Metal–CO Distances		
Re–C1	1.93 (1)	Re···O1	3.10 (1)
Re–C2	1.99 (1)	Re···O2	3.10 (1)
Re–C3	2.02 (1)	Re···O3	3.14 (1)
Re–C4	2.01 (1)	Re···O4	3.14 (1)
Re–C5	2.02 (1)	Re···O5	3.12 (1)
Pt–C6	1.89 (2)	Pt···O6	3.04 (1)
	C–O Bond Lengths		
C1–O1	1.17 (2)	C4–O4	1.13 (2)
C2–O2	1.12 (2)	C5–O5	1.10 (2)
C3–O3	1.11 (2)	C6–O6	1.15 (2)

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(13) The following methods were employed. Secondary extinction: Zachariasen, W. H. *Acta Crystallogr., Sect. A* **1968**, *A24*, 212. Numerical absorption: Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 61–66. Scattering factors: *Ibid.*, pp 99–101. Anomalous dispersion: *Ibid.*, pp 149–150. Computations: Sheldrick, G. M. "SHELX 76, a Program for Crystal Structure Determination", University of Cambridge, England, 1976.

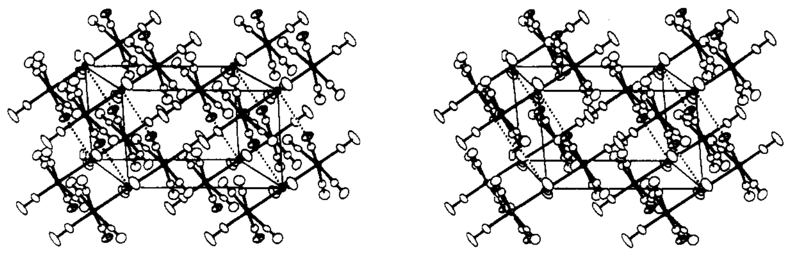

Figure 3. Packing diagram illustrating the weak intermolecular contact between platinum and oxygen atoms from two adjacent molecules. The Pt···O4′ distance is 3.48 (1) Å.

Table V. Comparison of Distances (Å) and Angles (deg) for $Re_2(CO)_{10}$[14] and $Re_2Pt(CO)_{12}$

	$Re_2(CO)_{10}$	$Re_2Pt(CO)_{12}$
M-M′	3.0413 (11)	2.8309 (5)
Re-CO(ax)	1.929 (7)	1.92 (1)
Re···O(ax)	3.075 (7)	3.10 (1)
Re-CO(eq) (av)	1.987 [15]	2.01 [1]
Re···O(eq) (av)	3.115 [13]	3.12 [2]
C-O(ax)	1.146 (10)	1.17 (2)
C-O(eq) (av)	1.129 [7]	1.12 [1]
M′-M-CO(ax)	176.34 (21)	178.4 (4)
M′-M-CO(eq) (av)	86.4 [25]	86.7 [15]
OC(ax)-M-CO(eq) (av)	93.7 [14]	93.3 [5]
M-C-O(ax)	177.54 (65)	177 (1)
M-C-O(eq) (av)	178.0 [12]	179 [1]
symmetry	$\sim D_{4d}$	$\sim D_{2h}$

structure factor amplitudes are available as supplementary information.

Results and Discussion

Solid-State Structure. The single-crystal X-ray diffraction analysis of $Re_2Pt(CO)_{12}$ shows that the molecule ideally possesses D_{2h} symmetry with octahedral coordination about each rhenium atom and square-planar (trans) geometry about the platinum (Figure 1). Since the platinum atom lies on the inversion center, the Re-Pt-Re angle is constrained to 180°.

The two sets of four equatorial carbonyls on rhenium are in an eclipsed configuration (Figure 2). Selected bond angles and distances for the compound are contained in Tables III and IV. All of the Pt-Re-CO(eq) angles are acute, ranging from 88.1 (4) to 84.6 (3)°, while the OC(ax)-Re-CO(eq) angles are all obtuse, ranging from 92.7 (6) to 93.8 (6)°. This indicates that the equatorial carbonyl groups are bent back slightly toward the platinum atom. The carbonyl groups on platinum are staggered between the equatorial carbonyls on rhenium (torsion angles C6-Pt-Re-C2, C6-Pt-Re-C4, C6-Pt-Re-C3, and C6-Pt-Re-C5 are equal to 51.3 (6), 38.0 (6), 128.4 (6), and 139.9 (6)°, respectively). The Re-Pt-C6 bond angle is 89.7 (4)°, indicating nearly perfect square-planar geometry about platinum. All M-CO angles are close to linear, ranging from 177 (1) to 180 (1)°.

The platinum-rhenium bond length of 2.8309 (5) Å (Table IV) is within 0.02 Å of the average between the Re-Re distance in $Re_2(CO)_{10}$[14] and the in-plane Pt-Pt distance in $[Pt_3(CO)_3(\mu\text{-}CO)_3]_n^{2-}$ (where n = 2, 3, 5).[15] A comparison of the metal-carbon distances of the CO's bound to rhenium in $Re_2(CO)_{10}$ with those in $Re_2Pt(CO)_{12}$ (Table V) shows that the distances are nearly equal. This is also true for the metal-oxygen and C-O bond distances with one notable exception. Although the C-O(ax) and C-O(eq) bond distances are similar (within experimental error) for $Re_2(CO)_{10}$, the C-O(ax) distance in the bimetallic carbonyl is 0.05 (2) Å longer than the average equatorial C-O distance. Both compounds have equatorial Re-C distances that are somewhat longer than the axial Re-C distance. A similar difference is also observed in the manganese and technetium analogues of $M_2(CO)_{10}$, and this lengthening of the equatorial M-C distances is attributed to the competition for d_π electron density between the mutually trans pairs of equatorial carbonyl ligands.[14,16]

Examination of intermolecular atomic distances suggests that there is a weak contact between platinum and the oxygen atoms from two adjacent molecules (Pt···O4′ = 3.48 (1) Å), allowing the geometry about platinum to approach that of an octahedron. As a result, infinite chains are formed, which run along the c axis of the crystal. This is illustrated in the packing diagram (Figure 3), which represents a projection of the unit cell along the a axis. Such an interaction is consistent with the fact that only four bands are observed in the CO stretching region of the solution IR spectrum, while six bands are seen in the solid-state spectrum. This interaction might also explain the rather low solubility of these compounds.

Although the title compounds are somewhat unusual in that they are square-planar complexes of platinum containing trans carbonyl groups,[17] linear bimetallic compounds of this general type have been known for some time. For example, PtM_2L_2 complexes where L = py with M = $CpMo(CO)_3$,[20] $Co(CO)_4$,[21] or $Mn(CO)_5$[22] and L = t-BuNC or $C_6H_{11}NC$ with M = $Co(CO)_4$, $Co(CO)_3PPh_3$, $Fe(CO)_3NO$, $Mn(CO)_5$, $CpMo(CO)_3$, or $CpW(CO)_3$[23] have been previously prepared and characterized. $Mn_2Pt(CO)_{10}(py)_2$ has been shown to have approximate D_{2h} symmetry,[24] like $Re_2Pt(CO)_{12}$. However, the pyridine complex is much more distorted, with Pt-Mn-C(eq) bond angles ranging from 68 to 97°.

Solution Studies. The binuclear reductive-elimination reaction of $Me_2Pt(COD)$ with $HM(CO)_5$ (M = Re, Mn) leads to the formation of the heterobimetallic carbonyl compounds $M_2Pt(CO)_{12}$ in high yield. Solution infrared studies of the reaction mixtures show that $Me_2Pt(CO)_2$[19] is formed as the reaction proceeds. Because this dicarbonyl is quite volatile, the reaction is best performed in a static CO atmosphere rather than in a CO flow. Although the dicarbonyl, like its precursor, reacts with $HM(CO)_5$ to form the bimetallic compounds, it reacts at a much slower rate, and hence its use offers no particular advantage.

Four carbonyl stretching modes are observed in solution infrared spectra of the bimetallic compounds (supplementary Figures S-2a and S-2b), as expected for an effective C_{4v}

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symmetry about the Re or Mn atoms and a trans configuration about the Pt center. The similar appearance of the spectra suggests that the two compounds are isostructural.

Collection of suitable ^{13}C NMR data was hampered by quadrupolar coupling (^{55}Mn, ^{185}Re, and ^{187}Re all have $I = {}^5/_2$) and the rather low solubility of the bimetallic compounds at low temperature. For $Re_2Pt(CO)_{12}$, two broad signals with half-widths of about 55 Hz were observed at room temperature. At −60 °C, these resonances narrowed to about 15 Hz and were centered at δ 190.3 (~8 C) and 183.7 (~2 C). These two resonances are presumably due to the eight equivalent equatorial and two equivalent axial carbonyl carbon atoms on rhenium.[25] Despite a careful search, the ^{13}CO resonance on Pt could not be observed. For $Mn_2Pt(CO)_{12}$ only a single, broad unresolved signal was observed at room temperature with a half-width of nearly 300 Hz. At −40 °C the signal was still quite broad ($w_{1/2} \sim 80$ Hz). Again, the ^{13}CO resonance on Pt was not observed.

It has recently been shown that binuclear reductive–elimination reactions between transition-metal alkyl and hydride complexes can occur by a variety of mechanistic routes.[27] Consequently, the organic ligand(s) may be eliminated as alkane(s) or aldehyde(s) depending on the nature of the reactants, the pathway(s), and the reaction conditions.[27b] In the reaction of $Me_2Pt(COD)$ with $HM(CO)_5$, spot tests for acetaldehyde[28] are negative.[29] Analysis of the gas above the reaction mixture by GC reveals that methane is formed in nearly quantitative yield. During the course of the reaction, substantial (approximately equimolar) amounts of $M_2(CO)_{10}$ are formed. Since $HM(CO)_5$ is stable in the presence of $M_2Pt(CO)_{12}$, this observation suggests that $M(CO)_5$ radicals are being generated, perhaps via a chain process.[30]

Conclusion. The binuclear reductive-elimination reaction of $Me_2Pt(COD)$ with excess $HM(CO)_5$ (M = Re, Mn) leads to the formation of the heterobimetallic carbonyls $M_2Pt(CO)_{12}$ in high yield with concomitant formation of $M_2(CO)_{10}$. A crystal structure determination for $Re_2Pt(CO)_{12}$ shows that the molecular ideally possesses D_{2h} symmetry with octahedral coordination about each rhenium atom and square-planar (trans) geometry about the platinum atom. The manganese analogue is probably isostructural.

Acknowledgment. This research was supported by NSF Grant DMR 80-20250 to the Materials Research Laboratory. NMR spectra were obtained in part under NSF Grant 79-16100 to the University of Illinois NSF Regional Instrumentation Facility. We also acknowledge the assistance of Dr. C. H. McAteer in obtaining the NMR spectra.

Note Added in Proof. The structure of $Mn_2Pt(CO)_{12}$ has been determined (Braunstein, P.; et al. *Nouv. J. Chim.*, in press).

Supplementary Material Available: Tables of the final thermal parameters (Table A) and final observed and calculated structure factor amplitudes (Table B) and figures showing the molecular ion multiplets (Figure S-1) and solution IR spectra (Figure S-2) (8 pages). Ordering information is given on any current masthead page.

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(25) At −60 °C the reported ^{13}C NMR spectrum (THF-d_8) of $Re_2(CO)_{10}$ is δ 192.8 [s, Re–CO(cis)] and 183.7 [s, Re–CO(trans)].[26]

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Synthesis and Structure of a Cobalt(I) *meso*-Tetraphenylporphyrin Complex, $[Co^I(TPP)][K\subset 222]_4Cl_3\cdot H_2O$

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Received November 2, 1983

Reduction of chlorocobalt(III) *meso*-tetraphenylporphyrin in chlorobenzene by an excess of 222 cryptated potassium 2-methyl-2-propanethiolate yields a cobalt(I) *meso*-tetraphenylporphyrin derivative, $[Co^I(TPP)][K\subset 222]_4Cl_3\cdot H_2O$ (**1**) of composition $C_{116}H_{174}N_{12}O_{25}Cl_3K_4Co$. The crystals of **1** are monoclinic, space group $C2/c$ with $a = 15.190$ (6) Å, $b = 21.313$ (8) Å, $c = 40.763$ (10) Å, $\beta = 101.58$ (2)°, $V = 12928$ Å^3, and $Z = 4$. The $(Co–N_p)_{av}$ bond distance in $[Co^ITPP]^-$ is 1.942 (3) Å. The porphyrin skeleton is quasi-planar although a few atoms deviate somewhat largely from their least-squares mean plane. When they are compared with the known Ni(II) porphyrin structures, the $(N–C_\alpha)_{av}$ bond distance appears somewhat lengthened and the $(C_\alpha–C_\beta)_{av}$ and $(C_\beta–C_\beta)_{av}$ bond lengths are slightly shortened. These small changes are most probably due to enhanced back-donation of the electron-rich cobalt(I) center toward the porphyrin π system.

Studies of model compounds and synthetic analogues for the active site of cobalt-substituted cytochrome P-450$_{CAM}$ have made chemical and structural investigations of mercaptocobalt porphyrins of interest.[1] In the course of such studies,[2] we have found that reduction of chlorocobalt(III) *meso*-tetraphenylporphyrin below the oxidation state II occurs by reaction with 222 cryptated potassium 2-methyl-2-propanethiolate in chlorobenzene. Reduction of cobalt(II) *meso*-tetraphenylporphyrin to the cobalt(I) derivative was first reported in 1965,[3] and other Co(I) porphyrins were obtained since.[4,5] However, to our knowledge no thiols or thiolates have been used as reducing agents although dielectronic cysteine reduction of vitamin B_{12} has been proposed in the enzymatic conversion of homocysteine to methionine.[6] We present here the structure of a compound,

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