an identical product upon workup as described here: ^1H NMR δ 9.87 (br s, 1, Et_3NH), 7.27 (2), 7.24 (2), and 7.12 (2) (each a s, H_m), 4.67 (br, 2, H_{iso}), 4.40 (sept, 2, H_{iso}), 3.78 (br, 2, H_{iso}), 2.92 (sept, 1, H_{iso}), 2.85 (sept, 2, H_{iso}), 2.49 (s, 3, WCMe), 2.17 (br q, 6, $HN(CH_2CH_3)_3$), 1.80 (12), 1.49 (6), 1.42 (12), 1.31 (6), and 1.22 (18) (each a br d, Me_{iso}), 0.66 (t, 9, $HN(CH_2CH_3)_3$). Anal. Calcd for $WC_{53}H_{88}S_3NCl$: C, 60.35; H, 8.41; Cl, 3.36. Found: C, 60.95; H, 8.66; Cl, 3.03.

W(CMe)(TIPT)$_3$. [Et_3NH][W(CMe)(TIPT)$_3$Cl] (0.69 g, 0.65 mmol) was dissolved in dichloromethane (20 mL). The reaction was stirred as $ZnCl_2$·dioxane (0.15 g, 0.66 mmol) was added as a solid over 1–2 min. The reaction mixture turned from yellow to dark red over the next 2 h. After 4 h pentane (20 mL) was added in order to precipitate any zinc salts remaining in solution. The resulting mixture was filtered through Celite, and the filtrate was evaporated to dryness in vacuo. The dark red, oily residue was dissolved in a minimum amount of pentane, and the solution was stored at −40 °C. Opaque, yellow-orange crystals (0.29 g, 48%) were isolated in two crops: ^1H NMR δ 7.01 (s, 6, H_m), 3.64 (sept, 6, H_{iso}), 2.90 (sept, 3, H_{iso}), 2.36 (s, 3, WCMe), 1.24 (d, 18, H_{iso}), 1.21 (d, 36, H_{iso}). The product was identified by comparison of its NMR spectrum with those of analogues (see above).

Registry No. **3**, 111975-79-2; [Et_3NH][**4** (M = Mo)], 111997-38-7; [Et_3NH][**4** (M = W)], 111997-40-1; LiTMT, 111975-80-5; TMTH, 1541-10-2; LiTIPT, 107847-82-5; (TMS)-TMT, 60253-72-7; Mo(C-*t*-Bu)Cl_3(dme), 98300-84-6; Mo(C-*t*-Bu)(TIPT)$_3$, 111975-81-6; W(C-*t*-Bu)Cl_3(dme), 83416-70-0; [W-(C-*t*-Bu)(TMT)$_3$]$_2$, 111997-41-2; [Et_3NH][W(C-*t*-Bu)(TIPT)$_3$Cl], 111975-83-8; W(C-*t*-Bu)(TIPT)$_3$, 111975-84-9; W(C_3-*t*-BuMe_2)-Cl_3(py), 91230-72-7; W(CMe)(TMT)$_3$(py), 111975-85-0; Mo(C-Pr)(TIPT)$_3$, 111975-86-1; W(C_3Me_3)(TIPT)$_3$, 111975-87-2; [Et_3NH][W(CMe)(TIPT)$_3$Cl], 111975-89-4; W(CMe)(TIPT)$_3$, 111975-90-7; Mo(C-*t*-Bu)[OCMe_2(CF_3)]$_3$, 90792-33-9; W-(C_3Me_3)Cl_3, 102342-00-7; $ZnCl_2$·dioxane, 16457-66-2; 4-octyne, 1942-45-6.

Systematic Synthesis of Mixed-Metal Clusters via Capping Reactions. Characterization of a Set of Octanuclear Carbido Clusters Involving Rhenium and Various Platinum Metals

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Received July 11, 1987

The cluster $[Re_7C(CO)_{21}]^{3-}$ reacts with a variety of platinum metal based electrophiles to afford the new mixed-metal clusters $[Re_7C(CO)_{21}ML_n]^{2-}$, where ML_n = $Rh(CO)_2$, Rh(CO)(PPh_3), Rh(COD), Ir(COD), Pd(C_3H_5), Pt(C_4H_7), and Pt(CH_3)$_3$. These complexes have been isolated as salts with various large cations and have been characterized by IR (ν_{CO}), ^1H NMR, and fast atom bombardment mass spectroscopies. Variable-temperature ^{13}C NMR spectroscopic studies of selected complexes show that each of these compounds adopts a 1,4-bicapped octahedral geometry in solution. This observation is in accord with the solid-state structure of $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$, which has been determined by X-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1/n$, with a = 13.412 (5) Å, b = 18.095 (6) Å, c = 20.686 (3) Å, and β = 107.21 (2)°, Z = 2, and the structure has been refined to $R(F)$ = 0.0618 and $R(wF)$ = 0.0688. Cyclic voltammetry studies reveal two oxidation waves for each compound, with $E_{1/2}$ strongly dependent on ML_n.

Introduction

The largest known rhenium carbonyl clusters are $[Re_7C(CO)_{21}]^{3-}$ and $[Re_8C(CO)_{24}]^{2-}$. These complexes were first prepared by Ciani and co-workers, who also showed their structures to consist of an octahedral $[\{Re(CO)_3\}_6C]^{4-}$ core, with one or two additional $Re(CO)_3^+$ caps.[1,2] Previous work in our group has resulted in the direct, high-yield synthesis of either $[Re_7C(CO)_{21}]^{3-}$ or $[Re_8C(CO)_{24}]^{2-}$ by sodium reduction of $Re_2(CO)_{10}$ at 200 °C.[3] Furthermore, we have discovered that $[Re_7C(CO)_{21}]^{3-}$ reacts with $Re_2(CO)_{10}$ to give $[Re_8C(CO)_{24}]^{2-}$, a reaction that can be viewed formally as the capping of one face of $[Re_7C(CO)_{21}]^{3-}$ by a $Re(CO)_3^+$ moiety. Considering the formal relationship between (η^5-C_5H_5)Re(CO)$_3$ (I) and $[Re_8C(CO)_{24}]^{2-}$ (II) suggests an analogy between $[Re_7C(CO)_{21}]^{3-}$ and $[C_5H_5]^-$. The same type of analogy has been drawn for Hawthorne's dicarbollide anion, $[C_2B_9H_{11}]^{2-}$,[4] and many other carboranes.[5] The Cp^-/Re_7^{3-} relationship suggests that mixed-metal clusters of the type $[Re_7C(CO)_{21}ML_n]^{2-}$ (III) might be broadly accessible.

The capping of a triangular face of a closo polyhedron has been treated theoretically. Mingos[6] has described the capping reaction as a condensation reaction between the

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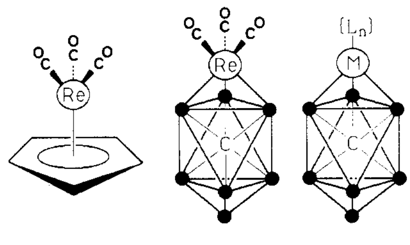
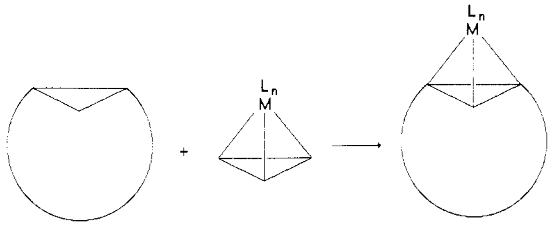


I II III

● = Re(CO)$_3$

polyhedron and a tetrahedron



The polyhedral electron count of such a condensation product is the sum of the electron counts of the reactant fragments minus the count of the common unit (in this case, a triangle). For a polyhedron of electron count x, the capped product shown above contains $x + 60 - 48 = x + 12$ electrons, i.e., ML_n^+ is a 12-electron fragment. The ML_n^+ moiety contributes nothing to the skeletal bonding of the cluster; the number of skeletal electron pairs, as defined by Wade,[7] remains constant.

Recent work has shown that $[Re_7C(CO)_{21}]^{3-}$ reacts directly with the late transition-metal electrophiles $[Cu(NCCH_3)_4][BF_4]$,[8] $[Ag(PPh_3)Cl]_4$,[8] and $Au(PPh_3)Cl$[8,9] to give the mixed-metal clusters $[Re_7C(CO)_{21}Cu(NCCH_3)]^{2-}$, $[Re_7C(CO)_{21}Ag(PPh_3)]^{2-}$, and $[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$, respectively. X-ray diffraction studies of $[\{Re_7C(CO)_{21}Ag\}_2(\mu\text{-}Br)]^{5-}$[8] and $[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$[9] have shown that in each case the heterometal atom caps the trianion on the face opposite the unique $Re(CO)_3$ to give 1,4-bicapped octahedra.[10] Given the current interest in mixed-metal clusters[11] and studies of capping reactions which yield such clusters,[12] we decided to explore the analogy represented by III for a wider range of transition-metal fragments, especially those of catalytically interesting platinum metals. Here we detail the synthesis and characterization of seven new mixed-metal complexes of the general type III, where ML_n = $Rh(CO)_2$, $Rh(CO)(PPh_3)$, Rh(COD), Ir(COD), $Pd(C_3H_5)$, $Pt(C_4H_7)$, and $Pt(CH_3)_3$ (COD = 1,5-cyclooctadiene; C_3H_5 = η^3-allyl; C_4H_7 = η^3-(2-methyl)allyl).

Experimental Section

All operations were carried out under nitrogen with the use of standard Schlenk techniques. Reaction solvents were dried and distilled immediately before use. $[Rh(CO)_2Cl]_2$,[13] $[Rh(COD)Cl]_2$,[14] $[Rh(CO)(PPh_3)Cl]_2$,[15] $[Ir(COD)Cl]_2$,[16] $[Pd(C_3H_5)Cl]_2$,[17] $[Pt(C_4H_7)Cl]_2$,[18] and $[Pt(CH_3)_3I]_4$[19] were prepared by literature methods. Salts of $[Re_7C(CO)_{21}]^{3-}$ were prepared by sodium reduction of $Re_2(CO)_{10}$ followed by metathesis with the appropriate cation.[3] $AgBF_4$ (Ozark-Mahoning) was used as received. IR spectra of pure compounds were recorded in acetone on a Perkin-Elmer Model 281B spectrophotometer. Reaction mixtures were monitored by infrared spectroscopy until the $[Re_7C(CO)_{21}]^{3-}$ starting material was completely consumed; in no instance was there any spectroscopic evidence for more than one product. ^1H and ^{13}C NMR spectra (360 and 90 MHz, respectively) were recorded on a Nicolet NT-360 instrument. Samples of compounds used in variable-temperature ^{13}C NMR studies were prepared from $[PPN]_3[Re_7C(CO)_{21}]$ which had been synthesized from ca. 50% ^{13}CO enriched $Re_2(CO)_{10}$. ^{31}P NMR spectra were recorded on a locally constructed spectrometer at 101 MHz, with chemical shifts referenced to external 85% H_3PO_4. Cyclic voltammetry data were obtained on a BAS-100 electrochemical analyzer with a platinum working electrode vs Ag/AgCl at 100 mV/s; all complexes were studied as 0.3 mM solutions in dichloromethane, with 0.1 M $[n\text{-}Bu_4N][ClO_4]$ as supporting electrolyte. Samples for mass spectrometry were suspended in a matrix of dithioerythritol/dithiothreitol and bombarded with a beam of high-energy xenon atoms; spectra were obtained by the staff of the Mass Spectrometry Center of the University of Illinois. Theoretical isotope patterns were calculated with the aid of the computer program MASPAN, written by Dr. M. A. Andrews in association with Professor H. D. Kaesz.[20] Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

$[Ph_4As]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$. $[Ph_4As]_3[Re_7C(CO)_{21}]$ (68.1 mg, 0.0223 mmol) and $[Pt(C_4H_7)Cl]_2$ (14.5 mg, 0.0254 mmol) were stirred in refluxing acetonitrile for 1 h. The solution volume was reduced under vacuum to ca. 3 mL, and diethyl ether was added until the solution turned cloudy. Cooling to −15 °C yielded dark red crystals (49.5 mg, 76%). Anal. Calcd for $C_{74}H_{47}As_2Re_7PtO_{21}$: C, 30.43; H, 1.62. Found: C, 30.64; H, 1.56. FAB-MS (negative ion): m/z (^{187}Re, ^{195}Pt) 2542 (M − Ph_4As), 2159 (M − $2Ph_4As$), 2104 ($Re_7C(CO)_{21}Pt$), 2104 − 28x, x = 1–6 ($Re_7C(CO)_{21}Pt - xCO$'s), 1909 ($Re_7C(CO)_{21}$).

$[PPN]_2[Re_7C(CO)_{21}Pt(CH_3)_3]$. Ten milliliters of a tetrahydrofuran (THF) solution of $[Pt(CH_3)_3I]_4$ (38.7 mg, 0.0264 mmol) was added to an equal volume of an acetone solution of $[PPN]_3[Re_7C(CO)_{21}]$ (53.5 mg, 0.0152 mmol). After overnight stirring at room temperature, the solution was taken to dryness. The residue was extracted into a 5/1 ethanol/acetone mixture; concentration and cooling of this solution gave the product as red crystals (37.6 mg, 77%). Anal. Calcd for $C_{97}H_{69}P_4N_2Re_7PtO_{21}$: C, 36.17; H, 2.16; N, 0.87. Found: C, 36.11; H, 2.32; N, 0.80. FAB-MS (negative ion): m/z (^{187}Re, ^{195}Pt) 2687 (M − PPN), 2447 ($[PPN][Re_7C(CO)_{21}]$), 2149 (M − 2PPN), 2134 ($Re_7C(CO)_{21}Pt(CH_3)_2$), 2091 ($Re_7C(CO)_{20}Pt(CH_3)$), 1909 ($Re_7C(CO)_{21}$), 1909 − 28x, x = 1–6 ($Re_7C(CO)_{21} - xCO$'s).

$[Ph_4As]_2[Re_7C(CO)_{21}Pd(C_3H_5)]$. $[Ph_4As]_3[Re_7C(CO)_{21}]$ (67.4 mg, 0.0221 mmol) and $[Pd(C_3H_5)Cl]_2$ (15.6 mg, 0.0426 mmol) were dissolved in acetonitrile to give a brown solution. This solution was stirred at room temperature for 30 min; the solvent was then removed under vacuum. The product was crystallized from dichloromethane/methanol (54.0 mg, 87%). Anal. Calcd for $C_{73}H_{45}As_2Re_7PdO_{21}$: C, 31.12; H, 1.61. Found: C, 30.83; H, 1.73. FAB-MS (negative ion): m/z (^{187}Re, ^{106}Pd) 2439 (M − Ph_4As), 2056 (M − $2Ph_4As$), 2015 ($Re_7C(CO)_{21}Pd$), 2015 − 28x, x = 1–12 ($Re_7C(CO)_{21}Pd - xCO$'s), 1909 ($Re_7C(CO)_{21}$).

$[PPN]_2[Re_7C(CO)_{21}Ir(COD)]$. Method 1. $[PPN]_3[Re_7C(CO)_{21}]$ (94.9 mg, 0.0268 mmol) and $[Ir(COD)Cl]_2$ (46.3 mg, 0.0689 mmol) were stirred in diglyme at 150 °C for 3 h. The solvent was

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then removed under vacuum and the residue extracted with 10 mL of acetone. Addition of 40 mL of methanol, followed by concentration and cooling, afforded red-black crystals (22.8 mg, 26%).

Method 2. A solution of "Ir(COD)$^{+}$"[21] was made by combining [Ir(COD)Cl$_2$] (35.1 mg, 0.0523 mmol) and AgBF$_4$ (9.5 mg, 0.049 mmol) in THF. The solution was filtered into an acetone solution of [PPN]$_3$[Re$_7$C(CO)$_{21}$] (60.0 mg, 0.0170 mmol). The resulting dark red solution was stirred at room temperature for 30 min. The product was then crystallized from acetone/methanol as in method 1 (37.6 mg, 67%). Anal. Calcd for C$_{102}$H$_{72}$P$_4$N$_2$Re$_7$IrO$_{21}$: C, 37.34; H, 2.21; N, 0.85. Found: C, 37.29; H, 2.29; N, 0.84. FAB-MS (negative ion): m/z (^{187}Re, ^{193}Ir) 2748 (M − PPN), 2640 ([PPN][Re$_7$C(CO)$_{21}$Ir]), 2210 (M − 2PPN), 2102 (Re$_7$C(CO)$_{21}$Ir), 2102 − 28x, x = 1–12 (Re$_7$C(CO)$_{21}$Ir − xCO's).

[Ph$_4$As]$_2$[Re$_7$C(CO)$_{21}$Rh(COD)]. Method 1. [Ph$_4$As]$_3$[Re$_7$C(CO)$_{21}$] (55.2 mg, 0.0181 mmol) and [Rh(COD)Cl]$_2$ (15.5 mg, 0.0314 mmol) were stirred in diglyme at 125 °C for 2 h. The solvent was evaporated under vacuum, and the residue extracted with 10 mL of acetone. Addition of 40 mL of methanol, followed by concentration and cooling, afforded dark red crystals of product (18.3 mg, 35%).

Method 2. A THF solution of "Rh(COD)$^{+}$" was made up by a procedure identical with that published by Osborn and Schrock[21] for the Ir analogue: THF solutions of [Rh(COD)Cl]$_2$ (20.0 mg, 0.0406 mmol) and AgBF$_4$ (7.0 mg, 0.036 mmol) were combined to give a yellow solution and a precipitate of AgCl. The solution was filtered into an acetone solution of [Ph$_4$As]$_3$[Re$_7$C(CO)$_{21}$] (43.4 mg, 0.0142 mmol) and the resulting product mixture treated as described above for [Re$_7$C(CO)$_{21}$Ir(COD)]$^{2-}$ to yield 34.0 mg (83%) of product. Anal. Calcd for C$_{78}$H$_{52}$As$_2$Re$_7$RhO$_{21}$: C, 32.51; H, 1.82. Found: C, 32.31; H, 1.77. ^{13}C NMR (CD$_2$Cl$_2$, 20 °C): δ 191.3, 197.1, 206.1 (all s, 9:9:3C, Re–CO), 425.2 (s, 1C, carbide). FAB-MS (positive ion): m/z (^{187}Re) 3269 (M + Ph$_4$As), 2886 (M), 2120 (M − 2Ph$_4$As).

[Et$_4$N]$_2$[R$_7$C(CO)$_{21}$Rh(CO)(PPh$_3$)]. A solution of [Rh(CO)(PPh$_3$)(acetone)$_2$][BF$_4$] (0.0354 mmol) was made up by chloride abstraction from [Rh(CO)(PPh$_3$)Cl]$_2$ by AgBF$_4$ in acetone and was transferred into an acetone solution of [Et$_4$N]$_3$[Re$_7$C(CO)$_{21}$] (51.3 mg, 0.0224 mmol). After 1 h of stirring at room temperature, the reaction solution was reduced in volume under vacuum to ca. 1 mL; 50 mL of chloroform was then added to give a cloudy solution. Storage of this solution at −15 °C for 9 days yielded small black crystals (19.2 mg, 34%). Anal. Calcd for C$_{57}$H$_{55}$N$_2$PRe$_7$RhO$_{22}$: C, 26.77; H, 2.17; N, 1.10. Found: C, 26.53; H, 2.13; N, 1.01. ^{31}P NMR ((CD$_3$)$_2$CO, 20 °C): δ 42.5 (d, $^1J_{\mathrm{Rh-P}}$ = 176 Hz). FAB-MS (negative ion): m/z (^{187}Re) 2432 (M − Et$_4$N), 2302 (M − 2Et$_4$N), 2274 (Re$_7$C(CO)$_{21}$Rh(PPh$_3$)), 2170 ([Et$_4$N][Re$_7$C(CO)$_{21}$Rh(CO)]).

[PPN]$_2$[Re$_7$C(CO)$_{21}$Rh(CO)$_2$]. [PPN]$_3$[Re$_7$C(CO)$_{21}$] (83.9 mg, 0.0238 mmol) and [Rh(CO)$_2$Cl]$_2$ (15.1 mg, 0.0388 mmol) were dissolved in dichloromethane to give a dark red-brown solution. After 20 min of stirring at room temperature, methanol was added to precipitate dark red crystals (65.9 mg, 88%). Anal. Calcd for C$_{96}$H$_{60}$P$_4$N$_2$Re$_7$RhO$_{23}$: C, 36.72; H, 1.93; N, 0.89. Found: C, 36.46; H, 1.67; N, 0.81. ^{13}C NMR (CD$_2$Cl$_2$, 20 °C): δ 179.7 (d, 2C, $^1J_{\mathrm{Rh-C}}$ = 75 Hz, Rh–CO), 191.2, 194.0, 204.8 (all s, 9:9:3C, Re–CO), 426.4 (s, 1C, carbide). No FAB mass spectrum could be obtained.

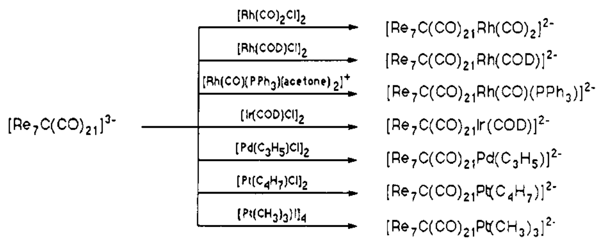
X-ray Structural Determination. Table I provides the details of the structural determination of [PPN]$_2$[Re$_7$C(CO)$_{21}$Pt(C$_4$H$_7$)]. Crystals suitable for diffraction studies were grown by slow evaporation of an acetone/methanol solution at room temperature and were mounted on glass fibers. Preliminary photographic characterization revealed 2/m Laue symmetry and systematic absences uniquely determined the space group to be $P2_1/n$. All examined specimens (nine in all) diffracted weakly. A profile-fitting procedure was used to improve the accuracy in the measurement of weak reflections. An empirical correction for absorption was applied; 252 data were used to fit a six-parameter ellipsoid model ($T_{\max}/T_{\min}$ = 0.124/0.046).

Table I. Crystal, Data Collection, and Refinement Parameters for [PPN]$_2$[Re$_7$C(CO)$_{21}$Pt(C$_4$H$_7$)]

(a) Crystal Parameters			
formula	C$_{98}$H$_{67}$N$_2$O$_{21}$P$_4$PtRe$_7$	V, Å^3	4796 (3)
crystal system	monoclinic	Z	2
space group	$P2_1/n$	d(calcd), g cm^{-3}	2.24
a, Å	13.412 (5)^a	μ(Mo Kα), cm^{-1}	109.7
b, Å	18.095 (6)	size, mm	0.20 × 0.21 × 0.35
c, Å	20.686 (3)	color	dark red
β, deg	107.21 (2)	temp, K	293
(b) Data Collection			
diffractometer	Nicolet R3m/μ	rflns collected	8161
radiation	Mo Kα	indpdnt reflns	7513
wavelength, Å	0.71073	R(int), %	1.71
monochromator	graphite	indpdnt rflns	3389
scan limits, deg	4 ≤ 2θ ≤ 48	w	5σ(F_o)
scan method	θ/2θ	std rflns	3 std/197 rflns
scan speed, deg min^{-1}	var. 4–10	decay	<1%
(c) Refinement			
$R(F)$, %	6.18	N_o/N_v	9.8
$R(wF)$, %	6.88	Δ/σ	0.027
GOF	1.148	$\Delta(\rho)$, e Å^{-3}	1.9 (1.06 Å Re(1))

^{a} Unit-cell parameters obtained from the least-squares fit of the angular settings of 25 reflections, 20° ≤ 2θ ≤ 25°.

Scheme I



The metal atom locations were determined by direct methods and the remainder of the non-hydrogen atoms located from subsequent Fourier syntheses. A disordered structure is required by Z = 2; the carbido carbon C(c) is located at an inversion center causing the superposition of the capping Re(CO)$_3$ and Pt(C$_4$H$_7$) groups. These metal atoms, Re(4) and Pt, were colocated at a common site and refined with each at half occupancy. All positional and thermal parameters were refined as variables in common to both. Two of the substituent atoms on these metal atoms, C(10) and C(11), were insufficiently separated to resolve individual positions and were refined as full occupancy composites; the remaining substituent atoms on Re(4) and Pt were located and refined at half occupancy. However, for these reasons, the bond parameters for the methallyl group and the CO groups on Re(4) are unreliable. The metal, P, and N atoms and the carbonyl groups of Re(1), Re(2), and Re(3) were refined with anisotropic thermal parameters. The remaining nor-hydrogen atoms were isotropically refined. Hydrogen atom contributions to the PPN cations were idealized. Table I-S provides atomic coordinates; Tables II-S and III-S list bond distances and angles, respectively. These tables are provided as supplementary information. A view of the Re$_7$PtC core is shown in Figure 6.

The computer programs and sources of scattering factors are contained in the SHELXTL (5.1) library (Nicolet Corp., Madison, WI).

Results and Discussion

Synthesis. [Re$_7$C(CO)$_{21}$]$^{3-}$ reacts with a number of platinum metal based electrophiles to give the new mix-

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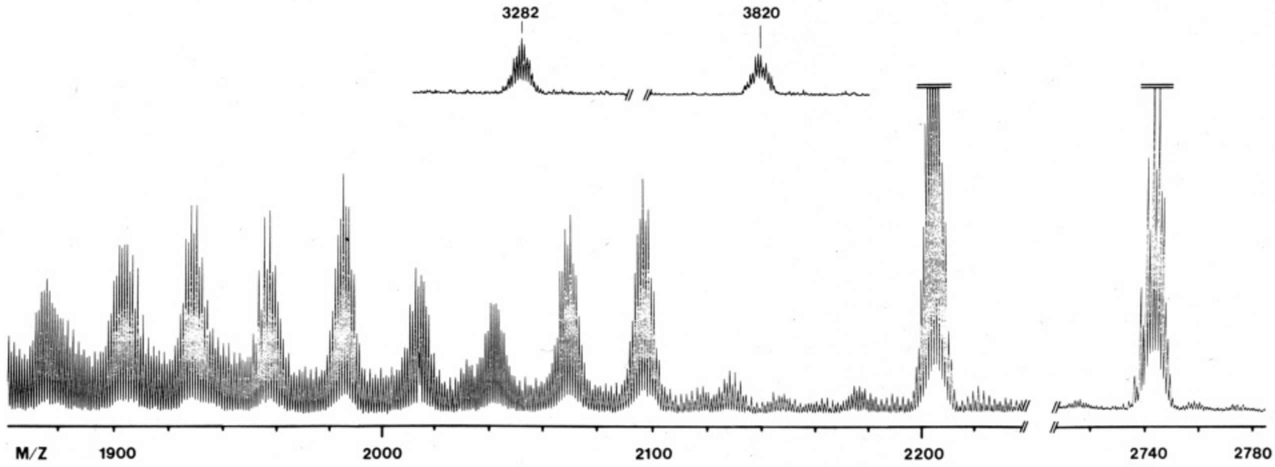

Figure 1. Fast-atom bombardment mass spectrum of $[PPN]_2[Re_7C(CO)_{21}Ir(COD)]$: (top) positive ion spectrum; (bottom) negative ion spectrum. See Experimental Section and Discussion for peak assignments.

Table II. Infrared Data for the Complexes $[Re_7C(CO)_{21}ML_n]^{2-}$

complex	ν_{CO}, cm^{-1}
$[PPN]_2[Re_7C(CO)_{21}Rh(CO)_2]$	2060 (w), 2020 (s), 2000 (vs), 1974 (w), 1947 (w), 1927 (w), 1890 (vw)
$[Et_4N]_2[Re_7C(CO)_{21}Rh(CO)(PPh_3)]$	2043 (w), 1999 (s, sh), 1992 (vs), 1961 (w), 1930 (w), 1915 (w), 1866 (vw)
$[Ph_4As]_2[Re_7C(CO)_{21}Rh(COD)]$	2041 (w), 1994 (vs), 1965 (w), 1937 (w), 1918 (w), 1882 (vw)
$[PPN]_2[Re_7C(CO)_{21}Ir(COD)]$	2042 (w), 1995 (vs), 1961 (w), 1939 (w), 1915 (w), 1884 (vw)
$[Ph_4As]_2[Re_7C(CO)_{21}Pd(C_3H_5)]$	2044 (w), 1993 (vs), 1964 (w), 1935 (w), 1918 (w), 1881 (vw)
$[Ph_4As]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$	2043 (w), 1993 (vs), 1964 (w), 1934 (w), 1917 (w), 1880 (vw)
$[PPN]_2[Re_7C(CO)_{21}Pt(CH_3)_3]$	2047 (w), 1998 (vs), 1967 (w), 1941 (w), 1919 (w), 1889 (vw)

ed-metal dianions $[Re_7C(CO)_{21}ML_n]^{2-}$ (see Scheme I). In cases where forcing conditions are required to effect reaction between $[Re_7C(CO)_{21}]^{3-}$ and a chloro-bridged transition-metal dimer (e.g., $[Rh(COD)Cl]_2$), reaction with the solvated metal-based cation (prepared by halide abstraction from the dimer by Ag^+ in a coordinating solvent) proceeds under much milder conditions. The clusters have been isolated as crystalline, air-stable salts of various large cations. All of the products have been characterized by elemental analysis as well as by ^1H NMR, IR, and FAB (fast-atom bombardment) mass spectroscopies.

Mass Spectrometry. FAB mass spectrometry has proven especially useful in determining the composition of large ionic compounds.[22,23] A typical FAB fragmentation pattern, of $[PPN]_2[Re_7C(CO)_{21}Ir(COD)]$, is shown in Figure 1. We have not observed signals arising from the parent ion $[M]^-$ in the negative ion spectra of these complexes; usually the signal at highest m/z is due to $[M - cation]^-$. (Occasionally a parent peak $[M]^+$ and a peak corresponding to $[M + cation]^+$ can be seen in the positive ion spectrum—upper trace, Figure 1.) Of the clusters in this study, only $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ and $[Re_7C(CO)_{21}Rh(COD)]^{2-}$ gave no negative-ion mass spectrum. The others all showed spectra consisting of peaks corresponding to $[M - cation]^-$, $[M - 2\ cations]^-$, and fragments of lower m/z due to loss of L_n, ML_n, and up to 12 carbonyls.

Figure 2 compares the theoretical and experimentally observed isotopic patterns for a representative cluster, $[Re_7C(CO)_{21}Pd(C_3H_5)]^{2-}$. The agreement is quite good, demonstrating that the mixed-metal clusters are not as susceptible to protonation in the mass spectrometer as is $[Re_7C(CO)_{21}]^{3-}$.[3]

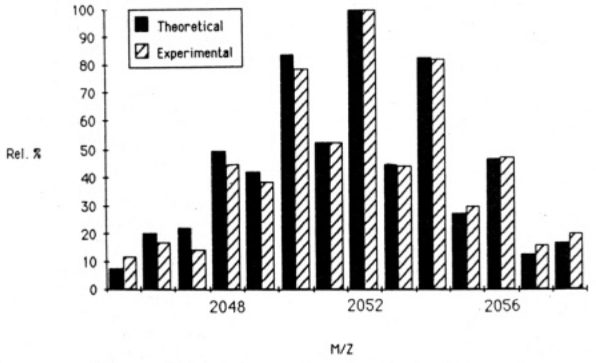

Figure 2. Comparison of observed and calculated isotope patterns for the ion $[Re_7C(CO)_{21}Pd(C_3H_5)]^-$. For all Re = ^{187}Re, C = ^{12}C, H = ^1H, O = ^{16}O, and Pd = ^{106}Pd, m/z 2056.

Infrared Spectroscopy. The infrared spectra of these compounds (Table II) exhibit a characteristic pattern of carbonyl absorptions consisting of five weak bands and one very strong band. The principal CO absorption is shifted 20–30 cm^{-1} to higher energy relative to that in $[Re_7C(CO)_{21}]^{3-}$, consistent with the lower electron density on the new clusters. The compounds $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ and $[Re_7C(CO)_{21}Rh(CO)(PPh_3)]^{2-}$ display an additional strong absorption arising from the carbonyl(s) bonded to the capping rhodium atom (see Figure 3). Only one absorption arising from rhodium-bound carbonyls is observed for $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ (at 2020 cm^{-1}), although the second band expected for the $Rh(CO)_2$ fragment[24] may be obscured by the very strong cluster absorption at 2000 cm^{-1}. The rhodium carbonyl stretch in $[Re_7C(CO)_{21}Rh(CO)(PPh_3)]^{2-}$, at 1999 cm^{-1}, is at significantly higher energy than those in $(\eta^5\text{-}C_5H_5)Rh(CO)(PPh_3)$ (1940 cm^{-1})[25] and $(\eta^5\text{-}C_5Me_5)Rh(CO)(PPh_3)$ (1924 cm^{-1}).[26] This observation

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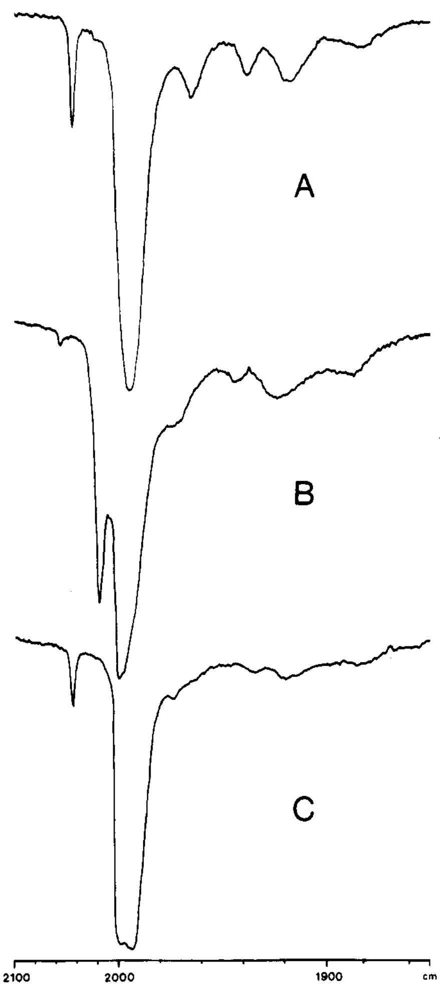

Figure 3. Infrared spectra (carbonyl region) of selected mixed-metal clusters in acetone: (a) $[Re_7C(CO)_{21}Rh(COD)]^{2-}$; (b) $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$; (c) $[Re_7C(CO)_{21}Rh(CO)(PPh_3)]^{2-}$.

implies that the $[Re_7C(CO)_{21}]^{3-}$ moiety is a weaker electron-donor than Cp^- toward a common ML_n^+ cap.

^{1}H NMR Spectroscopy. For each cluster, the chemical shifts of the ligands bonded to the capping metal are downfield of those of the corresponding cyclopentadienyl compound (see Table III). This result could be explained in terms of reduced electronic shielding of the protons in the Re_7ML_n clusters relative to the situation in the $CpML_n$ compounds. It should be noted, however, that other factors influencing the chemical shifts may be involved. For the complexes $(\eta^5\text{-}C_5H_4CF_3)M(COD)$,[31] where M = Rh or Ir, the trifluoromethylcyclopentadienide ligand, which is unquestionably more electron-withdrawing than Cp^-, has very little effect on the chemical shifts of the COD resonances relative to those in the Cp complexes. The same is true for $(\eta^5\text{-}C_5H_4Cl)Rh(COD)$ and $(\eta^5\text{-}C_5Ph_4Cl)Rh(COD)$.[32] It would therefore appear that simple electron-density arguments are insufficient to explain the ^{1}H NMR data.

Table III. ^{1}H NMR Data Comparison for the Complexes $[Re_7C(CO)_{21}ML_n]^{2-}$ and $CpML_n$

	chemical shifts[g]		
ML_n	$[Re_7C(CO)_{21}ML_n]^{2-}$	$CpML_n$	assignt
$Rh(CO)(PPh_3)$[a]	7.5–7.9 (m)	7.3–7.7	C_6H_5—
$Rh(COD)$[b]	1.72 (m, 4 H)	2.08 (8 H)	—CH_2—
	2.44 (m, 4 H)		
	4.56 (s, 4 H)	3.97 (4 H)	=CH—
$Ir(COD)$[c]	1.62 (m, 4 H)	1.90 (8 H)	—CH_2—
	2.36 (m, 4 H)		
	4.41 (s, 4 H)	3.83 (4 H)	=CH—
$Pd(C_3H_5)$[d]	3.92 (d, 2 H, J = 12.1)	2.14 (J = 11)	anti H
	4.74 (d, 2 H, J = 6.5)	3.11 (J = 6)	syn H
	5.56 (m, 1 H)	4.63	H_2CHCH_2
$Pt(C_4H_7)$[e]	2.30 (s, 3 H, J_{Pt} = 34.7)	2.16 (J_{Pt} = 34)	—CH_3
	2.83 (s, 2 H, J_{Pt} = 69.8)	2.20 (J_{Pt} = 111)	anti H
	4.18 (s, 2 H, J_{Pt} = 40.5)	3.52 (J_{Pt} = 61)	syn H
$Pt(CH_3)_3$[f]	1.88 (s, J_{Pt} = 71.4)	0.92 (J_{Pt} = 82.4)	—CH_3

[a] Solvents: Re_7, CD_3NO_2; Cp, $CDCl_3$ (ref 25). [b] Solvents: Re_7, CD_2Cl_2; Cp, $CDCl_3$ (ref 27). [c] Solvents: Re_7, CD_2Cl_2; Cp, $CDCl_3$ (ref 28). [d] Solvents: Re_7, $(CD_3)_2CO$; Cp, $CDCl_3$ (ref 17). [e] Solvents: Re_7, $(CD_3)_2CO$; Cp, C_6D_6 (ref 29). [f] Solvents: Re_7, $(CD_3)_2CO$; Cp, $CDCl_3$ (ref 30).

Table IV. ^{13}C NMR Data Comparison for Some of the Complexes $[Re_7C(CO)_{21}ML_n]^{2-}$ and Their (η^5-Cyclopentadienyl)ML_n Analogues

compound	$\delta_{\text{olefinic-C}}$	$\delta_{\text{aliphatic-C}}$	δ_{CO}	ref
$(\eta^5\text{-}C_5H_5)Rh(COD)$	62.1	32.3		33
$(\eta^5\text{-}C_5Cl_5)Rh(COD)$	80.4	32.1		34
$[Re_7C(CO)_{21}Rh(COD)]^{2-}$	80.9	29.9		this work
$(\eta^5\text{-}C_5H_5)Rh(CO)_2$			191.8	35
$[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$			179.7	this work
$(\eta^5\text{-}C_5H_5)Pt(CH_3)_3$		−20.7		30
$[Re_7C(CO)_{21}Pt(CH_3)_3]^{2-}$		21.7		this work

^{13}C NMR Spectroscopy. Table IV contains ^{13}C NMR data for the ligands bonded to the capping atoms of $[Re_7C(CO)_{21}Rh(COD)]^{2-}$, $[Re_7C(CO)_{21}Pt(CH_3)_3]^{2-}$, and $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ along with the analogous data for cyclopentadienyl compounds. Note that the chemical shifts for the COD ligand in $(\eta^5\text{-}C_5Cl_5)Rh(COD)$ and $[Re_7C(CO)_{21}Rh(COD)]^{2-}$ are very similar: the olefinic carbons at δ 80–81, are about 20 ppm downfield from those in CpRh(COD). Stronger electron donors on a metal center are expected to move the chemical shift of olefinic carbons bonded to that center to higher field because of the resulting higher degree of sp^3 hybridization at those carbons.[36] Increased electron density on platinum has also been shown to lead to upfield shifts in the resonances of adjoining methyl carbons.[37] On the other hand, increased electron density deshields carbonyls; therefore it appears that the rhodium atom in $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ is less electron-rich than that in $CpRh(CO)_2$. In sum, the ^{13}C NMR data in Table IV seem to agree with the model of $[Re_7C(CO)_{21}]^{3-}$ as a weaker electron donor than Cp^-.

Dynamic ^{13}C NMR spectroscopy has proven useful in the structural elucidation of $[Re_7C(CO)_{21}]^{3-}$ and its ad-

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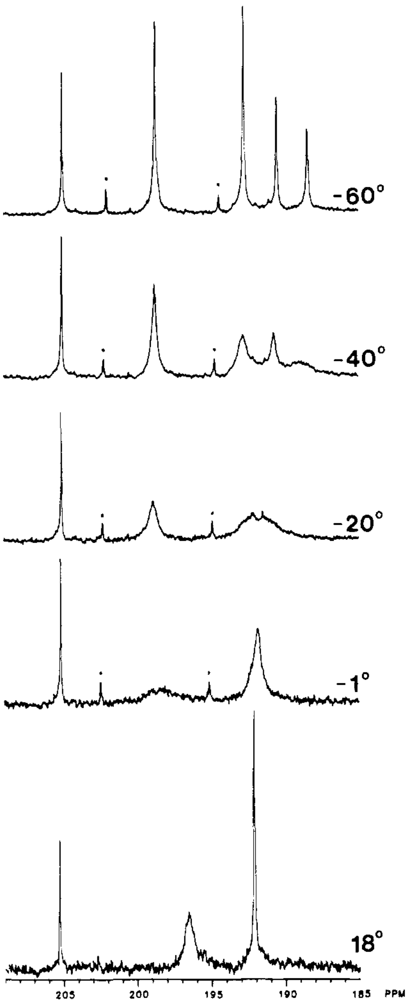
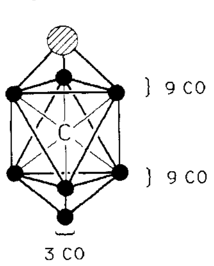


Figure 4. Variable-temperature ^{13}C NMR spectra (carbonyl region) of $[PPN]_2[Re_7C(CO)_{21}Pt(CH_3)_3]$; solvent, CD_2Cl_2. Resonances marked with an asterisk (*) arise from unreacted $[PPN]_3[Re_7C(CO)_{21}]$.

ducts.[2,3,9] Previous work[3,9] has shown that local carbonyl scrambling on each atom of a C_{3v} cluster framework (such as that adopted by $[Re_7C(CO)_{21}]^{3-}$ and the heteronuclear clusters $[Re_7C(CO)_{21}ML_n]^{2-}$) leads to a fast-exchange spectrum consisting of three singlets in a relative ratio of 3:9:9 (from lower to higher field). These resonances arise from, respectively, the carbonyls bonded to the capping rhenium atom, the carbonyls bonded to the three rheniums at the base of the ML_n cap, and the carbonyls bonded to three rheniums at the base of the $Re(CO)_3$ cap. The specific assignments follow from comparison with the room-temperature carbonyl chemical shifts reported for $[Re_8C(CO)_{24}]^{2-}$, namely, δ 204.0 (6C) and 191.3 (18C).[2] Three complexes, $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$, $[PPN]_2[Re_7C(CO)_{21}Pt(CH_3)_3]$, and $[PPN]_2[Re_7C(CO)_{21}Rh(COD)]$, have been studied by variable-temperature ^{13}C NMR (from 20 to -100 °C); a fourth, $[PPN]_2[Re_7C(CO)_{21}Rh(CO)_2]$, has been studied at room temperature (see Experimental Section). All four complexes show a 3:9:9 carbonyl pattern at room temperature, implying the 1,4-bicapped octahedral structure in solution for each.



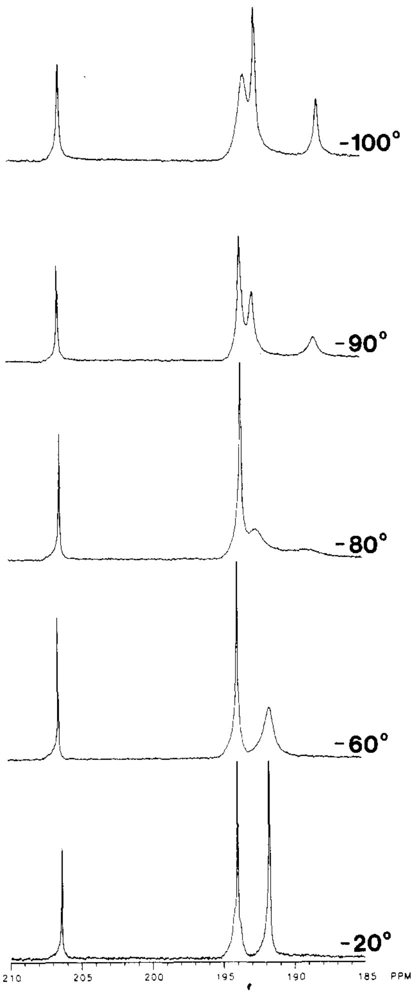


Figure 5. Variable-temperature ^{13}C NMR spectra (carbonyl region) of $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$; solvent, CD_2Cl_2.

The compound $[PPN]_2[ReC(CO)_{21}Pt(CH_3)_3]$ illustrates complete, sequential freezing out of carbonyl exchange (Figure 4). At room temperature, the ^{13}C NMR spectrum of this compound consists of the expected 3:9:9 pattern of carbonyl resonances at δ 205.2, 196.5, and 192.1. At -1 °C, the resonance at δ 196.5 begins to split into a 6:3 pair; at -20 °C, the resonance at δ 192.1 does the same. At -60 °C a fully resolved 3:6:6:3:3 pattern of carbonyl signals is observed at δ 205.0, 198.7, 192.7, 190.5, and 188.4. The carbide resonance remains invariant at δ 425.5. This pattern is analogous to the 6:12:6 carbonyl spectrum of $[Re_8C(CO)_{24}]^{2-}$ at -100 °C, taking into account the higher symmetry of that complex.[2]

The variable-temperature ^{13}C NMR spectra of $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$ are shown in Figure 5. The carbide resonance, not shown, appears at δ 432.9. In this compound, the carbonyl resonance furthest upfield (at δ 192.1) collapses first, in contrast to $[PPN]_2[Re_7C(CO)_{21}Pt(CH_3)_3]$, $[PPN]_2[Re_7C(CO)_{21}Au(PPh_3)]$,[9] $[PPN]_2[HRe_7C(CO)_{21}]$,[9] and $[PPN]_2[Re_7C(CO)_{21}Rh(COD)]$ (supplementary material). (We have no explanation for this diffeence at present. Either the two sets of nine carbonyls are being frozen out in reverse order or their chemical shift order is reversed.) At -80 °C, this resonance is split into two well-resolved signals, of relative ratio 6:3, at δ 192.6 and 188.3. At -100 °C these resonances are sharp, while the signal at δ 193.4 is beginning to broaden due to the

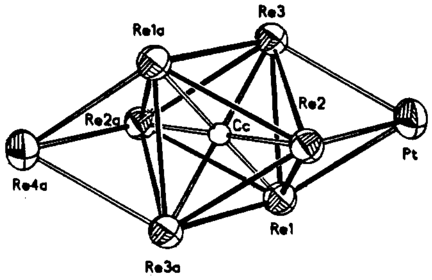


Figure 6. ORTEP diagram of the metal atom and carbide core of $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$. The carbide carbon atom lies on a crystallographic inversion center. Bond distances are as follows: Re(1)–Re(2), 2.990 (2); Re(1)–Re(3), 3.013 (2); Re(1)–RePt, 2.909 (2); Re(1)–Re(2a), 2.999 (2); Re(1)–Re(3a), 3.000 (2); Re(2)–Re(3), 3.018 (2); Re(2)–RePt, 2.859 (2); Re(2)–Re(3a), 2.973 (2); Re(3)–RePt, 2.935 (2); Re(1)–C(c), 2.125 (1); Re(2)–C(c), 2.110 (1); Re(3)–C(c), 2.127 (1). "RePt" is the composite Re(4)/Pt atom; see text for details.

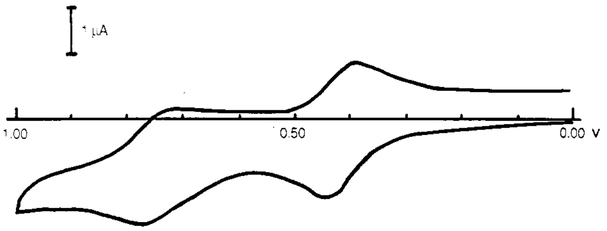


Figure 7. Positive-scan cyclic voltammogram of $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$.

slowing down of local exchange of that set of nine carbonyls.

X-ray Crystallography. The solid-state structure of $[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$, determined by an X-ray diffraction study of the PPN^+ salt, is a 1,4-bicapped octahedron, in agreement with the solution ^{13}C NMR data. The carbido carbon lies on a crystallographic inversion center, resulting in a 2-fold "end-to-end" disorder which superposes the capping $Re(CO)_3$ and $Pt(C_4H_7)$ groups. Figure 6 shows the Re_7PtC core of the molecule. In previously characterized Re_7M structures,[8,9] the octahedral face capped by the $Re(CO)_3$ group is significantly smaller in area than the face capped by M; in $[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$ these faces are crystallographically equivalent. In this respect $[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$ is very similar to $[Re_8C(CO)_{24}]^{2-}$, which also contains a crystallographic center of inversion at the carbide atom.[2] The X-ray data are not of high enough quality to draw any conclusions about the bonding of the $Pt(C_4H_7)$ cap to the cluster; in particular, we can make no comment about the degree of "slippage", if any, of the Pt vertex.[38]

Cyclic Voltammetry. The facile synthesis of several very similar clusters offers an opportunity to explore the effects of different ligands and capping metals on the electronic characteristics of such compounds. With this end in mind, we have studied these new clusters by cyclic voltammetry; a typical anodic scan, of $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$, appears in Figure 7. Two oxidation waves are observed: the first is quasi-reversible, the second almost completely irreversible. Numerical data for the first oxidation wave of each cluster appear in Table V. As can be seen, $E_{1/2}$ varies widely as a function of the ligands bonded to the capping metal atom. For example, replacing a carbonyl in $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ with the triphenylphosphine in $[Re_7C(CO)_{21}Rh(CO)(PPh_3)]^{2-}$ leads to a decrease of almost 200 mV in $E_{1/2}$. (Similarly, the oxidation potentials of $CpRh(CO)_2$ and $(C_5Ph_5)Rh(CO)_2$ are more than 500 mV higher than those of $CpRh(CO)(PPh_3)$ and $(C_5Ph_5)Rh(CO)(PPh_3)$, respectively.[39-41]) On the other hand, changing from a Rh(COD) cap to an Ir(COD) cap causes no change in $E_{1/2}$. As expected, the oxidation potential of $[Re_7C(CO)_{21}Pt(CH_3)_3]^{2-}$, which contains a Pt(IV) center, is much higher than that of $[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$, a Pt(II) complex. From these results we may conclude that while the electron removed in the electrochemical oxidation is not centered entirely on the capping metal atom, its energy is nevertheless strongly influenced by the nature of the capping moiety.

Table V. Cyclic Voltammetry Data for the Complexes $[Re_7C(CO)_{21}ML_n]^{2-}$

complex[a]	$E_{1/2}$,[b] mV	ΔE_p, mV
$[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$	626	125
$[Re_7C(CO)_{21}Rh(CO)(PPh_3)]^{2-}$	428	93
$[Re_7C(CO)_{21}Rh(COD)]^{2-}$	495	87
$[Re_7C(CO)_{21}Ir(COD)]^{2-}$	495	92
$[Re_7C(CO)_{21}Pd(C_3H_5)]^{2-}$	480	72
$[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$	418	65
$[Re_7C(CO)_{21}Pt(CH_3)_3]^{2-}$	644	64
$[Re_7C(CO)_{21}Re(CO)_3]^{2-}$ [c]	850	80

[a] All complexes studied as their PPN^+ salts. Conditions are given in the Experimental Section. [b] $E_{1/2} = (E_p{}^a + E_p{}^c)/2$, relative to Ag/AgCl. [c] Reference 3.

Conclusion

We have succeeded in synthesizing a set of closely related mixed-metal clusters involving a common $[Re_7C(CO)_{21}]^{3-}$ framework with various $ML_n{}^+$ caps. The structures of these compounds support an isolobal analogy between Cp^- and $[Re_7C(CO)_{21}]^{3-}$, although spectroscopic data suggest that the cluster is a weaker donor than Cp^- toward a common $ML_n{}^+$ cap. Nevertheless, the $[Re_7C(CO)_{21}]^{3-}$ unit can support capping units of the same metal that differ in size ($Rh(CO)_2$ vs $Rh(CO)(PPh_3)$) and in oxidation state ($Pt(C_4H_7)$ vs $Pt(CH_3)_3$). This suggests that important reactions such as ligand substitution and oxidative addition might occur at the capping metal center without disruption of the cluster framework. Future work will focus on this question of reactivity.

Acknowledgment. This work was supported at the University of Illinois by National Science Foundation Grants DMR 83-16981 and DMR 86-12860 to the Materials Research Laboratory and CHE 84-07233 to J.R.S. FAB mass spectra were obtaned with instrumentation supported in part by a grant from the National Institutes of Health (GM 27029).

Registry No. $[Ph_4As]_3[Re_7C(CO)_{21}]$, 107021-62-5; $[PPN]_3[Re_7C(CO)_{21}]$, 107021-61-4; $[Et_4N]_3[Re_7C(CO)_{21}]$, 99900-74-0; $[Pt(C_4H_7)Cl]_2$, 35770-44-6; $[Pt(CH_3)_3I]_4$, 18253-26-4; $[Pd(C_3H_5)Cl]_2$, 12012-95-2; $[Ir(COD)Cl]_2$, 12112-67-3; $[Rh(COD)Cl]_2$, 12092-47-6; $[Rh(CO)(PPh_3)(acetone)_2][BF_4]$, 111742-28-0; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[Ph_4As]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$, 111765-72-1; $[PPN]_2[Re_7C(CO)_{21}Pt(CH_3)_3]$, 111765-70-9; $[Ph_4As]_2[Re_7C(CO)_{21}Pd(C_3H_5)]$, 111765-74-3; $[PPN]_2[Re_7C(CO)_{21}Ir(COD)]$, 111793-36-3; $[Ph_4As]_2[Re_7C(CO)_{21}Ph(COD)]$, 111765-76-5; $[Et_4N]_2[Re_7C(CO)_{21}Rh(CO)(PPh_3)]$, 111793-34-1; $[PPN]_2[Re_7C(CO)_{21}Rh(CO)_2]$, 111765-66-3; $[PPN]_2[Re_7C(CO)_{21}Rh(CO)(PPh_3)]$,

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111822-64-1; $[PPN]_2[Re_7C(CO)_{21}Rh(COD)]$, 111793-56-7; $[PPN]_2[Re_7C(CO)_{21}Pd(C_3H_5)]$, 111793-54-5; $[PPN]_2[Re_7C(CO)_{21}Pt(C_4H_7)]$, 111793-55-6; $[PPN]_2[Re_7C(CO)_{21}uRe(CO)_3]$, 111765-68-5.

Supplementary Material Available: Tables listing atomic coordinates, bond distances, and bond angles and a figure of variable-temperature ^{13}C NMR spectra of $[PPN]_2[Re_7C(CO)_{21}Rh(COD)]$ (7 pages); tables of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Direct Synthesis and Interconversion of Large Rhenium Carbonyl Clusters

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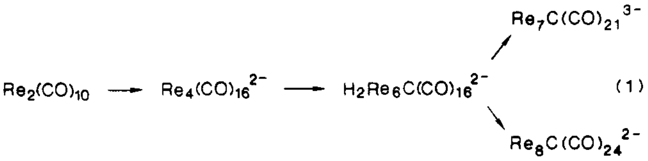
Received July 14, 1987

Treatment of $Re_2(CO)_{10}$ with sodium dispersion in glyme solvents provides direct syntheses of the rhenium carbonyl clusters $Re_4(CO)_{16}^{2-}$, $H_2Re_6C(CO)_{18}^{2-}$, $Re_7C(CO)_{21}^{3-}$, and $Re_8C(CO)_{24}^{2-}$, which are isolated as crystalline Et_4N^+ and $(PPh_3)_2N^+$ salts. The conditions and yields obtained are as follows: $Re_4(CO)_{16}^{2-}$, diglyme, 140 °C, 67%; $Re_7C(CO)_{21}^{3-}$, triglyme, 200 °C, 76%; $Re_8C(CO)_{24}^{2-}$, triglyme, 200 °C, 62%; and $H_2Re_6C(CO)_{18}^{2-}$, diglyme, 160 °C, 29%. Further experiments have indicated that the sequence of cluster building is $Re_2 \rightarrow Re_4 \rightarrow Re_6C$ followed by $Re_6C \rightarrow Re_7C$ or $Re_6C \rightarrow Re_8C$, depending on the relative amount of sodium and/or $Re_2(CO)_{10}$ present in the reaction. The direct interconversion of $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$ also has been demonstrated.

Introduction

The most systematic and broadly successful approach to the synthesis of large metal carbonyl clusters has been the "redox condensation" method of Chini and co-workers.[1,2] This procedure involves the interaction of two differently charged units (e.g., an anionic and a neutral complex), which coalesce with loss of carbon monoxide into a larger aggregate with an intermediate charge level.

We have reported straightforward syntheses of several large carbonyl clusters of ruthenium and osmium from the direct interaction of $M_3(CO)_{12}$ (M = Ru, Os) and sodium in ether solvents.[3] These reactions probably involve the growth of large anionic clusters from the attack of small anionic units on the neutral carbonyl clusters. We now report efficient preparations of several rhenium carbonyl clusters, from the analogous direct treatment of $Re_2(CO)_{10}$ with sodium under various conditions (see eq 1). These compounds, namely, $Re_4(CO)_{16}^{2-}$, $H_2Re_6C(CO)_{18}^{2-}$, $Re_7C(CO)_{21}^{3-}$, and $Re_8C(CO)_{24}^{2-}$, have been prepared previously by other means.[4-7] The solid-state geometries established for them are shown in Figure 1. In addition to the direct syntheses we also describe various interconversions among the compounds that illuminate possible pathways of cluster growth.



$$Re_2(CO)_{10} \longrightarrow Re_4(CO)_{16}^{2-} \longrightarrow H_2Re_6C(CO)_{16}^{2-} \begin{cases} \nearrow Re_7C(CO)_{21}^{3-} \\ \searrow Re_8C(CO)_{24}^{2-} \end{cases} \qquad (1)$$

Experimental Section

$Re_2(CO)_{10}$ was purchased from Strem Chemicals. Sodium was used as a 40% dispersion in mineral oil (Alfa). $Et_4NCl \cdot H_2O$ and $[(Ph_3P)_2N]Cl$ were purchased from Aldrich and used as received. ^{13}CO enriched $Re_2(CO)_{10}$ was prepared from photolysis of $Re_2(CO)_{10}$ in cyclohexane with 5 equiv of 90% ^{13}CO (Mound Laboratories) for 5 h in a pressure bottle. Diethyl ether, diglyme, triglyme, and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone ketyl before use. Unless otherwise specified, all operations were performed under a nitrogen atmosphere using standard techniques.

Infrared spectra were recorded on a Perkin-Elmer Model 281B spectrometer. Negative ion fast atom bombardment (FAB) mass spectra were obtained by Mr. J. Carter Cook, Jr., of the School of Chemical Sciences Mass Spectrometry Laboratory, on a VG-ZAB mass spectrometer system using tetraglyme or tetramethylene sulfone as the dispersing medium. 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.[8] NMR spectra were recorded on a Nicolet NT-360 spectrometer at 360 (^1H) and 90 MHz (^{13}C). Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences.

Preparation of $Re_4(CO)_{16}^{2-}$ Salts. Sodium dispersion (140 mg, 2.44 mmol of Na), freshly distilled diglyme (70 mL), and $Re_2(CO)_{10}$ (1.48 g, 2.27 mmol) were added to an oven-dried 100-mL three-necked flask. This mixture was heated at 140–150 °C for 20 h and formed a dark pink-red solution. After evaporation of ca. 50 mL of the diglyme, the mixture was added to 100 mL of aqueous Et_4NCl (8.0 g, 48.0 mmol). The red precipitate that formed was filtered, washed with water (150 mL), and dried in vacuo. Red crystals of $[Et_4N]_2[Re_4(CO)_{16}]$ were obtained from acetone/2-propanol by solvent diffusion at −20 °C (1.10 g, 0.76 mmol, 67%).

Anal. Calcd for $C_{32}H_{40}N_2O_{16}Re_4$: C, 26.44; H, 2.77; N, 1.93. Found: C, 26.84; H, 2.73; N, 1.69. IR (acetone): ν_{CO} 2006 (s), 1986 (m, sh), 1970 (vs), 1918 (m, sh), 1901 (m) cm^{-1} (lit.[4] ν_{CO} 2007

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