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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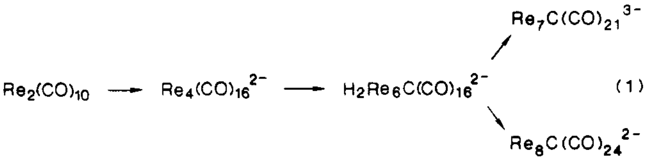
Treatment of $Re_2(CO)_{10}$ with sodium dispersion in glyme solvents provides direct syntheses of the rhenium carbonyl clusters $Re_4(CO)_{16}{}^{2-}$, $H_2Re_6C(CO)_{18}{}^{2-}$, $Re_7C(CO)_{21}{}^{3-}$, and $Re_8C(CO)_{24}{}^{2-}$, which are isolated as crystalline Et_4N^+ and $(PPh_3)_2N^+$ salts. 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.



(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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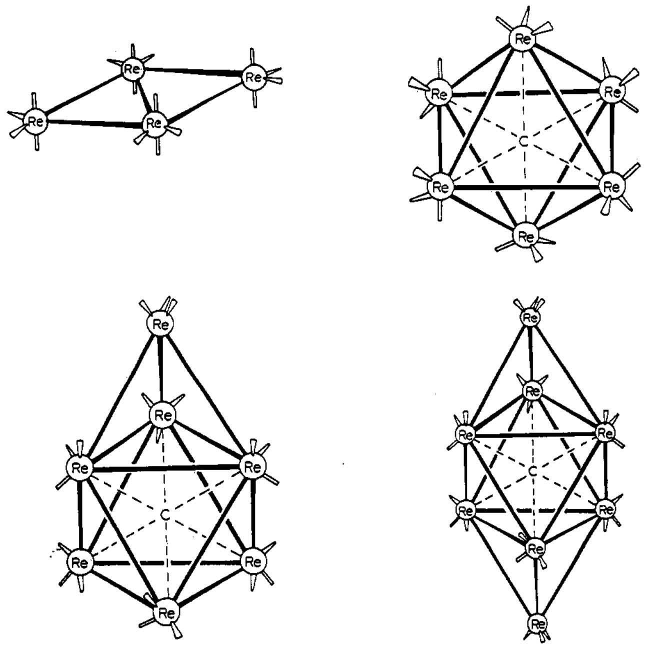

Figure 1. Molecular geometries established for $Re_4(CO)_{16}^{2-}$,[4] $H_2Re_6C(CO)_{18}^{2-}$,[5] $Re_7C(CO)_{21}^{3-}$,[6] and $Re_8C(CO)_{24}^{2-}$,[7] by X-ray diffraction studies.

(s), 1987 (m), 1969 (s), 1901 (m, v br) cm^{-1}).

$Re_4(CO)_{16}^{2-}$ was also isolated as the $(Ph_3P)_2N^+$ salt in similar yield. Negative ion FAB mass spectra for the $(Ph_3P)_2N^+$ salt (^{187}Re): *m/z* 1734 ($[Ph_3P)_2N][Re_4(CO)_{16}]^-$), 1196 ($[Re_4(CO)_{16}]^-$) as well as 1196 − 28*x*, *x* = 1–8 ($[Re_4(CO)_{16} - xCO]^-$).

Preparation of $Re_7C(CO)_{21}^{3-}$ Salts from $Re_2(CO)_{10}$ and Sodium. Dry triglyme (50 mL) and $Re_2(CO)_{10}$ (935 mg, 1.43 mmol) were added to an oven-dried 100-mL three-necked flask containing sodium dispersion. This mixture was heated at 200–210 °C for 6 h to give a light orange solution containing a bright red solid. The characteristic infrared bands of $Re_4(CO)_{16}^{2-}$ at 2006 (s), 1986 (m), and 1970 (vs) cm^{-1} were observed after 1 h; these were then replaced by bands of $H_2Re_6C(CO)_{18}^{2-}$ at 1998 (s, sh) and 1985 (s) cm^{-1} and finally bands of $Re_7C(CO)_{21}^{3-}$ at 1977 (s, sh) and 1968 (s) cm^{-1}. The cooled slurry was added to 150 mL of aqueous Et_4NCl (10 g, 60 mmol). After the solution was stirred for a few minutes, a red precipitate formed. This precipitate was filtered, washed with water (100 mL), and dried in vacuo. Crystallization of the residue from acetone/methanol by solvent diffusion at room temperature produced red crystals of $[Et_4N]_3[Re_7C(CO)_{21}]$ (710 mg, 0.31 mmol, 76%). Negative ion FAB mass spectrum (^{187}Re): *m/z* 2171 ($[Et_4N]_2[Re_7C(CO)_{21}]^-$), 2040 ($[Et_4N][Re_7C(CO)_{21}]^-$), 1909 ($Re_7C(CO)_{21}^-$) as well as 1909 − 28*x*, *x* = 1–11 ($[Re_7C(CO)_{21} - xCO]^-$). Anal. Calcd for $C_{46}H_{60}N_3O_{21}Re_7$: C, 24.16; H, 2.56; N, 1.84. Found: C, 24.08; H, 2.64; N, 1.83. IR (acetone): ν_{CO} 1978 (s, sh), 1969 (vs), 1943 (w), 1919 (vw), 1890 (m), 1854 (w) cm^{-1} (lit.[6] ν_{CO} 1977 (sh), 1968 (vs), 1940 (mw), 1920 (vw), 1890 (m), 1855 (w) cm^{-1}).

$Re_7C(CO)_{21}^{3-}$ was also isolated as the $(Ph_3P)_2N^+$ salt in similar yield. ^{13}C NMR spectrum of $[(Ph_3P)_2N]_3[Re_7C(CO)_{21})]$ prepared from $Re_2(^{13}CO)_{10}$ (20 °C, CD_2Cl_2): δ 422.8 (s, 1 C, μ_6-C), 210.2 (s, 3 C), 201.1 (s, 9 C), 195.2 (s, 9 C) (lit.[7] δ 423.6, μ_6-C).

Preparation of $Re_8C(CO)_{24}^{2-}$ Salts from $Re_2(CO)_{10}$ and Sodium. A solution of $Re_2(CO)_{10}$ (1.45 g, 2.22 mmol) and sodium dispersion (698 mg, 1.19 mmol of Na) in dry triglyme (70 mL) was heated at 190–210 °C for 80 h, yielding a dark red mixture and a rhenium mirror. Infrared analyses of the reaction mixture showed sequential formation of $Re_4(CO)_{16}^{2-}$, $H_2Re_6C(CO)_{18}^{2-}$, and finally $Re_8C(CO)_{24}^{2-}$. After evaporation of ca. 40 mL of the triglyme, the cooled mixture was added to 150 mL of aqueous Et_4NCl (6 g, 36 mmol). This mixture was held at 0 °C for 1 h to form a red precipitate, which was then collected, washed with water, and dried in vacuo. Dark red air stable crystals of $[Et_4N]_2[Re_8C(CO)_{24}]$ (840 mg, 0.34 mmol, 62%) were obtained from THF/methanol at −20 °C. Negative ion FAB mass spectrum (^{187}Re): *m/z* 2442 ($[Et_4N]_2[Re_8C(CO)_{24}]^-$), 2311 ($[Et_4N][Re_8C(CO)_{24}]^-$), 2180 ($Re_8C(CO)_{24}^-$) as well as 2180 − 28*x*, *x* = 1–13 ($[Re_8C(CO)_{24} - xCO]^-$). Anal. Calcd for $C_{41}H_{40}N_2O_{24}Re_8$: C, 20.23; H, 1.66 N, 1.15. Found: C, 20.27; H, 1.52; N, 1.35. IR (acetone): ν_{CO} 2011 (s, sh), 2004 (s), 1951 (w), 1932 (w), 1893 (w) cm^{-1} (lit.[7] ν_{CO} 2010 (sh), 2004 (s), 1950 (w), 1930 (w), 1890 (w) cm^{-1}).

$Re_8C(CO)_{24}^{2-}$ was isolated as the $(Ph_3P)_2N^+$ salt in similar yield.

Preparation of $[Et_4N]_2[H_2Re_6C(CO)_{18}]$ from $Re_2(CO)_{10}$ and Sodium. Dry diglyme (30 mL) and $Re_2(CO)_{10}$ (467 mg, 0.716 mmol) were added to an oven-dried three-necked flask containing sodium dispersion (25 mg, 0.435 mmol of Na). The reaction mixture was heated under reflux for 18 h; it was then a bright orange-red solution plus a bright red solid. The characteristic strong infrared bands of $Re_4(CO)_{16}^{2-}$ at 2006, 1986, and 1970 cm^{-1} were observed with those of $Re_2(CO)_{10}$ (2070 and 2014 cm^{-1}) after 2 h. The infrared spectrum of the product solution showed bands of $Re_2(CO)_{10}$, $H_2Re_6C(CO)_{18}^{2-}$ (at 1997 and 1986 cm^{-1}), and $Re_7C(CO)_{21}^{3-}$ (at 1978 and 1968 cm^{-1}). The cooled reaction mixture was filtered from the red solid ($Na_3[Re_7C(CO)_{21}]$) into 150 mL of aqueous Et_4NCl (10.0 g, 60 mmol). After this mixture was cooled to 0 °C for 1 h, the orange-brown solid that formed was filtered, washed with water (200 mL), and dried in vacuo. Unreacted $Re_2(CO)_{10}$ was extracted from this precipitate with 100 mL of cyclohexane (80 mg, 0.123 mmol, 17% recovered). The remaining solid was treated with dichloromethane (150 mL) in order to selectively dissolve the Et_4N^+ salt of $H_2Re_6C(CO)_{18}^{2-}$. This dichloromethane solution was filtered from the insoluble red $[Et_4N]_3[Re_7C(CO)_{21}]$, concentrated to a small volume (15–30 mL), and treated with 2-propanol (ca. 20 mL) to give red-orange crystals of $[Et_4N]_2[H_2Re_6C(CO)_{18}]$ (130 mg, 0.069 mmol, 29%) after cooling to −20 °C. Negative ion FAB mass spectrum (^{187}Re): *m/z* 1771 ($[Et_4N][H_2Re_6C(CO)_{18}]^-$), 1640 ($H_2Re_6C(CO)_{18}^-$) as well as 1640 − 28*x*, *x* = 1–8 ($[H_2Re_6C(CO)_{18} - xCO]^-$). Anal. Calcd for $C_{35}H_{42}N_2O_{18}Re_6$: C, 22.17; H, 2.23; N, 1.48. Found: C, 21.97; H, 2.36; N, 1.63. IR (acetone): ν_{CO} 1999 (s, sh), 1987 (vs), 1928 (w, sh), 1904 (m) cm^{-1} (lit.[5] ν_{CO} 1997 (s, sh), 1983 (s), 1925 (w), 1900 (m) cm^{-1}). ^{1}H NMR (CD_3CN, 20 °C): δ −19.6 (s) (lit. ($CD_3C(O)CD_3$) δ −19.5 (s)).

The red precipitate ($Na_3[Re_7C(CO)_{21}]$) isolated from the original reaction mixture was dissolved in 2 mL of acetone and added to 30 mL of aqueous Et_4NCl (2 g, 12 mmol) to give a red solid. After it was filtered, washed with water (50 mL), and dried in vacuo, this solid was identified as pure $[Et_4N]_3[Re_7C(CO)_{21}]$ by its IR spectrum. The yield was 90 mg (0.039 mmol, 19%).

Preparation of $H_2Re_6C(CO)_{18}^{2-}$ from $Re_4(CO)_{16}^{2-}$ and $Re_2(CO)_{10}$. A mixture of $[Et_4N]_2[Re_4(CO)_{16}]$ (187 mg, 0.129 mmol) and $Re_2(CO)_{10}$ (71 mg, 0.109 mmol) in diglyme (25 mL) was heated at reflux for 24 h. The solvent was removed under reduced pressure to give an orange-brown solid, which was washed with water (20 mL) and dried in vacuo. The dichloromethane-soluble fraction of this solid was extracted and crystallized by diffusion of 2-propanol at −20 °C to give red-orange crystals of $[Et_4N]_2[H_2Re_6C(CO)_{18}]$ (yield 125 mg, 0.066 mmol, 61%).

Preparation of $H_2Re_6C(CO)_{18}^{2-}$ in the Presence of D_2O. A 50-mL three-necked flask, a reflux condenser, a nitrogen inlet, a ground glass stopper, and a stir bar were washed twice with D_2O, and then the apparatus was assembled and dried with a heat gun under vacuum. Then $[Et_4N]_2[Re_4(CO)_{16}]$ (180 mg, 0.12 mmol), $Re_2(CO)_{10}$ (70 mg, 0.11 mmol), D_2O (10 µL, 0.55 mmol), and dried diglyme (25 mL) were added to the flask. After this mixture was heated at reflux for 24 h, the solvent was removed under reduced pressure. The orange-brown solid residue was washed with water (20 mL), dried in vacuo, and crystallized from dichloromethane/2-propanol. The ^{1}H NMR spectrum of this sample showed the hydride signal to have the same intensity relative to the protons of the tetraethylammonium salt (1:8:12) as the sample prepared in the absence of D_2O.

CO_2 Trapping Reaction. $Re_4(CO)_{16}^{2-}$ and $Re_2(CO)_{10}$. Diglyme (200 mL), $[Et_4N]_2[Re_4(CO)_{16}]$ (1.35 g, 0.93 mmol), and $Re_2(CO)_{10}$ (605 mg, 0.93 mmol) were added to a 300-mL three-necked flask equipped with a reflux condenser and nitrogen inlet. The nitrogen outlet on the reflux condenser was connected to two consecutive traps containing aqueous barium hydroxide solution (1 g in 40 mL per trap). The diglyme mixture was refluxed for 30 h under a nitrogen flow. After 1 h of heating, the first trap contained a white precipitate, which continued to form as the reaction proceeded. The resulting precipitate from the two traps was filtered, washed with water (150 mL) to remove barium hydroxide, and then dried in vacuo. This white precipitate was identified as $BaCO_3$ (120 mg, 0.61 mmol) from its IR spectrum in Nujol (ν_{CO} 1750 cm^{-1}). The diglyme in the reaction mixture was removed under reduced pressure, and the resulting red solid was washed with diethyl ether (20 mL). Dichloromethane (400 mL) was added to extract $[Et_4N]_2[H_2Re_6C(CO)_{18}]$. This solution was filtered, concentrated to a small volume (ca. 50 mL), and treated with 2-propanol (100 mL) to give the crystalline salt of $H_2Re_6C(CO)_{18}^{2-}$ (853 mg, 0.45 mmol, 48%). The remaining solid was treated with THF (300 mL) to extract $[Et_4N]_2[Re_8C(CO)_{24}]$ (480 mg, 0.19 mmol, 20%). The insoluble red solid remaining after these extractions was crystallized in acetone/methanol at -20 °C to give $[Et_4N]_3[Re_7C(CO)_{21}]$ (200 mg, 0.087 mmol, 16%). The amount of carbon dioxide trapped as barium carbonate accounted for 84% of the isolated products ($BaCO_3$, 0.61 mmol; Re_6C + Re_7C + Re_8C, 0.73 mmol).

CO_2 Trapping Reaction. $Re_2(CO)_{10}$ and Sodium. A solution of sodium dispersion (89 mg, 1.54 mmol), $Re_2(CO)_{10}$ (1.61 mg, 2.47 mmol), and diglyme (120 mL) was heated at 160 °C for 26 h. After workup and separation of the product mixture as described above, $[Et_4N]_2[H_2Re_6C(CO)_{18}]$ (640 mg, 0.34 mmol, 41%), $[Et_4N]_3[Re_7C(CO)_{21}]$ (200 mg, 0.087 mmol, 12%), and $[Et_4N]_2[Re_8C(CO)_{24}]$ (320 mg, 0.13 mmol, 21%) were obtained. The trapped $BaCO_3$ was filtered, washed with water, and dried (108 mg, 0.55 mmol, 67%). The amount of carbon dioxide trapped as barium carbonate accounted for 98% of the isolated products (Re_6C + Re_7C + Re_8C: 0.56 mmol).

Pyrolysis of $[Et_4N]_2[Re_4(CO)_{16}]$. A triglyme solution (10 mL) of $[Et_4N]_2[Re_4(CO)_{16}]$ (230 mg, 0.158 mmol) was heated at 200 °C for 8 h. The characteristic strong carbonyl bands of $H_2Re_6C(CO)_{18}^{2-}$, $Re_7C(CO)_{21}^{3-}$, and $Re_8C(CO)_{24}^{2-}$ were observed in the infrared spectrum of the product mixture. The solvent was removed under reduced pressure, and the various products were separated by extraction with the appropriate solvent as described in the preparation of $H_2Re_6C(CO)_{18}^{2-}$ and the CO_2 trapping reaction ($Re_4(CO)_{16}^{2-}$ and $Re_2(CO)_{10}$). The major product isolated was $H_2Re_6C(CO)_{18}^{2-}$ (110 mg, 0.058 mmol, 55%), with the minor products being $Re_7C(CO)_{21}^{3-}$ (30 mg, 0.013 mmol, 14%) and $Re_8C(CO)_{24}^{2-}$ (10 mg, 0.004 mmol, 5%).

Preparation of $Re_7C(CO)_{21}^{3-}$ from $H_2Re_6C(CO)_{18}^{2-}$, $Re_2(CO)_{10}$, and Sodium. Heating a mixture of $[Et_4N]_2[H_2Re_6C(CO)_{18}]$ (130 mg, 0.069 mmol), $Re_2(CO)_{10}$ (24 mg, 0.037 mmol), and sodium (20 mg, 0.35 mmol) in triglyme (15 mL) at 190 °C for 1 h produced a red precipitate and an orange solution. After metathesis with Et_4NCl and crystallization, pure $[Et_4N]_3[Re_7C(CO)_{21}]$ (69 mg, 0.030 mmol, 43%) was obtained.

Preparation of $Re_8C(CO)_{24}^{2-}$ from $Re_4(CO)_{16}^{2-}$ and $Re_2(CO)_{10}$. A mixture of $[Et_4N]_2[Re_2(CO)_{16}]$ (200 mg, 0.14 mmol), $Re_2(CO)_{10}$ (196 mg, 0.30 mmol), and triglyme (30 mL) was heated at 190–200 °C for 45 h. Infrared spectra of the reaction mixture indicated the intermediate formation of $H_2Re_6C(CO)_{18}^{2-}$. The solvent was removed under reduced pressure, and the red solid was crystallized to give $[Et_4N]_2[Re_8C(CO)_{24}]$ (280 mg, 0.11 mmol, 82%). The analogous reaction of $[(Ph_3P)_2N]_2[Re_4(CO)_{16}]$ with $Re_2(CO)_{10}$ provided the $(Ph_3P)_2N^+$ salt of $Re_8C(CO)_{24}^{2-}$ in similar yield.

Preparation of $Re_8C(CO)_{24}^{2-}$ from $H_2Re_6C(CO)_{18}^{2-}$ and $Re_2(CO)_{10}$. A mixture of $[Et_4N]_2[H_2Re_6C(CO)_{18}]$ (15 mg, 0.079 mmol), $Re_2(CO)_{10}$ (53 mg, 0.081 mmol), and triglyme (20 mL) was heated at 190–200 °C for 30 h. After solvent removal and crystallization, $[Et_4N]_2[Re_8C(CO)_{24}]$ (148 mg, 0.061 mmol, 76%) was obtained.

Reaction of $Re_7C(CO)_{21}^{3-}$ with $Re_2(CO)_{10}$ To Give $Re_8C(CO)_{24}^{2-}$. A mixture of $[Et_4N]_3[Re_7C(CO)_{21}]$ (175 mg, 0.076 mmol) and $Re_2(CO)_{10}$ (130 mg, 0.20 mmol) in triglyme (30 mL) was heated at 190–210 °C for 12 h. The solvent was removed under reduced pressure to give a red residue which was washed with water (20 mL) and diethyl ether (20 mL) and dried in vacuo. Crystallization of the precipitate afforded pure $[Et_4N]_2[Re_8C(CO)_{24}]$ (147 mg, 0.060 mmol, 79%). When a similar stoichiometric ratio of $[(Ph_3P)_2N]_3[Re_7C(CO)_{21}]$ to $Re_2(CO)_{10}$ (1:2.5) was used in this reaction, a comparable yield of the $(Ph_3P)_2N^+$ salt was obtained.

Reaction of $Re_8C(CO)_{24}^{2-}$ with Sodium To Give $Re_7C(CO)_{21}^{3-}$. Diglyme (10 mL), $[Et_4N]_2[Re_8C(CO)_{24}]$ (70 mg, 0.029 mmol), and sodium dispersion 35 mg, 0.61 mmol of Na) were added to an oven dried 50-mL three-necked flask equipped with a reflux condenser and carbon monoxide inlet. This mixture was heated at 140–150 °C under a carbon monoxide atmosphere for 1 h to give a light orange solution containing a red precipitate. The diglyme was removed under reduced pressure and the solid treated with 20 mL of aqueous Et_4NCl (2 g, 6.0 mmol). The red precipitate was filtered, washed with water (50 mL), and dried in vacuo. Red crystals of $[Et_4N]_3[Re_7C(CO)_{21}]$ (45 mg, 0.020 mmol, 69%) were obtained from acetone/methanol at -20 °C.

Cyclic Voltammetry. Cyclic voltammetry measurements of $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$ were made at a platinum electrode with a 0.1 M tetrabutylammonium perchlorate (TBAP) electrolyte. All potentials were referenced to the Ag/AgCl electrode. Both $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$ show no evidence of reduction from zero to -1.5 V. For $Re_7C(CO)_{21}^{3-}$, quasi-reversible waves are seen centered at 0.08 and 0.42 V with ΔE_p of 60 and 70 mV, respectively (at 100 mV/s). The voltammogram of $Re_8C(CO)_{24}^{2-}$ shows a quasi-reversible pattern centered at 0.85 V with ΔE_p = 80 mV (100 mV/s) and a largely irreversible pattern ($\Delta E_p \simeq 120$ mV) centered at 1.1 V.

Results and Discussion

Direct Syntheses from $Re_2(CO)_{10}$. $Re_4(CO)_{16}^{2-}$. Kaesz and co-workers reported that the reduction of $Re_2(CO)_{10}$ with excess sodium borohydride in refluxing THF produced $Re_4(CO)_{16}^{2-}$ in 20% yield.[4] We have found that the stoichiometric reaction of $Re_2(CO)_{10}$ with sodium in diglyme at 140–150 °C provides an improved yield (ca. 70%) of this dianion, which we have isolated as the Et_4N^+ and $(Ph_3P)_2N^+$ salts. If refluxing THF is employed, the complex is also formed, but in low yield (15–20%).

$Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$. These two clusters were prepared previously by the pyrolysis of $H_2Re(CO)_4^-$ in *n*-tetradecane with reported yields of 50% for $Re_7C(CO)_{21}^{3-}$[6] and 30% for $Re_8C(CO)_{24}^{2-}$.[7] We have realized the selective syntheses of these complexes in one-pot reactions from $Re_2(CO)_{10}$ and sodium in triglyme (eq 2 and 3). Crystalline Et_4N^+ or $(Ph_3P)_2N^+$ salts of these complexes have been isolated in 75% (Re_7C) and 60% (Re_8C) yields, respectively. In these syntheses, infrared spectra of the reaction mixtures indicate initial formation of $Re_4(CO)_{16}^{2-}$, which is then transformed into $H_2Re_6C(CO)_{18}^{2-}$ and finally into the respective product, depending on the ratio of starting materials used.

$$3.5Re_2(CO)_{10} + 3Na \xrightarrow{\Delta} Re_7C(CO)_{21}^{3-} \tag{2}$$

$$4Re_2(CO)_{10} + 2Na \xrightarrow{\Delta} Re_8C(CO)_{24}^{2-} \tag{3}$$

$H_2Re_6C(CO)_{18}^{2-}$. The treatment of $Re_2(CO)_{10}$ with a stoichiometric ratio of sodium (3:2) in refluxing diglyme (162 °C) affords $H_2Re_6C(CO)_{18}^{2-}$ in only 15–20% yield, and $Re_7C(CO)_{21}^{3-}$ is the major product isolated (50%). Our best direct synthesis of $H_2Re_6C(CO)_{18}^{2-}$ provides it in only 30% yield and requires the use of excess $Re_2(CO)_{10}$ (Re:Na = 3.3:2). In this case $Re_7C(CO)_{21}^{3-}$ and $Re_2(CO)_{10}$ are also isolated from the product mixture, each in ca. 20% yield. Ciani et al.[5] reported a 35% yield of $H_2Re_6C(CO)_{18}^{2-}$ from the pyrolysis of $H_2Re(CO)_4^-$ at 235 °C.

A more selective procedure for preparing $H_2Re_6C(CO)_{18}^{2-}$ is from the combination of $Re_4(CO)_{16}^{2-}$ and $Re_2(CO)_{10}$. The reaction of a 1.2:1 mole ratio (Re_4:Re_2) in refluxing diglyme gives $H_2Re_6C(CO)_{18}^{2-}$ in ca. 60% yield together with $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$ in less than 5% yield each. The combination of a stoichiometric ratio of the reactants (1:1) tends to generate less $H_2Re_6C(CO)_{18}^{2-}$ and more $Re_8C(CO)_{24}^{2-}$ (Re_6C, 50%; Re_8, 10–15%). The hexarhenium carbide is obtained as the major product (ca. 55% yield) from the pyrolysis of $Re_4(CO)_{16}^{2-}$ in triglyme (200 °C), whereas only small amounts of $Re_7C(CO)_{21}^{3-}$ (18%) and $Re_8C(CO)_{24}^{2-}$ (<5%) are isolated.

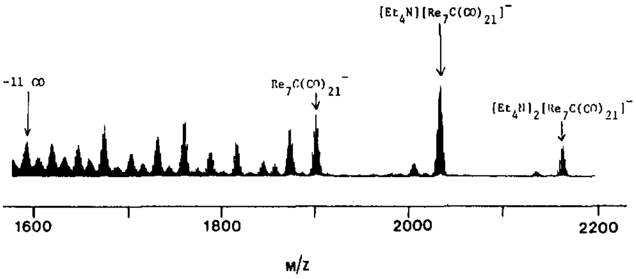

Figure 2. FAB negative ion mass spectrum of $[Et_4N]_3[Re_7C(CO)_{21}]$.

Negative Ion FAB Mass Spectral Analyses. The utility of fast atom bombardment (FAB) for ionizing involatile molecules is well established,[9] and recently the use of FAB-MS for characterizing high molecular weight ionic clusters has been spreading.[10,11] We have observed negative ion FAB mass spectra for these rhenium carbonyl clusters. For each complex, the FAB mass spectrum shows the isotope multiplet pattern for the molecular ion as well as ion multiplets corresponding to the loss of approximately half of the carbonyl ligands. In addition, the pattern(s) for the quaternary ammonium salt adduct(s) $[R_4N]_x[M]^-$ ($x = 1, 2$) are observed, as illustrated in the case of $[Et_4N]_3[Re_7C(CO)_{21}]$ (see Figure 2). However, a comparison of the calculated and observed isotope patterns for the molecular ion of $Re_7C(CO)_{21}^{3-}$ showed the observed peaks between the characteristic quartet (at *m/z* 1901, 1903, 1905, and 1907) to be represented at considerably higher percentage than theoretical values (see Figure 3). This is likely due to the presence of protonated ions, which would shift the quartet to one higher mass unit and produce a more evenly distributed envelope. The proton probably comes from water present in the dispersing medium. In fact, the "hydride" adduct $[HRe_7C(CO)_{21}]^{2-}$ has been synthesized by direct protonation of $Re_7C(CO)_{21}^{3-}$.[12]

Possible Pathways to $H_2Re_6C(CO)_{18}^{2-}$. Carbide Formation. Our previous work established that the clean transformation of $Ru_6(CO)_{18}^{2-}$ into a carbide cluster involved removal of the oxygen atom as carbon dioxide (see eq 4).[3] The evolution of carbon dioxide also occurs during

$$Ru_6(CO)_{18}^{2-} \xrightarrow{\Delta} Ru_6C(CO)_{16}^{2-} + CO_2 \qquad (4)$$

the reaction of $Re_4(CO)_{16}^{2-}$ and $Re_2(CO)_{10}$ to form the carbides $H_2Re_6C(CO)_{18}^{2-}$, $Re_7C(CO)_{21}^{3-}$, and $Re_8C(CO)_{24}^{2-}$. Barium carbonate is obtained in 65% yield, which accounts for over 80% of the isolated carbide products. Two pathways for Re_6C formation can be suggested. By analogy with eq 4, transformation of a Re_6 carbonyl cluster intermediate into $H_2Re_6C(CO)_{18}^{2-}$ is plausible. Suitable 86-electron formulations for the intermediate would be $Re_6(CO)_{20}^{4-}$ or $H_2Re_6(CO)_{20}^{2-}$. Although 20 CO ligands has not been observed for a stable octahedral cluster, ions up to $Re_6(CO)_{22}^+$ have been observed in gas-phase ion molecule reactions involving $Re_2(CO)_{10}$.[13] Another possible pathway involves the initial generation of $Re_4C(CO)_{14}^{2-}$ from $Re_4(CO)_{16}^{2-}$. The species $Re_4C(CO)_{14}^{2-}$ has 62 valence electrons, analogous to the known $Fe_4C(CO)_{12}^{2-}$,[14] and might have a similar butterfly arrangement of metal atoms. This latter pathway gains some credence from the recent isolation of the complex $Re_4C(CO)_{15}I^-$, the framework of which consists of a tetrahedrally distorted square of metal atoms surrounding the carbon atom.[15] Further reaction of a Re_4C species with $Re(CO)_5^-$ or $Re_2(CO)_{10}$ could lead to the Re_6C stage.

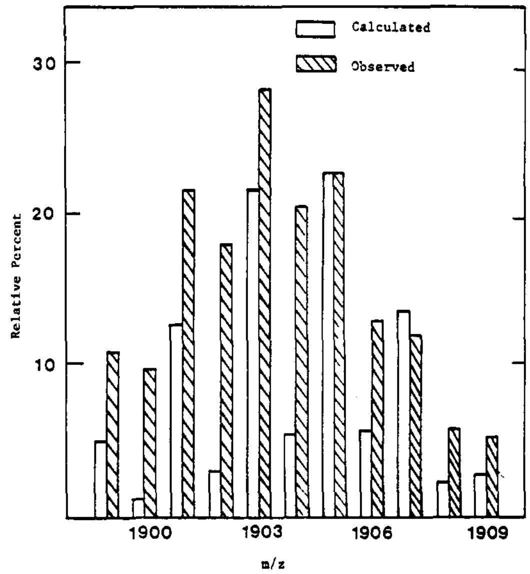

Figure 3. Comparison of observed and calculated isotope patterns for the ion $Re_7C(CO)_{21}^-$. The ion $^{187}Re_7{}^{12}C(^{12}C^{16}O)_{21}^-$ has *m/z* 1909.

Hydride Formation. Among the compounds described in this paper, the only one containing hydride ligands is $H_2Re_6C(CO)_{18}^{2-}$. Several experiments have been performed to investigate the source of the hydrides, but no definitive answer has been obtained. The addition of 5 equiv of D_2O to a diglyme solution of $Re_4(CO)_{16}^{2-}$ and $Re_2(CO)_{10}$ used to prepare $H_2Re_6C(CO)_{18}^{2-}$ provides no deuterium substitution, according to ^1H NMR analysis of the recrystallized product. ^1H NMR analysis of a solution of $H_2Re_6C(CO)_{18}^{2-}$ and D_2O (ca. 200 equiv) in dry THF shows no exchange into the cluster after several hours at room temperature. This result indicates that the hydrides are not sufficiently acidic to undergo exchange under these conditions. The reaction of $Re_2(CO)_{10}$ with sodium (2:3.2 ratio) produces a quantity of carbon dioxide similar to that from the reaction of $Re_2(CO)_{10}$ with $Re_4(CO)_{16}^{2-}$. The former reaction should show considerably increased carbon dioxide formation, if the hydride ligands were formed from the reduction of carbonyl by hydroxide ion present in solution (i.e., $[M] - CO + OH^-$ yielding $H[M]^- + CO_2$). Thus, these results indicate that the hydride ligands apparently do not originate from water or hydroxide in the reaction mixture. The solvent (diglyme) is the only obvious remaining source of protons, but we have not examined this directly.

Conversion of $H_2Re_6C(CO)_{18}^{2-}$ to $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$. Infrared monitoring of the reactions leading selectively to $Re_7C(CO)_{21}^{3-}$ or to $Re_8C(CO)_{24}^{2-}$ suggest the intermediate formation of $H_2Re_6C(CO)_{18}^{2-}$ in both cases. These conversions can be demonstrated directly. Thus, treatment of $H_2Re_6C(CO)_{18}^{2-}$ with sodium and $Re_2(CO)_{10}$

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affords $Re_7C(CO)_{21}^{3-}$ (isolated yield 40%), although a four-fold excess of sodium is needed under these conditions. Prolonged pyrolysis (30 h) of $H_2Re_6C(CO)_{18}^{2-}$ in triglyme (200 °C) affords $Re_8C(CO)_{24}^{2-}$ (yield 30%) as the only identifiable product without the formation of any observable $Re_7C(CO)_{21}^{3-}$. Treatment of $H_2Re_6C(CO)_{18}^{2-}$ with $Re_2(CO)_{10}$ (Re_6:Re_2 = 1:1) and heating the mixture in triglyme (190–200 °C) afford only $Re_8C(CO)_{24}^{2-}$ in ca. 80% isolated yield.

In the conversion of $H_2Re_6C(CO)_{18}^{2-}$ to the two larger clusters, the hydride ligands may be removed in one of three forms: as H_2, as two hydride ions (H^-), or as two protons (H^+). Since it is necessary to employ the appropriate quantity of reducing or oxidizing agent (sodium and/or $Re_2(CO)_{10}$) with $H_2Re_6C(CO)_{18}^{2-}$ to provide $Re_7C(CO)_{21}^{3-}$ or $Re_8C(CO)_{24}^{2-}$, respectively, loss of the hydride ligands as H_2 is the probable pathway. This would generate the formal intermediate "$Re_6C(CO)_{18}^{2-}$", which should react further in the manner observed. However, if they were removed as hydrides, a neutral intermediate (e.g., "$Re_6C(CO)_{18}$") would be generated, and this is not likely to be reduced to $Re_8C(CO)_{24}^{2-}$ in the presence of $Re_2(CO)_{10}$ only. The final possibility, removal as $2H^+$, would provide a more reduced species (e.g., "$Re_6C(CO)_{18}^{4-}$"), and the formation of $Re_7C(CO)_{21}^{3-}$ from $H_2Re_6C(CO)_{18}^{2-}$ is not likely to require the use of sodium as we have found.

Interconversion of $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$. The similar reaction temperature required for the preparation of $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$ suggests the possibility of their interconversion under appropriate conditions. In fact, the interaction of $Re_7C(CO)_{21}^{3-}$ with $Re_2(CO)_{10}$ (1:2.5 mole ratio) in triglyme (190 °C) produces $Re_8C(CO)_{24}^{2-}$ in ca. 80% yield (eq 5). Conversely, the

$$Re_7C(CO)_{21}^{3-} \underset{Na\ +CO}{\overset{Re_2(CO)_{10}}{\rightleftarrows}} Re_8C(CO)_{24}^{2-} \qquad (5)$$

reduction of $Re_8C(CO)_{24}^{2-}$ with excess sodium under a carbon monoxide atmosphere at 160 °C forms $Re_7C(CO)_{21}^{3-}$ in good yield (70%), presumably transforming the $Re(CO)_3$ cap into $Re(CO)_5^-$ under these strongly basic conditions. These results suggest that if $Re_7C(CO)_{21}^{3-}$ is generated in the direct synthesis of $Re_8C(CO)_{24}^{2-}$ (eq 3), it is easily converted to the octanuclear carbide dianion due to the high mole ratio of $Re_2(CO)_{10}$ present. More generally the conversion of $Re_7C(CO)_{21}^{3-}$ into $Re_8C(CO)_{24}^{2-}$ provides an experimental realization of the formal "capping reaction" shown in eq 6. Analogous capping reactions with a variety of platinum metal caps ML_n^+ have been successful and are described in a companion paper.[16]

$$Re_7C(CO)_{21}^{3-} + \text{“}Re(CO)_3^{+}\text{”} \rightarrow Re_8C(CO)_{24}^{2-} \qquad (6)$$

Registry No. $Re_2(CO)_{10}$, 14285-68-8; $[Et_4N]_2[Re_4(CO)_{16}]$, 111525-55-4; $[(Ph_3P)_2N]_2[Re_4(CO)_{16}]$, 111525-56-5; $[Et_4N]_3[Re_7C(CO)_{21}]$, 99900-74-0; $[(Ph_3P)_2N]_3[Re_7C(CO)_{21}]$, 107021-61-4; $Na_3[Re_7C(CO)_{21}]$, 111525-57-6; $[Et_4N]_2[Re_8C(CO)_{24}]$, 83267-48-5; $[(Ph_3P)_2N]_2[Re_8C(CO)_{24}]$, 111525-58-7; $[Et_4N]_2[H_2Re_6C(CO)_{18}]$, 85601-12-3; Na, 7440-23-5.

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Reactions of Transition-Metal–Propargyl Compounds with Dicobalt Octacarbonyl. New Heterobinuclear μ-Alkyne Complexes

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Reactions of transition-metal–propargyl complexes $[M]CH_2C{\equiv}CR$ with $Co_2(CO)_8$ in pentane at room temperature afford the trinuclear products $(CO)_3Co(\mu\text{-}RC_2CH_2[M])Co(CO)_3$ ($[M] = CpFe(CO)_2$, R = Ph (**1a**), Me (**1b**); $[M] = Mn(CO)_5$, R = Ph (**2**); $[M] = CpW(CO)_3$, R = Ph (**3a**), Me (**3b**); $[M] = CpMo(CO)_3$, R = Ph (**4**)) as purple solids of different degrees of stability (**1a**, **1b**, and **2** ≫ **3a**, **3b**, and **4**). Treatment of **1a** and **2** with CF_3CO_2H and alumina, respectively, leads to cleavage of the M–CH_2 bond with the formation of $(CO)_3Co(\mu\text{-}PhC_2Me)Co(CO)_3$ and $CpFe(CO)_2OC(O)CF_3$ (from **1a**). By contrast, **3a**, **3b**, and **4** react with CF_3CO_2H and alumina surprisingly to give heterobinuclear μ-alkyne complexes, $Cp(CO)_2M(\mu\text{-}RC_2Me)Co(CO)_3$ (**5a**, **5b**, and **6**, respectively) as air-stable, red solids. Complexes **1**–**6** were characterized by a combination of elemental analyses, FAB mass spectrometry, and IR and ^1H and ^{13}C NMR spectroscopy; the structure of **5a** was determined by single-crystal X-ray analysis. Crystal data: monoclinic, space group $P2_1/n$ with a = 8.825 (2) Å, b = 15.003 (2) Å, c = 14.035 (2) Å, β = 93.42 (1)°, and Z = 4. The structure was solved and refined to R = 0.0249 and R_w = 0.0268 by using 3918 independent reflections. The alkyne PhC_2Me is transversely bridging the Co–W bond (2.693 (1) Å), and its Me substituent is trans to Cp.

Introduction

Dicobalt octacarbonyl readily reacts with terminal and internal alkynes ($RC{\equiv}CR'$) to yield binuclear complexes of the type $(CO)_3Co(\mu\text{-}RC_2R')Co(CO)_3$ (I) which feature a transversely bridging alkyne ligand.[1] Corresponding reactions of $Co_2(CO)_8$ with organo-transition-metal complexes containing C≡C bonds have received relatively little attention. Rosenblum et al.[2] studied the reaction of di-

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