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Reactions of Carbon Monoxide with Coordinatively Unsaturated Rhenium(II) Dimers Possessing a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ Configuration. Cleavage of the Rhenium–Rhenium Bond and the Formation of Paramagnetic Derivatives of the Type $ReX_2(CO)_2(PR_3)_2$[1]

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Carbon monoxide reacts with the metal–metal bonded dimers $Re_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Pr, in refluxing ethanol, toluene, or acetonitrile to afford *trans*-$ReX_2(CO)_2(PR_3)_2$, a new class of carbonyl derivatives of rhenium(II). These paramagnetic 17-electron systems have been characterized by infrared, electronic absorption, X-ray photoelectron, and ESR spectroscopic techniques. The synthesis of $ReX_2(CO)_2(PR_3)_2$ is complicated by a variety of competing reactions. In the case of *trans*-$ReCl_2(CO)_2(PR_3)_2$, its decomposition to $ReCl(CO)_3(PR_3)_2$ and *trans*-$ReCl_4(PR_3)_2$ occurs under a variety of conditions thereby leading to a decrease in its yield with an increase in reaction time. The oxidation of a portion of the $Re_2Cl_4(PR_3)_4$ starting material to $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_6(PR_3)_2$ occurs by routes which do not involve reaction with CO. For example, the reaction of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ with refluxing ethanol affords a mixture of $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ and $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$. The characterizations of the new complexes $Re_2Cl_5(PR_3)_3$, where R = Et or *n*-Pr, are reported in full. The cleavage by CO of the metal–metal triple bond of $Re_2X_4(PR_3)_4$, species which possess a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ electronic configuration, is in marked contrast to the nonreactivity of dimers of the type $Re_2Cl_6(PR_3)_2$ and $Mo_2Cl_4(PR_3)_4$, which contain metal–metal quadruple bonds ($(\sigma)^2(\pi)^4(\delta)^2$ configuration).

Introduction

Since the discovery in the early 1960's of the existence of discrete *multiple* bonds between transition-metal atoms, there has been a steadily increasing interest in exploring and understanding the chemistry of these species, especially those in which *triple* and *quadruple* bonds exist between pairs of metal atoms.[2,3] Cotton and co-workers[3] have been pioneers in the discovery and structural characterization of compounds of chromium, molybdenum, tungsten, technetium, and rhenium of this type, and, very recently, theoretical advances (especially SCF–Xα–SW calculations),[4-9] coupled with detailed spectroscopic studies[5,10-12] have led to good understanding of the electronic structures of many of these species. Our interest in complexes of this type has involved investigations into two aspects of their chemical reactivity. First, we have been exploring the redox chemistry of low oxidation state metal–metal bonded dimers[13-15] which possess electronic configurations of the type $(\sigma)^2(\pi)^4(\delta)^a(\delta^*)^b(\pi^*)^0(\sigma^*)^0$, where $a = 1$ or 2 and $b = 0$–2, with the object of developing a reversible four-electron oxidant–reductant which retains its structural integrity. Second, we are interested in the use of these "coordinatively unsaturated" dimers as synthetic intermediates,[16,17] particularly in reactions where disruption of the strong metal–metal bond occurs.

In pursuing a study of the reactions of CO with the complex $Re_2Cl_4(PEt_3)_4$, an example of a molecule which possesses a Re–Re triple bond and a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ configuration,[9,13,18] we became interested in the possibility of synthesizing the complex $Re_2Cl_4(PEt_3)_4(CO)_2$ together with species in which substitution of some of the Cl^- or PEt_3 ligands might occur but without disruption of the metal–metal bond. The object was to determine the consequences of bonding the π-acceptor CO ligands upon both the Re–Re bond length and molecular geometry. However, we found that this reaction was extraordinarily complicated giving rise to products arising from both the cleavage of the Re–Re triple bond and the oxidation of the Re_2^{4+} core. Analogous reactions were found to occur with other complexes of the type $Re_2X_4(PR_3)_4$ and provide a route to the hitherto unknown paramagnetic rhenium(II) complexes $ReX_2(CO)_2(PR_3)_2$. Full details of our work are now reported.[19]

Experimental Section

Starting Materials. The complexes $Re_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Pr, were prepared as previously described[13] by the reaction of $(Bu_4N)_2Re_2X_8$ with the appropriate tertiary phosphine in refluxing ethanol. Commercial reagents and solvents were used as received. All phosphine ligands were obtained from Strem Chemicals, Inc. The carbon monoxide which was obtained from Matheson Gas Products was always dried before use.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere, and solvents were deoxygenated by purging with N_2 gas for several hours prior to use.

For product purification by column chromatography, the column was packed under a N_2 atmosphere using absorbent that had been purged with N_2 gas for at least 8 h. During the chromatographic separation of reaction products, N_2 gas was bubbled through the eluent.

A. Reactions of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ with Carbon Monoxide in Various Solvents. (i) Ethanol. (a) Short Reaction Time. $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.70 g) was added to 60 mL of ethanol, and the resulting suspension was refluxed. After CO had been bubbled through the refluxing reaction mixture for about 2 h, the solid starting material was no longer present, and the solution had turned a bright yellow-green. The solution was cooled to room temperature and evaporated to dryness on a rotary evaporator. The resulting residue was dissolved in 20 mL of hexane–toluene (1:1), and the resulting solution was placed on a 20 × 1.9 cm column made from 60–200 mesh silica gel and hexane–toluene (1:1). The composition and purity of all fractions were verified by thin-layer chromatography (TLC).

The column was initially eluted with 238 mL of hexane–toluene (1:1). The first 56 mL to come off the column was colorless. TLC showed that this fraction contained no complexes. The next 24 mL off the column contained a pale yellow band. When this fraction was evaporated to dryness, the resulting residue was of too small a quantity to characterize fully. The following 158 mL, which contained a bright green band, was evaporated to dryness. The residue was collected, washed with 2 mL of ethanol, and dried in vacuo to yield 0.15 g of the yellow-green complex $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$. Anal. Calcd for $C_{20}H_{42}Cl_2O_2P_2Re$: C, 37.9; H, 6.7; Cl, 11.2; mol wt 634. Found (for separate preparative samples): C, 38.0, 38.2; H, 6.6, 6.6; Cl, 10.8; mol wt in benzene 649; yield 20%. This complex was soluble in toluene, carbon tetrachloride, chloroform, ethanol, pentane, and diethyl ether. No decomposition of the solid was apparent even after it had been stored for several months in the air.

The column was next eluted with 150 mL of toluene, immediately followed by 75 mL of chloroform. The pale yellow solution that came off the column was evaporated to dryness and 2 mL of ethanol was added to the residue. A pale yellow product (0.16 g) was collected by filtration and dried in vacuo. Spectral and solubility measurements showed that this complex was $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$; yield 21%.

A green solution resulted upon eluting the column with an additional 255 mL of chloroform. This solution was evaporated to dryness and the resulting residue was dissolved in 5 mL of pentane. After about 2 min, tiny dark green crystals began to form. These crystals were filtered off and washed with additional pentane, but they turned to a powder when dried in vacuo. This product was the dimer

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$Re_2Cl_5(P(n\text{-}Pr)_3)_3$. Anal. Calcd for $C_{27}H_{63}Cl_5P_3Re_2$: C, 31.5; H, 6.2; Cl, 17.2. Found: C, 31.3; H, 6.0; Cl, 17.0; yield 23%. The complex was soluble in toluene and slightly soluble in pentane.

The column was finally eluted with 70 mL of ethanol to remove any remaining complexes which were still retained on the column. The resulting olive green fraction, when evaporated to dryness, gave a tar. The nature of this material is not known.

(b) Long Reaction Time. $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.12 g) was added to 60 mL of dry ethanol under a N_2 atmosphere. Carbon monoxide was bubbled through the solution for 12 h. The pale yellow solution was cooled to room temperature and evaporated to about 2 mL on the rotary evaporator. The pale yellow precipitate which had formed was filtered off and dried in vacuo. This product analyzed closely for $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$. Anal. Calcd for $C_{28}H_{42}ClO_3P_2Re$: C, 40.3; H, 6.8; Cl, 5.7; mol wt 626. Found: C, 39.3; H, 6.7; Cl, 5.6; mol wt in chloroform 645.

(ii) Toluene. (a) Short Reaction Time. $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.51 g) was added to 60 mL of dry toluene, and CO was bubbled through the refluxing solution for 0.5 h. The cooled bright yellow-green solution was evaporated to dryness on a rotary evaporator. The resulting crude product was chromatographed on a 21 × 1.9 cm column made from 60–200 mesh silica gel and hexane–toluene (1:1). A procedure exactly analogous to that described in section A(i)(a) afforded three complexes: $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$, 0.07 g, yield 13%; $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$, 0.11 g, yield 20%; $Re_2Cl_5(P(n\text{-}Pr)_3)_3$, 0.06 g, yield 13%. The spectral and solubility properties of these complexes formed were identical with those described in section A(i)(a).

(b) Long Reaction Time. $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.54 g) was added to 60 mL of dry toluene, and the refluxing solution was treated with CO for almost 13 h. The cherry red solution was cooled and evaporated to dryness on a rotary evaporator. When 500 mL of pentane was added to the residue, a green precipitate and a red solution resulted. The green complex $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ was filtered off, washed with pentane, and dried in vacuo. Anal. Calcd for $C_{18}H_{42}Cl_6P_2Re_2$: C, 23.9; H, 4.7. Found: C, 24.2; H, 4.8; yield 12%. The infrared and electronic absorption spectra of this product were identical with those of an authentic samples of this complex.[13]

The red filtrate was evaporated to dryness on a rotary evaporator to give a red-purple solid. This was dissolved in 10 mL of hexane–toluene (1:1) and then placed on a 21.5 × 1.9 cm column made from 60–200 mesh silica gel and hexane–toluene (1:1). The column was first eluted with 115 mL of hexane–toluene (1:1). The initial 54 mL to come off the column (a colorless solution) was discarded. The next 61 mL was a deep purple color which upon evaporation to dryness afforded a purple crystalline material. This product was collected, washed with 1 mL of ethanol, and dried in vacuo. Its infrared spectrum [ν(Re–Cl) at 322 cm^{-1}],[20] electronic absorption spectrum,[21] and microanalytical data were consistent with a complex of stoichiometry $ReCl_4(P(n\text{-}Pr)_3)_2$ containing a small amount of "lattice" hexane, i.e., $ReCl_4(P(n\text{-}Pr)_3)_2 \cdot C_6H_{14}$. Anal. Calcd for $C_{24}H_{56}Cl_4P_2Re$: C, 39.2; H, 7.7; Cl, 19.3. Found: C, 38.8; H, 7.7; Cl, 19.0, yield 4%.

The column was then eluted with an additional 21 mL of hexane–toluene (1:1), but when the pale pink solution was evaporated to dryness, only a trace of purple solid remained.

The column was then eluted with 218 mL of chloroform and this colorless fraction, upon evaporation to dryness and treatment with a small volume of ethanol (~5 mL), afforded only the rhenium(I) complex $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ which was identified by its spectral properties; yield 57%.

Continued elution with chloroform and ethanol did not result in the isolation of any further products.

(iii) Acetonitrile. $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.77 g) was dissolved in 50 mL of dry acetonitrile, and CO was bubbled through the refluxing solution for 2 h. The resulting green-yellow solution was taken to dryness on a rotary evaporator yielding a dark green residue which was dissolved in 15 mL of hexane–toluene (1:1) and was then chromatographed on a silica gel column. The usual workup procedure afforded 0.02 g of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$, 0.08 g of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$, and 0.135 g of a mixture of $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ and $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ as identified by infrared spectroscopy.[13] The yields of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ and $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ produced in this reaction were 2 and 9%, respectively.

(iv) 2-Methoxyethanol. $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.28 g) was added to 60 mL of 2-methoxyethanol, and CO was bubbled through the boiling solution for 20 h. The resulting pale yellow solution was cooled to room temperature and evaporated to give an oil. A small volume of ethanol (~5 mL) was added and the solution was then evaporated to ~1 mL. The resulting white product was filtered off, washed with a small amount of ethanol, and dried in vacuo. Microanalytical data were consistent with the stoichiometry $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$. Anal. Calcd for $C_{21}H_{42}ClO_3P_2Re$: C, 40.3; H, 6.8; Cl, 5.7. Found: C, 40.3; H, 6.4; Cl, 5.6; yield 46%.

B. Reactions of $Re_2Br_4(P(n\text{-}Pr)_3)_4$ with Carbon Monoxide in Ethanol. Treatment of a suspension of $Re_2Br_4(P(n\text{-}Pr)_3)_4$ (0.61 g) with CO in 80 mL of refluxing ethanol for almost 3 h afforded a yellow-green solution. This was cooled to room temperature and evaporated to dryness. The residue was dissolved in 39 mL of hexane–toluene (8:1) and placed on a 19.3 × 1.9 cm column made from 60–200 mesh silica gel and hexane–toluene (8:1).

The column was first eluted with 360 mL of hexane–toluene (8:1) to give a colorless solution. TLC showed that this solution did not contain any complex species. The column was then eluted with a further 310 mL of hexane–toluene (8:1). The yellow-green fraction was evaporated to dryness. The resulting olive green complex $ReBr_2(CO)_2(P(n\text{-}Pr)_3)_2$ was collected, washed with 1 mL of ethanol, and dried in vacuo. Anal. Calcd for $C_{20}H_{42}Br_2O_2P_2Re$: C, 33.3; H, 5.9; Br, 22.1. Found: C, 33.3; H, 6.1; Br, 22.0; yield 7%. The complex was soluble in the same solvents as its chloride analogue (see A(ii)).

The use of a further 135 mL of hexane–toluene (8:1) as the eluent resulted in a bright yellow-green solution. TLC showed that this was a mixture of two complexes: $ReBr_2(CO)_2(P(n\text{-}Pr)_3)_2$ and $ReBr(CO)_3(P(n\text{-}Pr)_3)_2$. However, elution with 218 mL of hexane–toluene (8:1), followed by 80 mL of toluene, gave a bright yellow fraction which was evaporated to dryness on a rotary evaporator. The yellow product was collected, washed with 1 mL of ethanol, and dried in vacuo. The product analyzed as $ReBr(CO)_3(P(n\text{-}Pr)_3)_2$. Anal. Calcd for $C_{21}H_{42}BrO_3P_2Re$: C, 37.6; H, 6.3; Br, 11.9. Found: C, 37.4; H, 6.2; Br, 11.8; yield 30%.

C. Reactions of $Re_2Cl_4(PEt_3)_4$ with Carbon Monoxide in Ethanol. The reaction between $Re_2Cl_4(PEt_3)_4$ (0.66 g) and CO in 60 mL of refluxing ethanol proceeded in the usual way. After a reflux time of 2.5 h, the yellow-green reaction solution was cooled to room temperature and evaporated to dryness. Fifty milliliters of hexane–toluene (1:1) was added to the residue, and this solution of the crude product was placed on a 21 × 1.9 cm column of 60–200 mesh silica gel and hexane–toluene (1:1).

The column was first eluted with 220 mL of hexane–toluene (1:1) which gave a colorless fraction which was discarded. Eluting with another 36 mL of hexane–toluene (1:1) resulted in a pale yellow solution, which when evaporated to dryness afforded an insignificant amount of solid material. A bright green band came off when the column was eluted with the next 212 mL of hexane–toluene (1:1). The fraction was evaporated to dryness and 1 mL of ethanol was added to the residue to give insoluble green crystals of $ReCl_2(CO)_2(PEt_3)_2$. The product was collected and dried in vacuo. Anal. Calcd for $C_{14}H_{30}Cl_2O_2P_2Re$: C, 30.6; H, 5.5; Cl, 12.9. Found: C, 30.1; H, 5.7; Cl, 13.8; yield 11%. This complex was extremely soluble in carbon tetrachloride, chloroform, benzene, ethanol, pentane, and diethyl ether.

After removal of the $ReCl_2(CO)_2(PEt_3)_2$, the column was eluted with 89 mL of hexane–toluene, followed by 85 mL of toluene. Evaporation of this pale yellow fraction to dryness yielded only a trace of material. Eluting next with 200 mL of chloroform gave a colorless fraction. The solution was evaporated to dryness and 10 mL of ethanol was added to the residue. When the ethanol was allowed to slowly evaporate to a volume of about 1 mL, off-white crystals of $ReCl(CO)_3(PEt_3)_2$ separated. These were filtered off and dried in vacuo. Anal. Calcd for $C_{15}H_{30}ClP_2O_3Re$: C, 33.2; H, 5.6; Cl, 6.5. Found: C, 33.2; H, 5.5; Cl, 6.6; yield 6%.

Next the column was eluted with 80 mL of chloroform to give a green fraction. The green fraction was evaporated to dryness and 5 mL of pentane was added to the residue. The grass green product which resulted was collected and dried in vacuo. Microanalytical data and spectral measurements showed it to be the dimer $Re_2Cl_5(PEt_3)_3$. Anal. Calcd for $C_{18}H_{45}Cl_5P_3Re_2$: C, 23.9; H, 5.0; Cl, 19.6; mol wt 903. Found: C, 24.2; H, 4.8; Cl, 19.3; mol wt in benzene 801; yield 16%.

D. Reactions of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$. (i) Carbon Monoxide. (a) A quantity of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ (0.12 g) was dissolved in 10 mL of absolute ethanol and CO was bubbled through the bright green solution for 3.5 h. The green reaction solution was then cooled and taken to dryness on a rotary evaporator. The infrared spectrum of the resulting bright green solid (0.1 g) confirmed it to be the unreacted starting material, $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$.

(b) $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ (0.1 g) was dissolved in 10 mL of absolute ethanol and 2 drops of tri-*n*-propylphosphine was added to the green solution. After 5 min of bubbling CO through the refluxing solution, the initial green color had changed to a pale yellow. The reaction was continued for 1 h and then cooled and evaporated to dryness. The resulting pale yellow residue (0.06 g), which was soluble in ethanol, diethyl ether, and acetone, was dried in vacuo. The infrared spectrum (Nujol mull) of this material showed that it was a mixture consisting predominantly of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ with a trace of unreacted $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$. The yield of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ was ~60%.

(ii) Tri-*n*-propylphosphine. $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ (0.2 g) was dissolved in 8 mL of ethanol, and to this was added 3 drops of tri-*n*-propylphosphine. The reaction mixture was then refluxed and the color of the solution changed rapidly from bright green to orange after 10 min of reaction. After 2.5 h of reflux, the orange solution was evaporated to low volume and the resulting orange solid (0.07 g) was filtered off, washed with a few milliliters of diethyl ether, and dried in vacuo. The pale orange solid (soluble in ethanol and acetone) was identified by its infrared spectrum as being predominantly $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ with a trace of *trans*-$ReCl_4(P(n\text{-}Pr)_3)_2$ [ν(Re–Cl) of the rhenium(IV) component occurred as a weak band at 320 cm^{-1}].[20]

(iii) Methanol–Hydrochloric Acid. A quantity of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ (0.20 g) was partially dissolved in 10 mL of CH_3OH–HCl (4:1). After 4 days of reflux, a red product (0.15 g) was filtered off, washed with methanol, and dried. The infrared spectrum of the red material was found to be a composite of the spectra of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ and *trans*-$ReCl_4(P(n\text{-}Pr)_3)_2$, but the microanalytical data for this material indicated that $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ was the major component. Anal. Calcd for $C_{21}H_{42}ClO_3P_2Re$: C, 40.3; H, 6.8. Calcd for $C_{18}H_{42}Cl_4P_2Re$: C, 33.3; H, 6.5. Found: C, 39.9; H, 6.6.

(iv) Chlorine–Carbon Tetrachloride. $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ (0.13 g) was dissolved in 50 mL of dry carbon tetrachloride. Upon passing a slow stream of chlorine into the bright green solution the color changed instantly to yellow. The refluxing reaction mixture was chlorinated for 1.5 h, and the resulting bright orange solution was cooled and then filtered to yield a light green solid. The green solid was washed with a small volume of carbon tetrachloride and diethyl ether and dried in vacuo. This product analyzed as a complex of stoichiometry $[(n\text{-}Pr)_3PCl]^+[ReCl_5(P(n\text{-}Pr)_3)]^-$. Anal. Calcd for $C_{18}H_{42}Cl_6P_2Re$: C, 30.0; H, 5.8; Cl, 29.6. Found: C, 29.8; H, 5.8; Cl, 29.4; yield 41%. This complex was soluble in acetone and acetonitrile.

The molar conductivity (Λ_m) of an acetonitrile solution of this complex (2.08×10^{-3} M) was 131 Ω^{-1} cm^2 mol^{-1}, consistent with the behavior of a 1:1 electrolyte.[22]

An ethanol solution of $[(n\text{-}Pr)_3PCl]ReCl_5(P(n\text{-}Pr)_3)$ when treated with 2 drops of tri-*n*-propylphosphine acquired a dark red coloration after ~3 h due to the formation of *trans*-$ReCl_4(P(n\text{-}Pr)_3)_2$.

(v) 2,2′-Bipyridyl. A quantity of bpy (0.15 g) was dissolved in 5 mL of toluene, and this solution was added to 0.3 g of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ dissolved in an equal volume of toluene. After 13 h of reflux, the reaction mixture had acquired a brown color, and a few black crystals were present on the boiling stick. After 3 days of reflux, the reaction mixture was cooled and the black crystals were filtered off, washed with toluene and diethyl ether, and dried in vacuo. The brown reaction filtrate, when reduced in volume, produced a black intractable oil. The crystalline reaction product (dark green on grinding) analyzed as a complex of stoichiometry $ReCl_2(CO)(bpy)(P(n\text{-}Pr)_3)$. Anal. Calcd for $C_{15}H_{29}Cl_2N_2OPRe$: C, 39.9; H, 4.8; Cl, 11.8; mol wt 601. Found: C, 39.6; H, 4.5; Cl, 12.3; mol wt in acetone 579; mol wt in chloroform 610; yield 21%; mp 235–240 °C dec.

The molar conductivity (Λ_m) of an acetone solution of the complex (2.32×10^{-3} M) was 5.0 Ω^{-1} cm^2 mol^{-1}, consistent with this complex having a nonionic structure.[22]

(vi) 1,2-Bis(diphenylphosphino)ethane. Ethanol (10 mL) was syringed into an intimate mixture of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ (0.13 g) and dppe (0.085 g), and the resulting bright green solution was refluxed. A white precipitate formed after 10 min and, after an additional 10 min of refluxing, the reaction mixture was cooled and the white material was filtered off, washed with ethanol and diethyl ether, and dried in vacuo. This product analyzed as a complex of stoichiometry $ReCl(CO)_2(dppe)_2$. Anal. Calcd for $C_{54}H_{48}ClO_2P_4Re$: C, 60.35; H, 4.52; Cl, 3.3. Found: C, 59.9; H, 4.4; Cl, 3.5; yield 14%; mp 268 °C dec. This complex was soluble in nitromethane and nitrobenzene but insoluble in acetone, acetonitrile and ethanol.

The molar conductivity (Λ_m) of a nitromethane solution of this complex (5.76×10^{-3} M) was 0.4 Ω^{-1} cm^2 mol^{-1}. A similar measurement in nitrobenzene (1.86×10^{-3} M) yielded a value of $\Lambda_m = 5.4 \times 10^{-3}$ Ω^{-1} cm^2 mol^{-1}. Therefore, $ReCl(CO)_2(dppe)_2$ is a nonelectrolyte in these solvents.[22]

E. Other Reactions Relating to the Carbonylation of $Re_2X_4(PR_3)_4$. (i) Reaction of the $Re_2Cl_8^{2-}$ Anion with Carbon Monoxide–Tri-*n*-propylphosphine. A quantity of the salt $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (0.3 g) was partially dissolved in 20 mL of absolute ethanol, and a slow stream of CO was bubbled through the solution for 0.5 h at 23 °C. Addition of tri-*n*-propylphosphine (1 mL) caused an immediate color change from blue to a dark green. The reaction mixture was then refluxed with CO bubbling through the solution, and during a period of 37 h, the dark green solution changed to a green-brown and finally acquired a light orange color. After a total reaction time of 40 h, the contents of the flask were chilled to 0 °C while CO bubbled through the solution. The resulting crop of straw-colored crystals which formed was filtered off, washed with a few milliliters of cold ethanol, and dried in vacuo. This product was identified as $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ by infrared spectroscopy; yield 70%.

(ii) Reaction of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ with Ethanol. (a) $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (1.01 g) was suspended in 60 mL of ethanol and refluxed for 2 h. After this period, the dark green solution was cooled and 0.19 g of unreacted $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (identified by its infrared spectrum)[13] was filtered off. The green filtrate was reduced to dryness on a rotary evaporator. The dark green residue was dissolved in 15 mL of hexane–toluene (1:1) and was chromatographed on a silica gel column. Eluting with 80 mL of hexane–toluene (1:1) gave a colorless fraction which, when evaporated, produced no detectable residue. Eluting with a further 190 mL of hexane–toluene (1:1) gave a pale yellow fraction which yielded 0.141 g of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$. The remaining green band on the column was eluted with 75 mL of hexane–toluene (1:1) which, when evaporated to dryness, afforded 0.19 g of green $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ identified by its infrared spectrum and microanalysis. Anal. Calcd for $Re_2Cl_5[P(C_3H_7)_3]_3$: Cl, 17.2. Found: Cl, 17.0. There was no evidence for the formation of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ in this reaction.

(b) A quantity of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (0.50 g) was dissolved in 50 mL of toluene, and the solution was refluxed for 2 h. The resulting gray solution was evaporated to dryness (rotary evaporator) to yield 0.48 g of unreacted $Re_2Cl_4(P(n\text{-}Pr)_3)_4$, as identified by its infrared spectrum.[13]

(iii) Reaction of $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ with Carbon Monoxide. $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ (0.71 g) was suspended in 50 mL of ethanol, and carbon monoxide was bubbled through the refluxing solution for 4 h. The green solid was filtered off (0.68 g) and was identified as $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ by its infrared spectrum.[13] A similar reaction in toluene resulted in quantitative recovery of the starting material.

Physical Measurements. Infrared spectra in the region 4000–200 cm^{-1} were recorded as Nujol mulls using a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded on Beckman DU-2 and Cary 14 spectrophotometers. X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum $K\alpha_1$–$K\alpha_2$ line (1486.6 eV) was used as the excitation source. Full details of the experimental procedure are described elsewhere.[23,24] Magnetic susceptibilities were determined by the Gouy technique using $Hg[Co(SCN)_4]$ as the calibrant and also by the Faraday method using the Faraday magnetic balance at the University of Arizona. The magnetic measurements were made at only one temperature, approximately 25 °C. Corrections for the ligand diamagnetism were estimated from Pascal's constants. X-Band ESR spectra were recorded on glasses at 100 K or on solids at room temperature using a Varian E-109 spectrometer. Conductivity measurements were carried out using an Industrial Instruments bridge, Model RC 16B2.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

Carbonylation Reactions of $Re_2X_4(PR_3)_4$. The reactions between CO and $Re_2X_4(PR_3)_4$, where X = Cl when R = Et

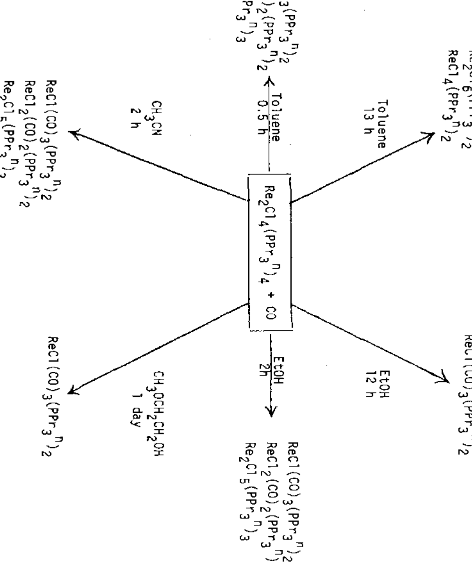


Figure 1. Product distributions for the reaction of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ with CO in various solvents.

or *n*-Pr and X = Br when R = *n*-Pr, in refluxing ethanol, toluene, or acetonitrile are extremely complex and lead to the formation of mixtures of $ReX_2(CO)_2(PR_3)_2$, X = Cl or Br, $ReX(CO)_3(PR_3)_2$, X = Cl or Br, $Re_2Cl_5(PR_3)_3$, $Re_2Cl_6(PR_3)_2$, and *trans*-$ReCl_4(PR_3)_2$. The product distribution depends upon the starting material, the choice of solvent, and the reaction time. The reactions of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$, which were those we studied in greatest detail, are summarized in the reaction scheme shown in Figure 1.

In all instances, the reaction of CO with $Re_2X_4(PR_3)_4$ in refluxing ethanol (and toluene and acetonitrile in the case of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$) for periods of less than 3 h afforded complexes of the type $ReX_2(CO)_2(PR_3)_2$, a new class of rhenium(II) carbonyl derivatives. Other products isolated from these same reaction mixtures were $ReX(CO)_3(PR_3)_2$, which are members of a well-known class of rhenium(I) carbonyl complexes,[25] and, in the case of X = Cl, the new "mixed" oxidation state rhenium dimers $Re_2Cl_5(PR_3)_3$, where R = Et or *n*-Pr.

Extending the reaction times to 12 h or more in the case of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ (see Figure 1) resulted in the disappearance of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ and $Re_2Cl_5(P(n\text{-}Pr)_3)_3$, an increase in the yield of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$, and, using toluene as solvent, the additional appearance of the higher oxidation state species *trans*-$ReCl_4(P(n\text{-}Pr)_3)_2$ and $Re_2Cl_6(P(n\text{-}Pr)_3)_2$.

Preliminary attempts to monitor the progress of the reactions using IR and NMR spectroscopy proved to be unsatisfactory and were abandoned in favor of the workup of the individual reactions and isolation of the reaction products.[26] In most cases, column chromatography (silica gel) was necessary to separate the complex reaction mixtures. Up to 70% of the total rhenium could be accounted for in the combined yields of these products, but in many instances, much lower total yields were obtained. At no time were we able to isolate or obtain evidence for the formation of stable carbonyl derivatives in which the Re–Re bond remains intact.

The new complexes prepared in this work are listed in Table I, together with a summary of their spectral properties. Since the properties of $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ and *trans*-$ReCl_4(P(n\text{-}Pr)_3)_2$ (and its hexane solvate) agree with those reported previously in the literature[13,20] for samples of these complexes which were obtained by different preparative routes, they will not be discussed further.

Probable Mechanisms of the Metal–Metal Bond Breaking and Oxidation Reactions of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$. The relatively

Table I. Spectroscopic Properties of Complexes Resulting from the Carbonylation Reactions of $Re_2X_4(PR_3)_4$

				IR, cm^{-1}			XPS, eV			
complex		medium[a]	electronic absorption max (2000–400 nm),[b] nm	medium[a]	ν(C–O)	ν(Re–Cl)	Re $4f_{7/2}$[d]	Cl $2p_{3/2}$	P 2p	C 1s
$ReCl(CO)_3(P(n\text{-}Pr)_3)_2$	I	NM	<400	NM C_6H_6	1944 vs, 1884 vs 1940 s, 1887 s	274 m	41.5 (1.4)		~131.5	285.0
$ReCl(CO)_3(PEt_3)_2$	II	NM	<400	NM	1948 s, 1904 s	280 m–s				
$ReBr(CO)_3(P(n\text{-}Pr)_3)_2$	III	C_6H_6	445 (90)	NM C_6H_6	1942 s, 1883 s 1942 s, 1890 m					
$ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$	IV	NM DR C_6H_6	650 m, 430 s 650 m, 430 s 650 (84), ~478 sh, 425 (2100)	NM C_6H_6	1901 vs 1906 vs	302 s	41.6 (1.3)	198.4	~131.3	285.0
$ReCl_2(CO)_2(PEt_3)_2$	V	NM	655 m, 415 vs	NM	1912 s	310 s, 303 sh				
$ReBr_2(CO)_2(P(n\text{-}Pr)_3)_2$	VI	DR	690 m, 467 s	NM	1904 vs					
$Re_2Cl_5(P(n\text{-}Pr)_3)_3$	VII	NM C_6H_6	1375 s, 720 m,[c] 555 sh, ~470 sh 1355 (2340), 370 (1640)	NM		337 s, 315 m–s, ~300 sh				
$Re_2Cl_5(PEt_3)_3$	VIII	NM	1460, 720 m[c]	NM		344 s, 321 m, 298 w				
$[(n\text{-}Pr)_3PCl][ReCl_5(P(n\text{-}Pr)_3)]$	IX	acetone	1530 vw, br, 1340 w, 1160 w, 1110 w, 750 m, 690 w, 640 m	NM		330 sh, 325 sh, 317 s	43.4 (1.5)	e	~132.2	285.0
$ReCl_2(CO)(bpy)(P(n\text{-}Pr)_3)$	X	acetone	645 m, ~475 sh, 455 s	NM CH_3CN	1835 vs 1848 s	305 s, 278 s	41.1 (2.0)	198.2	~130.7	285.0
$ReCl(CO)_2(dppe)_2$	XI	NM	<400	NM	1837 s, 1795 s		40.4 (1.7)	198.0	131.3	285.0

[a] Abbreviations: NM, Nujol mull; DR, diffuse reflectance. [b] Molar extinction coefficients given in parentheses. [c] 720-nm band due to contamination by $Re_2Cl_6(P(n\text{-}Pr)_3)_2$. [d] Full-width half-maximum (fwhm) values for Re $4f_{7/2}$ peaks given in parentheses. [e] Complex Cl 2p binding energy spectrum due to two sets of overlapping Cl 2p doublets (see text).

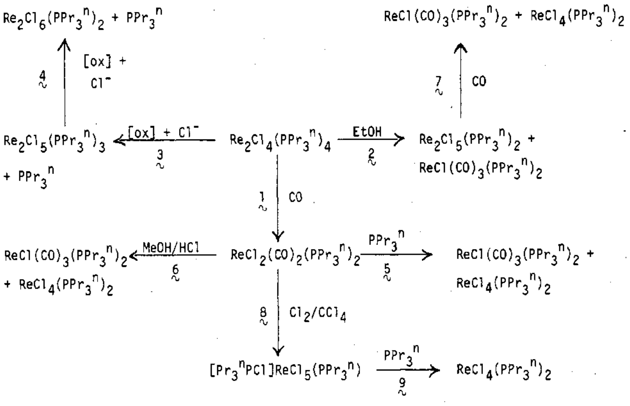


Figure 2. Scheme outlining the reactions which probably occur in the $Re_2Cl_4(P(n\text{-}Pr)_3)_4$–CO system. In reactions 3 and 4, [ox] represents an oxidizing agent.

simple Re–Re bond cleavage reaction which takes place when $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ is reacted with CO (eq 1) is unfortunately

$$Re_2Cl_4(P(n\text{-}Pr)_3)_4 + 4CO \rightarrow 2ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2 \quad (1)$$

complicated by a variety of competing redox reactions which lead to its conversion and that of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ to $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$, $Re_2Cl_5(P(n\text{-}Pr)_3)_3$, $Re_2Cl_6(P(n\text{-}Pr)_3)_2$, and $ReCl_4(P(n\text{-}Pr)_3)_2$. From the product distributions (see Figure 1) and other reactivity studies, we have attempted to explain the course of these carbonylation reactions. We believe that the reactions which are most likely to occur in the $Re_2Cl_4(P(n\text{-}Pr)_3)_4$–CO system are those summarized in Figure 2 (numbered 1–9).

Although pure $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ does not react further with CO in refluxing ethanol, the addition of phosphine causes its rapid conversion to $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$. This reaction (5) occurs even in the absence of CO but in this instance is also accompanied by the formation of some $ReCl_4(P(n\text{-}Pr)_3)_2$. Similarly, the reaction of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ with CH_3OH–HCl (6) affords a mixture of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ and $ReCl_4(P(n\text{-}Pr_3)_2$, the rhenium(I) complex being the major component. Accordingly, any release of free phosphine or HCl in the reaction between $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ and CO will favor the formation of $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ While the detailed mechanisms of reactions 5 and 6 are unknown, it is possible that they involve a disproportionation step (e.g., $3Re(II) \rightarrow 2Re(I) + Re(IV)$) which does not proceed when CO alone is reacted with $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$.

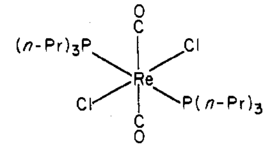
Paralleling the formation of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$, the rhenium dimer $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ is likewise obtained in maximum yield after about 2 h and thereafter decomposes. We believe that this complex can be formed by at least two routes. In the first of these, the reaction of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ with refluxing ethanol (2) occurs (even in the absence of CO) to produce $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ and $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$; under these conditions we find no evidence for the formation of any $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$. Since $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ does not react with toluene or acetonitrile, the oxidation of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ to $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ in these solvents must occur by routes which are independent of the solvent. It has previously been shown[15,27] that complexes of the type $Re_2X_4(PR_3)_4$, where X = Cl, Br, or I, may be oxidized in two reversible one-electron steps to $Re_2X_4(PR_3)_4^+$ and $Re_2X_4(PR_3)_4^{2+}$. The very low value of the first oxidation potential[28] makes these species very susceptible to oxidation. The formation of any mild oxidant (including Cl_2 or adventitious O_2) in the reaction between $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ and CO will therefore generate the monocation, which we have found[15,29] reacts rapidly with Cl^- to form $Re_2Cl_5(P(n\text{-}Pr)_3)_3$, subsequently releasing 1 equiv of phosphine (see reaction 3). $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ can in turn be oxidized to $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ via reaction 4.[13,15,29]

Studies on the reactions of CO with $Re_2Cl_5(PRPh_2)_3$, where R = Me or Et, in refluxing benzene or toluene show[30] that these dimers are converted to mixtures of $ReCl(CO)_3(PRPh_2)_2$, *trans*-$ReCl_4(PRPh_2)_2$, and other as yet unidentified species, thereby explaining why $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ is rapidly consumed upon extending the reaction with CO beyond about 2 h (reaction 7).

We have also found that $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ is oxidized to the rhenium(IV) salt $[(n\text{-}Pr)_3PCl]ReCl_5(P(n\text{-}Pr)_3)$ by chlorine–carbon tetrachloride solutions (reaction 8) and this complex, upon treatment with tri-*n*-propylphosphine (reaction 9) produces *trans*-$ReCl_4(P(n\text{-}Pr)_3)_2$. Thus, this rhenium(IV) complex can be produced by at least one of four reactions (5–9).

Properties and Structure of $ReX_2(CO)_2(PR_3)_2$. The properties of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ appear to be representative of this new class of rhenium(II) carbonyl derivatives. It is soluble in a variety of polar and nonpolar solvents, is a monomer in benzene, and possesses a room-tempmerature magnetic moment of 2.1 μ_B, a value which is consistent with its formulation as a derivative of rhenium(II) (t_{2g}^5 configuration). The solid-state room-temperature ESR spectrum of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ is broad (fwhm ~450 G) and centered at a g_{av} value of 2.25. Its NMR spectrum in $CDCl_3$ consists of one broad band which is centered around δ 1.6. The Me_4Si signal is also very broad, a consequence of the paramagnetic nature of the complex. This is further evidence for the complex being a rhenium(II) t_{2g}^5 species, since paramagnetic rhenium(III) (t_{2g}^4) complexes have *sharp* resonances, shifted relative to those of their diamagnetic analogues.[33]

The infrared spectrum of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ is in accord with a trans disposition of both Re–CO and Re–Cl bonds, possessing both single ν(CO) and ν(Re–Cl) absorptions (Table I). Accordingly, it most likely has an all-trans geometry, similar to that exhibited by certain ruthenium(II) complexes of this type.[34]



In contrast to the common occurrence of tertiary phosphine complexes of rhenium(I) and rhenium(III) carbonyl halides,[25] the only previous report of rhenium(II) carbonyl species is an account by Chatt et al.[25b] of the isolation and characterization of monocarbonyl derivatives of the types $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]X$, where X = $FeCl_4$, Br_3, I_3, or PF_6, and $[ReCl(CO)(PMe_2Ph)_4]FeCl_4$. Our synthetic procedure is quite different from that utilized by Chatt et al.[25b] and provides a route to the previously unknown neutral dicarbonyls. The isoelectronic dinitrogen complexes of rhenium(II), $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]X$, have also been isolated by Chatt and co-workers[35] but exist in both green and purple forms. Although it is not clear where the difference between the two forms lies, their gross stereochemistry is probably the same.[35] These complexes are presumably close structural analogues of green $ReX_2(CO)_2(PR_3)_2$, since they show electronic absorption bands at 620 nm (green form) and 590 nm (purple form) which resemble the bands located between 650 and 690 nm in the related spectra of the dicarbonyl derivatives (Figure 3 and Table I). However, the difference in the number of carbonyl groups present in "isoelectronic" $ReCl_2(CO)_2(PR_3)_2$ and $[ReCl(CO)(PR_3)_4]^+$ does result in a significant difference in the XPS of these complexes. The appropriate Re $4f_{7/2}$ binding energies for $ReCl(CO)_3(P(n\text{-}$

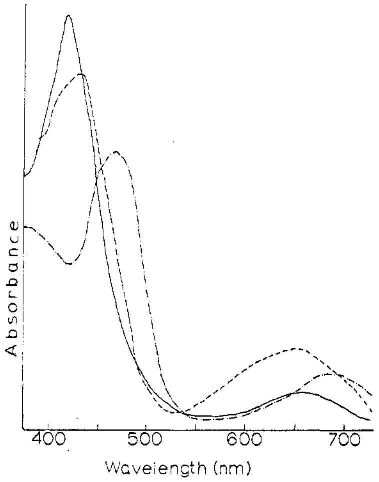


Figure 3. Electronic absorption spectrum of $ReCl_2(CO)_2(PEt_3)_2$ as a Nujol mull (—) and the diffuse reflectance spectra of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ (- - -) and $ReBr_2(CO)_2(P(n\text{-}Pr)_3)_2$ (–·–·–).

Table II. Comparison of the Re $4f_{7/2}$ Binding Energies for Carbonyl and Dinitrogen Complexes of Rhenium(I) and Rhenium(II)[a]

complex	Re $4f_{7/2}$, eV
$ReCl(CO)_3(P(n\text{-}Pr)_3)_2$	41.5
$ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$	41.6
$ReCl(CO)(PMe_2Ph)_4$	40.5[b]
$[ReCl(CO)(PMe_2Ph)_4]^+FeCl_4^-$	42.1[b]
$ReCl(N_2)(PMe_2Ph)_4$	40.5[b]
$[ReCl(N_2)(PMe_2Ph)_4]^+FeCl_4^-$	42.2[b]

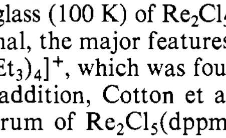
[a] Binding energies are internally referenced to a C 1s energy of 285.0 eV for the carbon atoms of the PR_3 ligands. [b] Data taken from ref 36.

$Pr)_3)_2$ and $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ are given in Table II, and these data are compared with that for carbonyl and dinitrogen complexes of the type $[ReCl(Y)(PR_3)_4]^{n+}$, where Y = CO or N_2 and n = 0 or 1.[36] In the case of the monocarbonyl and dinitrogen complexes, oxidation from Re(I) to Re(II) is not accompanied by any change in the ligand environment about the metal center, and accordingly, the increase in positive charge is reflected by a chemical shift of +1.5 eV. Since this same ligand arrangement is not present in the neutral dicarbonyl complex $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$, we would not necessarily expect this complex to possess the same Re 4f binding energies as $[ReCl(Y)(PMe_2Ph)_4]^+$. The reason that the Re 4f energies of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ and $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ are virtually identical is that a decrease in metal oxidation state is paralleled by an increase in the number of carbonyl groups bound to the metal. The increased electron-withdrawing effect of three vs. two CO groups compensates for the expected decrease in positive charge in going from Re(II) to Re(I). The result is the near coincidence of the metal binding energies of these complexes.

Preliminary studies of the substitution chemistry of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ show that it reacts with 2,2′-bipyridyl in refluxing toluene to afford the green monocarbonyl $ReCl_2(CO)(bpy)(P(n\text{-}Pr)_3)$. As with the monocarbonyl cations $[ReCl(CO)(PR_3)_4]^+$ described by Chatt et al.,[25b] this complex has its $\nu(CO)$ mode at a much lower frequency (1835 cm^{-1}) than in the parent neutral dicarbonyl complex $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$. This shift is consistent with the displacement of CO and $P(n\text{-}Pr)_3$ by 2,2′-bipyridyl, a ligand which possesses less net back-acceptor capability. The electronic absorption spectrum of $ReCl_2(CO)(bpy)(P(n\text{-}Pr)_3)$ (ν_{max} at 645 nm) resembles that of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$, while the XPS of $ReCl_2(CO)(bpy)(P(n\text{-}Pr)_3)$ shows Re 4f binding energies which are a little lower (Table I) than those of $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$, as a result of loss of one of the π-back-bonding CO ligands.

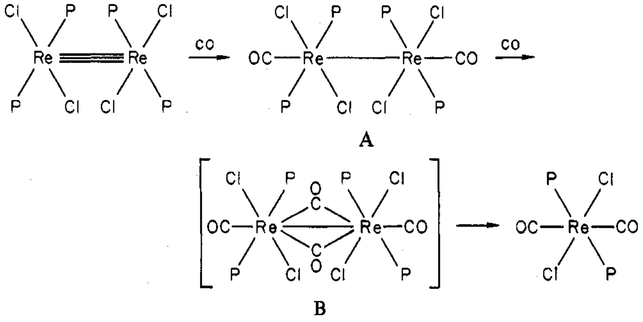
Just as the addition of tri-n-propylphosphine to $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$ leads to its rapid reduction to $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ (Figure 2), so 1,2-bis(diphenylphosphino)ethane in refluxing ethanol affords the white rhenium(I) complex $ReCl(CO)_2(dppe)_2$. Although a species of this same stoichiometry has previously been reported by Freni et al.[37] and proposed to have the ionic structure *cis*-$[Re(CO)_2(dppe)_2]^+Cl^-$, the complex prepared in the present study forms nonconducting solutions in nitromethane and nitrobenzene and has an infrared spectrum (Nujol mull) which is quite different ($\nu(CO)$ at 1837 and 1795 cm^{-1}) from that reported by Freni et al.[37] ($\nu(CO)$ at 1945 and 1888 cm^{-1} for a Nujol mull). These two complexes are apparently structural isomers and our sample may possess a six-coordinate structure (18-electron system) containing one of the dppe ligands bound in a monodentate fashion. A seven-coordinate structure (20-electron system) containing two dppe chelate rings seems less likely. Further work is planned in order to more fully characterize this complex, but these studies are at present hindered by the very low yields in which it has been obtained.

Preparation and Characterization of $Re_2Cl_5(PR_3)_3$ (R = Et or n-Pr). While complexes of the type $Re_2Cl_5(PRPh_2)_3$, where R = Me or Et, can be prepared by the direct reaction of $(Bu_4N)_2Re_2Cl_8$ with the appropriate phosphine,[13] the related derivatives with triethyl- and tri-n-propylphosphines cannot be so prepared since further reduction to $Re_2Cl_4(PR_3)_4$ occurs very rapidly.[13] As a result of the present study, we have found that the reaction of $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ in refluxing ethanol yields a mixture of $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ and $ReCl(CO)_3(P(n\text{-}Pr)_3)_2$ which can easily be separated. This dimer, and its triethylphosphine analogue, can also be isolated from the reaction between $Re_2Cl_4(PR_3)_4$ and CO in refluxing ethanol or toluene. $Re_2Cl_5(PR_3)_3$, where R = Et or n-Pr, are soluble in ethanol, toluene, acetone, and chloroform and slightly soluble in pentane. The $\nu(Re\text{–}Cl)$ modes (Table I) are comparable with those of the previously characterized derivatives $Re_2Cl_5(PRPh_2)_3$, where R = Me or Et,[13] and their electronic absorption spectra possess the characteristic intense broad absorption band centered at about 1400 nm (Table I) which is shown by other species containing a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic configuration[10d,13,38] and which may be assigned[10d] to a $\delta \rightarrow \delta^*$ transition. Accordingly, they presumably have the eclipsed structure[13]



The solid-state room-temperature ESR spectrum of $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ is very broad and asymmetric. The midpoint between the band minimum and maximum gives a g value of 2.3–2.4. As observed for the paramagnetic dicarbonyl $ReCl_2(CO)_2(P(n\text{-}Pr)_3)_2$, the signal is skewed to lower (<2) g values. An ethanol glass (100 K) of $Re_2Cl_5(P(n\text{-}Pr)_3)_3$ displays a complex ESR signal, the major features of which resemble those of $[Re_2Cl_4(PEt_3)_4]^+$, which was found[27] to have $g_{\parallel} < 2$ and $g_{\perp} \sim 2.2$. In addition, Cotton et al.[39] report that the X-band ESR spectrum of $Re_2Cl_5(dppm)_2$, where dppm = bis(diphenylphosphino)methane, is likewise broad and complex. The similarity of the ESR spectrum of $Re_2Cl_5(PR_3)_3$ with those of $[Re_2Cl_4(PEt_3)_4]^+$ and $Re_2Cl_5(dppm)_2$ indicates that in $Re_2Cl_5(PR_3)_3$ the unpaired electron is coupled to two Re nuclei each with spin $^5/_2$.

Relationship between the Reactivities of Rhenium Dimers Containing Metal–Metal Triple and Quadruple Bonds. Most reactions of the octahalodirhenate(III) anions, species which possess a Re–Re quadruple bond and a $(\sigma)^2(\pi)^4(\delta)^2$ ground state electronic configuration,[2,3] occur with the retention of the metal–metal bond although under certain circumstances this bond may break, as in its photochemical cleavage[40] upon ultraviolet irradiation of acetonitrile solutions of $(Bu_4N)_2Re_2Cl_8$. One type of interaction between $Re_2X_8^{2-}$ (or $Re_2X_6(PR_3)_2$) and various ligands, which might so weaken the Re–Re bond that it eventually dissociates, is that involving a nonsterically hindered π-acceptor ligand such as CO. This type of ligand may compete with the electrons used in the Re–Re π bonding (d_{xz}–d_{xz} and d_{yz}–d_{yz} overlaps)[2] thereby weakening the metal–metal bonding. However, we find that no such reaction occurs when $Re_2Cl_6(P(n\text{-}Pr)_3)_2$ is treated with CO in refluxing ethanol; neither does such a reaction occur between CO and the molybdenum(II) dimers $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(dppm)_2$, where dppm = bis(diphenylphosphino)methane, in dichloromethane.[41] In contrast to this situation, the rhenium(II) dimers, which possess the same molecular structures as their molybdenum(II) analogues but different electronic structures (i.e., triple vs. quadruple M–M bonds), react very rapidly with CO to produce $ReX_2(CO)_2(PR_3)_2$. This difference in reactivity is probably a consequence of differences in the electronic structure of the M_2^{n+} units and is not associated directly with variations in the ligand sets since isoelectronic $Re_2Cl_6(PR_3)_2$ and $Mo_2Cl_4(PR_3)_4$ have different combinations of Cl^- and PR_3 ligands, yet neither reacts with CO. It is possible that in $Re_2X_4(PR_3)_4$, overlap between the antibonding orbitals of π symmetry on CO and the metal-based π-bonding molecular orbitals is now more favored compared to the situation with $Re_2Cl_6(PR_3)_2$ and $Mo_2Cl_4(PR_3)_2$, thereby leading to an intermediate such as $Re_2Cl_4(P(n\text{-}Pr)_3)_4(CO)_2$ (A) which contains terminal CO groups collinear with the Re–Re bond. The coordination of these π-acceptor CO ligands may so weaken the Re–Re bond that the metal centers become susceptible to further nucleophilic attack by CO to form a second intermediate B, containing both terminal and bridging CO groups. B would be an 18-electron metal–metal bonded dimer, but severe steric crowding about the eight-coordinate metal atoms would likely favor its conversion to the dicarbonyl monomer.



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Registry No. I, 66900-38-7; II, 66841-03-0; III, 66841-02-9; IV, 61863-65-8; V, 66841-01-8; VI, 66841-00-7; VII, 61840-79-7; VIII, 61840-74-2; IX, 66808-73-9; X, 66826-66-2; XI, 66808-72-8; $Re_2Cl_4(P(n\text{-}Pr)_3)_4$, 55400-08-3; $Re_2Cl_6(P(n\text{-}Pr)_3)_2$, 41021-44-7; *trans*-$ReCl_4(P(n\text{-}Pr)_3)_2$, 66808-71-7; $Re_2Br_4(P(n\text{-}Pr)_3)_4$, 58298-33-2; $Re_2Cl_4(PEt_3)_4$, 55400-06-1; $[(n\text{-}Pr)_3PCl]^+[ReCl_5(P(n\text{-}Pr)_3)]^-$, 66808-70-6; $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$, 14023-10-0.

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