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The Reactions of Carbon Monoxide with the Series of Dirhenium Species $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$ (n = 0, 1, 2) Possessing Rhenium–Rhenium Bond Orders of 4, 3.5 and 3

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The complexes $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_n$, where n = 0, 1 or 2, which possess Re–Re multiple bonds of orders 3, 3.5 and 4, respectively, react with carbon monoxide in 2-methoxyethanol to afford the reductive cleavage product $ReCl(CO)_3(PMe_2Ph)_2$ in high yield. In other solvents (ethanol and toluene), these reactions are complicated by competing side reactions which can result in redox chemistry at the dirhenium units without the incorporation of CO into the products. The reactions in ethanol and toluene lead to the formation of $Re_2Cl_5(PMe_2Ph)_3$, $Re_2Cl_6(PMe_2Ph)_2$, trans-*$ReCl_4(PMe_2Ph)_2$, $ReCl(CO)_2(PMe_2Ph)_3$ and/or $ReCl_3(CO)(PMe_2Ph)_3$, in addition to $ReCl(CO)_3(PMe_2Ph)_2$, depending upon the reaction conditions. The electrochemical properties of the carbonyl containing products $ReCl(CO)_2(PMe_2Ph)_3$, $ReCl(CO)_3(PMe_2Ph)_2$ and $ReCl_3(CO)(PMe_2Ph)_3$, as well as those of the previously described rhenium(II) dicarbonyl complex $ReCl_2(CO)_2(P\text{-}n\text{-}Pr_3)_2$, have been studied using the cyclic voltammetry technique.*

Introduction

The reactivity of dinuclear metal centers containing metal–metal multiple bonds with π-acceptor ligands is well-documented [1, 2]. The resulting cleavage reactions often provide a route to monomeric products not available from simple substitution reactions of parent mononuclear complexes. An interesting example is the isolation of the paramagnetic complexes $ReX_2(CO)_2(PR_3)_2$, possessing the relatively rare mononuclear Re(II) oxidation state, from the reactions of the triply bonded dirhenium(II) species $Re_2X_4(PR_3)_4$ (X = Cl, Br; R = Et, n-Pr) with carbon monoxide [2a]. Other products of these surprisingly complex reactions are the cleavage products $ReCl(CO)_3(PR_3)_2$ and $ReCl_4(PR_3)_2$ and complexes resulting from oxidation of the Re_2^{4+} core, *viz.*, $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_6(PR_3)_2$. No evidence was obtained in this study [2a] to support the formation of stable carbonyl derivatives in which the Re–Re bond remains intact.

As a logical development of this work, we have investigated the reactions of the series of complexes $Re_2Cl_4(PMe_2Ph)_4$, $[Re_2Cl_4(PMe_2Ph)_4]PF_6$ and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ with carbon monoxide. These molecules, which we have recently isolated and structurally characterized [3], possess bond orders of 3, 3.5, and 4, the oxidations being achieved by sequential loss of electrons from the δ* molecular orbital of $Re_2Cl_4(PMe_2Ph)_4$. The purpose of our investigation was two-fold. First, we were interested in comparing the results with those reported in the earlier study in which the $Re_2Cl_4(PR_3)_4$ starting materials contained the trialkyl phosphines PEt_3 or $P\text{-}n\text{-}Pr_3$ [3], as well as noting any reactivity differences which might exist between members of the series in which the Re–Re bond order varies from 3 to 3.5 to 4. Secondly, we were interested in exploring by electrochemistry the redox chemistry of the carbonyl products so obtained, with the objective of assessing what effect replacing a phosphine ligand with a carbon monoxide ligand would have on the properties of the metal center.

Experimental

Starting Materials

The complexes $Re_2Cl_4(PMe_2Ph)_4$, $[Re_2Cl_4(PMe_2Ph)_4]PF_6$ and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ were prepared as described previously [3], the neutral species being oxidized to the monocation and dication by the use of nitrosonium hexafluorophosphate. The complex *trans*-$ReCl_2(CO)_2(P\text{-}n\text{-}Pr_3)_2$ was prepared by the action of carbon monoxide upon $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ [2(a)]. Commercial reagents and solvents were used as received and stored over molecular sieves. Dimethylphenylphosphine was obtained from Strem Chemicals, Inc. Matheson Gas Products supplied the carbon monoxide which was dried before use.

Reaction Procedures

All reactions were carried out in a nitrogen atmosphere, and solvents were deoxygenated by

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purging with N_2 gas for several hours prior to use. The carbon monoxide reactions were performed at atmospheric pressure unless otherwise specified.

For product separation by column chromatography, the column was packed under a N_2 atmosphere using solvents which had been purged thoroughly with N_2.

A. Reactions of $Re_2Cl_4(PMe_2Ph)_4$ with Carbon Monoxide in Various Solvents

(i) Ethanol

$Re_2Cl_4(PMe_2Ph)_4$ (0.20 g, 0. 19 mmol) was added to 30 ml of dry ethanol, and the resulting suspension was refluxed. After CO had been bubbled through the reaction mixture for about 5 h, the solution was a yellow-green color with an insoluble green precipitate. The solid was filtered off and washed with toluene followed by diethyl ether to yield 0.15 g of recovered starting material. The yellow-green filtrate was evaporated to dryness on a rotary evaporator and the resulting light green residue of $Re_2Cl_5(PMe_2Ph)_3$ was collected, washed with diethyl ether and dried in vacuo; yield, 0.04 g (22%). This complex was identified by IR spectroscopy and cyclic voltammetry as being similar to other phosphine complexes of the type $Re_2Cl_5(PR_3)_3$ [4]. Cyclic voltammetric measurements on a 0.2 *M* tetra-n-butyl ammonium hexafluorophosphate-dichloromethane solution of this complex showed that it possesses a one-electron oxidation at $E_{1/2} = +0.46$ V and a one-electron reduction at $E_{1/2} = -0.65$ V *vs.* SCE. The direct reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with PMe_2Ph in MeOH–HCl at room temperature gives, as determined by electrochemistry, a mixture of $Re_2Cl_6(PMe_2Ph)_2$ and the form of $Re_2Cl_5(PMe_2Ph)_3$ that was obtained in the reaction between $Re_2Cl_4(PMe_2Ph)_4$ and CO in ethanol.

(ii) Toluene

(a) Short Reaction Time: $Re_2Cl_4(PMe_2Ph)_4$ (0.33 g, 0.31 mmol) was suspended in 60 ml of dry toluene and the refluxing solution was treated with CO for 4 h. The red-gold colored solution was stripped to dryness under vacuum and the resulting residue was washed with 5 ml of hexane–toluene (1:1). The residue dissolved partially to yield an orange-yellow solution and a blue-green solid, $Re_2Cl_5(PMe_2Ph)_3$, which was collected, washed with additional toluene then diethyl ether and dried *in vacuo*; yield 0.18 g (60%). *Anal.* Calcd for $C_{24}H_{33}Cl_5P_3Re_2$: C, 29.90; H, 3.45. Found: C, 29.86; H, 3.58.

This complex possessed the expected paramagnetism ($\mu_{eff} = 1.55$ B.M. by the Evans Method) and voltammetric half wave potentials at +0.46 V and −0.65 V *vs.* SCE as present in the CV of the samples isolated from ethanol (see A(i)). However, these electrochemical features were accompanied by an additional oxidation at +0.38 V and an additional reduction at −0.93 V. The currents associated with these four couples are very similar. We believe that the product isolated from toluene may be a mixture of two isomers of $Re_2Cl_5(PMe_2Ph)_3$. If so, then our attempts to interconvert these isomers or separate them were unsuccessful. However, an examination of the low temperature ESR spectrum of the toluene product (CH_2Cl_2 glass at −160 °C) showed that while it exhibits many of the same features as the sample of $Re_2Cl_5(PMe_2Ph)_3$ obtained from the octachlorodirhenate(III) reaction, the pattern is more complex and appears to be an overlap of two signals. The complex ESR signal is centered at ~2.8 kG, and resembles very closely that previously reported for other compounds of this type [2a, 4].

The orange-yellow hexane–toluene filtrate that remained following the isolation of $Re_2Cl_5(PMe_2Ph)_3$ was placed on a 20 × 1.9 cm column made from 60–200 mesh silica gel and hexane–toluene (1:1). The column was initially eluted with 150 ml of hexane–toluene (1:1) followed by 100 ml of toluene but no significant quantity of product was obtained. The column was next eluted with 150 ml of dichloromethane, and the resulting yellow-green solution was collected. Evaporation of the solution to a low volume (~5 ml) and subsequent chilling to 0 °C for 12 h yielded a bright yellow crystalline product, $ReCl(CO)_2(PMe_2Ph)_3$; yield, 0.08 g (19%). *Anal.* Calcd for $C_{26}H_{33}ClO_2P_3Re$: C, 45.15; H, 4.81. Found: C, 44.73; H, 5.09. ^1H NMR and IR spectral data were consistent with those previously reported in the literature for the isomer with a *cis*-arrangement of CO ligands and a meridonal arrangement of phosphine ligands [5, 6].

Finally, the column was eluted with 150 ml of ethanol, and a colorless solution was collected. Evaporation of the solvent yielded the white solid *trans*-$ReCl(CO)_3(PMe_2Ph)_2$, 0.06 g (16%). The complex was characterized by a comparison of its IR and ^1H NMR spectra to those reported previously [5, 6].

(b) Intermediate Reaction Time. $Re_2Cl_4(PMe_2Ph)_4$ (0.31 g, 0.29 mmol) was added to 60 ml of dry toluene and CO was bubbled through the refluxing solution for 12 h. The resulting solution was green, and a quantity of the blue-green complex $Re_2Cl_5(PMe_2Ph)_3$ was also present; the latter was isolated and characterized as described in A(ii)(a). Yield, 0.09 g (32%).

The green reaction filtrate solution was reduced in volume to approximately 20 ml and the resulting bright green solid was filtered off, washed with diethyl ether and dried *in vacuo*. The IR spectrum and cyclic voltammogram of this product were consistent with it being $Re_2Cl_6(PMe_2Ph)_2$ [4]; yield, 0.06 g (24%).

The remaining filtrate was evaporated to dryness to yield an orange-yellow residue. This was dissolved in 5 ml of hexane–toluene (1:1) and chromatographed in the usual way (see A(ii)(a)). The column was first eluted with 150 ml hexane-toluene (1:1), the evaporation of which yielded no products. Elution with 100 ml of toluene gave a pale purple solution which yielded a bright purple residue upon evaporation. This was dissolved in 10 ml of methanol and the solution chilled to 0 °C for 24 h. A crop of white needles admixed with a purple precipitate was filtered off and dried. The cyclic voltammogram of this mixture showed it to be composed of *trans*-$ReCl(CO)_3(PMe_2Ph)_2$, fully characterized in A(ii)(a), and *trans*-$ReCl_4(PMe_2Ph)_2$ ($E_{1/2}$(red) = −0.15 V *vs.* SCE) [4].

The column was finally eluted with 50 ml of chloroform resulting in the collection of a bright green band. Reduction of the volume and addition of diethyl ether afforded a small quantity of the yellow-green crystalline complex $ReCl_3(CO)(PMe_2Ph)_3$; yield, 0.08 g (19%). *Anal.* Calcd for $C_{25}H_{33}Cl_3OP_3$-Re: C, 40.88; H, 4.53. Found: C, 39.36; H, 4.49. The ^1H NMR data indicated the presence of lattice diehtyl ether. The spectroscopic properties of this product as well as its melting point (201–211 °C) confirmed its identity [5].

(c) Long Reaction Time. $Re_2Cl_4(PMe_2Ph)_4$ (0.25 g, 0.23 mmol) was suspended in 50 ml of dry toluene and refluxed under a constant flush of CO for 24 h. The solution was cooled to room temperature, and a quantity of blue-green $Re_2Cl_5(PMe_2Ph)_3$ was filtered off, washed with diethyl ether and dried *in vacuo*; yield, 0.12 g (53%). Identification was based upon its characteristic spectroscopic and electrochemical properties.

The filtrate was evaporated to dryness, to give a pale green residue that was dissolved in 5 ml of hexane–toluene (1:1) and chromatographed on silica gel as described in A(ii)(a). Elution with toluene (80 ml) gave *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ (0.03 g, 11%) while a yellow band eluted using 200 ml of chloroform yielded $ReCl_3(CO)(PMe_2Ph)_3$ (0.12 g, 35%). Both complexes were characterized on the basis of their spectroscopic and electrochemical properties.

(iii) 2-Methoxyethanol

$Re_2Cl_4(PMe_2Ph)_4$ (0.52 g, 0.49 mmol) was added to 40 ml of dry 2-methoxyethanol and CO was bubbled through the boiling solution for 4 h. The solvent was distilled under reduced pressure from the almost colorless solution to give a pale blue oil. Dissolution of the oil in 2 ml of hot 2-methoxyethanol followed by chilling to 0 °C for 5 h afforded a crop of white crystals of *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ that were washed with a small quantity of cold ethanol and dried *in vacuo*; yield, 0.08 g. The colorless ethanol washing was reduced in volume to ~2 ml and chilled to 0 °C. A further crop of white crystals were collected; combined yield 0.27 g (48%). The identity of this complex was confirmed by its spectroscopic [5, 6] and electrochemical properties.

B. Reaction of $Re_2Cl_4(PMe_2Ph)_4$ with Carbon Monoxide Under Pressure

$Re_2Cl_4(PMe_2Ph)_4$ (0.20 g, 0.19 mmol) was reacted with CO in 30 ml of refluxing toluene for 5 h under the pressure afforded by a mercury bubbler system [7]. A work-up procedure analogous to that described in A(ii)(c) afforded the products $Re_2Cl_5(PMe_2Ph)_3$ (0.10 g, 54%), *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ (0.03 g, 14%), and $Re_3(CO)(PMe_2Ph)_3$ (0.09 g, 32%).

C. Reaction of $[Re_2Cl_4(PMe_2Ph)_4]PF_6$ with Carbon Monoxide in Various Solvents

(i) Ethanol

$[Re_2Cl_4(PMe_2Ph)_4]PF_6$ (0.20 g, 0.16 mmol) was refluxed in 50 ml of ethanol for 10 h under a stream of CO. At the end of this time, no reaction had occurred, and only starting material was recovered.

(ii) Toluene

Reaction in refluxing toluene for up to 15 h failed to proceed to any significant extent.

(iii) 2-Methoxyethanol

$[Re_2Cl_4(PMe_2Ph)_4]PF_6$ (0.15 g, 0.12 mmol) was added to 10 ml of 2-methoxyethanol, and CO was bubbled through the refluxing solution for 3 h. The resulting pale blue solution was stripped to dryness under reduced pressure to give a blue oil. The oil was dissolved in 2 ml of methanol and chilled to 0 °C for 12 h, by which time a crop of white crystals had deposited. These were collected, washed with a small amount of cold methanol and dried *in vacuo*. Characterization based on cyclic voltammetry and IR spectroscopy showed the product to be *trans*-$ReCl(CO)_3(PMe_2Ph)_2$; yield 0.13 g (90%).

D. Reactions of $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ with Carbon Monoxide in Various Solvents

(i) Ethanol

$[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ (0.10 g, 0.07 mmol) was refluxed in 20 ml of ethanol under a stream of CO for 12 h. The resulting solution was green with an olive green precipitate of $[Re_2Cl_4(PMe_2Ph)_4]PF_6$. Reduction of the volume to 5 ml induced further precipitation of the solid which was filtered off, washed with diethyl ether and dried *in vacuo*; yield, 0.08 g.

(ii) Toluene

(a) Short Reaction Time. A reaction procedure analogous to that described in D(i) with a reaction time of 5 h, resulted only in the isolation of the reduced species $[Re_2Cl_4(PMe_2Ph)_4]PF_6$.

(b) Intermediate Reaction Time. A quantity of $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ (0.54 g, 0.40 mmol) was suspended in 50 ml of dry toluene and refluxed under CO for 12 h. The resulting reaction mixture was stripped to dryness under reduced pressure to give a residue that appeared to be a mixture of green and purple materials. The residue dissolved partially in 10 ml of hexane–toluene (1:1) to leave an insoluble green solid that was shown by cyclic voltammetry to be an approximately 50:50 mixture of $[Re_2Cl_4(PMe_2Ph)_4]PF_6$ and $Re_2Cl_6(PMe_2Ph)_2$.

The orange-red solution was chromatographed using the procedure described in A(ii)(a) to give *trans*-$ReCl_4(PMe_2Ph)_2$ (0.04 g, 6%) upon elution with toluene, and $ReCl_3(CO)(PMe_2Ph)_3$ (0.08 g, 14%) using chloroform as eluent.

(c) Long Reaction Time. $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ (0.28 g, 0.21 mmol) was added to 40 ml of dry toluene and carbon monoxide was bubbled through the refluxing solution for 24 h. At the end of this period, a bright green solid, identified by cyclic voltammetry as $Re_2Cl_6(PMe_2Ph)_2$, was filtered off from the reddish-gold filtrate. Reduction in the volume of the filtrate by one-third resulted in the precipitation of more of this product; combined yield 0.04 g (27%). Further evaporation of the toluene filtrate to about 10 ml afforded a green-grey solid (0.08 g), which was shown to be a mixture of $Re_2Cl_5(PMe_2Ph)_3$ and $[Re_2Cl_4(PMe_2Ph)_4]PF_6$.

The reaction filtrate which remained at this time, was reduced to dryness on a rotary evaporator. The residue was dissolved in ethyl acetate-petroleum ether (1:4) and placed at the top of an alumina column packed in the same solvent mixture. Elution with 100 ml of ethyl acetate–petroleum ether (1:10) gave a colorless solution which yielded a crop of white crystalline *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ upon reduction in volume to approximately 1 ml. The product was collected, washed with small amounts of cold diethyl ether and dried *in vacuo*; yield 0.04 (16%). Further elution of the column with 75 ml of ethyl acetate–petroleum ether (1:2) gave a yellow band which yielded yellow $ReCl_3(CO)(PMe_2Ph)_3$ upon evaporation; yield 0.06 g (19%). Finally the column was treated with ethyl acetate, to give a trace of the purple complex *trans*-$ReCl_4(PMe_2Ph)_2$, identified by cyclic voltammetry [4].

(iii) 2-Methoxyethanol

A quantity of $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ (0.27 g, 0.20 mmol) was suspended in 5 ml of 2-methoxyethanol and CO was bubbled through the refluxing solution for 4 h. The pale blue reaction solution was then reduced to dryness under vacuum. The resulting oil was washed repeatedly with petroleum ether (total volume 50 ml) and the extract was reduced to ~2 ml by which time the white product $ReCl(CO)_3(PMe_2Ph)_2$ had precipitated; yield 0.15 g (64%). *Anal.* Calcd for $C_{19}H_{22}ClO_3P_2Re$: C, 39.23; H, 3.81. Found: C, 39.04; H, 3.90. ^1H NMR and IR spectroscopies showed that the product was a mixture of the so-called *trans*-isomer (containing *trans*-phosphine ligands and a meridonal disposition of CO ligands), and the isomer in which the CO ligands are in a facial arrangement [5].

Physical Measurements

Infrared spectra of Nujol mulls were recorded in the region 4000–400 cm^{-1} between KBr plates on a Beckman IR-12 spectrophotometer. Solution IR spectra were measured in dichloromethane or chloroform in the 2300–1700 cm^{-1} region. Nuclear magnetic resonance spectra were recorded using a Perkin-Elmer R-32 spectrometer. Resonances were referenced internally to the impurity in the deuterated solvent used. Electrochemical measurements were made in dichloromethane containing 0.2 *M* tetra-n-butyl ammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values were determined as $(E_{p,a} + E_{p,c})/2$ and are referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature. Voltammetric experiments were performed using a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. A determination of the room temperature magnetic moment of a dichloromethane solution of $Re_2Cl_5(PMe_2Ph)_3$ was done by the Evans Method [8, 9], using a PE-R32 spectrometer. The X-band ESR spectra of $Re_2Cl_5(PMe_2Ph)_3$ were recorded on toluene–dichloromethane glasses (0.6 mol fraction of toluene) at -160 °C using a Varian E-109 spectrometer.

Analytical Procedures

Elemental microanalyses were performed by Dr. H. D. Lee and Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

Carbonylation of $Re_2Cl_4(PMe_2Ph)_4$

The reactions between carbon monoxide and the neutral complex in refluxing toluene are extremely complex, leading to the formation of mixtures of $Re_2Cl_5(PMe_2Ph)_3$, $Re_2Cl_6(PMe_2Ph)_2$, *trans*-$ReCl_4(PMe_2Ph)_2$, $ReCl(CO)_2(PMe_2Ph)_3$, *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ and $ReCl_3(CO)(PMe_2Ph)_3$. The product distribution depends to a large extent upon the reaction time; the complex $ReCl(CO)_2(PMe_2Ph)_3$, for example, is isolated provided the reaction times do not exceed 4–5 hours. The complexity of these reactions and the types of complexes isolated resemble those reported previously [2(a)] for the carbonylation of $Re_2Cl_4(PR_3)_4$, where R = Et or n-Pr. However, they differ in two important respects, namely, our failure to isolate a dicarbonyl derivative of rhenium(II), *viz.*, $ReCl_2(CO)_2(PMe_2Ph)_2$, and the isolation of two products of the reductive carbonylation of $Re_2Cl_4(PMe_2Ph)_4$, *i.e.*, $ReCl(CO)_2(PMe_2Ph)_3$ and *trans*-$ReCl(CO)_3(PMe_2Ph)_2$, rather than only $ReCl(CO)_3(PR_3)_2$ in the case of R = Et or n-Pr [2(a)]. While we did not isolate $ReCl_2(CO)_2(PMe_2Ph)_2$ it is probable that it is formed as the initial non-reductive cleavage product. Since we have shown that for $ReCl_2(CO)_2(PR_3)_2$ (R = Et or n-Pr) there are a variety of pathways by which these complexes decompose to give $ReCl(CO)_3(PR_3)_2$ and *trans*-$ReCl_4(PR_3)_2$, it seems more than likely that $ReCl_2(CO)_2(PMe_2Ph)_2$ is formed but decomposes quickly, primarily to the rhenium(I) carbonyl species.

The non-carbonyl containing products $Re_2Cl_5(PMe_2Ph)_3$ and $Re_2Cl_6(PMe_2Ph)_2$ are formed by routes which do not involve reaction with CO. Specifically in the case of $Re_2Cl_5(PMe_2Ph)_3$, this occurs by oxidation of $Re_2Cl_4(PMe_2Ph)_4$ to $[Re_2Cl_4(PMe_2Ph)_4]^+$ (this is easily accomplished by reaction with adventitious oxygen, for example [4]), and subsequent reaction of the monocation with any chloride it can scavenge. Note that in the case of the reaction of $Re_2Cl_4(PMe_2Ph)_4$ with CO in ethanol, the only product isolated is $Re_2Cl_5(PMe_2Ph)_3$. This same reaction course ensues in the absence of CO and provides a convenient method of preparing this complex. Similar behavior has been observed in the case of the conversion of $Re_2Cl_4(P\text{-n-}Pr_3)_4$ to $Re_2Cl_5(P\text{-n-}Pr_3)_3$ [2(a)].

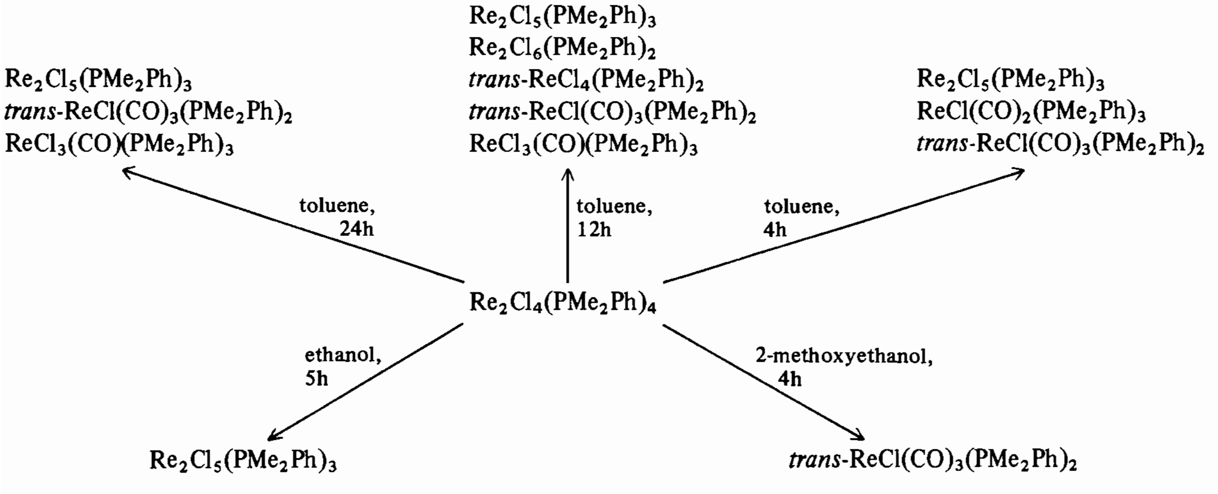
The rhenium(III)–carbonyl derivative $ReCl_3(CO)(PMe_2Ph)_3$ was formed in the reaction between $Re_2Cl_4(PMe_2Ph)_4$ and CO in toluene when reaction times of 12–24 hours were used, the yield increasing as the reaction time was increased. While we are uncertain of the mechanism by which this complex is formed it is noteworthy that analogous products were not obtained in the case of the trialkylphosphine derivatives [2(a)].

Of the preceding reactions, only those which resulted in the formation of $Re_2Cl_5(PMe_2Ph)_3$ (with ethanol or toluene as reaction solvents) or $ReCl_3(CO)(PMe_2Ph)_3$ (toluene as solvent) constitute useful synthetic procedures. While *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ was isolated under a variety of conditions when toluene was used as the solvent, its yield was quite low. However, with 2-methoxyethanol as the reaction solvent and quite short reaction times (*ca.* 4 hours), *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ was found to be the major product (*ca.* 50%) from the reaction between $Re_2Cl_4(PMe_2Ph)_4$ and carbon monoxide. In probing the reasons for such enhanced reactivity and selectivity, a control reaction was carried out by refluxing $Re_2Cl_4(PMe_2Ph)_4$ in 2-methoxyethanol in the absence of carbon monoxide. This was done to ensure that a CO moiety was not being abstracted from the solvent. Since no reaction was observed, it is presumed that the higher boiling point of 2-methoxyethanol as well as the increased solubility of the complex $Re_2Cl_4(PMe_2Ph)_4$ in this solvent are factors which favor the reductive cleavage reaction proceeding quickly to completion without competing side reactions (*i.e.* those leading to the formation of $Re_2Cl_5(PMe_2Ph)_3$, $Re_2Cl_6(PMe_2Ph)_2$, *trans*-$ReCl_4(PMe_2Ph)_2$ and $ReCl_3(CO)(PMe_2Ph)_2$).

A summary of the products obtained from the reaction of $Re_2Cl_4(PMe_2Ph)_4$ is shown in Scheme I.

Carbonylation of $[Re_2Cl_4(PMe_2Ph)_4]PF_6$

The reactivity of the monocation with carbon monoxide is much lower than that of the analogous neutral and dicationic complexes, a result which may be explained in terms of its extreme insolubility in the solvents of choice. Thus no reactivity was observed in ethanol or toluene. However, the isolation



Scheme I. Product distributions for the reactions of $Re_2Cl_4(PMe_2Ph)_4$ with CO.

of a nearly quantitative yield of *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ was achieved in 2-methoxyethanol.

Carbonylation of [$Re_2Cl_4(PMe_2Ph)_4$](PF_6)$_2$

Certain reaction conditions (reflux in ethanol or for relatively short periods in toluene) favor the reduction of the dication to the relatively unreactive monocation, a reaction course which is not surprising in view of the ease with which this one-electron reduction has been demonstrated to occur electrochemically [3]. Longer reaction times afforded the same assortment of carbonyl containing complexes (except $ReCl(CO)_2(PMe_2Ph)_3$) and non-carbonyl species ($Re_2Cl_6(PMe_2Ph)_2$, $Re_2Cl_5(PMe_2Ph)_3$ and *trans*-$ReCl_4(PMe_2Ph)_2$ that are formed from $Re_2Cl_4(PMe_2Ph)_4$ (see Scheme I). Once again, with 2-methoxyethanol as the solvent, the complex $ReCl(CO)_3(PMe_2Ph)_2$ was the principal reaction product. However, in contrast to the other reactions in which *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ (*i.e.* a *trans*-disposition of phosphine ligands and a meridonal arrangement of CO ligands) is the only isomer to be isolated, the conversion of [$Re_2Cl_4(PMe_2Ph)_4$](PF_6)$_2$ to $ReCl(CO)_3(PMe_2Ph)_2$ gives this isomer admixed with one in which the CO ligands are in a facial arrangement [5].

Electrochemical Properties of Carbonyl Complexes of Rhenium

Surprisingly, there is a dearth of data dealing with the electrochemical properties of carbonyl containing complexes of rhenium(I). Following our recent studies delineating the electrochemical behavior of rhenium(I) isocyanide complexes containing the [$Re(CNR)_6$]$^+$, [$Re(CNAr)_6$]$^+$ and [$Re(CNR)_4(PR_3)_2$]$^+$ cations (R = alkyl and Ar = aryl) [10–12], we have taken this opportunity to examine the related behavior of $ReCl(CO)_2(PMe_2Ph)_3$ and $ReCl(CO)_3(PMe_2Ph)_2$. The isocyanide complexes exhibit a reversible one-electron oxidation in the potential range +0.5 V to +1.2 V *vs.* SCE [10–12], and a similar process was found to characterize the carbonyl complexes as determined by the cyclic voltammetry (CV) technique. The cyclic voltammograms of 0.2 *M* tetra-n-butylammonium hexafluorophosphate–dichloromethane solutions of these complexes are shown in Fig. 1. The voltammetric half-wave potential for $ReCl(CO)_2(PMe_2Ph)_3$ *vs.* SCE is +0.82 V (see Fig. 1a). For sweep rates (ν) between 50 and 400 mV/s, the ratio $i_p/\nu^{1/2}$ was constant and $i_{p,a}/i_{p,c} \simeq 1$ in accord with diffusion control. The potential separation between anodic and cathodic peaks, ΔE_p, was 90 mV for a sweep rate of 200 mV/s. With our cell configuration [13], these properties are consistent with this being a reversible electron-transfer process. A second oxidation which is irreversible occurs at $E_{p,a} = +1.25$ V *vs.* SCE. Controlled potential electrolysis at +0.9 V showed that the first oxidation corresponds to a one-electron process although a CV of the resulting solution showed that some decomposition had occurred. For the *trans*-isomer of $ReCl(CO)_3(PMe_2Ph)_2$ (Fig. 1c), the corresponding redox process occurs at $E_{1/2} = +1.18$ V and also approaches electrochemical reversibility ($i_{p,a}/i_{p,c} \simeq 1$ and $\Delta E_p = 85$ mV/s at $\nu = 200$ mV/s), while the *fac*-isomer is characterized by $E_{p,a} = +1.46$ V (Fig. 1d), there being no perceptible current associated with the return reduction wave. The shift of the oxidation to more positive potentials upon changing from $ReCl(CO)_2(PMe_2Ph)_3$ to $ReCl(CO)_3(PMe_2Ph)_2$ reflects the effect on the metal center of replacing a σ-donating phosphine with a π-accepting carbon monoxide ligand. This leads to an increase in the positive charge at the metal center and a concomitant increase in the difficulty of oxidizing such species. This trend of increasing positive potentials with increase in the number of carbonyl ligands is further demonstrated in the case of $ReCl(CO)_4(PMe_2Ph)$ [14], the CV of which did not reveal an oxidation below +1.7 V *vs.* SCS (the limit of our measurements).

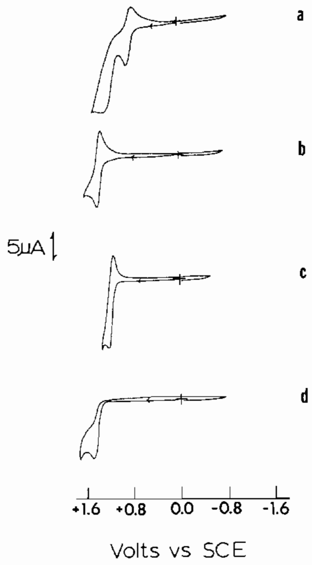


Fig. 1. Cyclic voltammograms (scan rate 200 mV/s at a Pt-bead electrode) in 0.2 *M* tetra-n-butylammonium hexafluorophosphate–dichloromethane: (a) $ReCl(CO)_2(PMe_2Ph)_3$; (b) $ReCl_3(CO)(PMe_2Ph)_3$; (c) *trans*-$ReCl(CO)_3(PMe_2Ph)_2$; (d) *fac*-$ReCl(CO)_3(PMe_2Ph)_2$.

The rhenium(II) dicarbonyl complex *trans*-$ReCl_2(CO)_2(P\text{-}n\text{-}Pr_3)_2$ is a 17-electron species [2a] and displayed the expected electrochemistry, namely, a one-electron reduction to the 18-electron monoanion [*trans*-$ReCl_2(CO)_2(P\text{-}n\text{-}Pr_3)_2$]$^-$ with $E_{1/2} = -0.99$ V *vs.* SCE, and a one-electron oxidation at $E_{1/2} \approx +0.80$ V *vs.* SCE. While the reduction appears to be reversible, there being no evidence for isomerization accompanying this electron-transfer [15], in the case of the oxidation the coupled waves have $i_{p,a}/i_{p,c}$ ratios of less then 1 at $\nu = 200$ mV/s, implying a lack of reversibility for this process on the CV time scale. Thus, following the oxidation at $E_{p,a} = +0.86$ V, the reverse scan shows the coupled reduction wave at +0.75 V together with a wave at ~+0.2 V that can be attributed to a chemical product that is formed following oxidation to the relatively unstable 16-electron cation $[ReCl_2(CO)_2(P\text{-}n\text{-}Pr_3)_2]^+$.

The rhenium(III) complex $ReCl_3(CO)(PMe_2Ph)_3$ exhibits a one-electron oxidation at $E_{1/2} = +1.38$ V *vs.* SCE (Fig. 1b). This process approaches reversibility and indicates that the 17-electron cation that is formed possess reasonable stability.

Conclusions

The reactions of carbon monoxide with the series of dirhenium complexes $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_n$ (n = 0, 1 or 2), possessing Re–Re bond orders of 3, 3.5 and 4, respectively, afford the rhenium(I) carbonyl complexes $ReCl(CO)_2(PMe_2Ph)_3$ or $ReCl(CO)_3(PMe_2Ph)_2$ as the principal products of the reductive cleavage of the metal–metal bonds. These pathways are complicated by the occurrence of competing side reactions (especially in ethanol and toluene) in which the dirhenium units undergo redox reactions (affording $Re_2Cl_5(PMe_2Ph)_3$ or $Re_2Cl_6(PMe_2Ph)_2$) without the incorporation of CO. The course of the reactions that lead to the rhenium(I) carbonyls, accords with the strong tendency of multiply bonded dimetal species to be cleaved by π-acceptor ligands [1, 16]. The reactions of CO with $Re_2Cl_6(PMe_2Ph)_2$, to produce $ReCl(CO)_4(PMe_2Ph)$ [14], and with $(n\text{-}Bu_4N)_2Re_2Cl_8$, which in acetonitrile affords $Re(CO)_5Cl$ and $[Re(CO)_2(NCCH_3)_4{}^+]_2[ReCl_6{}^{2-}]$ [17], show similarities to the results obtained in the present investigation and demonstrate the generality of these reductive cleavage reactions.

Acknowledgements

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14 A sample of $ReCl(CO)_4(PMe_2Ph)$ was prepared in 40% yield from the reaction of $Re_2Cl_6(PMe_2Ph)$ with CO in 2-methoxyethanol following reflux for 7 h. The sample was chromatographed on a Fluorosil column (100–200 mesh); elution with 1:1 petroleum ether–diethyl ether and subsequent work-up gave this complex as white crystals. Microanalytical data, and IR and ^1H NMR spectroscopy indicated that *trans*-$ReCl(CO)_3(PMe_2Ph)_2$ was present in small amounts as an impurity. *Anal.* Calcd. for $C_{12}H_{11}ClO_4PRe$: C, 30.55; H, 2.35. Found: C, 31.66; H, 2.54. The spectroscopic properties of $ReCl(CO)_4(PMe_2Ph)$ were in good agreement with similar data reported for samples of this complex prepared by an alternative procedure [6].

15 Isomerization accompanying the oxidation of the complexes $Mo(CO)_2(CNR)_2(PR_3)_2$ to their 17-electron cations is known to occur (see, K. A. Conner and R. A. Walton, *Organometallics, 2,* 169 (1983)). Note that these molybdenum species $[Mo(CO)_2(CNR)_2(PR_3)_2]^{0,+1}$ are isoelectronic with $[ReCl_2(CO)_2(PR_3)_2]^{-1,0}$.

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