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Preliminary communication

# COMPLEX HALIDES OF THE TRANSITION METALS. XXII.[1] CLEAVAGE OF THE RHENIUM-RHENIUM QUADRUPLE BOND OF $Re_2X_4(PR_3)_4$ BY CARBON MONOXIDE: THE ISOLATION AND CHARACTERIZATION OF RHENIUM(II) CARBONYL DERIVATIVES OF THE TYPE $ReX_2(CO)_2(PR_3)_2$

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## Summary

Reaction of the metal-metal bonded dimers $Re_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or $Pr^n$, with carbon monoxide provides a route to previously unknown paramagnetic rhenium(II) carbonyl derivatives of the type $ReX_2(CO)_2(PR_3)_2$.

Our recent isolation and characterization of the rhenium(II) complexes of the type $Re_2X_4(PR_3)_4$, where X = Cl or Br,[2-4] and the discovery that they may be reversibly oxidized to the rhenium(III) dimers $Re_2X_6(PR_3)_2$,[2] has led us to explore their reactivity towards carbon monoxide and other small molecules. We have found that reaction with carbon monoxide provides a route to the hitherto unknown rhenium(II) complexes $ReX_2(CO)_2(PR_3)_2$ and we now report preliminary details of our results.

The reaction between carbon monoxide and $Re_2X_4(PR_3)_4$, where X = Cl when R = Et or $Pr^n$ and X = Br when R = $Pr^n$, in refluxing ethanol or toluene is extremely

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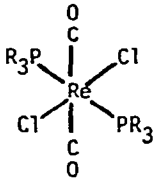
complex and leads to the formation of mixtures of $ReX_2(CO)_2(PR_3)_2$, $ReX(CO)_3(PR_3)_2$, $Re_2Cl_5(PR_3)_3$, $Re_2Cl_6(PR_3)_2$ and/or <u>trans</u>-$ReCl_4(PR_3)_2$. The product distribution depends both upon the choice of solvent and reaction time. Short reaction times (2 h or less) favor the formation of $ReX_2(CO)_2(PR_3)_2$, whereas prolonged reaction periods lead to conversion to $ReX(CO)_3(PR_3)_2$ and other non-carbonyl containing products.

The synthetic procedure which gave the highest yield of $ReX_2(CO)_2(PR_3)_2$ is as follows. About 0.7 g of $Re_2Cl_4(PPr^n_3)_4$ was added to 60 ml dry deoxygenated ethanol and carbon monoxide was bubbled through the refluxing reaction mixture for almost 2 h. The resulting bright yellow-green solution was cooled to room temperature and then evaporated to dryness. The solid residue was extracted into 20 ml hexane/toluene (1:1) and the mixture of products separated by column chromatography on silica gel (column size 20x1.9 cm). The column was eluted with hexane/toluene (1:1) to give bright green crystalline $ReCl_2(CO)_2(PPr^n_3)_2$ (20% yield and with chloroform to yield both $ReCl(CO)_3(PPr^n_3)_2$ (21% yield) and $Re_2Cl_5(PPr^n_3)_3$ (23% yield). Satisfactory microanalyses were obtained for all products.

The reaction between $Re_2Cl_4(PEt_3)_4$ and carbon monoxide in refluxing ethanol for 2.5 h proceeded in an analogous fashion to that described above to afford $ReCl_2(CO)_2(PEt_3)_2$, $ReCl(CO)_3(PEt_3)_2$ and $Re_2Cl_5(PEt_3)_3$, while the reaction involving $Re_2Br_4(PPr^n_3)_4$ produced a mixture of $ReBr_2(CO)_2(PPr^n_3)_2$ and $ReBr(CO)_3(PPr^n_3$ which could be separated by column chromatography.

We note that the reaction between $Re_2Cl_6(PEt_3)_2$ and carbon monoxide in refluxing ethanol or toluene is very slow and does not appear to result in any significant quantities of carbonyl containing species.[5]

The properties of $ReCl_2(CO)_2(PPr^n_3)_2$ appear to be representative of this new class of rhenium(II) carbonyl derivatives. It is soluble in benzene, toluene, carbon tetrachloride, chloroform, ethanol, pentane and diethyl ether. It is monomeric in benzene (found, 649; calcd., 634) and possesses a room temperature magnetic moment of 2.1 B.M., a value which is consistent with its formulation as a derivative of rhenium(II) ($t_{2g}^5$ configuration). Its infrared spectrum is in accord with a trans disposition of both Re-CO and Re-Cl bonds ($\nu_{CO}$: 1906(vs) cm (benzene), 1901(vs) $cm^{-1}$ (nujol); $\nu_{ReCl}$ 302(s) $cm^{-1}$ (nujol)). Accordingly it appears to have the all-trans geometry shown in (I), similar to that exhibited by certain ruthenium(II) complexes of this type.[6]



(I)

In contrast to the common occurrence of tertiary phosphine complexes of both rhenium(I) and rhenium(III) carbonyl halides,[7,8] the only previous report of rhenium(II) carbonyl species is a recent account by Chatt et al[8] 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[8] and provides a route to the unknown neutral dicarbonyls.

The unexpected ease with which carbon monoxide cleaves the Re-Re quadruple bond of $Re_2X_4(PR_3)_4$ suggests that a detailed investigation of such reactions is desirable in view of the synthetic potential of the strongly reducing, coordinativity unsaturated $[ReX_2(PR_3)_2]$ moiety. Such studies are currently underway and will be reported in full at a later date.

## Acknowledgements

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