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Dicarbonyldinitrogen complexes of rhenium(I)

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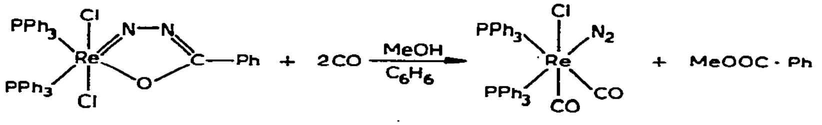
The recent report[1] of three rhenium(I) carbonyl dinitrogen complexes, $[Re(NH_2)(CO)_3(N_2)L]$ ($L = PMe_2Ph$ or $AsMe_2Ph$), and $[Re(NH_2)(CO)_2(N_2)(PMe_2Ph)_2]$ prompts us to report an analogous series of compounds $[ReCl(CO)_2(N_2)L_2]$ prepared by an extension of our previously published method[2]. The compound (I) reacts with carbon monoxide in refluxing benzene/methanol to yield the dicarbonyldinitrogen complex (II)



(I) (II)

The monomeric compound (II) is a diamagnetic, air-stable, yellow crystalline solid, whereas the carbonyl dinitrogen amido-complexes[1] appear to be markedly air-sensitive. The complex (II) is relatively inert, it does not react with carbon monoxide in refluxing solvents below 120°, nor with dry hydrogen chloride at 20°. Oxidation by chlorine in chloroform yields 2 mols. CO and 1 mol. N_2. Reaction with $Ph_2PCH_2CH_2PPh_2$ yields $[ReCl(CO)(Ph_2PCH_2CH_2PPh_2)_2]$[3] and 2 mole equivalents of gas.

The infrared spectrum of (II) (chloroform) shows strong bands at 2105, 2020, and 1930 cm^{-1}. In the $^{15}N_2$ analogue, these are found at 2060, 2000, and 1930 cm^{-1}. Evidently the two higher frequency vibrations are coupled and there is no pure $\nu(N{\equiv}N)$. Moelwyn-Hughes and Garner[1] assign a band at about 2220 cm^{-1} in each of their amido compounds to $\nu(N{\equiv}N)$. These higher frequencies may correlate with the lower stabilities of their compounds but because of coupling they would not be expected to give exact information about the nature of the bonding in the metal–dinitrogen system.

Analogues of (II) which contain other tertiary phosphines (PR_3) are synthesised by the following series of reactions:

$$(I) \xrightarrow[\text{solvent}]{PR_3} [ReCl_2(\cdot N{=}NCOPh)(Pr_3)_3] \xrightarrow[MeOH/C_6H_6]{CO} [ReCl(CO)_2(N_2)(PR_3)_2]$$

The unexpectedly high stabilities of these compounds, even though strongly π-bonding carbon monoxide groups are present with the dinitrogen, emphasises that the satisfaction of the donor function of the dinitrogen is probably more important for complex formation than the satisfaction of its acceptor function[4]. Thus rhenium(I) appears to have energy levels particularly favourable for the formation of σ-bonds to dinitrogen.

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