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Preliminary communication

A HYDROXY-CARBENE DINITROGEN COMPLEX OF RHENIUM

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Summary

trans-$[ReCl(CO)_2(N_2)(PPh_3)_2]$ reacts with $MeLi/H^+$ to give an hydroxy-carbene dinitrogen complex, *trans*-$[ReCl\{C(OH)Me\}(CO)(N_2)(PPh_3)_2]$. This product was unexpected, since under similar conditions *trans*-$[ReCl(CO)_3(PPh_3)_2]$ gives *trans*-$[ReMe(CO)_3(PPh_3)_2]$ and $[MnCp(CO)_2(N_2)]$ gives $[MnCp(CO)_2\{N_2(Me)H\}]$.

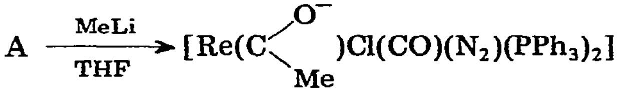
There is only one example of nucleophilic attack upon coordinated dinitrogen, and that in a complex which also contains CO ligands, $[MnCp(CO)_2(N_2)]$, reaction 1 [1].

$$[MnCp(CO)_2(N_2)] \xrightarrow[(2)\,H^+]{(1)\,RLi} [MnCp(CO)_2(RN{=}NH)] \qquad (1)$$

(R = Me or Ph)

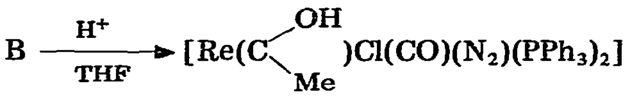
We wish to define sites which activate N_2 towards such attack, and have studied the reaction of the electron-poor complex *trans*-$[ReCl(CO)_2(N_2)(PPh_3)_2]$ (A) [2] ($\nu(N_2)$ 2120 cm^{-1}, $E_{1/2}^{ox}$ 1.1 V versus saturated calomel electrode in tetrahydrofuran (THF) - 0.2M $[Bu_4N][BF_4]$) with MeLi.

We find that A reacts rapidly at room temperature with an excess of MeLi in THF, to give after quenching with HBF_4 (aq), HCl(g), or CF_3COOH an hydroxy-carbene complex, C, in ca. 60% yield according to reactions 2 and 3.



$$A \xrightarrow[THF]{MeLi} [Re(C(O^-)Me)Cl(CO)(N_2)(PPh_3)_2] \qquad (2)$$

(B)



$$\mathrm{B} \xrightarrow[\mathrm{THF}]{\mathrm{H^+}} [\mathrm{Re}(\mathrm{C}\overset{\mathrm{OH}}{\underset{\mathrm{Me}}{<}})\mathrm{Cl(CO)(N_2)(PPh_3)_2}] \qquad (3)$$

(C)

We did not detect products derived from attack upon N_2, nor from metathesis of the Cl ligand with Me. Our evidence for the course and products of these reactions is as follows. The product, C, which we have isolated as an orange crystalline solid, is a non-conductor in 1,2-dichloroethane. Bands were observed in its infrared spectrum at 2050 cm^{-1}, s, $\nu(N\equiv N)$, 1895 cm^{-1}, s, $\nu(CO)$, and 1280 cm^{-1}, m, $\nu(C—O)$. The ^{15}N analogue of C shows bands at 1990 cm^{-1}, s, 1895 cm^{-1}, s, and 1280 cm^{-1}, m. There is no band assignable to $\nu(OH)$ in the spectrum of C. The ^1H NMR spectrum of C and of its ^{15}N analogue are identical, viz. δ 1.8 (s, intensity 3, Me) δ 7—8 (m, intensity 30, aryl) and δ 14.0 (s, intensity 1, OH) ppm. The last resonance disappeared upon addition of D_2O to the CD_2Cl_2 solution of C. The ^{31}P NMR spectrum shows a singlet at 123.2 ppm upfield from trimethylphosphite in C_6D_6. These data and the analysis are consistent with the formulation $[Re\{C(OH)Me\}(CO)Cl(N_2)(PPh_3)_2]$ and with the structure shown in Fig. 1. The intramolecular hydrogen bonding to the halide ligand has been suggested for the stabilisation of the hydroxy-carbene complex $[Re\{C(OH)Me\}(CO)_4Cl]$ [3]. We have characterised the intermediate B, the initial product of the reaction of A with MeLi, by solution infrared spectroscopy. The bands at 2110 and 1920 cm^{-1} of A in THF disappear immediately upon addition of MeLi-THF whilst new bands are observed at 2035 and 1875 cm^{-1}. This is consistent with the formation of the single intermediate, B, reaction 2.

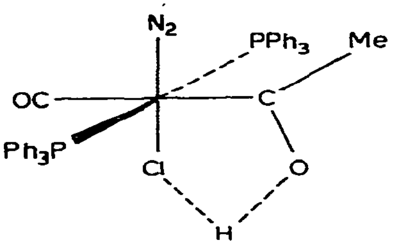


Fig. 1.

In contrast to *trans*-$[Re(CO)_2Cl(N_2)(PPh_3)_2]$, *trans*-$[ReCl(CO)_3(PPh_3)_2]$ (D) reacts with MeLi in THF, under identical conditions to those used for reaction 2, to give the metathesis product, E, via reaction 4.

$$\mathrm{D} \xrightarrow[\mathrm{THF}]{\mathrm{MeLi}} \textit{trans}\text{-}[\mathrm{ReMe(CO)_2(PPh_3)_2}] \qquad (4)$$

(E)

$\nu(CO)$ 1910, 1950 cm^{-1}, s; $\nu(CO)$ 1885, 1925 cm^{-1}, s; $\nu(CH)$ 2870, 2935 cm^{-1} ^1H NMR spectrum (CD_2Cl_2); δ −1.0 (t, intensity 3, Me), δ 7—8 (m, intensity 30, aryl) ppm.

It is rather surprising that the complexes A and D follow distinctly different reaction pathways with MeLi. The oxidation potential of D is some 350 mV more positive than that of A, $E_{1/2}^{ox}$ (D) = +1.37 V vs. SCE THF - 0.2 *M* $[NBu_4]$-$[BF_4]$, which suggests that the metal centre of D is more electrophilic than that of A. However Darst has shown [3] that $[ReCl(CO)_5]$ reacts with MeLi/H^+ to give an hydroxy-carbene complex although its redox potential (ca. +1.9 V) is a further 500 mV more positive [3].

The factors which determine the site of RLi attack when this reagent has an apparent choice between metal, carbon monoxide and dinitrogen ligands in the same molecule are of considerable fascination. We are presently examining the reactivity towards RLi reagents of certain new "electron-poor" rhenium-dinitrogen complexes in an attempt to explore these factors further [4].

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