

Preliminary communication

A CARBYNE COMPLEX OF RHENIUM(V) BY PROTONATION AT
 NITROGEN OF AN ISONITRILE COMPLEX OF RHENIUM(I)

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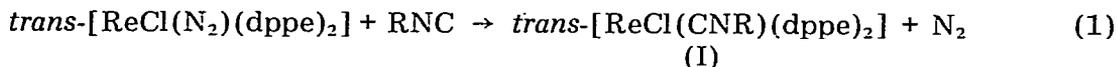
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Summary

The complexes *trans*-[ReCl(CNR)(dppe)₂] (I, R = Me or *t*-Bu) have been prepared by displacement of dinitrogen from *trans*-[ReCl(N₂)(dppe)₂]. I (R = Me) reacts with HBF₄ to give the carbyne-type complex *trans*-[ReCl{CNH(Me)}(dppe)₂]BF₄.

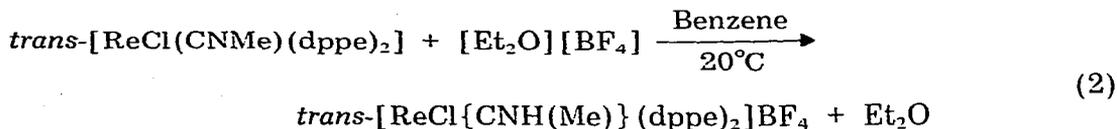
When bound at electron-rich sites, isonitriles are rendered susceptible to attack at their nitrogen atom by electrophilic reagents. Examples of such an attack at terminal isonitrile has hitherto been confined to complexes of molybdenum and tungsten [1]. Here we describe a new example where isonitrile ligates an electron-rich rhenium site.

Since dinitrogen-bonding sites are particularly electron-rich, we have adopted our earlier strategy [1] of displacing dinitrogen with isonitrile (reaction 1) to give the yellow rhenium complexes (I, R = Me or *t*-Bu). The reaction is slow, taking 3 days reflux in THF under an argon atmosphere in presence of an excess of isonitrile.



The complexes I have very low $\nu(\text{N}\equiv\text{C})$ values (R = Me, 1840; R = *t*-Bu, 1920 cm^{-1}) and their *trans*-configuration follows from the singlet resonance in their ³¹P NMR spectra (C₂H₂Cl₂ solution). They are mononuclear in C₂H₄Cl₂ solution.

The electron-releasing properties of this rhenium site render the ligating isonitrile susceptible to attack by electrophiles. Thus we find that I (R = Me) undergoes protonation at nitrogen when treated with [Et₂OH][BF₄] to give the buff, carbyne-type complex *trans*-[ReCl{CNH(Me)}(dppe)₂]BF₄ (II) (reaction 2).



Complex II has the *trans*-structure (^{31}P singlet), $\nu(\text{NH})$ 3250 cm^{-1} [$\nu(\text{ND})$ 2410 cm^{-1} in deuterio analogue] and $\delta(\text{NH})$ $3.9\text{--}4.2\text{ ppm}$ ($\text{C}^2\text{H}_2\text{Cl}_2$ solution). It conducts as a 1/1 electrolyte in CH_3NO_2 . It has no band due to $\text{N}\equiv\text{C}$ in its IR spectrum but a band at 1575 cm^{-1} is assigned to $\nu(\text{N}=\text{C})$ of the carbyne-type ligand. The NCH_3 ^1H resonance is the expected doublet (δ 1.55 ppm , $J(\text{NH})$ 5.1 Hz), which collapses to a singlet on addition of D_2O or irradiation at the N—H resonance. We are extending this reaction to other isonitriles and to alkylating agents.

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References

- 1 J. Chatt, A.J.L. Pombeiro, R.L. Richards, G.H.D. Royston, K.W. Muir and R. Walker, *J. Chem. Soc. Commun.*, (1975) 708; J. Chatt, A.J.L. Pombeiro and R.L. Richards, *J. Chem. Soc. Dalton*, in press.
- 2 J. Chatt, C.M. Elson, A.J.L. Pombeiro, R.L. Richards and G.H.D. Royston, *J. Chem. Soc. Dalton*, (1978) 165.