

Preliminary communication

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PREPARATION OF A TETRAHYDROBORATE COMPLEX OF  
 RHENIUM(I), *cis*-[Re( $\eta^2$ -BH<sub>4</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]

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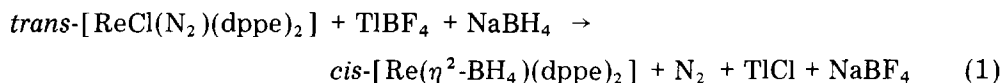
Summary

Dechlorination reactions of the dinitrogen and the isocyanide complexes *trans*-[ReClL(dppe)<sub>2</sub>] (I: L = N<sub>2</sub>; II: L = CNMe; dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) by TlBF<sub>4</sub>, in the presence of NaBH<sub>4</sub> afford *cis*-[Re( $\eta^2$ -BH<sub>4</sub>)(dppe)<sub>2</sub>] (which has a static tetrahydroborate ligand) and the hydride complex *trans*-[ReH(CNMe)(dppe)<sub>2</sub>], respectively.

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As part of our work on the activation of small molecules, such as dinitrogen [1], isocyanides [2] or alkynes [3], by electron-rich transition-metal centres, we have recently isolated the unsaturated [ReCl(dppe)<sub>2</sub>] complex which has a trigonal bipyramidal geometry [4], and which may be involved in some of the dinitrogen displacement reactions of *trans*-[ReCl(N<sub>2</sub>)(dppe)<sub>2</sub>] (I) by those substrates. In view of the participation of hydride complexes in the metal-promoted reductions of this type of substrate [5], we attempted the preparation of the series [ReX(dppe)<sub>2</sub>] (X = hydride or hydride-donor ligand) in order to gain knowledge of the effect of the X ligand on the ability of such centres to interact with dinitrogen, isocyanides, alkynes, etc.

Treatment of a THF solution of the dinitrogen complex I with NaBH<sub>4</sub> in the presence of TlBF<sub>4</sub> gives a species (obtained as red crystals from a dichloromethane extract), formulated as the 16-electron tetrahydroborate complex *cis*-[Re( $\eta^2$ -BH<sub>4</sub>)(dppe)<sub>2</sub>] (III, eq. 1) on the basis of microanalytical data, molar conductivity measurements (it is a non-electrolyte in 1,2-dichloroethane) and IR and NMR spectroscopy.



The IR bands of the  $\text{BH}_4^-$  ligand in complex III are observed at 2400m, 2330w(br)  $\text{cm}^{-1}$  ( $\text{B-H}_t$  stretching  $A_1, B_1$  modes) and 1188s  $\text{cm}^{-1}$  ( $\text{BH}_2$  deformation  $B_2$  mode), in agreement with those reported for other borohydride compounds, e.g.,  $[\text{RuH}(\eta^2\text{-BH}_4)\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]$  [6]. Although the mode of coordination of  $\text{BH}_4^-$  is not defined by the IR data of complex III, its bidentate character and rigid coordination is confirmed by the following NMR spectroscopic data.

Two broad resonances (each of them integrating for 2 protons) are observed in the  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ), at 1.27 and  $-9.0$  ppm, which can be assigned to the two equivalent terminal ( $\text{BH}_2$ ) and bridging ( $\text{ReH}_2\text{B}$ ) protons, respectively, of the static  $\text{BH}_4^-$  ligand.

The bidentate character of the borohydride implies a *cis*-geometry for complex III, and this is confirmed by the detection of a proton phenyl triplet ( $\delta$  6.42 ppm,  $J$  7.3 Hz, 4H) upfield from the usual phenyl range, which is diagnostic [7] of a *cis*-dppe geometry in hexa-coordinate bis(dppe) complexes. Two equally intense singlet resonances are observed in the  $^{31}\text{P}$  NMR spectrum, in agreement with the two sets of phosphorus nuclei. The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum shows a very broad resonance, as reported [6] for  $[\text{RuH}(\eta^2\text{-BH}_4)\{\text{PhP}(\text{CH}_2\text{CH}_2\text{-CH}_2\text{PPh}_2)_2\}]$ .

Although the non-fluxional behaviour of the  $\text{BH}_4^-$  ligand may result from a variety of factors, a considerable  $\pi$ -electron release from the electron-rich  $\{\text{Re}^I(\text{dppe})_2\}$  centre to an empty B-H(bridging) antibonding orbital [8] presumably plays a role.

In the formation of complex III, labilization of the  $\text{Re-N}_2$  bond in the parent compound is probably the result of the replacement of the  $\pi$ -electron-donor chloride ligand by borohydride. However, isocyanides are known to be much less selective ligands than dinitrogen [9] and, accordingly, dechlorination of *trans*- $[\text{ReCl}(\text{CNMe})(\text{dppe})_2]$  (II), by reaction with  $\text{TlBF}_4$  in the presence of  $\text{NaBH}_4$ , leads to *trans*- $[\text{ReH}(\text{CNMe})(\text{dppe})_2]$  (IV), the isocyanide ligand being retained during the replacement of chloride by hydride, presumably via a borohydride intermediate.

Complex IV has  $\nu(\text{CN})$  at ca. 1835  $\text{cm}^{-1}$  and, in the  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ), the hydride resonance is observed as a quintet ( $^2J(\text{PH})$  20.5 Hz) at  $\delta$   $-7.6$  ppm.

The reactions described here show that  $\text{Tl}^+$  behaves as an efficient chloride abstractor of the  $\{\text{ReCl}(\text{dppe})_2\}$  centre, which then is able to bind  $\text{BH}_4^-$  or a derived hydride. The labilization of the  $\text{Re-N}_2$  bond upon dechlorination of the metal centre allows formation of a vacant coordination position required for the stabilization, by chelation, of a  $\text{BH}_4^-$  ligand, which then has an unusual rigid binding to the metal. We are presently extending this type of study to the preparation of other hydride complexes and to compounds with other anionic ligands (such as alkoxide, fluoride, etc.).

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