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Preliminary communication

Direct formation of acylazo- and aroylazo-rhenium(III) complexes from rhenium(I) dinitrogen complexes

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SUMMARY

The complexes $[ReCl(N_2)(PMe_2Ph)_4]$ and $[ReCl(N_2)(PMe_2Ph)_3(pyridine)]$ react with organic acid halides, RCOCl, to form acylazo- and aroylazo-complexes, $[ReCl_2(N_2COR)(PMe_2Ph)_3]$, for which X-ray diffraction studies confirm the formation of the N–C bond; the osmium complex $[OsCl_2(N_2)(PEt_2Ph)_3]$ does not undergo analogous reactions.

Generally, dinitrogen in its stable coordination complexes is no more reactive than molecular nitrogen, except sometimes in its ability to bind to another coordination centre[1]. However, certain molybdenum and tungsten bis-dinitrogen complexes react with organic acid halides and hydrogen halides according to eqns. (1) and (2)[2,3].

$$[M(N_2)_2(PR_3)_4] \xrightarrow{RCOX} [M(N_2COR)(PR_3)_4X] \xrightarrow{HX} [M(N_2HCOR)(PR_3)_4X_2] \quad (1)$$

$$[M(N_2)_2(PR_3)_4] \xrightarrow{HX} [M(N_2H_2)(PR_3)_4X_2] \quad (2)$$

Reaction (1) is of particular interest in that it is essentially the reverse of the usual route to rhenium(I) dinitrogen complexes, $[ReCl(N_2)(PR_3)_4]$, which are made by alcoholysis of rhenium(III) benzoylazo-complexes $[ReCl_2(N_2COPh)(PR_3)_3]$ in the presence of an excess of the phosphine[4]. We now find that the yellow dinitrogen complexes $[ReCl(N_2)(PMe_2Ph)_4]$ and $[ReCl(N_2)(PMe_2Ph)_3(pyridine)]$ react with an excess of acetyl chloride or benzoyl chloride to form the deep red azo-complexes, *mer*-$[ReCl_2(N_2COR)(PMe_2Ph)_3]$ (A, $R = CH_3$; B, $R = Ph$). Crystals of (B) are identical with those of $[ReCl_2(N_2COPh)(PMe_2Ph)_3]$ prepared from $[ReOCl_3(PR_3)_2]$ and $PhCONHNH_2$ [5], for which there is a full X-ray structural analysis[6]. The acetyl product (A) is stable in solution but readily reconverts even at room temperature to the parent dinitrogen complexes by reaction with an excess of the phosphine or pyridine respectively, especially in the presence of an alcohol. The benzoyl complex is more stable and needs an excess of added ligand in refluxing methanol to effect the reconversion[4].

Preliminary experiments indicate that the preparation of acylazo-rhenium(III) complexes from rhenium(I) dinitrogen complexes is general; it is the only method at present available for their preparation. They cannot be prepared from $[ReOCl_3(PR_3)_2]$ and an acylhydrazine, analogously to their aromatic analogues.

The acylation or aroylation of ligating dinitrogen is accompanied by the loss of the second dinitrogen ligand from the molybdenum and tungsten complexes (eqns. (1) and (2)) and by the loss of a labile phosphine or pyridine ligand from the rhenium complex. The presence of the labile ligand seems to be essential because there is no evidence of any reaction between $[ReCl(N_2)(Diphos)_2]$ and acetyl or benzoyl chlorides. Protonation of the rhenium dinitrogen complex in analogy with eqn. (2) has not been achieved; generally the metal is protonated instead[4]. Neither have we been able to acylate, aroylate, or protonate the dinitrogen in $[OsCl_2(N_2)(PEt_2Ph)_3]$. Evidently the tendency of the dinitrogen ligand to take part in this type of reaction falls markedly along the series $[W(N_2)_2(PR_3)_4] > [ReCl(N_2)(PR_3)_4] > [OsCl_2(N_2)(PR_3)_3]$.

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