Methyleneamido-complexes of Rhenium(III)

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Summary Methyleneamido-complexes have been obtained by the deprotonation of alkylimido-complexes by bases such as pyridine.

DISUBSTITUTED methyleneamido-complexes obtained by the reaction of a lithium ketimide, $LiNCR^1R^2$ (R^1 and R^2 = alkyl or aryl), on halogeno-transition-metal complexes, are now well known,[1] but such a route is not available to the parent methyleneamido-complexes. Here we report a novel reaction which has given the stable methyleneamido-complexes, (I) (R = Ph, Me, or Et), and a monoalkylmethyleneamido-complex.

The reaction was found in attempts to displace the NMe ligand as methylaminylene (methylnitrene) by the reaction of *trans*-complexes of the type (II) with neutral ligands such as carbon monoxide or pyridine. No evidence of free nitrene activity was found although the action of CO on $[ReCl_3(NMe)(PPh_3)_2]$ produced *cis*- and *trans*-$[ReCl(CO)_3(PPh_3)_2]$ and a trace of HCN. However, pyridine reacted smoothly with the blue complexes (II) or with *cis*-$[ReCl_3(NMe)(PMePh_2)_2]$ according to reaction 1. Evidently the hydrogen is activated sufficiently, by electron withdrawal into the rhenium in the linear Re–N–Me system, to protonate pyridine. Thus the N–Me is closer to a ligating nitrene in character than to an anionic methylimido-ligand. Hydrogen chloride reconverts (I) into (II) (reaction 2).

$$\textit{trans}\text{-}\underset{\text{(II)}}{[ReCl_3(NMe)(PPh_2R)_2]} + 2py \longrightarrow$$

$$\underset{\text{(I)}}{[ReCl_2(N{=}CH_2)(py)(PPh_2R)_2]} + py{\cdot}HCl \qquad (1)$$

$$\text{(I)} + 2HCl \longrightarrow \text{(II)} + py{\cdot}HCl \qquad (2)$$

A sterically hindered base such as triethylamine also deprotonates (II) but stable products are obtained only in the presence of potential ligands (reaction 3). The complex

$$\textit{trans}\text{-}[ReCl_3(NMe)(PMe_2Ph)_2] + PMe_2Ph + NEt_3 \longrightarrow$$

$$\underset{\text{(III)}}{[ReCl_2(N{=}CH_2)(PMe_2Ph)_3]} + NEt_3{\cdot}HCl \qquad (3)$$

$[ReCl_3(NPh)(PPh_3)_2]$ (IV) does not react with pyridine at room temperature but under reflux gives the product $[ReCl_3(NPh)(py)_2]$.

Analyses, molecular weights, and i.r. and ^1H n.m.r. data support and confirm the structures assigned to complexes (I) and show that the phosphine ligands are in *trans*-positions. The methylene resonances are at τ *ca.* 11·7. The ^1H n.m.r. spectrum of (III) is sufficient to assign its complete configuration. It has a *meridianal* arrangement of phosphine ligands with the $N{=}CH_2$ ligand *trans* to the unique phosphine, and the methylene resonance at τ 11·3 is split into two triplets by the ^{31}P nuclei. All of the complexes (II) have an i.r. band at *ca.* 1310 cm^{-1} which appears to be associated with the NMe group because it is not present in the spectra of the complexes (I), (III), or (IV).

The complex *trans*-$[ReCl_3(NEt)(PMePh_2)_2]$ reacts with neat pyridine to give a solution of $[ReCl_2(N{=}CHCH_3)(py)(PMePh_2)_2]$, identified from its ^1H n.m.r. spectrum, but not isolated. The unique proton absorbs at τ 11·2 and its absorption is split by the CH_3 and the equivalent *trans* phosphorus nuclei.

The green solid methyleneamido-complexes (I), but not their solutions, are stable in air. We were unable to deprotonate the complexes (II) any further to form HCN complexes or free hydrogen cyanide, even with bipyridine.

The $N{=}CH_2$ radical is isoelectronic with nitrogen oxide and similarly should give bent or linear M–N–C systems according to the electronic requirements of the metal. In our complexes the rhenium requires three electrons to satisfy the effective atomic number rule and so should contain a linear Re–N–C system.

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[1] M. Kilner and J. N. Pinkney, *J. Chem. Soc.* (*A*), 1971, 2887, and references therein.