A Novel Route to Methyleneamido Ligands by Protonation of Nitriles Ligating an Electron-rich Centre. Synthesis of *trans*-$[ReCl(NCR)(dppe)_2]$ (R = Alkyl or Aryl, dppe = $Ph_2PCH_2CH_2PPh_2$) and $[ReCl(N{=}CHC_6H_4OMe\text{-}4)(dppe)_2][BF_4]$

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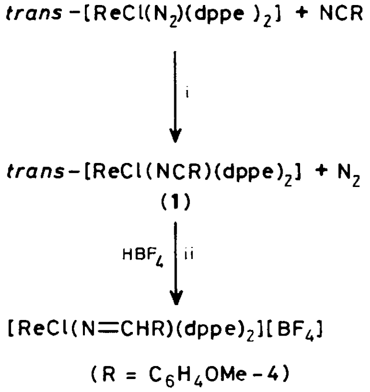
Treatment of *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with NCR affords *trans*-$[ReCl(NCR)(dppe)_2]$ (**1**; R = Me, C_6H_4Me-4, C_6H_4OMe-4, or C_6H_4F-4); (**1**, R = C_6H_4OMe-4) gives $[ReCl(N{=}CHR)(dppe)_2][BF_4]$ on treatment with HBF_4.

The complex chemistry of methyleneamido-ligands, N=CRR′ (R, R′ = H, alkyl, or aryl), has not received wide attention, in spite of their potential ability to act as either one- or three-electron donors. Metal complexes of these ligands are most generally prepared by treatment of a metal halide with LiNCRR′,[1] but a number of other routes are known, *e.g.*, reductive coupling of two nitrile molecules at a group V metal centre;[2] formal insertion of nitrile into a metal–carbon,[3] metal–hydrogen,[3] or metal–phosphorus[4] bond; deprotonation of alkylimido complexes of rhenium(v).[5] In these preparations, the metals are in intermediate or high oxidation states. We now report a new synthesis of these ligands utilising ligation of nitriles to an electron-rich metal centre. Following our studies on the activation of unsaturated nitrogenase substrates at d^6 dinitrogen-binding metal centres,[6,7] we have found that nitriles bound at such a centre undergo electrophilic attack at carbon to give methyleneamido-ligands.

Treatment of *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with NCR in toluene or thf (tetrahydrofuran) under tungsten-filament irradiation gives the compounds *trans*-$[ReCl(NCR)(dppe)_2]$ (**1**; R = Me, C_6H_4Me-4, C_6H_4OMe-4, or C_6H_4F-4) [reaction (i) in Scheme 1], isolated as red or orange solids which have ν(NC) at 2185—2170 cm^{-1} in their i.r. spectra, below the range observed for the free ligands (2250—2210 cm^{-1}).

An *X*-ray crystal structure determination of the thf/CH_2Cl_2 solvate of (**1**; R = Me)[8] shows that the complex has essentially octahedral geometry with the end-on linear acetonitrile ligand *trans* to chloride. The N–C bond length is in the range usually observed for nitrile complexes,[9] but the Re–N distance is shorter than those in nitrile complexes with less electron-rich rhenium centres, either in the same or in higher oxidation



Scheme 1

states;[10] it is also shorter than the estimated single bond distance.[11]

These data are consistent with the strong π-electron release from the rhenium(I) centre of compounds (**1**), which causes their low ν(NC) values.

Thus these ligands might be expected to undergo electrophilic attack and this was demonstrated for (**1**, R = C_6H_4OMe-4) which undergoes protonation by $[Et_2OH][BF_4]$ in CH_2Cl_2 to give the monosubstituted methyleneamido-complex $[ReCl(N{=}CHC_6H_4OMe\text{-}4)(dppe)_2][BF_4]$ [reaction (ii), Scheme 1] as a pale-yellow solid (50—60% yield). In its $^{13}C\{^1H\}$ n.m.r. spectrum (CD_2Cl_2, 298 K) the methylene-amido-carbon resonates as a singlet at δ 113.9 (rel. $SiMe_4$) which splits into a doublet, as expected, in the ^1H-coupled spectrum (J_{CH} 164.3 Hz). The C–H proton has a high field ^1H ABCDX-type resonance centred at δ −7.0 (rel. $SiMe_4$) due to coupling to the four non-equivalent phosphorus nuclei which, in turn, show a complex ABCD-type ^{31}P resonance pattern.

The analogous ligand N=CHMe is also produced by protonation and has been spectroscopically characterised in solution [*e.g.* δ(N=CH*Me*) 3.3, d, $^3J_{HH}$ 6.4 Hz; δ(N=C*H*Me) −2.5, m], but the complex is too labile to obtain analytically pure.

These reactions, which are distinct from previously known chemistry of nitriles,[2,3,5,9,12] result from their activation towards β-electrophilic attack when bound to the strongly electron-releasing rhenium site. Therefore, they extend to a further nitrogenase substrate the mode of ligation-induced reactivity which we have previously observed for isocyanides,[6] alkyne-derived allene,[13] and vinylidene[14] species, as well as for dinitrogen.[15]

It should be noted that nitriles, NCR, are reductively cleaved by nitrogenase to RCH_3 and NH_3.[16] We have established[15] that β-electrophilic attack is the first step on the route to reductive cleavage of N_2 to $2NH_3$ and the reaction reported here may well be the first step in the related reductive cleavage of NCR at a suitable metal centre.

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