Dinitrogen- and Carbonyl-complexes as Bases Towards Trimethylaluminium

By J. Chatt,* R. H. Crabtree, and R. L. Richards
(*A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton* BN1 9QJ)

Summary The order of relative basic strengths, THF > *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ > *trans*-$[Mo(N_2)_2(dpe)_2]$ > *trans*-$[W(N_2)_2(dpe)_2]$ > *trans*-$[ReCl(N_2)(PMe_2Ph)_2\{P(OMe)_3\}_2]$ > *trans*-$[ReCl(CO)(PMe_2Ph)_4]$ > Et_2O > *mer*-$[OsCl_2(N_2)(PEt_2Ph)_3]$ (THF = tetrahydrofuran, dpe = $Ph_2PCH_2CH_2PPh_2$) towards trimethylaluminium in benzene has been deduced from ^1H n.m.r. studies of the equilibrium between trimethylaluminium, the above compounds, and Et_2O.

Various aluminium(III) species form adducts with carbonyl complexes by bonding to the oxygen atom of one or more carbonyl groups,[1-3] and it was briefly reported that triethylaluminium appears to react analogously with *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ to form the adduct, obtained as an oil.[4]

We now report the isolation of adducts formed from a number of dinitrogen complexes and a carbonyl analogue with trimethylaluminium (see Table). All are crystalline 1:1 adducts except that from the osmium compound. Each shows a characteristic lowering ($\Delta\nu$) of $\nu(X{\equiv}Y)$ (where X = C, Y = O or X = Y = N) relative to that of the starting complex and a shift of the trimethylaluminium ^1H n.m.r. resonance relative to free trimethylaluminium (Table). The marked lowering of ν (CO) or ν (N_2) on adduct formation suggests that terminal oxygen or terminal nitrogen is the point of attachment of the trimethylaluminium, since these frequencies should be raised by attachment to the metal or the chloride ligand.[5] Furthermore, the characteristic ^1H n.m.r. and i.r. patterns of the tertiary phosphine ligands change only slightly on adduct formation, thus these ligands are not abstracted on reaction.

$$[\text{metal–}(X{\equiv}Y)] + AlMe_3{\cdot}Et_2O \underset{30^\circ}{\overset{\text{benzene}}{\rightleftharpoons}} [\text{metal–}(X{\equiv}Y){\cdot}AlMe_3] + Et_2O \qquad (1)$$

Hydrolysis destroys the adducts, regenerating the parent carbonyl or dinitrogen complexes in nearly quantitative yield. Addition of diethyl ether, however, sets up equilibria (1) whose constants *K* we have determined by relating the concentration of the various species to their integrated peak heights in the ^1H n.m.r. spectrum of the equilibrated benzene solutions. An averaged resonance for the trimethylaluminium protons was observed at a value intermediate between those of the adduct (A) and $AlMe_3{\cdot}Et_2O$ (B), the mole fraction of each species being given by $\tau_{obs} = n_A\tau_A + n_B\tau_B$.

The values of *K* obtained indicate that towards trimethylaluminium, the order of relative basic strength is THF > *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ > *trans*-$[Mo(N_2)_2(dpe)_2]$ > *trans*-$[W(N_2)_2(dpe)_2]$ > *trans*-$[ReCl(N_2)(PMe_2Ph)_2\{P(OMe)_3\}_2]$ > *trans*-$[ReCl(CO)(PMe_2Ph)_4]$ > Et_2O > *mer*-$[OsCl_2(N_2)(PEt_2Ph)_3]$. There is no correlation between $\Delta\nu$ values nor ^1H n.m.r. shifts and this order.

Thus co-ordinated dinitrogen in the majority of cases studied has a greater basic strength than diethyl ether. In particular *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$, which has the lowest ν (N_2) of the parent complexes, gives the highest *K*.

Table

Compound	ν (cm^{-1})[a]	$\Delta\nu$ (cm^{-1})[a]	$AlMe_3$ resonance[a,b] ($\tau \pm 0{\cdot}02$)	*K*
THF	—	—	—	70
trans-$[ReCl(N_2)(PMe_2Ph)_4]$[c]	1923	29	10·03	20·6
trans-$[Mo(N_2)_2(dpe)_2]$[c]	1979[d]	96[d]	10·37	33(16·5)[e]
trans-$[W(N_2)_2(dpe)_2]$[f]	1953[d]	91[d]	10·20	15(7·5)[e]
trans-$[ReCl(N_2)(PMe_2Ph)_2–\{P(OMe)_3\}_2]$	2000	54	10·03	5·5
trans-$[ReCl(CO)(PMe_2Ph)_4]$	1782	102	10·01	3·3
Et_2O	—	—	—	1
mer-$[OsCl_2(N_2)(PEt_2Ph)_3]$[f]	2063	81	9·93	0·3
Al_2Me_6	—	—	10·33	—

[a] In benzene solution. [b] Relative to Me_4Si. [c] First isolated in collaboration with Dr. E. A. Jeffery. [d] Of asymmetric vibrational absorption. [e] Halved for comparative purposes to account for the presence of two basic sites on the molecule. [f] Adduct slowly decomposes.

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