Formation of Dinitrogen Complexes by Nucleophilic Attack at a Singly Bent Aryldiazenido Ligand (N_2R) in [(η^5-MeC_5H_4)Mn$(CO)_2(N_2R)$][BF_4] and [(η^5-C_5H_5)Re$(CO)_2(N_2R)$][BF_4]

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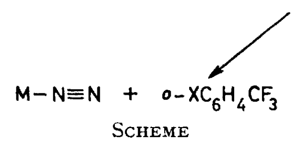
Summary The new aryldiazenido complexes [(η^5-Me-C_5H_4)Mn$(CO)_2(N_2R)$][BF_4] (R = *o*-$CF_3C_6H_4$, *o*-FC_6H_4, or Ph) and [(η^5-C_5H_5)Re$(CO)_2(N_2R)$][BF_4] (R = *o*-$CF_3C_6H_4$) react with nucleophiles such as I^-, Cl^-, Br^-, CN^-, or SCN^- to give the dinitrogen complexes [(η^5-MeC_5H_4)Mn$(CO)_2N_2$] and [(η^5-C_5H_5)Re$(CO)_2N_2$].

Some of the few reactions displayed by co-ordinated dinitrogen in well-defined compounds are alkylation, acylation, and aroylation using certain alkyl, acyl, and aroyl halides, to form compounds containing a metal-bound NNC group, for example an alkyldiazenido ligand (N_2R). Aryl halides do not react because of their weak co-ordinating ability and the difficulty of cleaving the carbon–halogen bond.[1] Thus, the direct conversion of co-ordinated dinitrogen into an aryldiazenido ligand has not been achieved, even though a large number and variety of aryldiazenido complexes now exist, and these are generally quite stable.[2] However, there has been no previous indication of the reverse reaction, namely dearylation of an aryldiazenido ligand to yield the dinitrogen complex. We now report two examples.

The manganese complex[3] [(η^5-MeC_5H_4)MnH$(CO)_2SiPh_3$] reacts with [RN_2][BF_4] in acetone at room temperature with elimination of $HSiPh_3$ to yield the aryldiazenido complex [(η^5-MeC_5H_4)Mn$(CO)_2(N_2R)$][BF_4] [(**1**); R = (**a**) *o*-$C_6H_4CF_3$, (**b**) *o*-C_6H_4F, (**c**) Ph]. The reaction, and the stability of the product, are sensitive to the ring substituent in R and decrease in the order $CF_3 > F > H \gg OMe$; (**1c**) could not be isolated and no aryldiazenido complex was observed for R = *p*-$MeOC_6H_4$. The *X*-ray structure of (**1a**) confirms that the aryldiazenido group is co-ordinated in the 'singly-bent' geometry, with dimensions Mn–N 1·693(7), N–N 1·211(8) Å, Mn–N–N 171·8(8), N–N–C 125·6(9)°.[4]

The aryldiazenido complexes (**1a**—**c**) are smoothly converted into the dinitrogen complex [(η^5-MeC_5H_4)Mn-$(CO)_2N_2$] (**2**), by stirring an acetone solution at room temperature with solid KI under argon. The progress could be followed easily by solution i.r. spectra (AgCl cells), for example the strong absorptions due to (**1a**) at 2090, 2045 [ν(CO)], and 1795 [ν(NN)] cm^{-1} become steadily replaced by ones at 1970, 1911 [ν(CO)], and 2160 [ν(NN)] cm^{-1} of (**2**) assigned by comparison[5] with [(η^5-C_5H_5)Mn-$(CO)_2N_2$]. Upon complete reaction the products were separated and identified by g.l.c.–mass spectroscopy and i.r. spectroscopy to be (**2**) (*m/e* 218) and *o*-$CF_3C_6H_4I$ (*m/e* 272). Similar reactions occurred with potassium salts of other nucleophiles such as Br^-, Cl^-, CN^-, and SCN^-. The dinitrogen complex (**2**) can be reconverted into the aryldiazenido complex (**1**) by stirring with an appropriate aryldiazonium tetrafluoroborate in acetone at room temperature; (**1d**; R = *p*-FC_6H_4) synthesized in this way exhibited ν(NN) at 1796 cm^{-1}, but, when [*p*-$FC_6H_4{}^{14}N^{15}N$][BF_4] was used, this absorption was completely absent and instead ν($^{14}N^{15}N$) occurred at 1770 cm^{-1} showing conclusively that the reaction is indeed a displacement of co-ordinated N_2 by [RN_2]$^+$ rather than the diazonium salt being simply a source of R or R^+ which might add to the existing dinitrogen ligand.



Scheme

It appears that the 'singly-bent' aryldiazenido group in (**1**) is susceptible to attack by nucleophiles X^- according to the Scheme Other 'singly-bent' aryldiazenido complexes do not, in general, show similar behaviour, even when they are chosen to be cationic, to contain the strongly electron-withdrawing o-CF_3 group, or to have nearly comparable ν(NN) values Some examples [with ν(NN)] that we have examined are (all with $R = o\text{-}CF_3C_6H_4$) $[Fe(CO)_2(PPh_3)_2(N_2R)]^+$ (1718)[6], $[Ru(CO)_2(PPh_3)_2(N_2R)]^+$ (1669, 1595, 1570, and 1540),[7] and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(N_2R)]$ (1613 and 1564) [8]

Only by synthesizing {analogously, from $[(\eta^5\text{-}C_5H_5)ReH(CO)_2SiPh_3]$[9]} the closely similar rhenium complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2R)][BF_4]$ (**3**, $R = o\text{-}CF_3C_6H_4$)† have we so far been able to find another example, an acetone solution of (**3**) [i r (CH_2Cl_2) ν(CO) 2090, 2030, and ν(NN) 1760 cm^{-1}] reacted with KI more rapidly than (**1a**) to give $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2)]$[10] [i r ($Me_2CO$) ν(CO) 1960, 1898 and ν(NN) 2142 cm^{-1}, *m/e* 334, 336]

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