Manganese Carbonyl–Diaza-allyl Complexes. Mn–N Bond Formation by Decarbonylation of Carbamoyl-type Complexes

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Summary The cyclic carbamoyl complexes $[(CO)_4\text{MnC(O)}\cdot\text{N}(\text{R}^2)\cdot\text{C}(\text{R}^1)\text{:}\text{NR}^2]$ undergo both thermal and photochemical decarbonylation to form novel π-diaza-allyl complexes $(CO)_4\text{MnN}(\text{R}^2)\cdot\text{C}(\text{R}^1)\cdot\text{NR}^2$; attempts to reverse the process by treatment with CO at high pressures and temperatures gave only $[(CO)_5\text{MnN}(\text{R}^2)\text{C}(\text{R}^1)\text{:}\text{NR}^2]$; no evidence was obtained for insertion into the Mn–N bonds.

Although amido($-NR_2$) and carbamoyl[$-C(O)NR_2$] groups are isoelectronic with alkyl and acyl groups, metal carbonyl complexes containing such substituents are relatively uncommon.[1] Furthermore, in contrast to the carbo-groups, interconversions between amido- and carbamoyl groups are unknown in such complexes although this mechanism has been proposed for the metal carbonyl catalysed carbonylation of secondary amines.[2] We wish to report the formation of the cyclic carbamoyl complexes (I), their thermal and photochemical decarbonylation to diaza-allyl complexes (II),† and the failure to re-insert CO into Mn–N bonds.

Treatment of $Mn(CO)_5Br$ with lithiated amidines, $\text{R}^2\text{NC}(\text{R}^1)\text{NR}^2\text{Li}$, affords the pale yellow carbamoyl complexes (I).[3] Four terminal ν(CO) stretching frequencies are observed in the i.r. spectrum together with a medium intensity absorption at *ca.* 1700 cm^{-1}. The latter is up to *ca.* 100

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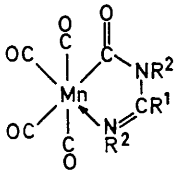
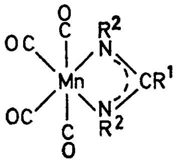
† Satisfactory C, H and N analyses were obtained for each complex.

cm^{-1} higher than is found for [*cis*-$M(CO)_4(NH_2R)(CONHR)$] (M = Mn,[4] Re[5]) and is attributed to conjugation and ring size effects. In view of our failure to insert CO into Mn–N bonds the formation of the carbamoyl complex probably proceeds by nucleophilic attack at a carbonyl group of $Mn(CO)_5Br$, a mechanism which has been suggested for other carbamoyl forming reactions,[6]



(I)

	R¹	R²
a;	Ph	Ph
b;	Ph	*p*-tolyl
c;	Me	Ph
d;	Ph	H



(II)

	R¹	R²
a;	Ph	Ph
b;	Ph	*p*-tolyl

Pyrolysis of (Ia) in Nujol or cyclohexane [130—140°, 15h, 1100 p.s.i. N_2] caused the i.r. absorption at 1698 cm^{-1} to disappear and new absorptions due to $Mn_2(CO)_{10}$[7] and (IIa) to appear. Despite variation over a range of temperatures and pressures, formation of $Mn_2(CO)_{10}$ could not be prevented. U.v. irradiation of (I, a and b) in cyclohexane at ambient temperature achieved the same decarbonylation reaction to form (II, a and b) in high yields. The carbonyl stretching frequencies closely resemble those of π-$C_3H_5Mn(CO)_4$,[8] and a similar delocalised π-system is indicated for complexes (II) by the n.m.r. spectrum of (IIb, R² = *p*-tolyl, R¹ = Ph) in CCl_4 which showed only one *p*-Me signal at all temperatures between +40 and −50 °C. These complexes are the first examples of 3-atom pseudo-π-allyl systems containing two nitrogen atoms and their method of preparation is the first known example of the decarbonylation of a carbamoyl-transition metal derivative to form a metal–nitrogen bond.

As part of a general study of the high pressure reactions of metal–nitrogen bonded species, it was of interest to attempt to reverse the decarbonylation process. Treatment of (IIa) with CO [3000 p.s.i., 125 °C, 48 h], in a high pressure i.r. cell[9] produced no evidence for the reformation of (Ia) by insertion into a Mn–N bond. Instead, formation of a new species (III), was detected, which on the basis of the i.r. spectrum in the 2100—1500 cm^{-1} region and its comparison with the spectra of other reported carbonyl species, is identified as $Mn(CO)_5N(Ph){\cdot}C(Ph){:}NPh$. Further carbonylation of this first example of an amido-manganese carbonyl complex could not be achieved. After removal of the CO and substituting nitrogen (1000 p.s.i.), complex (III) disproportionated to $Mn_2(CO)_{10}$ on heating, although (IIa) was observed transiently during this process. (III) persisted at room temperature under an atmosphere of CO and efforts are being directed at present towards its isolation.

We thank the SRC for research grants in support of this work.

(*Received*, *4th May* 1972; *Com.* 753.)

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