Organonitrogen Groups in Metal Carbonyl Complexes. Part X. Carbonylation Studies

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A possible mechanism for the carbonylation of amines and other nitrogen-containing molecules, which involves insertion into a transition metal–nitrogen bond, has been tested. Attempts to insert carbon monoxide into such bonds of $[M(\eta^5\text{-}C_5H_5)(CO)_2X]$ [M = Mo or W; X = $N{:}CR_2$ (R = Bu^t or *p*-tolyl), R_2CNCR_2 (R = Ph, *p*-tolyl, or *p*-$CF_3C_6H_4$), RNC(R′)NR (R = R′ = Ph; R = Ph, R′ = *p*-tolyl)], $[Mn(CO)_4X]$ {X = RNC(R′)NR (R = R′ = Ph)}, and $[Fe(\pi\text{-}C_5H_5)(CO)_2(NPh_2)]$, produced $[\{(\eta^5\text{-}C_5H_5)M(CO)_n\}_2]$ (M = Mo or W, $n = 3$: M = Fe, $n = 2$) and/or the binary metal carbonyls. No evidence was obtained for the formation of carbamoyl complexes.

PRIMARY and secondary amines react catalytically with carbon monoxide in the presence of low-valent transition-metal complexes to yield amides and ureas.[1] Dimethylamine, in the presence of cobalt carbonyl produced *NN′*-dimethylformamide [2] and a mechanism involving the formation of $[Co(NMe_2)(CO)_4]$, followed by insertion of carbon monoxide into the cobalt–nitrogen bond to form carbamoyl complexes, was suggested.[3,4] Such complexes are well documented,[5] but are usually synthesized directly from an amine and a metal carbonyl without a pressure of carbon monoxide.[5] Thus an alternative mechanism for the carbonylation of amines involves nucleophilic attack of the amine at the carbon atom of a co-ordinated carbon monoxide molecule, followed by loss of a proton.[6] The present work relates to determining the plausibility of carbon monoxide insertion into transition metal–nitrogen bonds, which has been widely referred to on many previous occasions. Various organonitrogen complexes have been subjected to high CO

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[1] A. Rosenthal and I. Wender, ' Organic Syntheses *via* Metal Carbonyls,' eds. I. Wender and P. Pino, Interscience, New York, 1968, vol. 1, p. 405.

[2] H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Amer. Chem. Soc.*, 1953, **75**, 3148.

[3] H. W. Sternberg, I. Wender, *Chem. Soc. Spec. Publ.* No. **13**, 1959, 35.

[4] R. F. Heck, ' Mechanisms of Inorganic Reactions,' A.C.S. Monograph No. **49**, Amer. Chem. Soc., New York, 1965, 181.

[5] R. J. Angelici, *Accounts Chem. Res.*, 1972, **5**, 335.

[6] R. J. Angelici and R. W. Brink, *Inorg. Chem.*, 1973, **12**, 1067.

pressures at temperatures up to 185 °C, and the reactions monitored by i.r. spectroscopy.

Known amino (R_2N) derivatives of low-valent transition metals which are active as catalysts in the carbonylation reactions of amines and related compounds are rare and restricted almost entirely to complexes of iron.[7] But such complexes are not directly analogous to the suggested intermediates since the nitrogen atom usually adopts a bridging position reinforcing a metal–metal bond in a dinuclear unit. Except for $[Fe(\pi\text{-}C_5H_5)(CO)_2N<]$ derivatives, no directly analogous complexes are known, their instability being related to the hardness of nitrogen compared with the soft low-valent transition-metal centre. Softening the nitrogen by incorporating it into a π system leads to complexes having $M{-}N{=}CR_2$ or $M{-}N\leqslant$ groups and such complexes have been used in the present study. Any carbamoyl complexes formed would have additional stability from the delocalised π system of the $-C(O)N{:}CR_2$ group. Such a group is known already in the complex $Li[Cr(CO)_5\{C(O)N{:}CPh_2\}]$.[8]

Carbonylation and decarbonylation studies of organonitrogen complexes

Complex	Ref. ‡	Solvent §	Pressurising gas	Max. conditions t/°C	Max. conditions P/atm	Reaction time/h	Products †
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N{:}CBu^t_2)]$	*a*	N	CO	170	270	16	$[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, $[Mo(CO)_6]$
$[W(\eta^5\text{-}C_5H_5)(CO)_2(N{:}CBu^t_2)]$	*a*	N	CO	170	240	13	$[\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, $[W(CO)_6]$
$[W(\eta^5\text{-}C_5H_5)(CO)_2\{N{:}C(p\text{-}MeC_6H_4)_2\}]$	*a*	N	CO	160	230	14	$[\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, $[W(CO)_6]$
$[W(\eta^5\text{-}C_5H_5)(CO)_2(Ph_2CNCPh_2)]$	*a, b*	N	CO	170	210	18	$[\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, $[W(CO)_6]$
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{(p\text{-}MeC_6H_4)_2CNC(p\text{-}MeC_6H_4)_2\}]$	*a, b*	N	CO	185	210	45	$[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, $[Mo(CO)_6]$
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}]$	*a, b*	N	CO	175	310	72	$[Mo(CO)_6]$,trace $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{PhNC(Ph)NPh\}]$	*c*	N	CO	150	330	24	$[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, $[Mo(CO)_6]$
$[W(\eta^5\text{-}C_5H_5)(CO)_2\{(p\text{-tolyl})NC(Ph)N(p\text{-tolyl})\}]$	*c*	N	CO	160	300	18	$[\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, $[W(CO)_6]$
$[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NPh_2)]$	*d*	N	N_2	150	190	2	Non-carbonyl materials
$[Mn(CO)_4\{CON(Ph)C(Ph)NPh\}]$	13	N	N_2	140	75	12	$[Mn(CO)_4\{PhNC(Ph)NPh\}]$, $[Mn_2(CO)_{10}]$
		C_6H_{12}	N_2	170	140		$[Mn(CO)_4\{PhNC(Ph)NPh\}]$, $[Mn_2(CO)_{10}]$
$[Mn(CO)_4\{PhNC(Ph)NPh\}]$	13	N	CO	125	200	12	$[Mn_2(CO)_{10}]$, $[Mn(CO)_5\text{-}\{PhNC(Ph)NPh\}]$
$[Mn(CO)_4(NH_2Bu^n)(COHNBu^n)]$	*e*	N	CO	18	270	4	$[Mn_2(CO)_{10}]$ *
		N	N_2	100	180	16	$[Mn_2(CO)_{10}]$, $[Mn(CO)_5]^-$
$[Co\{(C_5H_{10}N)CO\}(CO)_3(PPh_3)]$	*f*	N	N_2	150	200	4	Non-carbonyl materials

* Weak absorptions at *ca.* 2 030 and 1 955 cm^{-1} detected also, possibly due to $[Mn(CO)_3(NH_2Bu^n)_2CONHBu^n]$ † Products were identified by i.r. spectroscopy. ‡ References to preparation of complexes are given. § N = Nujol.

[a] M. Kilner and C. Midcalf, *J. Chem. Soc.* (*A*), 1971, 292; H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 153 and 1535. [b] K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc.* (*A*), 1970, 2279. [c] T. Inglis and M. Kilner, *J.C.S. Dalton*, 1975, 930. [d] P. L. Pauson and G. R. Knox, personal communication. [e] R. J. Angelici, *Chem. Comm.*, 1965, 486; R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta*, 1968, **2**, 3. [f] J. Palagyi and L. Marko, *J. Organometallic Chem.*, 1969, **17**, 453.

EXPERIMENTAL

High-pressure i.r. cells,[9] which can be heated and maintained at temperatures up to 220 °C, were used in conjunction with a modified Perkin-Elmer 257 spectrophotometer for the spectral studies. The complexes formed in the reactions were identified by comparing their i.r. absorption frequencies with those of authentic samples or with literature values.

Typically, $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N{:}CBu^t_2)]$ was mixed with Nujol (20 ml) and the mixture added to the high-pressure cell against a counter current of nitrogen. After assembling the complete cell it was pressurised with nitrogen, which was later vented, before pressurising with carbon monoxide to 200 atm. The reaction cell was compensated with an identical cell containing Nujol which was kept at the same temperature and pressure as the reaction cell. At room temperature two absorptions at 1 967 and 1 883 cm^{-1} were detected, and became more intense as the temperature was raised to 80 °C and as more complex dissolved in Nujol. A new absorption (1 920 cm^{-1}) was discernible after $1\frac{1}{2}$ h at 125 °C (total reaction time 4 h) and as the temperature was raised to 150 °C, the new absorption, now enhanced in intensity, was accompanied by a slightly less intense peak at *ca.* 1 990 cm^{-1}. These new absorptions gained intensity during 17 h at the expense of the absorptions of the starting material, and were eventually replaced by absorptions at 2 056w, 1 985s, 1 959vs, 1 916s, *ca.* 1 912s, sh cm^{-1} assigned to $[Mo(CO)_6]$ (lit.[10] 1 989 cm^{-1}) and $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ (lit.[11] 1 960vs, 1 916vs). Prolonged heating under *ca.* 230 atm of CO resulted in the enhanced intensity of the 1 985 cm^{-1} absorption at the expense of the other absorptions. As the sample cooled no notable changes in the spectra occurred.

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[8] M. J. Doyle, M. F. Lappert, G. M. McLaughlin, and J. McMeeking, *J.C.S. Dalton*, 1974, 1494.

[9] W. Rigby, R. Whyman, and K. Wilding, *J. Phys. E., Sci. Instrum.*, 1970, **3**, 572.

[10] G. Bor, *Spectrochim. Acta*, 1962, **18**, 817.

[11] F. A. Cotton, A. O. Liehr, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

Throughout the study no new absorptions were detected in the 1 600—1 800 cm^{-1} region which could be assigned to the $-C(O)N{:}CR_2$ group.

RESULTS AND DISCUSSION

The metal carbonyl complexes studied have organonitrogen groups of the following types, (i) $-N{:}CR_2$, (ii) R_2CNCR_2, (iii) $R'NC(R)NR'$, (iv) $-NR_2$, and (v) $CON<$ (see Table). Heating of the compounds under carbon monoxide pressures led ultimately to the binary carbonyl (Table) irrespective of the type of attached organonitrogen group. Cyclopentadienyl complexes proceeded through the mixed π-cyclopentadienyl carbonyl complex prior to the loss of the hydrocarbon ligand.

$$[(\eta^5\text{-}C_5H_5)M(CO)_2X] \xrightarrow{CO} [\{(\eta^5\text{-}C_5H_5)M(CO)_3\}_2] \xrightarrow{CO} [M(CO)_6]$$

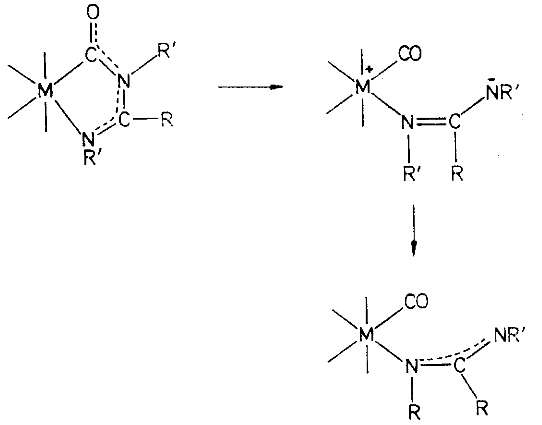
M = Mo or W

X = $N{:}CR_2, R_2CNCR_2$, or $R'NC(R)NR'$

Careful monitoring of the carbamoyl carbonyl stretching region produced no evidence for the formation of such carbamoyl intermediates under a variety of conditions.

The involvement of carbamoyl complexes as intermediates in the carbonylation of amines is generally accepted.[12] Even at ambient temperature the carbamoyl group is cleaved from $[Mn(CO)_4(Bu^nNH_2)(CONHBu^n)]$ in the presence of carbon monoxide (280 atm) so carbamoyl complexes are expected to have at the most only a transient existence under catalytic conditions. Since decacarbonyldimanganese is generally the least efficient carbonylation catalyst of the triad $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, and $[Co_2(CO)_8]$ [1] a very short lifetime for the other metal–carbamoyl intermediates is expected. Thus the failure to detect the products of insertion and the slow loss of the original complex may be explained in terms of the transient nature of the carbamoyl intermediates, and a slow insertion stage.

Alternatively the spectral changes could arise solely from metal–nitrogen bond cleavage. Support is given to this interpretation by the studies on $[Mn(CO)_4\{CON(Ph)C(Ph)NPh\}]$ in which the carbamoyl group has an additional attachment to the metal through the imino-nitrogen atom. Decarbonylation yielded $[Mn(CO)_4\{PhNC(Ph)NPh\}]$ but attempts at recarbonylation (125 °C max., 200 atm CO) to generate the original, relatively thermally stable, carbamoyl complex (m.p. 120 °C decomp.) over 12 h failed, although the latter complex is stable under these conditions.[13] Failure to detect this and other known carbamoyl complexes by insertion into metal–nitrogen bonds adds credence to the view that such a process does not occur to any appreciable extent. Interestingly, evidence was obtained for the formation of $[Mn(CO)_5\{N(Ph)C(Ph)NPh\}]$. Decarbonylation of carbamoyl complexes has not been reported previously, and indeed cleavage of the carbamoyl group proceeds by loss of the amino-group rather than by loss of carbon monoxide.[6] A similar process may have occurred for the amidino-complex, except that the organonitrogen group is not completely displaced from the metal because of its attachment through a second nitrogen atom. Unlike other carbamoyl complexes, hydrogen transfer to the displaced amino-group is not involved here; any charge imbalance is compensated by a slight adjustment of electron density in the delocalised π-system.



Many of the complexes studied have the nitrogen ligand acting as a three-electron group through either unidentate or bidentate attachment to the metal. Under carbon monoxide pressures bidentate groups often become unidentate and vacate a co-ordination position subsequently occupied by carbon monoxide,[14] but such a process did not occur for the aza-allyl (R_2CNCR_2) complexes. Also the methyleneamino-group failed to become a one-electron donor group.

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