Organonitrogen Groups in Metal Carbonyl Complexes. Part VIII. Diaza-allyl Derivatives of Manganese

By **Thomas Inglis, Melvyn Kilner,* Timothy Reynoldson,** and (Mrs) **Elinor E. Robertson,** Department of Chemistry, The University of Durham, South Road, Durham DH1 3LE

Lithioamidines, R′N(Li)·C(R):NR′, react with [Mn(CO)$_5$X] (X = Cl, Br, or I) to yield carbamoyl-type complexes, [Mn(CO)$_4${CO·N(R′)·C(R):NR′}], which, in contrast to previously reported carbamoyl complexes, can be decarbonylated by u.v. irradiation to form [Mn(CO)$_4${R′N·C(R):NR′}] complexes. Various bonding modes are discussed for each organonitrogen group, and structures are suggested on the basis of limited spectroscopic data. Thermolysis of [Mn(CO)$_4${CO·N(Ph)·C(Ph):NPh}] also caused decarbonylation of the carbamoyl group, but when achieved under a high pressure of carbon monoxide the first example of an amino-manganese carbonyl complex, [Mn(CO)$_5${N(Ph)·C(Ph):NPh}], was also formed.

THE substitution of nitrogen into an allyl group for a skeletal carbon atom (together with its attached atom or group) in many ways leaves the group little changed, the group retaining, for example, the potential to act as a one- or three-electron donor to low-valent transition metals. Previous papers in this series[1] have been concerned with one such organonitrogen group, R_2CNCR_2, which has been shown to act as a three electron h^3-ligand to molybdenum, tungsten,[1] and manganese.[2] In many respects the σ–π type attachment of the latter group

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[1] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 153; 1535.

[2] K. Farmery, M. Kilner, C. Midcalf, and Miss C. A. Payling, Abstr. IVth International Conf. Organometallic Chemistry, Bristol, 1969, p. 55.

mirrors the bonding in π-allyl complexes, particularly in the fluxional changes which occur in solution,[1] but in other respects the groups differ markedly. For example, the absence of a substituent in the 2-position allows an aza-allene ($\mathrm{R_2C{=}\overset{+}{N}{=}CR_2}$) conformation to be adopted ($\mathrm{R_2C}$ planes orthogonal) purely by rotation about a C–N bond. Such a bonding mode has been shown by *X*-ray crystallography[3] to occur for one form of $[(\pi\text{-}\mathrm{C_5H_5})\mathrm{Mo(CO)_2\{}(p\text{-tolyl})_2\mathrm{CNC}(p\text{-tolyl})_2\}]$.

TABLE 1

I.r. spectral data for the amidino-manganese complexes

Complex	ν(CO) Stretching frequencies ($\mathrm{cm^{-1}}$) (terminal)	(carbamoyl [c])
$[\mathrm{Mn(CO)_4\{CO{\cdot}NHC(Ph){:}NH\}}]$ [a]	2090m—s, 1992s,br, 1954s	1615s
$[\mathrm{Mn(CO)_4\{CO{\cdot}N(Ph){\cdot}C(CH_3){:}NPh\}}]$ [b]	2085m, 2004s, 1986vs, 1972vs	1694m
$[\mathrm{Mn(CO)_4\{CO{\cdot}N}(p\text{-tolyl}){\cdot}\mathrm{C(CH_3){:}N}(p\text{-tolyl})\}]$	2082m, 1993s, 1980s, 1942vs [d]	1663m
	2081w, 1997m, 1984vs, 1969s [b]	1674m
$[\mathrm{Mn(CO)_4\{CO{\cdot}N(Ph){\cdot}C(Ph){:}NPh\}}]$ [b]	2083s, 2004s, 1988vs, 1974vs	1698s
$[\mathrm{Mn(CO)_4\{CO{\cdot}N}(p\text{-tolyl}){\cdot}\mathrm{C(Ph){:}N}(p\text{-tolyl})\}]$	2083s, 2002s, 1987vs, 1972vs	1695m
$[\mathrm{Mn(CO)_4\{PhN{\cdot}C(CH_3){:}NPh\}}]$ [b]	2096w, 2017s, 1996s, 1955s	
$[\mathrm{Mn(CO)_4\{PhN{\cdot}C(Ph){:}NPh\}}]$ [b]	2093w, 2010m, 1995s, 1950s	
$[\mathrm{Mn(CO)_4\{}(p\text{-tolyl})\mathrm{N{\cdot}C(Me){:}N}(p\text{-tolyl})\}]$ [b]	2095w, 2013m—s, 1990s, 1954s	
$[\mathrm{Mn(CO)_4\{}(p\text{-tolyl})\mathrm{N{\cdot}C(Ph){:}N}(p\text{-tolyl})\}]$ [b]	2095w, 2010s, 1992s, 1950s	

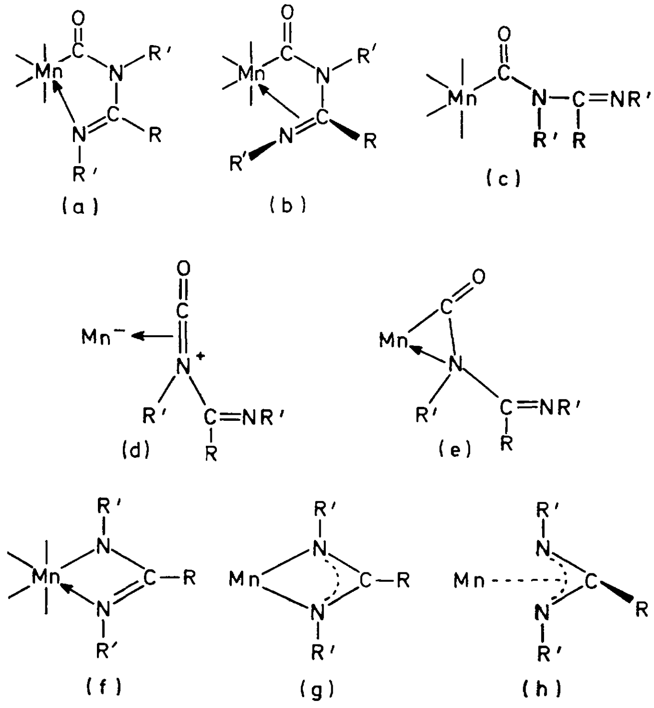
[a] $\mathrm{CHCl_3}$ Solution. [b] Cyclohexane solution. [c] KBr Disc.

The notable differences in chemistry associated with the introduction of nitrogen into a π-allyl skeleton have led us to the study of diaza-allyl complexes, particularly those of the amidino-group $[\mathrm{R'N{\cdot}C(R){:}NR'}]$.[4] In addition to being isoelectronic with the π-allyl group, this group is also isoelectronic with the carboxylato-group (see Figure), which when bidentate tends to bond so that the metal lies in the same plane as the $\mathrm{CO_2}$ unit.[5] Thus on proceeding down the pseudo-allyl isoelectronic series from the π-allyl to the carboxylato-group the bonding mode to the metal appears to change from the metal lying above the ligand plane, *e.g.* $[(\pi\text{-}\mathrm{C_3H_5})_2\mathrm{Ni}]$,[6] to lying in the ligand plane, *e.g.* $[(\mathrm{C_6H_6})\mathrm{Mo}(\pi\text{-}\mathrm{C_3H_5})(\mathrm{O_2CCH_3})]$.[7]

Unlike manganese(I)–alkyl bonds, the corresponding manganese–amino ($\mathrm{Mn{-}NR_2}$) bond lacks robustness, and no examples are known, but softening of the nitrogen with –C(S)Ph, $\mathrm{-C_6H_4S}$,[8] or $\mathrm{R_2C{:}}$[9] substituents leads to thermally stable complexes. The last feature occurs in the $\mathrm{R'NC(R){:}NR'}$ group, but here the possible formation of carbamoyl complexes[10,11] is an additional complication, since such complexes do not usually decarbonylate to amino-derivatives.

RESULTS AND DISCUSSION

(A) *Complexes of the Type* $[\mathrm{Mn(CO)_4\{CO{\cdot}N(R'){\cdot}C(R){:}NR'\}}]$.—Amidino-complexes were synthesised by a metathetical reaction involving lithioamidines and bromopentacarbonylmanganese(I) in ether solvent. The pentacarbonyl complexes each exhibit five ν(CO) stretching frequencies (Table 1), although in polar solvents complete resolution of all the absorptions was not always achieved. Four absorptions are positioned in the terminal metal–carbonyl region (1900—2100 $\mathrm{cm^{-1}}$), consistent with a *cis*-$\mathrm{Mn(CO)_4}$ moiety, and one in the 1700 $\mathrm{cm^{-1}}$ region which we assign to a predominently carbamoyl carbonyl stretching vibration. Thus the complexes are formulated $[\mathrm{Mn(CO)_4\{CO{\cdot}N(R'){\cdot}C(R){:}NR'\}}]$.



Possible bonding modes for the $\mathrm{-CO{\cdot}N(R'){\cdot}C(R){:}NR'}$ and $\mathrm{-N(R'){\cdot}C(R){:}NR'}$ groups

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[3] H. M. M. Shearer and J. D. Sowerby, results communicated in M. Kilner, *Adv. Organometallic Chem.*, 1970, **10**, 115.

[4] T. Inglis, M. Kilner, and T. Reynoldson, *J.C.S. Chem. Comm.*, 1972, 774.

[5] T. Inglis, *Inorg. Chim. Acta, Rev.*, 1973, **7**, 35.

[6] H. Dietrich and R. Uttech, *Naturwiss.*, 1963, **50**, 613.

[7] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 1403.

[8] W. Hieber and M. Gscheidmeier, *Chem. Ber.*, 1966, **99**, 2312; E. Lindner and H. Weber, *Z. Naturforsch.*, 1969, **24B**, 453; E. Lindner, R. Grimmer, and H. Weber, *Angew. Chem. Internat. Edn.*, 1970, **9**, 639.

[9] M. Kilner and C. Midcalf, *J. Chem. Soc.* (*A*), 1971, 292.

[10] R. J. Angelici, *Chem. Comm.*, 1965, 486; R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta*, 1969, **2**, 3.

[11] S. Fukuoka, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, 1968, **33**, 2973.

Some possible bonding modes for the $R'N{\cdot}C(R){:}NR'$ group, based on the above data are given in the Figure. Structures (a) and (b) have bidentate 3-electron-donor groups forming 5-membered rings, the difference arising from the possibility of either the nitrogen lone-pair of electrons or the π-electrons of the C–N bond providing the second attachment to the metal. Otherwise they are both basically carbamoyl derivatives. Structure (c) has a conventional carbamoyl group but the metal remains a 16-electron system; this unlikely structure is not consistent with the ν(CO) stretching data. Finally the organo-group may bond as an aza-keten group $[R'R''\overset{+}{N}{=}C{=}O$ ($R'' = R'N{:}CR$); (d) and (e)], which is analogous to the mode of attachment of the nitrogen ligands in $[(\pi\text{-}C_5H_5)Mo(CO)_2(R_2CNCR_2)]$[3] and $[Mn(CO)_4(CH_2{\cdot}CH_2{\cdot}NCH_2)]$.[12] Structures involving rings containing oxygen as well as two nitrogen atoms are dismissed on the basis of 1600—1700 cm^{-1} absorptions.

Structure (a) is preferred on the basis of a 5-membered metallocyclic ring rather than a 3-membered ring, and on the stereochemistry of the group. In (b) the MnC(O)N and NCN planes are non-coincident, and against extensive delocalisation of the ligand group favoured by i.r. data. The 3-membered ring structure (e) should absorb in the carbonyl stretching region higher than normal carbamoyl complexes and close to those of related acyl derivatives (Table 2), because of the involvement of the nitrogen lone-pair in bonding with the metal.

TABLE 2

Comparison of 'carbonyl' stretching frequencies of amidino-complexes with those of related acyl and carbamoyl complexes

Complex	Diluant	Absorption	Ref
$[Mn(CO)_4\{CO{\cdot}NH{\cdot}C(C_6H_5){:}NH\}]$	KBr	1613s	*a*
$[Mn(CO)_4\{CO{\cdot}N(C_6H_5){\cdot}C(C_6H_5){:}NC_6H_5\}]$	KBr	1673	*a*
$[Mn(CO)_4\{CO{\cdot}N(C_6H_5){\cdot}C(CH_3){:}NC_6H_5\}]$		1668	*a*
$[Mn(CO)_4\{(NH_2CH_3)CONHCH_3\}]$	KBr	1610w 1540m	*b*
$[Mn(CO)_4\{(NC_5H_{10})COCH_3\}]$	CCl_4	1613	*c*
$[Mn(CO)_4COCH_2CH_2NEt_2]$	C_6H_{12}	1660	*d*
$[Mn(CO)_4COCH_2C_5H_4N]$	C_6H_{12}	1668	*d*
$[Fe(\pi\text{-}C_5H_5)(CO)_2CON(C_2H_5)_2]$	Mull	1534	*e*
$[Fe(\pi\text{-}C_5H_5)(CO)_2CONHC_2H_5]$	$CH_3C_6H_{11}$	1622	*b*

[a] This work. [b] Ref. 10. [c] K. A. Keblys and A. H. Filbey, *J. Amer. Chem. Soc.*, 1960, **82**, 4204. [d] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1966, **5**, 293. [e] R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1918.

In addition, for structure (e) an i.r. absorption ν(CN) in the 1600 cm^{-1} region would be expected, but although bands do occur in the two regions predicted, other absorptions [*e.g.* (III) and (IV), Table 3] are not satisfactorily explained with this model. Thus we tend to favour structure (a).

Only limited structural data are provided by ^1H n.m.r. studies. Use of methyl substituents on *N*-aryl groups produced only a singlet signal for the methyl protons although the two *p*-tolyl groups would appear to be in different environments. The immediate conclusion must be that such groups are insensitive to the differences, both electronic and steric, between the two nitrogen atoms, but this feature is rather surprising when *p*-methyl substituents proved so valuable for monitoring rotation about a C–N axis and interchange of σ–π bonding in $[(\pi\text{-}C_5H_5)M(CO)_2\{R_2C{\cdot}N{:}CR_2\}]$ ($M = Mo$ or W)[1] complexes. That *para*-substituents are insensitive to the electronic and/or steric effects at nitrogen thus seems unacceptable although the steric effects in particular operating in the $R'N{\cdot}C(R){:}NR'$ and $R_2C{\cdot}N{:}CR_2$ groups will be different. Interchange of the two ends of the $R'N{\cdot}C(R){:}NR'$ group is possible and further studies using different substituents are in progress in an attempt to interpret the available data more fully.

TABLE 3

I.r. absorptions of $[Mn(CO)_4\{CO{\cdot}N(R'){\cdot}C(R){:}NR'\}]$ associated with the OCNCN skeleton

		Absorptions ($\bar{\nu}$/cm^{-1})			
R	R′	I	II	III	IV
Me	Ph	1668s	1610m—s	1495m	1420s
Me	*p*-tolyl	1671m 1659m	1602s	1508m—s	1415m, 1403m
Ph	Ph	1673s	1586s	1500m—s	1411s
Ph	*p*-tolyl	1664s	1590m	1514sh 1510ms	1419w 1393m—s
Ph	H	1613vs	1605sh	1524m	1487m

I.r. data in the 1600—1400 cm^{-1} region are recorded in Table 3. From inspection of structure (a) it may be seen that the organo-nitrogen group has fragments which bear close analogy with those of amide ($-CON\langle$) and amidine [$-N(R'){\cdot}C(R){:}NR'$] groups, both of which have characteristic symmetric and asymmetric stretching vibrations involving their three skeletal atoms.[13,14] Two vibrations will be particularly relevant for each group, the asymmetrical and symmetrical OCN or NCN stretching vibrations, but extensive mixing of the vibrations will occur such that the highest absorption band, predominantly the OCN asymmetrical stretching vibration, will move to higher frequencies compared with related groups having the OCN skeleton. A further consequence of the mixing is a lowering of the absorption which is predominantly the symmetrical NCN stretching vibration. The effect on the highest frequency absorption is adequately illustrated with reference to related carbamoyl complexes in Table 2, where data on related acyl derivatives are also collected.

Two mechanisms are feasible for the formation of the carbamoyl-type complexes, one involving a metathetical reaction (1) (elimination of lithium halide), followed by nucleophilic attack at a carbonyl group by the imino-nitrogen atom and a redistribution of electron density. An alternative mechanism (2) which is analogous to that which occurs in forming other carbamoyl complexes,[10]

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[12] E. W. Abel, R. J. Rowley, R. Mason, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1974, 72.

[13] 'Irscot Infrared Structural Correlation Tables,' eds., R. G. J. Miller, H. A. Willis, and H. J. Hediger, Heyden and Son, Ltd., London, 1965, Table 5, and refs. therein.

[14] D. C. Prevorsek, *J. Phys. Chem.*, 1962, **66**, 769.

involves initial nucleophilic attack at a carbonyl group, elimination of lithium halide and finally co-ordination of the imino-nitrogen atom at the vacant co-ordination site. The elucidation of the adopted mechanism using unsymmetrical amidines of the type R′N(Li)·C(R):NR″ proved not to be possible since in solution the lithioamidines are associated, and react as though they are a mixture of R′N(Li)·C(R):NR″ and R′N:C(R)·N(Li)R″.[15]

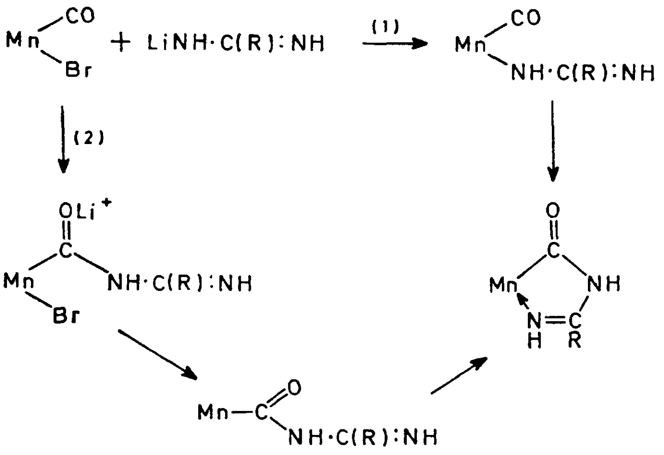
TABLE 4

I.r. spectral data for $[Mn(CO)_4X_2]$ complexes in the ν(CO) stretching region

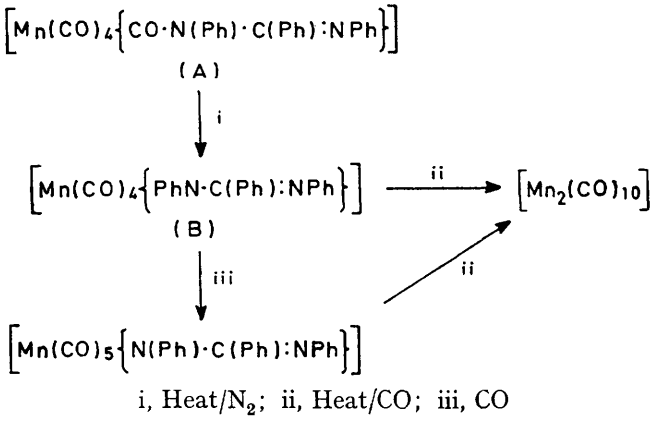
Complex		Stretching frequencies ($\bar{\nu}$/cm^{-1})			
$[Mn(CO)_4(Ph_2C{\cdot}N{:}CPh_2)]$ [a]	$CHCl_3$	2104w	2033s	2020sh	1965s
$[Mn(CO)_4\{PhN{:}C(Ph){\cdot}NPh\}]$ [b]	C_6H_{12}	2093w	2010m	1995s	1950s
$[Mn(CO)_4(CH_2{\cdot}CH{:}CH_2)]$ [c]	C_2Cl_4	2075m	1997s	1979vs	1964vs
$[Mn(CO)_4(CF_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CF_3)]$ [d]	$CHCl_3$	2123w	2055s	1973s	1950s
$[Mn(CO)_4(S_2CPh)]$ [e]	CCl_4	2100w	2022s	2017sh	1972s
$[Mn(CO)_4\{S_2P(C_2H_5)_2\}]$ [f]	C_6H_{14}	2092m	2014vs	2000s	1963s
$[Mn(CO)_4S_2C_2(CN)_2]^-$ [g]	$CHCl_3$	2075w	2010vs	1982s	1933m

[a] K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc.* (*A*), 1970, 2279. [b] This work. [c] H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 1960, **15B**, 682, and ref. 19. [d] Ref. 20. [e] Ref. 8. [f] Ref. 21. [g] J. Locke and J. A. McCleverty, *Chem. Comm.*, 1965, 102; C. R. Jenkins, *J. Organometallic Chem.*, 1968, **15**, 441.

(B) *Complexes of the Type* $[Mn(CO)_4\{R'N{\cdot}C(R){:}NR'\}]$.—In view of the known decarbonylation reactions of acyl derivatives of metal carbonyls to form alkyl derivatives,[16] the carbamoyl-type complexes were heated in a high-pressure i.r. cell [17] under *ca.* 90—160 atm pressures of nitrogen or carbon monoxide and the spectral changes monitored. Under both sets of conditions new absorptions (later attributed to $[Mn(CO)_4\{R'N{\cdot}C(R){:}NR'\}]$) were detected. New i.r. absorptions which occurred after prolonged heating at high pressures of carbon monoxide are ascribed to a $Mn(CO)_5$ moiety, and since a carbamoyl ν(CO) frequency could not be detected the formulation $[Mn(CO)_5\{N(Ph){\cdot}C(Ph){:}NPh\}]$ is tentatively suggested, rather than the corresponding MnC(O)N< derivative. This complex exists at ambient temperatures in a saturated solution of carbon monoxide but readily decarbonylates, particularly when heated to 140—150 °C under nitrogen (90 atm), to $[Mn(CO)_4\{PhN{\cdot}C(Ph){:}NPh\}]$ and $[Mn_2(CO)_{10}]$.



Acyl derivatives of manganese carbonyl are known to decarbonylate when heated to yield alkyl complexes, a reaction which can be reversed under carbon monoxide pressures.[16] Although the decarbonylation step for the carbamoyl complexes reported here can be similarly achieved, recarbonylation of the manganese–nitrogen bond is shown not to occur, in keeping with the findings for other organonitrogen complexes.[18] However a $[Mn(CO)_5(NRR')]$ type complex was detected (although not isolated) and this in itself is unusual. All previous attempts to prepare such amino-complexes *via* conventional synthetic routes have been unsuccessful.[18] Interestingly, the attempted thermal decarbonylation of $[Mn(CO)_4(NH_2Bu^n)CONHBu^n]$ under carbon monoxide pressures yielded $[Mn_2(CO)_{10}]$ at 50 °C during 16 h, with no evidence for an intermediate Mn–N-containing species. Indeed the complexes $[Mn(CO)_4\{CO{\cdot}N(R'){\cdot}C(R){:}NR'\}]$ furnish the first examples of carbamoyl complexes which decarbonylate with the formation of metal–nitrogen bonds.



i, Heat/N_2; ii, Heat/CO; iii, CO

$[Mn(CO)_4\{R'N{\cdot}C(R){:}NR'\}]$ Complexes were synthesised more efficiently and conveniently by u.v. irradiation of the carbamoyl complexes in cyclohexane solution.

Solution i.r. spectra, recorded in Table 1, consist of

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[15] R. L. Shriner and F. W. Neumann, *Chem. Rev.*, 1944, **35**, 351.

[16] K. Noack, U. Schaerer, and F. Calderazzo, *J. Organometallic Chem.*, 1967, **8**, 517; T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598.

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

[18] M. Kilner, unpublished results.

[19] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.

[20] M. Kilner and A. Wojcicki, *Inorg. Chem.*, 1965, **4**, 591.

[21] E. Lindner and K.-M. Matejcek, *J. Organometallic Chem.*, 1970, **24**, C57; 1972, **34**, 195.

three medium and a weak absorption in the carbonyl stretching region consistent with a tetracarbonyl complex with C_{2v} symmetry. The frequencies are compared in Table 4 with those complexes of other 3-electron donors which formally occupy two co-ordination positions, but the modes of attachment differ somewhat. The π-allyl group bonds so that the metal is above the plane of the allyl group, equidistant from each of the skeletal carbon atoms, whereas for the acetylacetonato-group the metal is expected to lie in the O_2C_3 plane, *e.g.* $[Rh(CO)_2\{CF_3\cdot CO\cdot CH\cdot CO\cdot CF_3\}]$.[22] The amidino-group may adopt either mode but at this time it is not possible to deduce which type occurs.

It is relevant here to note that the carboxylato-group acts as a unidentate group to manganese and forms only complexes of the type $[Mn(CO)_5OC(O)R]$.[23] Also the carboxylato-group has a distinct preference to act as a bridging group in low-valent complexes rather than a bidentate group as in $[\{Rh(CO)_2OC(O)CH_3\}_2]$.[24] Thus the amidino-group in manganese carbonyl complexes shows a closer analogy with the π-allyl group rather than with the isoelectronic carboxylato-group.

^{1}H N.m.r. studies, particularly of N-*p*-tolyl derivatives, showed the *p*-methyl substituents to be magnetically equivalent, no splitting of the sharp signal being observed at temperatures down to −50 °C. It is tempting to conclude from these data that the amidino-group bonds symmetrically towards the metal, but caution is required particularly when similar data were recorded for $[\overline{Mn(CO)_4\{CO\cdot N(R')\cdot C(R)\!:\!N}R'\}]$ complexes which are expected to have substituents R′ in different environments. Attempts to synthesise further amidino-complexes more amenable to spectroscopic investigation are being made in an effort to resolve these structural/bonding aspects.

EXPERIMENTAL

NN′-Diphenylbenzamidine,[25] *NN*′-di-*p*-tolylbenzamidine,[26] *NN*′-diphenylacetamidine,[27] and *NN*′-di-*p*-tolylacetamidine [27] were synthesised by standard methods, and benzamidine obtained from its hydrochloride which was obtained commercially. The free amidine was obtained from the hydrochloride hydrate by a standard method,[28] sublimed *in vacuo* at *ca.* 55 °C, and stored under nitrogen at −10 °C. n-Butyl-lithium, *ca.* 2·7M in hexane, was used as supplied commercially without purification. Complexes $[Mn(CO)_5X]$ (X = Cl, Br, or I) were prepared from decacarbonyldimanganese.[29] Hydrocarbon solvents and diethyl ether were dried over extruded sodium, and dichloromethane freshly distilled from phosphoric oxide. All solvents were pumped to remove dissolved air, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed with rigorous exclusion of air.

I.r. spectra in the range 4000—200 cm^{-1} were recorded with a Perkin-Elmer 457 spectrophotometer and ^{1}H n.m.r. spectra at 60 MHz with a Varian A56/60D spectrometer. Thermal decarbonylation and carbonylation studies were accomplished using a balanced pair of high-pressure i.r. cells and monitored with a modified Perkin-Elmer 257 spectrophotometer in the 2200—1500 cm^{-1} region. Mass spectra were obtained with an A.E.I. MS 9 instrument at 70 eV and an accelerating potential of 8 kV. Samples were inserted directly into the ion source at temperatures between 80 and 220 °C.

Carbon, hydrogen, and nitrogen contents of the complexes were determined with a Perkin-Elmer 240 Elemental Analyser, and manganese content by atomic absorption spectroscopy using a Perkin-Elmer 403 spectrophotometer. Molecular-weight measurements were obtained by cryoscopy in benzene, or by osmometry using a Mecrolab osmometer.

The synthetic route adopted for the amidino-complexes involved the preparation of lithioamidines at low temperatures and the reaction at ambient temperature of the white suspension in ether with bromopentacarbonylmanganese. Other carbonyl halides were suitable but the bromide was preferred on account of the ease and efficiency of its preparation from $[Mn_2(CO)_{10}]$. Conversion into the pale yellow amidino-complexes $[Mn(CO)_5\{N(R')\cdot C(R)\!:\!NR'\}]$ as monitored by i.r. spectroscopy appeared quantitative, but the isolation of the material from solution by crystallisation techniques proved difficult and inefficient, and final yields of *ca.* 50% were obtained. Solutions of the products decomposed readily in the air, but the solids could be handled in the air for very short periods without noticeable deterioration. Pure samples left at room temperatures even under nitrogen for several days showed detectable contamination.

Reaction of $LiNH\cdot C(Ph)\!:\!NH$ *with* $[Mn(CO)_5Br]$.—A suspension of lithiobenzamidine was formed from the amidine (0·26 g, 2·2 mmol) and Bu^{n}Li (1·15 ml; 1·48M) in ether (70 ml) by mixing at −196 °C, allowing the mixture to warm, then stirring the mixture of the green solution and white precipitate at ambient temperature for 1·5 h. Attempts to follow the progress of this reaction by i.r. spectroscopy proved unsuccessful since the lithio-derivative has absorption peaks in the ν(C:N) region in identical positions to those of the parent amidines. Addition of this mixture to solid $[Mn(CO)_5Br]$ (0·58 g, 2·1 mmol) and stirring for an additional 1·75 h gave a yellow-orange solution and a fine light-coloured precipitate (LiBr). Filtration of the mixture, and evaporation of the filtrate, after addition of hexane (10 ml), gave a yellow powder. Extraction with dichloromethane followed by filtration of the extracts through alumina, and evaporation to small bulk gave pale green plates of $[Mn(CO)_4\{CO\cdot NH\cdot C(Ph)\!:\!NH\}]$ (m.p. 144 °C, decomp.) [Found: C, 46·2; H, 1·95; N, 8·9; Mn, 17·5. $C_{12}H_7MnN_2O_5$ requires C, 45·87; H, 2·25; N, 8·92; Mn, 17·5%), *m/e* (P^+), 314.

Reaction of $LiN(Ph)C(Ph)\!:\!NPh$ *with* $[Mn(CO)_5Br]$.—A suspension of lithioamidine (2·7 mmol) in ether (130 ml) was added to $[Mn(CO)_5Br]$ (1·0 g, 3·6 mmol) and the mixture was stirred for 3 h at room temperature. Activated alumina (*ca.* 10 g) was then added and the mixture filtered. The residue was washed with ether (2 × 10 ml), and the com-

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[22] N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, *Chem. Comm.*, 1967, 1041.

[23] M. L. H. Green, A. G. Massey, J. T. Moelwyn-Hughes, and P. L. I. Nagy, *J. Organometallic Chem.*, 1967, **8**, 511; R. B. King and R. N. Kapoor, *ibid.*, 1968, **15**, 457.

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bined filtrate and washings evaporated to dryness *in vacuo*. Recrystallisation of the residue from dichloromethane–hexane yielded yellow crystals of $[Mn(CO)_4\{CO{\cdot}N(Ph){\cdot}C(Ph){:}NPh\}]$, m.p. 120 °C (decomp.) [Found: C, 61·95; H, 3·30; N, 6·0%; *M*, 503, 510 (osmometry, benzene). $C_{24}H_{15}MnN_2O_5$ requires C, 61·79; H, 3·24; N, 6·01%; *M*, 466], *m/e* (P^+), 466.

Reaction of $LiN(p\text{-tolyl}){\cdot}C(Ph){:}N(p\text{-tolyl})$ *with* $[Mn(CO)_5Br]$.—The lithio-reagent formed from the amidine (1·33 g, 4·4 mmol) and Bu^nLi (1·65 ml; 2·68M) in ether solution (150 ml) was added to $[Mn(CO)_5Br]$ (1·20 g, 4·4 mmol), and the procedure outlined above for $LiN(Ph)C(Ph){:}NPh$ followed. Yellow-green crystals (m.p. 132 °C, decomp.) of $[Mn(CO)_4\{CO{\cdot}N(p\text{-tolyl}){\cdot}C(Ph){:}N(p\text{-tolyl})\}]$ were obtained by crystallisation of the crude product from dichloromethane–hexane; yield 50·4% [Found: C, 63·3; H, 3·75; N, 5·25; Mn, 11·15%; *M*, 530 (osmometry C_6H_6). $C_{26}H_{19}MnN_2O_5$ requires C, 63·20; H, 3·87; N, 5·17; Mn, 11·12%; *M*, 494]; mass spectrum: *m/e* 494 (P^+), 466 $(P - CO)^+$, 410 $(P - 3CO)^+$, 382 $(P - 4CO)^+$, 354 $(P - 5CO)^+$; ^1H n.m.r. τ (CH_2Cl_2): 2·97 (13H, multiplet), 7·75 (6H, sh). The latter signal remained sharp at −30 °C. $(p\text{-Tolyl})N{:}C(Ph)NH(p\text{-tolyl})$ in CS_2 exhibits signals at τ 2·63(5H), 2·98(8H), and 7·60(6H).

Reaction of $LiN(Ph){\cdot}C(CH_3){:}NPh$ *with* $[Mn(CO)_5Br]$.—The lithioamidine suspension prepared from frozen solutions of $HN(Ph){\cdot}C(CH_3){:}NPh$ (0·312 g, 1·48 mmol) and Bu^nLi (0·55 ml; 2·68M in hexane) in ether (60 ml) was mixed at room temperature with $[Mn(CO)_5Br]$ (0·41 g, 1·49 mmol), and the procedure described previously followed. Yellow-green translucent crystals of $[Mn(CO)_4\{CO{\cdot}N(Ph){\cdot}C(CH_3){:}NPh\}]$ (m.p. 136—138 °C) were obtained by crystallisation of the crude product from dichloromethane–hexane (Found: C, 56·4; H, 3·3; N, 6·95; Mn, 13·6%. $C_{19}H_{13}MnN_2O_5$ requires C, 56·4; H, 3·24; Mn, 13·6; N, 6·93%); mass spectrum: *m/e* 404 (P^+), 376 $(P - CO)^+$, 348 $(P - 2CO)^+$, 320 $(P - 3CO)^+$, 292 $(P - 4CO)^+$, 264 $(P - 5CO)^+$; ^1H n.m.r. τ (CH_2Cl_2): 2·6 (10H, multiplet) and 8·27 (3H). The latter signal remained a sharp singlet down to −34 °C.

Reaction of $LiN(p\text{-tolyl}){\cdot}C(CH_3){:}N(p\text{-tolyl})$ *with* $[Mn(CO)_5Br]$.—The above procedure was followed using the amidine (1·17 g, 4·90 mol), Bu^nLi (1·82 ml; 2·67M in hexane) and $[Mn(CO)_5Br]$ (1·36 g, 4·95 mol) in ether (100 ml). Pale yellow crystals (m.p. 128—132 °C) of $[Mn(CO)_4\{CO{\cdot}N(p\text{-tolyl}){\cdot}C(CH_3){:}N(p\text{-tolyl})\}]$ were isolated [Found: C, 59·3; H, 4·55; Mn, 11·9; N, 6·35. $C_{21}H_{17}MnN_2O_5$ requires C, 59·5; H, 3·97; Mn, 12·7; N, 6·51%]; mass spectrum: *m/e* 432 (P^+), 404 $(P - CO)^+$, 376 $(P - 2CO)^+$, 348 $(P - 3CO)^+$, 320 $(P - 4CO)^+$, and 292 $(P - 5CO)^+$; ^1H n.m.r. τ $(CDCl_3)$: 7·67 and 8·75. The signal due to the phenyl groups was obscured by the signal due to residual $CHCl_3$.

Thermal Decarbonylation of $[Mn(CO)_4\{CO{\cdot}N(Ph){\cdot}C(Ph){:}NPh\}]$.—The complex (*ca.* 80 mg) was mixed with the solvent (Nujol or cyclohexane, 20 ml) and added to a high-pressure i.r. cell,[17] which was then pressurised with nitrogen (*ca.* 70 atm) and slowly heated. The reaction was monitored in the 2200—1500 cm^{-1} region, and after 16 h at 140 °C new absorptions occurred at 2045, 2010, 1995, 1980sh, and 1950 cm^{-1} which are assigned to a mixture of $[Mn_2(CO)_{10}]$ and $[Mn(CO)_4\{PhN{\cdot}C(Ph){:}NPh\}]$. Release of the nitrogen pressure and its replacement with carbon monoxide (200 atm) and adjustment of the temperature to 125 °C produced new absorptions at 2135w, 2050s, and 2000m—s (assigned to $[Mn(CO)_5\{PhN{\cdot}C(Ph){:}NPh\}]$) during 16 h but traces of the starting material remained. These final traces disappeared during the following 24 h. Replacement of the carbon monoxide pressure by a pressure of nitrogen (*ca.* 60 atm), and lowering of the temperature to 100 °C caused the reappearance of $[Mn(CO)_4\{PhN{\cdot}C(Ph){:}NPh\}]$, (2093w, 2010m, 1995s, and 1950s cm^{-1}). After 2 h at 140—150 °C $[Mn_2(CO)_{10}]$ was detected, and after a further 12 h at 145 °C only $[Mn_2(CO)_{10}]$ (2040m, 2010s, and 1980w—m cm^{-1}) remained.

U.v. Irradiation of $[Mn(CO)_4\{CO{\cdot}N(R'){\cdot}C(R){:}NR'\}]$ *Complexes*.—A solution (*ca.* 10^{-3}M) of the complex in cyclohexane was irradiated in a quartz flask *ca.* 20 cm from a 100 W Hg lamp. The solutions darkened from pale yellow-green as the decarbonylation reaction proceeded, and reaction was allowed to continue for between 2 and 3 h. The reactions were monitored by i.r. spectroscopy, and terminated when the absorptions associated with the initial complex failed to decrease in intensity during a 15 min period. Except when very dilute solutions were used, complete conversion into the decarbonylated complexes was not achieved.

After irradiation the solutions were filtered through alumina, then reduced to small bulk *in vacuo*. The resultant complexes were obtained by applying fractional crystallisation techniques at −20 °C, but overall yields tended to be less than 40%. Greatest losses were sustained in the separation process. The deep yellow crystals slowly decomposed in air at ambient temperatures, whereas solutions of the complexes in organic solvents in which they are very soluble were particularly susceptible to decomposition in air. The complexes failed to give mass spectra, thermal decomposition occurring in the source chamber before the complex could be volatilised.

$[Mn(CO)_4\{(p\text{-tolyl})N{\cdot}C(Me){:}N(p\text{-tolyl})\}]$, Found: C, 59·4; H, 4·3; Mn, 13·9; N, 7·1. $C_{20}H_{17}MnN_2O_4$ requires C, 59·5; H, 4·24; Mn, 13·6; N, 6·94%; parent peak in the mass spectrum was not detected.

$[Mn(CO)_4\{PhN{\cdot}C(CH_3){:}NPh\}]$, Found: C, 57·4; H, 3·45; Mn, 14·35; N, 7·55%; *M*(cryoscopy in C_6H_6), 420. $C_{18}H_{13}MnN_2O_4$ requires C, 57·5; H, 3·46; Mn, 14·65; N, 7·46%; *M*, 438.

$[Mn(CO)_4\{(p\text{-tolyl})N{\cdot}C(Ph){:}N(p\text{-tolyl})\}]$, Found: C, 64·7; H, 4·25; N, 5·25. $C_{25}H_{19}MnN_2O_4$ requires C, 64·4; H, 4·11; N, 6·01%; ^1H n.m.r. τ (CCl_4): 2·67—3·48 (various sharp signals, 13H), 7·72(6H), (CH_2Cl_2): 2·97 (multiplet 13H), and 7·75(6H) [$(p\text{-tolyl})NH{\cdot}C(Ph){:}N(p\text{-tolyl})$ τ (CS_2): 2·63(5H), 2·98(8H), 7·60(6H)]. No splitting of the CH_3 signal was observed at −50 °C.

$[Mn(CO)_4\{(p\text{-tolyl})NC(Ph){:}N(p\text{-tolyl})\}C_6H_{12}]$, Found: C, 67·7; H, 4·25; N, 5·2. $C_{25}H_{19}MnN_2O_4$ requires C, 67·6; H, 5·64; N, 5·09%.

$[Mn(CO)_4\{PhN{\cdot}C(Ph){:}NPh\}]$, Found: C, 63·2; H, 3·8; Mn, 12·5; N, 6·5. $C_{23}H_{15}MnN_2O_4$ requires C, 63·0; H, 3·42; Mn, 12·5; N, 6·39%.

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