Organonitrogen Groups in Metal Carbonyl Complexes. Part VII.† Methyleneamino-derivatives of Iron Carbonyls

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$(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$, formed in the reactions of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, Br, I) with $Bu^t_2C{:}NLi$, is the sole derivative of this type isolated, although evidence is presented for the existence of a diphenyl derivative in solution. $Fe(CO)_4X_2$ (X = I, Br) reacts with $R'R''C{:}NLi$ ($R' = R''$ = Ph, *p*-tolyl; R' = Ph, $R'' = Bu^t$) to form $Fe_2(CO)_6I(N{:}CR'R'')$ and $[Fe(CO)_3N{:}CR'R'']_2$, for which structures with bridging methyleneamino-groups are assigned on the basis of i.r. and Mössbauer spectroscopic data. All complexes are formed in low yield. The novel $Fe_2(CO)_6I(N{:}CR'R'')$ complexes are of structural interest since they contain bridging groups of widely differing sizes and bridging characteristics.

ORGANONITROGEN groups acting as three electron donors in iron carbonyl complexes are well documented,[1] and such complexes have the nitrogen atom usually in a bridging position linking two metals, although groups bridging three metals are not uncommon.[1] The structures are characterised by short metal–metal distances, small FeNFe angles, and small dihedral angles. Such features were found by *X*-ray crystallographic studies[2] for the methyleneamino-bridged complex $[Fe(CO)_3N{:}C(p\text{-tolyl})_2]_2$ (I; $R^1 = R^2 = R^3 = R^4 = p$-tolyl), which was obtained in small yield by the reaction of $Fe_2(CO)_9$ with the azine $(p\text{-tolyl})_2C{:}NN{:}C(p\text{-tolyl})_2$.[3] Alternative routes to this type of methyleneamino-complex have been explored with the intention of studying this organonitrogen group in this bridging mode of bonding.

Previous studies of methyleneamino-derivatives[4] have been concerned primarily with complexes having terminally bound groups *e.g.* $[(\pi\text{-}C_5H_5)M(CO)_2N{:}CR_2]$ (M = Mo, W; R = Bu^t, Ph, *p*-tolyl, $p\text{-}CF_3C_6H_4$, *etc.*) and only for certain complexes does thermolysis lead to the synthesis of bridged dinuclear $[(\pi\text{-}C_5H_5)M(CO)N{:}CR_2]_2$ complexes. The requirement that each metal satisfies the noble gas rule implies that ten electrons are involved in the bonding in the M_2N_2 ring system. Since either six or eight electrons are commonly involved in M_2X_2 bridging units and ten electron units are rare, these Group VI metal derivatives were considered atypical, and efforts were directed preferentially towards iron carbonyl derivatives. Studies of three types of complexes, $[(\pi\text{-}C_5H_5)Fe(CO)N{:}CR_2]$, $[Fe_2(CO)_6I(N{:}CR_2]$, and $[Fe(CO)_3N{:}CR_2]_2$ are now reported.

RESULTS AND DISCUSSION

The Monocarbonyl Complexes $[(\pi\text{-}C_5H_5)Fe(CO)N{:}CR_2]$.—The reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2X]$ (X = Cl, Br, I) with $Bu^t_2C{:}NLi$ produced $[(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2]$ as an air and light sensitive blue oil, which decomposed slowly at ambient temperatures in an atmosphere of nitrogen. In contrast, the reactions of the dicarbonyl chloride with $R_2C{:}NSiMe_3$ (R = Ph, Bu^t) under refluxing conditions in monoglyme solution for several hours produced $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in high yield; for R = Ph a small amount of the azine $Ph_2C{:}NN{:}CPh_2$ was isolated also. In the reaction with $Ph_2C{:}NLi$, a new i.r. absorption at 1946 cm^{-1} indicated the formation of a carbonyl species in solution at low temperatures, but all attempts to isolate and purify the complex at low temperatures led to its decomposition. The close similarity of certain aspects of the i.r. spectrum of this complex [*e.g.* ν(CO) 1946 cm^{-1} in ether] with that of $[(\pi\text{-}C_5H_5)Fe(CO)_2N{:}CBu^t_2]$ [ν(CO) 1953 cm^{-1} in $CHCl_3$] indicate that $[(\pi\text{-}C_5H_5)Fe(CO)N{:}CPh_2]$ may have been formed in solution, although we cannot eliminate entirely the possibility that a 2-aza-allyl/allene[5,6] complex, $(\pi\text{-}C_5H_5)Fe(CO)(Ph_2CNCPh_2)$, was formed.

$(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$ has a similar blue colour and a similar camphor-like odour to the corresponding molybdenum and tungsten analogous,[4a] but is much more unstable towards air and light, and readily loses carbon monoxide. The mass spectrum and i.r. confirm the mononuclear formulation. A single sharp methyl signal in the ^1H n.m.r. spectrum (Table 1) was observed at all temperatures between ±40° with only a small movement in position due to temperature effects. A linear FeNC skeleton is inferred. Rotation of the methyleneamino-group about the multiple M–N bond is possible in the same way as postulated for $[(\pi\text{-}C_5H_5)Mo(CO)_2N{:}CBu^t_2]$[4b] but was not detected.

$[(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2]$ undergoes rapid decomposition with iodine to produce an inseparable oily mixture of non-carbonyl compounds, in contrast to the reactions of $[\pi\text{-}C_5H_5)M(CO)_2N{:}CR_2]$ (M = Mo, W) complexes.[4b]

No evidence was found for a dinuclear complex $[(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2]_2$ having two three-electron organonitrogen bridging groups. Steric factors are most probably responsible for the preferred mononuclear formulation, but such restrictions do not occur for the

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† Part VI is reference 4*e*.

[1] M. Kilner, 'Nitrogen Groups in Metal Carbonyl Complexes,' *Adv. Organometallic Chem.*, 1970, **10**, 115.

[2] D. Bright and O. S. Mills, *Chem. Comm.*, 1967, **245**.

[3] M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Comm.*, 1965, **543**; G. R. Knox and P. L. Pauson, personal communication.

[4] (*a*) K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc.* (*A*), 1970, **2279**; (*b*) M. Kilner and C. Midcalf, *J. Chem. Soc.* (*A*), 1971, **292**; (*c*) M. Kilner and J. N. Pinkney, *J. Chem. Soc.* (*A*), 1971, **2887**; (*d*) H. R. Keable and M. Kilner, *J. Chem. Soc.* (*A*), 1972, **153**; (*e*) H. R. Keable, M. Kilner, and Mrs. E. E. Robertson, *J.C.S. Dalton*, 1974, **639**.

[5] H. R. Keable and M. Kilner, *J.C.S. Dalton* (*A*), 1972, **1535**.

[6] D. Biggs, D. T. Clarke, H. R. Keable, and M. Kilner, *J.C.S. Dalton*, 1973, **2143**.

$N{:}CPh_2$ group and a *trans*-dinuclear formulation, *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)N{:}CPh_2]_2$, cannot be entirely eliminated. For comparison both $[(\pi\text{-}C_5H_5)Mo(CO)_2N{:}CPh_2]$ and $[(\pi\text{-}C_5H_5)Mo(CO)_2N{:}CPh_2]_2$ are known.[4e]

TABLE 1

I.r. and ^1H n.m.r. spectral data

	ν(CO) Stretching frequencies (cm^{-1})	^1H n.m.r. (τ)
$(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$	1953s [a]	5·61(5), 8·94(18) [c]
$(\pi\text{-}C_5H_5)Fe(CO)N{:}CPh_2$ (?)	1946s [a]	
$[Fe(CO)_3N{:}CPh_2]_2$	2047m, 2041s, 1994s, 1979vvw,[b] 2065, 2035, 1988 [e]	2·80 [d]
$[Fe(CO)_3N{:}C(p\text{-tolyl})_2]_2$	2071m, 2038s, 1992s, 1976vvw,[b] 2055, 2020, 1975 [e]	2·94(4), 7·66(3),[d] 2·93(3·9), 7·63(3) [e]
$[Fe(CO)_3N{:}CPhBu^t]_2$	2073m 2036s, 1994s, 1987s,1971m [b]	2·80(5), 8·84(9) [d]
$Fe_2(CO)_6I(N{:}CPh_2)$	2083m, 2050s, 2016s, 2006s, 1982vvw [b]	2·68 [d]
$Fe_2(CO)_6I[N{:}C(p\text{-tolyl})_2]$	2084m, 2053s, 2018s, 2008s, 1980vw [b]	2·87(4), 7·63(3) [d]
$Fe_2(CO)_6I(N{:}CPhBu^t)$	2082m, 2048s, 2014s, 2008s, 1995vw [b]	2·70(5), 8·78(9) [d]

[a] Chloroform solution. [b] Cyclohexane solution. [c] Perdeuteriomethylcyclohexane solution. [d] Carbon disulphide solution. [e] Carbon tetrachloride solution; M. M. Bagga, G. R. Knox, and P. L. Pauson, personal communication.

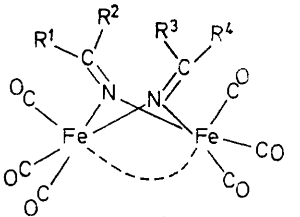
The Dinuclear Complexes $[Fe(CO)_3N{:}CR'R'']_2$.—$R'R''C{:}NLi$ ($R' = R'' =$ Ph, *p*-tolyl; $R' =$ Ph, $R'' = Bu^t$) reacted with $Fe(CO)_4I_2$ in ether solution to form complexes of the type $[Fe(CO)_3N{:}CR'R'']_2$ together with small amounts of $[Fe_2(CO)_6I(N{:}CR'R'')]$, which were separated by chromatography on silica using cyclohexane as the eluting agent. The former complexes were all air stable yellow-orange crystalline complexes. When $Bu^t_2C{:}NLi$ was used as the reactant the only product obtained was iron pentacarbonyl, identified by i.r. spectroscopy and mass spectrometry.

Bagga, Knox, and Pauson[3] prepared the complexes $[Fe(CO)_3N{:}CR_2]_2$ (R = Ph, *p*-tolyl) in ⩽2·2% yield by an alternative route from $Fe_2(CO)_9$ and the corresponding azine in benzene at the reflux temperature. We have attempted the preparation of these types of complexes from $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ with $Ph_2C{:}NN{:}CPh_2$ using (i) the reactants alone in a sealed tube at 100—150° for up to 24 h, (ii) irradiation of the reactants in ether solution at the ambient temperature for up to 24 h, and (iii) heating the reactants in ether solution at the reflux temperature for up to 48 h. [$Fe(CO)_5$ and the azine were heated also at 100—120° in petroleum ether and in toluene (at 80 and 150° in a sealed tube)]. Similar reactions were attempted also with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. In most cases decomposition of the iron carbonyls amounted to between 10—20% and most of the starting materials were recovered unchanged. I.r. spectroscopy and chromatography of the reaction mixture using alumina gave no indication of the formation of any organonitrogen complexes. Pauson *et al.*[3] demonstrate that a thermal route from $Fe_2(CO)_9$ is possible, but the conditions of temperature and/or solvent are apparently very critical to obtain even a small yield. The alternative route *via* $Fe(CO)_4X_2$ complexes produced yields of 8—9%, and was therefore preferred.

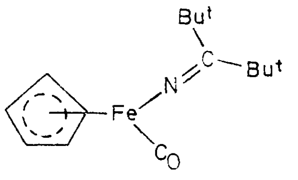
For the $[Fe(CO)_3N{:}CR_2]_2$ complexes in solution, the number and arrangement of carbonyl absorptions in the i.r. spectra are similar to those observed for other $[Fe_2(CO)_6X_2]$ complexes[7,8] and indicate similar structures to that determined by *X*-ray crystallographic techniques for $[Fe(CO)_3N{:}C(p\text{-tolyl})_2]_2$.[2]

The two methyleneamino-groups act as three electron bridging atoms between the iron atoms. The observed ν(CO) frequencies are *ca.* 5—20 cm^{-1} to higher energy than those of the structurally related complexes $[Fe(CO)_3SPh]_2$[7] and $[Fe(CO)_3PPh_2]_2$,[8] which may indicate, since nitrogen bases are in general stronger Lewis bases than either sulphur or phosphorus bases, that the methyleneamino-group is more efficient at reducing the electron density at the metal through π-bonding.

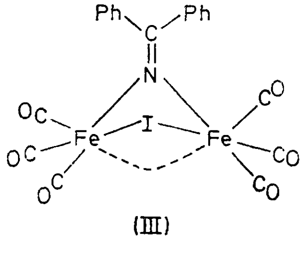
Compared with the i.r. spectra of $[Fe(CO)_3N{:}CR_2]_2$ (R = Ph, *p*-tolyl), $[Fe(CO)_3N{:}CPhBu^t]_2$ exhibits in solution two additional ν(CO) stretching frequencies (bands are of medium to strong intensity) resulting from the lowering of the symmetry of the molecule on introducing an asymmetrically substituted methyleneamino-group. Although two geometrical isomers are theoretically possible, evidence from fractional crystallisations, chromatography on silica, and ^1H n.m.r. studies indicated the presence of only one isomer, which for steric reasons is expected to be the isomer (I; $R^1 = R^4 = Bu^t$; $R^2 = R^3 =$ Ph). Models based upon the structure of $[Fe(CO)_3N{=}C(p\text{-tolyl})_2]_2$ indicate that a t-butyl substituent would distort the adjacent $Fe(CO)_3$ moiety, particularly by causing the unique carbonyl group to be displaced towards the second bridging position. This steric hindrance[9] restricts the available space for the



(I)



(II)



(III)

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[7] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3600.

[8] R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711.

[9] R. Snaith, C. Summerford, K. Wade, and B. K. Wyatt, *J. Chem. Soc. (A)*, 1970, 2635.

second bridging group, and is thought to prevent the formation of the *syn*-isomer as well as $[Fe(CO)_3N{:}CBu^t_2]_2$.

The mass spectra confirmed the molecular formulations and the presence of six carbonyl groups in each complex. Similar metal containing ions were detected; and each spectrum was free of mononuclear metal species. Thus the presence of bridging groups binding the metal atoms is highly likely. All the spectra showed strong peaks corresponding to the doubly charged ions $[Fe_2(N{:}CR'R'')_2]^{2+}$. It is notable that when $R' = Bu^t$ and $R'' = Ph$, the predominant fragmentation of $[Fe_2(N{:}CBu^tPh)_2]^+$ is through two successive losses of $[Bu^tC{:}N]$, a fragmentation path similar to that observed previously for $[(\pi\text{-}C_5H_5)M(CO)L(N{:}CBu^tPh)]$ ($M = Mo$, W; $L = CO$; $M = Mo$, $L = PPh_3$).[4c]

The Mössbauer spectral data for the complexes $[Fe(CO)_3N{:}CR'R'']_2$ are recorded in Table 2. The low isomer shift values (δ) reflect the high *s*-electron density at the metal nucleus arising from two main factors, the strong σ-donation of the nitrogen base into iron orbitals with some 4*s* character, and π-bonding of filled metal *d*-orbitals with empty orbitals of the ligand. These two effects are considered to predominate; it has been shown from studies involving a variety of Lewis bases with varying degrees of back-co-ordination that forward σ-donation into orbitals involving the iron 3*d* orbitals, which has the opposite effect of increasing the shielding and diminishing the *s*-electron density at the iron nucleus, is less important.[10]

TABLE 2

Mössbauer spectral data at 77 K

Complex	Isomer shift δ/mm s^{-1}	Quadrupole splitting Δ/mm s^{-1}	Half width mm s^{-1}
$[Fe(CO)_3N{:}CPh_2]_2$	0·03	0·87	0·23
$[Fe(CO)_3N{:}C(p\text{-tolyl})_2]_2$	0·01	0·85	0·19
$[Fe(CO)_3N{:}CPhBu^t]_2$	0·05	0·87	0·24
$Fe_2(CO)_6I(N{:}CPh_2)$	0·16	1·70	0·25

Similar Mössbauer parameters to those observed for the bismethyleneamino-bridged complexes have been observed for $[Fe_2(CO)_6(PhHC{:}NNHPh)]$ (δ, 0·03 mm s^{-1}; Δ, 0·87 mm s^{-1}),[11] and a related structure has been proposed. Rupture of the N–N bond of the organonitrogen ligand is considered to produce PhHC:N- and PhNH-groups which bridge between the $Fe(CO)_3$ moieties. Such a structure is preferred to the alternative structure having the *o*-metallated bridging ligand system $[C_6H_4CH_2NNHPh]$.

The Heterobridged Dinuclear Complexes $Fe_2(CO)_6(N{:}CR'R'')I$.—These complexes were obtained in small yield as deep red crystals ($R' = R'' = Ph$) or deep red oils ($R' = R'' = p$-tolyl; $R' = Ph$, $R'' = Bu^t$) from the reactions of $Fe(CO)_4I_2$ with $R'R''C{:}NLi$ and were separated from the major product $[Fe(CO)_3N{:}CR'R'']_2$ by chromatography on silica. Spectroscopic data relating to the complexes are given in Tables 1 and 2. The formal replacement of a bridging methyleneamino-group in symmetrically bridged complexes by the electronegative iodine [structure (III)] effectively reduces the electron density at the metal and is seen to be reflected in the higher i.r. absorption frequencies of the carbonyl groups. The lowering of the symmetry of the bridging unit is reflected in the appearance of an additional ν(CO) absorption for the heterobridged complexes compared with the homo-bridged complexes, but on the basis of the i.r. spectrum it is not possible to assign planar or puckered Fe_2NI bridging units.

The mass spectra of the $[Fe_2(CO)_6(N{:}CR'R'')I]$ complexes confirm their molecular formulation and the presence of six carbonyl groups. The persistence of the complexes to fragment without loss of iodine and without formation of mononuclear metal species is in keeping with other polynuclear bridged complexes, for which the metal cluster does not fragment until all the terminally attached groups have been lost.[12] An interesting feature of the $[Fe_2(CO)_6(N{:}CPhBu^t)I]$ complex is again the fragmentation through loss of $[Bu^tCN]$ in preference to [PhCN] from $[Fe_2(N{:}CPhBu^t)I]^+$.

The nature of the Fe_2NI bridging unit is of particular interest [13] since the bridging characteristics of nitrogen and iodine in iron complexes are apparently opposed. In general, the geometry of bridging units depends on the co-ordination of the metal, the size of the bridging atoms, their repulsion across the ring, and the presence or absence of metal–metal bonds.[14] Ideally a comparison between $[Fe(CO)_3NR_2]_2$ and $[Fe(CO)_3I]_2$ would be most appropriate, but the latter complex is not known, and consequently general features of the crystal structures of $[Fe(CO)_3NH_2]_2$ [15] and $[Fe(NO)_2I]_2$ [14] are compared instead. Unfortunately the number of co-ordinated groups is not the same for each, but valuable trends can nevertheless be obtained. Organonitrogen groups bridge between metals so that the M–N–M and N–M–N angles are small, and in complexes having metal–metal bonds the dihedral angles are also comparatively small (see ref. 1). In $[Fe(CO)_3NH_2]_2$, for example, the angles are 74, 78, and 78° respectively. In contrast the large size of iodine restricts symmetrically iodine bridged units to approximately planar arrangements although the angles at iodine are similar to those at nitrogen in related complexes (*i.e.* FeIFe angle in $[Fe(NO)_2I]_2$ is 73°).[14] Metal–metal distances for the latter complexes are long {*e.g.* 3·05 Å for $[Fe(NO)_2I]_2$} compared with symmetrically nitrogen bridged complexes {2·40 Å for $[Fe(CO)_3NH_2]_2$}. Whereas the iron atoms of $[Fe(CO)_3NH_2]_2$ can be considered to be square based pyramidally co-ordinated,[15] the vacant octahedral position being associated with a

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[10] R. Greatrex and N. N. Greenwood, *Discuss. Faraday Soc.*, 1969, **47**, 126; R. L. Collins and R. Pettit, *J. Chem. Phys.*, 1963, **39**, 3433.

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[12] D. B. Chambers, F. Glocking, and J. R. C. Light, *Quart. Rev.*, 1968, **12**, 317.

[13] M. Kilner and C. Midcalf, *Chem. Comm.*, 1971, 944.

[14] L. F. Dahl, E. R. de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 1969, **91**, 1653 and references therein.

[15] L. F. Dahl, W. Costello, and R. B., King, *J. Amer. Chem. Soc.*, 1968, **90**, 5422.

metal–metal bond, the metal–metal interaction of $[Fe(NO)_2I]_2$ is across the planar Fe_2I_2 ring, conferring five-fold co-ordination on each iron atom.[14] Thus the preference of bridging iodines for planar arrangements and long metal–metal distances contrasts with the small dihedral angles and short metal–metal distances observed for nitrogen bridged systems.

The Mössbauer spectral data (Table 2) for $[Fe_2(CO)_6(N{:}CR'R'')I]$ show considerable differences from the parameters for $[Fe(CO)_3N{:}CR'R'']_2$ complexes. The larger isomer shift values observed for the former reflect the expected decrease in σ-donation from the bridging atoms and the decrease in π-bonding when nitrogen is replaced by iodine. The iodine bridged complexes exhibit large quadrupole splittings indicating a significant distortion of the pseudo-octahedral co-ordination of iron found for $[Fe(CO)_3N{:}C(C_6H_4\text{-}p\text{-}Me)_2]_2$; indeed a tendency towards a planar Fe_2NI ring may be indicated, although for a complex with a truly planar bridging unit a higher quadrupole splitting is expected.[10]

A recent *X*-ray crystal structural determination [16] of the complex $[Fe_2(CO)_6(N{:}CPh)_2I]$ has shown the geometry of the $[Fe_2(N{:}CPh_2)]$ unit to be virtually unchanged from that observed for $[Fe(CO)_3N{:}C(p\text{-tolyl})_2]_2$ [2] and that the nitrogen is the most dominant atom in determining the geometry of the Fe_2NI bridging unit. A short metal–metal bond is observed (2·44 Å) which produces a small FeIFe angle at iodine (55·2°). This angle is notably smaller, to an extent of about 18°, than the lowest previously observed angles. For comparative purposes, the complexes $[Fe(NO)_2I]_2$ [14] and α-NBI_4 [17] have MIM angles of 73 and 74° respectively. Co-ordination of the iron atoms in $Fe_2(CO)_6(N{:}CPh_2)I$ is distorted and does not correspond to any regular figure.

Treatment of $[Fe_2(CO)_6I(N{:}CPh_2)]$ with $Ph_2C{:}NLi$ in a 1 : 1 molar proportion produced an excellent yield of $[Fe(CO)_3N{:}CPh_2]_2$, and illustrates a possible synthetic route to other mixed bridged complexes. Studies are continuing with this objective.

EXPERIMENTAL

$R_2C{:}NH$ ($R = Bu^t$, Ph, *p*-tolyl),[18] $Bu^tPhC{:}NH$,[18] $Ph_2C{:}NLi$,[19] $Ph_2C{:}NSiMe_3$,[20] $Bu^t_2C{:}NLi$,[21] $Bu^t_2C{:}NSiMe_3$,[20] $PhBu^tC{:}NLi$,[4c] $(p\text{-tolyl})_2C{:}NLi$,[19] $Fe(CO)_4X_2$ (X = Br, I),[22] and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, Br, I) [23] were prepared by standard routes. Triphenylphosphine was recrystallised from hexane before use, and iodine purified by sublimation *in vacuo*. Hydrocarbon solvents and diethyl ether were dried over extruded sodium, monoglyme distilled from lithium aluminium hydride, and chloroform 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 and in darkness.

Spectra.—I.r. spectra in the range 4000—200 cm^{-1} were recorded with a Grubb–Parsons Spectromaster and Perkin-Elmer SP 457 spectrophotometers, and ^1H n.m.r. spectra at 60 MHz with a Perkin-Elmer R10 or Varian A56/60 spectrometer. 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°. Mössbauer spectra at 77 K were recorded at the P.C.M.U., Harwell.

Analysis.—Carbon, hydrogen, and nitrogen contents were determined with a Perkin-Elmer 240 elemental analyser and iodine content by fusion of the complex with potassium, followed by the volumetric determination of iodide ions. Molecular weights were determined in benzene by cryoscopy or osmometry using a Mecrolab osmometer.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ *with* $Bu^t_2C{:}NLi$.—A solution of $Bu^t_2C{:}NLi$ (2 mmol) in ether (10 ml) was added to a frozen solution of $(C_5H_5)Fe(CO)_2Cl$ (0·42 g, 2·0 mmol) in ether (100 ml). The mixture when slowly warmed and kept at room temperature for $\frac{1}{2}$ h became deep blue, slowly evolved gas, and deposited a fine white powder. After separation by filtration the residue was shown by i.r. spectroscopy and qualitative tests to consist of lithium chloride, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, and a non-carbonyl oily decomposition product. Evaporation of the filtrate (20°, 10^{-1} mmHg) gave an oily blue residue which was extracted with hexane (2 × 50 ml). Removal of the hexane (20°, 10^{-1} mmHg) gave $(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$ as a blue oil, which was vacuum distilled into a cooled receiver (20°, 10^{-3} mmHg) [yield, 0·32 g (55%)] (Found: C, 62·1; H, 8·1; N, 4·8; CO, 9·55; *M*, 295. $C_{15}H_{23}FeNO$ requires C, 62·28; H, 7·96; N, 4·84; CO, 9·68%; *M*, 289), ν(CO) 1947s (Nujol), ν(CN) 1610w, mbr cm^{-1} (Nujol), *m/e* (P^+) 289, m^* [$P^+ \longrightarrow (P - CO)^+$] 235.

Similar reactions occurred using $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ and $(\pi\text{-}C_5H_5)Fe(CO)_2I$ as starting materials.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ *with* $Bu^t_2C{:}NSiMe_3$.—$(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (1·84 g, 10 mmol) and $Bu^t_2C{:}NSiMe_3$ (10 mmol) were refluxed for 48 h in monoglyme (100 ml). No gas evolution was observed, and the carbonyl chloride was slowly converted to $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, the only product detected by i.r. spectroscopy and chromatography on alumina.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ *with* $Ph_2C{:}NLi$.—A solution of $Ph_2C{:}NLi$ (2 mmol) in a hexane–ether mixture (20 ml) was added to a frozen solution of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (0·42 g, 2 mmol) in ether (20 ml) at −196°. The mixture, when slowly warmed to room temperature, became dark in colour and slowly evolved gas over 1 h. The solution was reduced in bulk (25°, 10^{-1} mmHg) and chromatographed on neutral alumina. Elution with a light petroleum–ether mixture (4 : 1) gave $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, both identified by i.r. spectroscopy. I.r. spectroscopy also indicated the presence of a monocarbonyl species [ν(CO) 1946 cm^{-1}] present in small quantity but attempts to isolate this product by low temperature recrystallisation and chromatography failed.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ *with* $Ph_2C{:}NSiMe_3$.—

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$Ph_2C{:}NSiMe_3$ (10 mmol) was added to a solution of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (1·84 g, 10 mmol) in monoglyme (30 ml). After 48 h at the reflux temperature the only product detected and isolated was $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, which was identified by i.r. spectroscopy and analysis.

Attempted Reaction of $(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$ *with* Ph_3P.—No reaction occurred between triphenylphosphine (0·524 g, 2 mmol) and $(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$ (0·58 g, 2 mmol) in hexane (100 ml) at the reflux temperature over 48 h.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$ *with Iodine.*—Iodine (0·25 g, 1 mmol) in hexane (200 ml) was added slowly to $(\pi\text{-}C_5H_5)Fe(CO)N{:}CBu^t_2$ (0·58 g, 2 mmol) in hexane (100 ml). Rapid decomposition of the carbonyl complex resulted in an inseparable black oil.

Reaction of $Fe(CO)_4I_2$ *with* $Ph_2C{:}NLi$.—A solution of $Ph_2C{:}NLi$ (5 mmol) in diethyl ether (10 ml) was added to a cooled solution of $Fe(CO)_4I_2$ (2·11 g, 5 mmol) also in diethyl ether (100 ml). On warming slowly to room temperature and stirring for 1 h the slow evolution of carbon monoxide ceased and the solution darkened in colour. The ether was removed *in vacuo* (20°, 10^{-1} mmHg), and the residue extracted with n-hexane (3 × 20 ml). The n-hexane was then removed from the extracts (20°, 10^{-1} mmHg), the residue dissolved in the minimum quantity of warm cyclohexane, and the solution chromatographed on a 3 ft Silicar column, using cyclohexane as eluant. Two fractions were separated, the first a deep red colour and the second a yellow-orange colour. The solvent was removed (20°, 10^{-1} mmHg) from each fraction, the residues dissolved separately in hot n-hexane, and the solutions left to give respectively crystals of (*a*) $Fe_2(CO)_6(N{:}CPh_2)I$ [m.p. 138—139° (decomp.), 0·6 g, 4%] and (*b*) $[Fe(CO)_3N{:}CPh_2]_2$ (m.p. 136—138°, 1·3 g, 8%) at −20° [(*a*) Found: C, 38·85; H, 1·65; N, 2·35; I, 21·3. $C_{19}H_{10}Fe_2INO_6$ requires C, 38·84; H, 1·70; N, 2·38; I, 21·63%. m/e (P^+) 587. ν(CO), Nujol mull: 2075m, 2040s, 2000s, 1988s, 1976s, and 1948vvw cm^{-1}; (*b*) Found: C, 60·1; H, 3·1; N, 4·35; *M*, 635. $C_{32}H_{20}Fe_2N_2O_6$ requires C, 60·00; H, 3·13; N, 4·38%; *M*, 640. m/e (P^+) 640. ν(CO), Nujol mull: 2071m, 2034s, 1985s, 1974s, 1968sh, 1961s, and 1935vvw cm^{-1}].

Reaction of $Fe(CO)_4I_2$ *with* (p-tolyl)$_2C{:}NLi$.—A solution of (p-tolyl)$_2C{:}NLi$ (5 mmol) in diethyl ether (10 ml) was added to a cooled solution of $Fe(CO)_4I_2$ (2·11 g, 5 mmol) in diethyl ether (100 ml), and the reaction carried out as described above. The first deep red fraction produced $Fe_2(CO)_6(N{:}C$-p-tolyl)$_2$I, as a deep red oil (yield 3%) (Found: C, 40·9; H, 2·25; N, 2·2; I, 20·5. $C_{21}H_{14}Fe_2INO_6$ requires C, 40·97; H, 2·27; N, 2·27; I, 20·65%). m/e (P^+) 615. ν(CO), Nujol mull: 2079m, 2048s, 2013s, 2000s, 1984s cm^{-1}. The second orange fraction produced orange needle-like crystals of $[Fe(CO)_3N{:}C(p\text{-tolyl})_2]_2$ [0·28 g (8%), decomp. 157° without melting] (Found: C, 61·8; H, 3·9; N, 4·0; *M* (benzene), 681. $C_{36}H_{28}Fe_2N_2O_6$ requires C, 62·07; H, 4·02; N, 4·02%; *M*, 696). m/e (P^+) 696. ν(CO), Nujol mull: 2070m, 2030s, 1992s, 1984s, 1977s, and 1962vvw cm^{-1}.

Reaction of $Fe(CO)_4I_2$ *with* $PhBu^tC{:}NLi$.—A solution of $PhBu^tC{:}NLi$ (5 mmol) in diethyl ether (10 ml) was added to a cooled solution of $Fe(CO)_4I_2$ (2·11 g, 5 mmol) in diethyl ether (100 ml) and the reaction carried out as described above. The first deep red fraction produced $[Fe_2(CO)_6(N{:}CPhBu^t)I]$ (4%) as a deep red oil (Found: C, 35·95; H, 2·4; N, 2·4; I, 22·25. $C_{17}H_{14}Fe_2INO_6$ requires C, 35·97; H, 2·47; N, 2·47; I, 22·40%). m/e (P^+) 567. ν(CO), Nujol mull: 2081m, 2044s, 2009s, 1987s, 1980s, and 1963vw cm^{-1}. The second orange fraction produced orange needle-like crystals of $[Fe(CO)_3N{:}CPhBu^t]_2$ (0·3 g, 9%), m.p. 160° (decomp.) (Found: C, 56·1; H, 4·7; N, 4·75; *M* (benzene), 595. $C_{28}H_{28}Fe_2N_2O_6$ requires C, 56·0; H, 4·66; N, 4·66%; *M*, 600). m/e (P^+) 600. ν(CO), Nujol mull: 2064m, 2028s, 1991s, 1984s, and 1959s cm^{-1}.

Reaction of $Fe(CO)_4I_2$ *with* $Bu^t_2C{:}NLi$.—A solution of $Bu^t_2C{:}NLi$ (5 mmol) in diethyl ether (10 ml) was added to a cooled solution of $Fe(CO)_4I_2$ (2·11 g, 5 mmol) in diethyl ether (100 ml). The mixture, when slowly warmed and kept at room temperature for 1 h, darkened in colour and evolved carbon monoxide. The i.r. spectrum of the solution showed almost total consumption of the carbonyl iodide. The only product was obtained by distillation and identified by i.r. spectroscopy, mass spectroscopy, and analysis as pentacarbonyl iron (yield, 30—40%).

Reaction of $Fe(CO)_4Br_2$ *with* $Ph_2C{:}NLi$.—A solution of $Ph_2C{:}NLi$ (10 mmol) in diethyl ether (10 ml) was added to a cooled solution of $Fe(CO)_4Br_2$ (3·28 g, 10 mmol) in diethyl ether (100 ml) and the reaction carried out as described above. Chromatography gave one orange-yellow fraction from which yellow needle-like crystals of $[Fe(CO)_3N{:}CPh_2]_2$ were obtained (0·13 g, 2%) (Found: C, 60·2; H, 3·5; N, 4·7. $C_{32}H_{20}Fe_2N_2O_6$ requires C, 60·00; H, 3·13; N, 4·38%).

Reaction between $[Fe_2(CO)_6(N{:}CPh_2)I]$ *and* $Ph_2C{:}NLi$.—$Ph_2C{:}NLi$ (0·5 mmol) in ether (5 ml) was added to a cooled solution of $[Fe_2(CO)_6(N{:}CPh_2)I]$ (0·29 g, 0·5 mmol) in hexane (5 ml). The reaction was shown by i.r. spectroscopy to be complete after ½ h. Removal of the solvent from the reaction mixture (20°, 10^{-1} mmHg) gave a waxy residue which was extracted with hot hexane (2 × 2 ml). On cooling the combined extracts, orange-yellow needle-like crystals of $[Fe(CO)_3N{:}CPh_2]_2$ (0·3 g, 94%) were obtained, and identified by i.r. spectroscopy, mass spectroscopy, and elemental analysis.

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