Carbene Complexes. Part 12.[1] Electron-rich Olefin-derived Neutral Mono- and Bis-(carbene) Complexes of Low-oxidation-state Manganese, Iron, Cobalt, Nickel, and Ruthenium †

By **Michael F. Lappert** * and **Peter L. Pye**, School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The electron-rich olefin $[\text{:}\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}]_2$ ($L^R{}_2$; R = Me or Et) provides a ready source of various thermally stable neutral mono- and bis-(carbene) complexes of Fe, Ru, Co, and Ni and, with greater difficulty, of Mn^I. Noteworthy is the range of co-ordination numbers, formal metal oxidation states, and geometries (tetrahedral, square planar, trigonal bipyramidal, or octahedral) of the complexes. Amongst the 29 new complexes are the novel neutral bis(carbene) species $[Fe(L^{Me})_2(NO)_2]$, $[Co(CO)(L^{Et})_2(NO)]$, *trans*-$[Fe(CO)_3(L^{Me})_2]$, $[Ni(CO)_2(L^{Et})_2]$, $[Fe(CO)_2I_2(L^{Me})_2]$, and $[Ni(L^{Me})_2(NO_3)_2]$; the last is the only diamagnetic nickel(II) dinitrate. Infrared spectra show that ν(CO) is low compared with analogous (*e.g.* phosphine) complexes; $\nu(CN_2)$ is in the range 1 480—1 540 cm^{-1}, the upper end being characteristic of the higher-oxidation state metal complexes. This trend is also observed in ^{13}C n.m.r. chemical shifts when $C_{carb.}$ moves to higher field ($C_{carb.}$ is generally 200—230 p.p.m. downfield from $SiMe_4$); $[Ru_3(CO)_{11}L^{Et}]$ shows only one CO resonance, an indication of fluxionality, whereas $[Fe_2(CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)L^{Et}]$ exists at 25 °C in solution as a mixture of *cis* and *trans* isomers.

WE have previously reported on the reactions of electron-rich olefins $[\text{:}\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}]_2$ ($L^R{}_2$; R = Me or Et) with low-valent Group 6 transition-metal carbonyl complexes $[M(CO)_6]$ (M = Cr, Mo, or W), or some of their derivatives, and the chemistry of the complexes so formed.[1-3] We now report results of reactions between an electron-rich olefin $L^R{}_2$ with some carbonyl complexes of manganese, iron, ruthenium, cobalt, and nickel. These are summarised in Schemes 1—3, and the characterisation of the new complexes (1)—(29) is shown in Table 1. Complex (3) has previously been described,[4] but its reported ^1H n.m.r. spectrum shows it to have been impure.

Carbeneiron(0) complexes are usually rather labile (*e.g.* refs. 5—9). They may be synthesised by oxidative-addition procedures involving $[Fe(CO)_4]^{2-}$,[6,10,11] or an adaptation of the original Fischer carbene synthetic technique from $[Fe(CO)_5]$,[8,9] but other routes have also been described.[12,13] None of these procedures leads to the simple bis(carbene) derivative $[Fe(CO)_3(carbene)_2]$. In contrast, such a complex, (4), is obtained in high yield from $[Fe(CO)_5]$ and $L^{Me}{}_2$ (see Scheme 1). Unlike *trans*-$[Fe(CO)_3(PPh_3)_2]$,[14] *trans*-$[Fe(CO)_3(L^{Me})_2]$, (4), is very reactive even in the solid state, although thermally stable, but the mixed carbene–phosphine species *trans*-$[Fe(CO)_3L^{Me}(PR_3)]$ [R = Ph (5) or Et (6)] are much more inert. The tetrahedral dinitrosyl complex $[Fe(CO)_2(NO)_2]$,[15] formally containing Fe^{-II}, is also remarkably responsive to CO substitution and both mono- and bis-(carbene) derivatives are easily obtained, *i.e.* $[Fe(CO)L^{Me}(NO)_2]$ (1) and $[Fe(L^{Me})_2(NO)_2]$ (2). Fischer-type mono(carbene) complexes related to (1) have been reported,[16] but the thermal robustness of complexes containing the ligand $\text{:}\overline{\mathrm{CN(R)CH_2CH_2N}}\mathrm{R}$ (L^R) permits

---

† No reprints available.

[1] Part 11, P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Dalton*, 1977, preceding paper.

[2] Part 10, M. F. Lappert and P. L. Pye, *J.C.S. Dalton*, 1977, 1283.

[3] Part 9, M. F. Lappert, P. L. Pye, and G. M. McLaughlin, *J.C.S. Dalton*, 1977, 1272; M. F. Lappert and P. L. Pye, *Proc. 2nd Internat. Conf. Molybdenum Chem.*, Oxford, 1976.

[4] Part 8, B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Dalton*, **1974**, 1827.

[5] D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[6] M. Green, F. G. A. Stone, and M. Underhill, *J.C.S. Dalton*, 1975, 939.

[7] E. O. Fischer, M. J. Beck, C. G. Kreiter, J. Lynch, J. Müller, and E. Winkler, *Chem. Ber.*, 1972, **105**, 162.

[8] E. O. Fischer and H. J. Kollmeier, *Angew. Chem. Internat. Edn.*, 1970, **9**, 309.

[9] E. O. Fischer and H. J. Beck, *Angew. Chem. Internat. Edn.*, 1970, **9**, 72.

[10] K. Öfele, *Angew. Chem. Internat. Edn.*, 1969, **8**, 916.

[11] Part 7, B. Çetinkaya, M. F. Lappert, G. M. McLaughlin, and K. Turner, *J.C.S. Dalton*, 1974, 1591.

[12] W. Petz, *Angew. Chem. Internat. Edn.*, 1974, **13**, 273.

[13] J. Daub, H. Erhardt, J. Kappler, and V. Trautz, *J. Organometallic Chem.*, 1974, **69**, 423.

[14] A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, 1963, **2**, 151.

[15] L. Malatesta and A. Arànco, *J. Chem. Soc.*, 1957, 3803.

[16] E. O. Fischer, F. R. Kreissl, and E. Winkler, *Chem. Ber.*, 1972, **105**, 588.

more forcing reaction conditions to be employed in their synthesis [allowing isolation of thermally stable bis-(carbene) derivatives] and subsequent study in solution (chemical reactivity and spectroscopy).

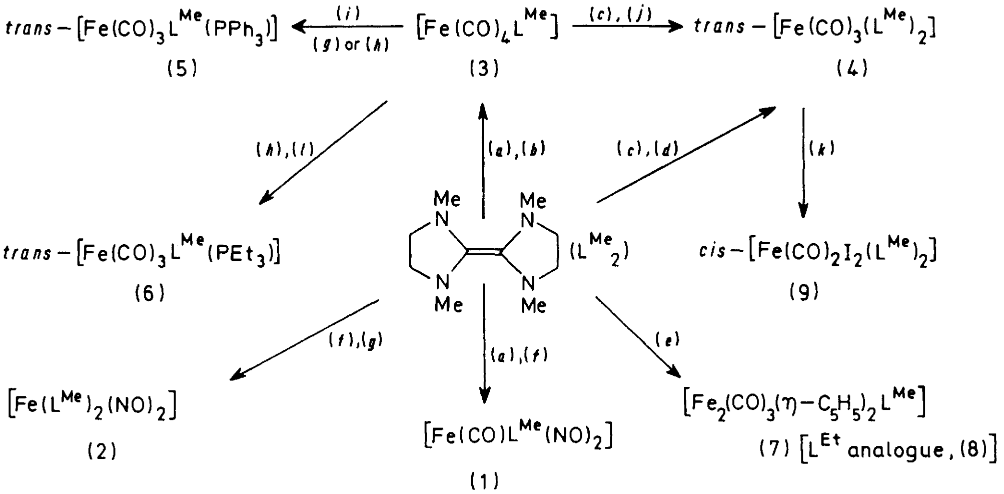
trigonal-bipyramidal complex (4) has the carbene ligands mutually *trans* and the three equatorial CO ligands are unable to withdraw sufficient electron density from the metal, whereas in the tetrahedral complex (2) removal of the charge by the NO groups is facilitated. The reaction of I_2 with (4) does not cause carbene-ligand displacement {in contrast to PPh_3 loss

TABLE 1

Neutral mono- and bis-(carbene) complexes of low-valent manganese, iron, ruthenium, cobalt, and nickel, and their characterisation

Complex [a]	Yield (%)	M.p. (θ_c/°C)	Colour	Analysis (%) [b] C	H	N
$[Fe(CO)L^{Me}(NO)_2]$ (1)	45	47	Dark red-brown	29.4 (29.7)	4.3 (4.2)	22.9 (23.1)
$[Fe(L^{Me})_2(NO)_2]$ (2)	60	234	Deep purple	38.7 (38.5)	6.4 (6.4)	27.0 (26.9)
$[Fe(CO)_4L^{Me}]$ (3)	75	48—50	Yellow	40.3 (40.6)	3.9 (3.8)	10.6 (10.5)
trans-$[Fe(CO)_3(L^{Me})_2]$ (4)	95	140	Deep yellow	46.3 (46.4)	6.0 (6.0)	16.5 (16.6)
trans-$[Fe(CO)_3L^{Me}(PPh_3)]$ (5)	90	215 (decomp.)	Deep yellow	62.1 (62.4)	5.0 (5.0)	5.7 (5.6)
trans-$[Fe(CO)_3L^{Me}(PEt_3)]$ (6)	80	94	Cream	47.2 (47.2)	7.3 (7.1)	7.8 (7.9)
$[Fe_2(CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2L^{Me}]$ (7)	80	210 (decomp.)	Intense green	51.3 (51.0)	4.7 (4.7)	6.8 (6.6)
$[Fe_2(CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2L^{Et}]$ (8)	65	170—171	Intense green	53.3 (53.1)	5.5 (5.3)	6.2 (6.2)
$[Fe(CO)_2I_2(L^{Me})_2]$ (9)	65	166 (decomp.)	Brown	25.5 (25.6)	3.8 (3.6)	9.8 (10.0)
$[Ru_3(CO)_{11}L^{Et}]$ (10)	25	113	Crimson-red	29.1 (29.3)	1.9 (1.9)	3.8 (3.8)
$[Co(CO)_2L^{Me}(NO)]$ (11)	80	*ca.* −5	Scarlet	34.4 (34.6)	4.1 (4.2)	17.4 (17.3)
$[Co(CO)(L^{Me})_2(NO)]$ (12)	90	136 (decomp.)	Crimson-brown	41.9 (42.2)	6.5 (6.4)	22.2 (22.3)
$[Co(CO)(L^{Et})_2(NO)]$ (13)	90	100	Crimson-brown	48.9 (48.8)	7.7 (7.6)	18.9 (19.0)
$[Co(CO)L^{Et}(NO)(PPh_3)]$ (14)	60	139—141	Crimson-brown	61.5 (61.8)	6.0 (5.8)	8.3 (8.3)
$[Mn(CO)_2(\eta\text{-}C_5H_4Me)L^{Me}]$ (15)	1	*c*	Straw yellow		*d*	
$[Ni(CO)_3L^{Me}]$ (16)	90	*ca.* 0	White	40.0 (40.0)	4.3 (4.2)	11.8 (11.6)
$[Ni(CO)_3L^{Et}]$ (17)	85	*ca.* −15	White	45.0 (44.7)	5.4 (5.2)	10.6 (10.4)
$[Ni(CO)_2(L^{Me})_2]$ (18)	95	200 (decomp.)	Pale yellow	46.4 (46.3)	6.6 (6.4)	18.0 (18.0)
$[Ni(CO)_2(L^{Et})_2]$ (19)	90	178	Pale yellow	52.0 (52.3)	7.6 (7.7)	15.4 (15.3)
$[Ni(CO)_2L^{Me}(PPh_3)]$ (20)	95	143	Pale yellow	63.2 (63.2)	5.4 (5.3)	6.0 (5.9)
$[Ni(CO)_2L^{Et}(PPh_3)]$ (21)	95	154 (decomp.)	Pale yellow	64.6 (64.4)	5.9 (5.8)	5.6 (5.6)
$[Ni(CO)_2L^{Me}\{P(C_6H_{11})_3\}]$ (22)	90	163	Pale yellow	61.0 (60.9)	9.0 (8.8)	5.9 (5.7)
cis-$[NiCl_2(L^{Me})_2]$ (23)	90	230 (decomp.)	Orange-yellow	37.3 (36.9)	6.4 (6.2)	16.9 (17.2)
cis-$[NiI_2(L^{Me})_2]$ (24)	90	293 (decomp.)	Burgundy red	23.8 (23.6)	4.0 (4.0)	10.8 (11.0)
cis-$[NiI_2(L^{Me})(PPh_3)]$ (25)	90	190—192	Dark red-brown	40.9 (41.0)	4.0 (3.8)	4.3 (4.2)
$[Ni(L^{Me})_2(NO_3)_2]$ (26)	95	220	Yellow-orange	31.7 (31.7)	5.5 (5.3)	22.0 (22.2)
$[Ni_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2(\mu\text{-}L^{Et})]$ (27)	25	*c*	Red-brown	51.4 (53.8)	6.1 (6.0)	6.8 (7.0)
fac-$[MnBr(CO)_3(L^{Me})_2]$ (28)	5	*c*	Pale yellow		*e*	
trans-$[NiCl_2(L^{CH_2Ph})_2]$ (29)	75	254 (decomp.)	Orange	64.3 (64.8)	5.8 (5.8)	9.1 (8.9)

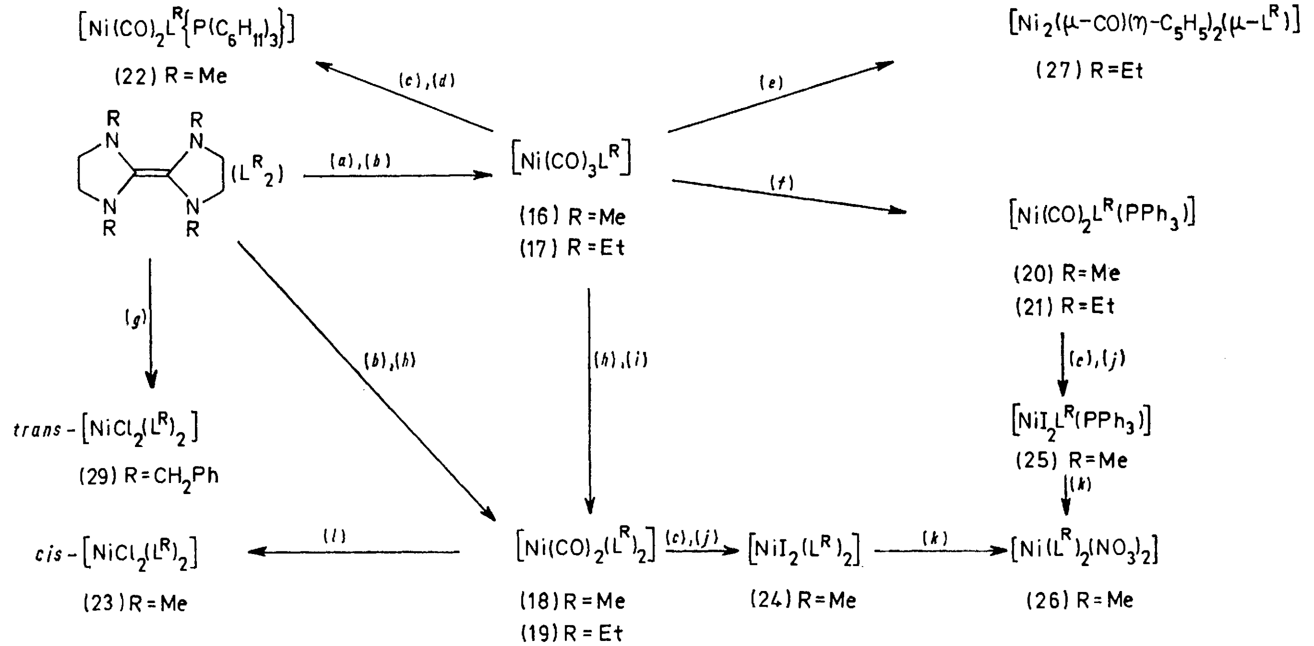
[a] L^{Me} = $\overline{:CN(Me)CH_2CH_2N}Me$, L^{Et} = $\overline{:CN(Et)CH_2CH_2N}Et$. [b] Calculated values are given in parentheses. [c] Not recorded. [d] I.r. characterisation only. [e] I.r. and ^1H n.m.r. characterisation only.



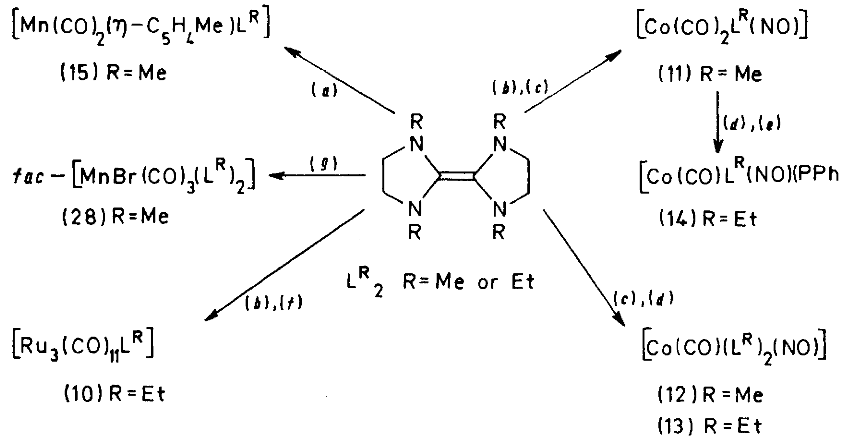
SCHEME 1 Synthesis and reactions of mono- and bis-(carbene) complexes of iron. (*a*) Hexane, 65 °C; (*b*) $[Fe(CO)_5]$; (*c*) decalin, 160—180 °C; (*d*) $[Fe(CO)_5]$ or $[Fe(CO)_3(nbd)]$; (*e*) xylene, 140 °C, $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$; (*f*) $[Fe(CO)_2(NO)_2]$; (*g*) $C_6H_{11}Me$, 100 °C; (*h*) hexane, 25 °C, *hν*; (*i*) PPh_3; (*j*) $L^{Me}{}_2$; (*k*) CH_2Cl_2, 10 °C, I_2; (*l*) PEt_3

Unlike *trans*-$[Fe(CO)_3(L^{Me})_2]$ (4), complex (2) is resistant to aerial oxidation. This is attributed primarily to its different stereochemistry. Thus the from *trans*-[Fe(CO)$_3$(PPh$_3$)$_2$]},[14,17] but results in eventual CO loss, forming brown *cis*-[Fe(CO)$_2$I$_2$(L^{Me})$_2$], (9), a further demonstration of the strong M–C$_{carb.}$ bond.

Although the iron(I) dimer [{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] has afforded complexes derived from phosphines,[18] phosphites,[19] or isocyanides,[20] hitherto no carbene analogues were described. Thermally, one terminal CO is substituted to afford the intensely dark green {*cf.* [Fe$_3$(CO)$_{12}$]} [Fe$_2$(CO)$_3$(η-C$_5$H$_5$)$_2$L^R] [R = Me (7) or Et (8)], but no bis(carbene) complex was observed.



SCHEME 2 Synthetic routes to mono- and bis-(carbene) complexes of nickel. (*a*) Hexane, 60—65 °C; (*b*) [Ni(CO)$_4$]; (*c*) CH$_2$Cl$_2$, 0 °C; (*d*) P(C$_6$H$_{11}$)$_3$; (*e*) toluene, 80 °C, [Ni(η-C$_5$H$_5$)$_2$]; (*f*) hexane, 25 °C, PPh$_3$; (*g*) tetrahydrofuran, 65 °C, [NiCl$_2$(PPh$_3$)$_2$]; (*h*) C$_6$H$_{11}$Me, 90—100 °C; (*i*) L$^R_2$; (*j*) I$_2$; (*k*) Me$_2$CO, 25 °C, Ag[NO$_3$]; (*l*) CH$_2$Cl$_2$, −25 °C, Cl$_2$



SCHEME 3 Synthesis of neutral mono- and bis-(carbene) complexes of cobalt, ruthenium, and manganese. (*a*) Decalin, 180 °C, *hν*, [Mn(CO)$_3$(η-C$_5$H$_4$Me)]; (*b*) hexane, 65 °C; (*c*) [Co(CO)$_3$(NO)]; (*d*) C$_6$H$_{11}$Me, 100 °C; (*e*) PPh$_3$; (*f*) [Ru$_3$(CO)$_{12}$]; (*g*) toluene, 110 °C, [MnBr(CO)$_3$(PPh$_3$)$_2$]

Unlike other substitution reactions of [Ru$_3$(CO)$_{12}$], L$^{Et}_2$ only caused substitution of one carbonyl ligand to yield [Ru$_3$(CO)$_{11}$L^{Et}] (10); monosubstituted species of this type are very rare, although [Ru$_3$(CO)$_{11}$(PPh$_3$)] has been identified;[21] reaction normally proceeds further until the trisubstituted cluster is obtained;[21–23] indeed, a kinetic study[22] of the reaction between [Ru$_3$(CO)$_{12}$] and PPh$_3$ failed to detect any trace of the mono-derivative, although [Ru$_3$(CO)$_{10}$(PPh$_3$)$_2$] was detected. We consider that [Ru$_3$(CO)$_9$(L^R)$_3$] is not likely to be

---

[17] W. Hieber and J. Muschi, *Chem. Ber.*, 1965, **98**, 3931.

[18] R. J. Haines and A. L. Du Preez, *Inorg. Chem.*, 1969, **8**, 1459.

[19] D. C. Harris, E. Rosenberg, and J. D. Roberts, *J.C.S. Dalton*, 1974, 2398.

[20] M. J. Boylan, J. Bellerby, J. Newman, and A. R. Manning, *J. Organometallic Chem.*, 1974, **47**, C33.

[21] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 2094.

[22] A. J. Poë and M. V. Twigg, *J.C.S. Dalton*, 1974, 1860.

intrinsically unstable, but the high temperature required for its formation from $[Ru_3(CO)_{12}]$ has precluded its isolation.

In the light of the results with $[Fe(CO)_2(NO)_2]$ (see Scheme 1), the isoelectronic $[Co(CO)_3(NO)]$ and $[Ni(CO)_4]$ complexes were examined. Each readily afforded mono- or bis-(carbene) derivatives (Schemes 2 and 3); complexes of type $[Co(CO)(L^R)_2(NO)]$ [R = Me (12) or Et (13)] have not previously been observed in carbene-metal chemistry.

Neither carbenecobaltate(−I) nor carbenenickel(0) species are well known: examples of the former (taking NO as a unipositive ligand) are restricted to the very labile or air-sensitive $[Co(CO)_2\{C(OR)(NR'_2)\}(NO)]$ [16] and $[CoBr(CO)\{CH(NMe_2)\}(PPh_3)_2]$; [24] all the reported nickel(0) complexes [16,25-27] are thermally unstable, the least reactive, *e.g.* $[Ni(CO)_3\{C(OR)(NR'_2)\}]$,[16] decomposing above −30 °C. We have found that pure $[Ni(CO)_3L^R]$ [R = Me (16) or Et (17)] are quite stable at room temperature, and also up to *ca.* 60 °C in hexane solution, whereas the bis(carbene) complexes $[Ni(CO)_2(L^R)_2]$ [R = Me (18) or Et (19)] are stable even at >150 °C. Similarly, the cobaltate(−I) complexes $[Co(CO)_2L^R(NO)]$ (11) and $[Co(CO)(L^R)_2(NO)]$ (12 and (13) are unaffected by heating to 100 °C. The mono(carbene) derivatives (11) and (16) readily lose CO on reaction with tertiary phosphines, affording species such as $[Co(CO)L^R(NO)(PPh_3)]$ (14) and $[Ni(CO)_2L^R(PPh_3)]$ (20) or (21), or $[Ni(CO)_2L^R\{P(C_6H_{11})_3\}]$ (22).

Because of our current interest in paramagnetic carbenemetal complexes,[28] we sought to examine the class $[NiX_2(L^R)_2]$ (X = anionic ligand). Thus, tertiary phosphine complexes of Ni^{II} are often paramagnetic, *e.g.* $[NiCl_2(PPh_3)_2]$,[29a] and we have often observed similar behaviour of complexes containing PPh_3 and L^R (R = Me or Et) ligands.

As described previously,[4] attempted neutral-ligand substitution *via* $[NiCl_2(PPh_3)_2]$ had also led to halide-ion displacement. However, oxidation of $[Ni(CO)_2(L^{Me})_2]$ (18) or $[Ni(CO)_2L^{Me}(PPh_3)]$ (20) with the appropriate dihalogen affords in high yield *cis*-$[NiCl_2(L^{Me})_2]$ (23), $[NiI_2(L^{Me})_2]$ (24), or *cis*-$[NiI_2(L^{Me})(PPh_3)]$ (25). The square-planar *cis* stereochemistry of (23) has been inferred from the observation of two $\nu(NiCl_2)$ bands, at 320 and 305 cm⁻¹ (Table 2) {*e.g.* for *cis*-$[NiCl_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), $\nu(NiCl_2)$ at 330 and 320 cm⁻¹; [29b] but for *trans*-$[NiCl_2(PEt_3)_2]$,[29b] $\nu(NiCl_2)$ at 402 cm⁻¹}, and for (25) by ^1H n.m.r. spectroscopy (Table 3). The carbene-ring CH_2 protons are observed initially as a broad AA′BB′ multiplet, but a slow *cis* $\rightleftharpoons$ *trans* equilibrium is developed in solution, shown by the partial disappearance of the multiplet to a sharp singlet and the build up of a second N–CH_3 signal.

Although a *trans* arrangement of neutral unidentate ligands is generally observed in unidentate square-planar nickel(II) complexes, these are normally produced by direct reaction of the ligand with a nickel(II) precursor, *e.g.* ref. 29*a* for phosphine complexes, and not, as in our case, indirectly *via* oxidative addition of X_2 to Ni^0: the isomer obtained may therefore be influenced by the preparative route. Some support for this has come from our more recent studies with the tetra-*N*-benzyl-substituted olefin $L^{CH_2Ph}{}_2$ which has been found [30] to react rather differently, in general not affording ionic carbenemetal complexes. Thus, unlike $L^{Me}{}_2$ or $L^{Et}{}_2$,

TABLE 2

Selected i.r. data ($\bar{\nu}_{max.}$/cm⁻¹) for neutral mono- and bis-(carbene) complexes of low-valent manganese, iron, ruthenium, cobalt, and nickel

Complex	ν(CO)	$\nu(CN_2)$ [a]	Others
(1)	2 003s [b]	1 510m–s	ν(NO) 1 751s, 1 709s [b]
(2)		1 510s	ν(NO) 1 664s, 1 618s [a]
(3)	2 040m, 1 959s, 1 938s [b]	1 500m	
(4)	1 959vw, 1 841vs [c]	1 505m	
(5)	1 962vw, 1 870vs [d]	1 504m	
(6)	1 969vw, 1 867vs [b]	1 500m	
(7)	1 920vs,[e] 1 712s [f,g]	1 498m	
(8)	1 921vs,[e] 1 711s [f,g]	1 481m	
(9)	2 011s 1 982s [a]	1 512m	
(10)	2 096w, 2 087m, 2 042s, 2 022s 2 011s, 1 986vw (sh), 1 981s, 1 965m, 1 950vw [b]	1 497m	
(11)	2 025s, 1 963s [d]	1 511m–s	ν(NO) 1 741s [d]
(12)	1 911s [d]	1 506m	ν(NO) 1 665s [d]
(13)	1 910s [d]	1 491m	ν(NO) 1 667s [d]
(14)	1 935s [d]	1 492m	ν(NO) 1 692s [d]
(15)	1 906s, 1 823s [a]	1 507m	
(16)	2 058s, 1 978vs [b]	1 503m [h]	
(17)	2 055s, 1 976s, 1 972s [b]	1 495m [h]	
(18)	1 938vs, 1 865vs [d]	1 505m	
(19)	1 935vs, 1 859vs [d]	1 491m	
(20)	1 978s, 1 903vs [d]	1 506m	
(21)	1 972s, 1 998vs [b]	1 492m	
(22)	1 965s, 1 900vs [a]	1 497m	
(23)		1 535s, 1 515 (sh)	$\nu(NiCl_2)$ 326ms, 305m [a]
(24)		1 525s, 1 507 (sh)	
(25)		1 535s, 1 510 (sh)	
(26)		1 538s, 1 512 (sh)	
(27)	1 794s [f,i]	1 490w (?)	
(28)	1 995s, 1 899s, 1 880s [a]	1 503m	
(29)		1 510vs	$\nu(NiCl_2)$ 397s [a]

[a] Dilute Nujol mull between CsI plates. [b] Hexane solution. [c] Benzene solution. [d] $C_6H_{11}Me$ solution. [e] Terminal CO. [f] Bridging CO. [g] $CHCl_3$ solution. [h] Neat liquid. [i] CH_2Cl_2 solution.

---

[23] J. P. Candlin and A. C. Shortland, *J. Organometallic Chem.*, 1969, **16**, 289.

[24] A. J. Hartshorn, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1975, 929.

[25] W. Petz, *J. Organometallic Chem.*, 1973, **55**, C42.

[26] W. Petz, *J. Organometallic Chem.*, 1974, **72**, 369.

[27] L. Knauss and E. O. Fischer, *J. Organometallic Chem.*, 1971, **31**, C68.

[28] *Cf.* M. F. Lappert, J. J. MacQuitty, and P. L. Pye, *J.C.S. Chem. Comm.*, 1977, 411.

[29] (*a*) See C. A. McAuliffe, ' Transition Metal Complexes of P, As, and Sb Ligands,' MacMillan, London, 1973; (*b*) P. M. Boorman and A. J. Carty, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 101.

[30] M. F. Lappert and P. L. Pye, unpublished work.

which displace Cl^- from $[NiCl_2(PPh_3)_2]$,[4] $L^{CH_2Ph}{}_2$ affords neutral square-planar *trans*-$[NiCl_2(L^{CH_2Ph})_2]$ (29); *i.e.* ligand displacement from a nickel(II) precursor leads to the *trans* isomer [one $\nu(NiCl_2)$ band at 397 cm^{-1}].

Reaction of $Ag[NO_3]$ with (24) afforded $[Ni(L^{Me})_2(NO_3)_2]$ (26) (unassigned stereochemistry, but probably *cis*), which was also unexpectedly diamagnetic, unlike all the reported tertiary phosphine nickel(II) dinitrate complexes.[29a] The mono(carbene) di-iodide (25) underwent an unusual disproportionation on reaction with $Ag[NO_3]$, yielding the diamagnetic dinitrate (26) and paramagnetic $[Ni(NO_3)_2(PPh_3)_2]$.

TABLE 3

Selected ^1H n.m.r. chemical-shift data [a] for neutral mono- and bis-(carbene) complexes of low-valent manganese, ruthenium, iron, cobalt, and nickel

		Resonance				
Complex	Solvent	NCH_2CH_2N	NCH_3	NCH_2	$N-(CH_2)-CH_3$	Others
(1)	C_6H_6	7.60	7.40			
(2)	C_6H_6	7.30	6.90			
(3)	C_6H_6 [b]	7.45	7.10			
(4)	C_6H_6	7.25	6.50			
(5)	C_6H_6	7.47	6.73			
(6)	C_6H_6	7.40	6.76			
(7)	$CDCl_3$ [c]	6.8,[d] 6.92 [e]	6.28,[d] 6.42 [e]			5.34,[d,f] 5.60 [e,f]
(8)	$(CD_3)_2CO$	6.6,[d] 7.18 [e]		5.0—6.5 (m)	8.55 (t),[e] 8.7 (t) [d]	5.36,[d,f] 5.6 [d,f] 5.52,[e,f] 5.7 [e,f]
(9)						
(10)	C_6H_6	7.58		6.60 (q)	9.16 (t)	
(11)	C_6H_6	7.55	7.40			
(12)	C_6H_6	7.27	6.95			
(13)	C_6H_6	7.13		6.37	8.95	
(14)	C_6H_6	7.17 (m)		6.90 (q)	9.15 (t)	
(15)						
(16)	C_6H_6	7.42	7.20			
(17)	C_6H_6	7.30		6.58 (q)	9.05 (t)	
(18)	C_6H_6	7.25	6.9			
(19)	C_6H_6	7.15		6.30 (q)	8.95 (t)	
(20)	C_6D_6	7.3	7.1			
(21)	C_6D_6	7.05		6.50 (q)	9.0 (t)	4.52 [f]
(22)	C_6H_6	7.27	6.92			
(23)	CH_2Cl_2	6.61	6.35			
(24)	$CDCl_3$	6.57	6.35			
(25)	$CDCl_3$	6.80,[g] 6.65 [h]	6.51, 6.42 [h]			
(26)	CH_2Cl_2	6.60	6.35			
(27)	$C_6D_5CD_3$	7.40		6.25 (q)	9.01 (t)	
(28)	$CDCl_3$	6.60	7.15			
(29)	$CDCl_3$	6.80		4.20		

[a] All the resonances are singlets unless otherwise stated (t = triplet, q = quartet, m = multiplet) and quoted in τ relative to $SiMe_4$ ($=\tau$ 10) recorded at 60 MHz. [b] Values in $CDCl_3$; NCH_2CH_2N, τ 6.35; NCH_3 6.68. [c] Signals were broad and poorly resolved. [d] *trans* Isomer. [e] *cis* Isomer. [f] η-C_5H_5. [g] Broad resonance at 35 °C: became sharper on heating. [h] Slow build up of second set of sharp signals (*ca.* 24 h); may be due to *cis* $\rightleftharpoons$ *trans* isomerisation.

The square-planar arrangement of ligands [also supported by the yellow to red colour of the complexes (23)—(26)] may be rationalised in terms of the strong $M-C_{carb.}$ σ bond and the associated high ligand-field strength of L^R, causing the relative instability in all cases of a tetrahedral compared to a spin-paired d^8 square-planar complex.[31a] Thus electronic, rather than steric, factors are considered to be controlling.

An interesting reaction was that between $[Ni(CO)_3L^{Et}]$ (17) and $[Ni(\eta\text{-}C_5H_5)_2]$ giving a product, (27), considered to be a rare example [31b] of a complex containing a bridging carbene ligand. This complex, $[Ni_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2(\mu\text{-}L^{Et})]$ (27), is so formulated (*i*) by analogy with $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$, which is prepared from $[Ni(CO)_4]$ and $[Ni(\eta\text{-}C_5H_5)_2]$, and (*ii*) from spectroscopic data (see below).

It is surprising that carbenemanganese complexes derived from electron-rich olefins are elusive (Scheme 3), especially so because other stable carbenemanganese complexes are known (see, for example, refs. 32—35). Thus, $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$ afforded $[Mn(CO)_2(\eta\text{-}C_5H_4Me)L^{Me}]$ (15) in $<1\%$ yield (identified by i.r. only), and $[MnBr(CO)_3(PPh_3)_2]$ gave *fac*-$[MnBr(CO)_3(L^{Me})_2]$ (28) in *ca.* 5% yield (characterised by i.r. and ^1H n.m.r. spectroscopy).

The complexes $[Mn_2(CO)_{10}]$, $[MnBr(CO)_5]$, or $[Mn(CO)_5Me]$ failed to afford characterisable carbenemanganese complexes: $[Mn_2(CO)_{10}]$ and $[MnBr(CO)_5]$ were reduced to $[Mn(CO)_5]^-$ and $[Mn_2(CO)_{10}]$, respectively, and reduction may also have been the fate of $[Mn(CO)_5Me]$. In view of the ease with which ligands such as PPh_3 displace CO in carbonylmanganese complexes generally,[36] the results with electron-rich olefins

---

[31] (*a*) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972; (*b*) D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[32] E. O. Fischer and A. Maasböl, *Chem. Ber.*, 1967, **100**, 2445.

[33] P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 760.

[34] C. H. Game, M. Green, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 351.

[35] D. H. Bowen, M. Green, D. M. Grove, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 1189.

[36] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

L^R_2 (R = Me or Et) appear to be anomalous. Previously we have observed a close parallel between the general reactivity towards transition-metal complexes of L^R_2 and PPh_3 (see ref. 1 and earlier papers).

Spectroscopic Properties.—These are summarised in Tables 2 (i.r.), 3 (^{1}H n.m.r.), and 4 (^{13}C n.m.r.). Generally, the values of ν(CO) and ν(NO) are amongst the lowest recorded for each class of complex (*e.g.* see ref. 37), a further illustration of the extremely strong σ-donor strength of the carbene (L^R) ligand, and $\nu(CN_2)$ is in the 1 480—1 540 cm^{-1} region.

A similar trend is found in the nitrosyl complexes examined. Thus, $[Co(CO)_2(NO)(PPh_3)]$ has ν(CO) at 2 036 and 1 982 cm^{-1} and ν(NO) at 1 760 cm^{-1}, and $[Co(CO)(NO)(PPh_3)_2]$ has ν(CO) at 1 957 and ν(NO) at 1 714 cm^{-1};[40] these bands are at significantly higher frequency than their electron-rich olefin-derived carbene analogues (11) and (14) (Table 2). In contrast, Fischer-type carbene complexes are similar to the triphenylphosphine complexes. For example, $[Co(CO)_2\{C(OR)(NR'_2)\}(NO)]$ has ν(CO) at 2 025 and 1 963 cm^{-1} and ν(NO) at 1 742 cm^{-1},[16] and $[Fe(CO)\{C(OR)(NR'_2)\}(NO)_2]$ has ν(CO) at 2 002 cm ^{1} and ν(NO) at 1 752 and 1 710 cm^{-1}.[16] The complex $[Ni_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2(\mu\text{-}L^{Et})]$ (27) formulated as having a bridging carbene, contains the expected single bridging carbonyl band at 1 794 cm^{-1}; the normally medium-to-strong band at *ca.* 1 500 cm^{-1} observed for $\nu(CN_2)$ in terminal L^R complexes is, as expected, not seen, although there was a very weak band at 1 490 cm^{-1}, attributed to a vibration involving the C_5H_5 moiety.

TABLE 4

Carbon-13 n.m.r. chemical-shift data [a] for neutral mono- and bis-(carbene) complexes of low-valent manganese, iron, ruthenium, cobalt, and nickel

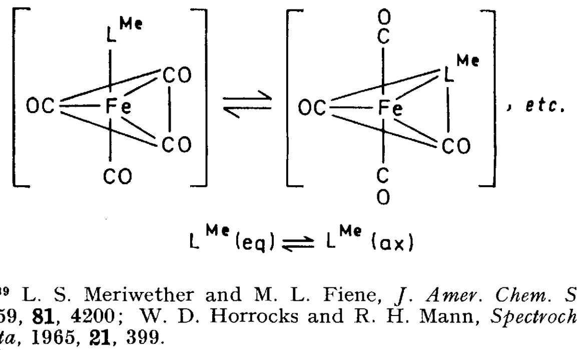
Complex	Solvent	Resonance				
		$C_{carb.}$	CO	NCH_2CH_2N	NCH_3	Others
(1)	C_6D_6	220.4	225.8	51.8	37.6	
(2)	CD_2Cl_2	231.2		52.0	37.6	
(3)	C_6D_6	212.8	217.2 [b]	51.2	38.9	
(4)	C_6D_6	222.4	225.9 [b]	51.3	39.4	
(8)	CD_2Cl_2	214 ± 2 [c]	214 ± 2 [c]	47.4		45.3,[d] 13.5,[e] 87.4, 87.2,[f] 88.2, 85.9 [g]
(10)	$C_6D_5CD_3$	198.6	204.9 [b]	47.0		47.0,[d] 13.0 [e]
(13)	C_6D_6	228.4 [h]	221.3 [h]	47.9		45.3,[d] 13.4 [e]
(17)	C_6D_6	214.4	199.1 [b]	47.8		45.1,[d] 13.3 [e]
(19)	C_6D_6	223.4	205.4 [b]	47.6		45.0,[d] 13.4 [e]
(23)	$CDCl_3$	194.5		51.4	37.9	
(24)	$CDCl_3$	208.8		51.9	37.1	
(25)	$CDCl_3$	206.3		51.8	37.4	

[a] All the values are quoted in p.p.m. relative to $SiMe_4$ (= 0 p.p.m.); samples run in 8- or 10-mm tubes at 30 °C. [b] All the CO groups are equivalent. [c] Signals not assigned; bridging CO groups were not observed. [d] NCH_2. [e] CCH_3. [f] $\eta\text{-}C_5H_5$, *cis* isomer. [g] $\eta\text{-}C_5H_5$, *trans* isomer. [h] Signals were broadened due to $^1J(^{13}C-^{59}Co)$.

The complex $[Fe(CO)_4L^{Me}]$ (3) has three ν(CO) bands, unlike the related, but less symmetric, $[Fe(CO)_4\{CN(Me)C(Me)\text{:}C(H)S\}]$ which shows four distinct bands.[6] Complex (3) is therefore believed to be similar to $[Fe(CO)_4\{CN(Me)CH\text{:}CHNMe\}]$:[10] the crystal structure [38] of the latter shows the carbene ligand in an axial position, but with deviations from an ideal trigonal-bipyramidal (t.b.p.) arrangement. The disubstituted iron(0) complexes $[Fe(CO)_3(L^{Me})Q]$ (4)—(6) all show one very strong band, characteristic of the *trans* t.b.p structure. (A *cis* arrangement is only found in complexes containing a chelate ligand, such as dppe.[37]) The binuclear species $[Fe_2(CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2L^R]$ (7) and (8) have only a single terminal and a single bridging carbonyl band, at 1 920 and 1 710 cm^{-1}, respectively; evidence for *cis* and *trans* isomers was not obtained.

The complex $[Ni(CO)_3L^{Et}]$ (17) is rather unusual in as much as the *E* mode is resolved in hexane solution (Δν *ca.* 4 cm^{-1}): the selection rules governing this system also apply to *fac*-$[M(CO)_3L_3]$ complexes, where the *E* mode is similarly resolved in *fac*-$[W(CO)_3(L^{Me})_3]$ (ref. 2). The disubstituted nickel(0) complexes clearly show increased lowering of ν(CO) when substituting a carbonyl group by L^{Me} rather than PPh_3; thus, for $[Ni(CO)_2(L^{Me})_2]$ (18), ν(CO) is at 1 938 and 1 865 cm^{-1}, which may be compared with 1 978 and 1 903 cm^{-1} in $[Ni(CO)_2L^{Me}(PPh_3)]$ and *ca.* 2 007 and 1 952 cm^{-1} in $[Ni(CO)_2(PPh_3)_2]$.[39]

N.m.r. Generally, the complexes all exhibited single first-order ^{1}H n.m.r. spectra for the *N*-alkyl and *N*-CH_2CH_2N protons. Of interest was the re-examination of $[Fe(CO)_4L^{Me}]$ (3). The previous report [4] indicated the presence of doublet signals for the *N*-Me and ring CH_2 groups; this is in fact incorrect, sharp singlets being observed which persist to below −90 °C, indicating a low barrier to site exchange:



---

[37] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, London, 1967.

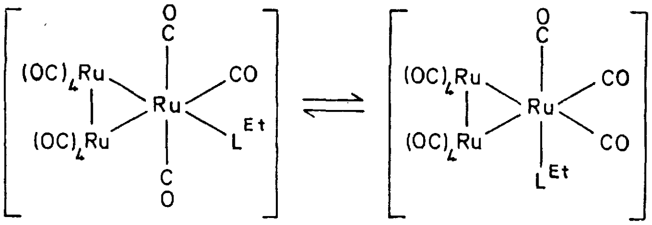
[38] G. Huttner and W. Gartzke, *Chem. Ber.*, 1972, **105**, 2714.

[39] L. S. Meriwether and M. L. Fiene, *J. Amer. Chem. Soc.*, 1959, **81**, 4200; W. D. Horrocks and R. H. Mann, *Spectrochim. Acta*, 1965, **21**, 399.

[40] W. Hieber and J. Ellermann, *Chem. Ber.*, 1963, **96**, 1643.

A similar result was obtained on re-examination of the ^{13}C n.m.r. spectra of (3);[41] even at -90 °C only one CO resonance was observed. The values of $\delta(C_{carb.})$ for the complexes examined are generally comparable to values of δ(CO) found in the same complexes, but can be distinguished by off-resonance studies in which the height of the signal attributable to $C_{carb.}$ diminishes appreciably.[2,3] Several trends are clearly noticeable: (*i*) δ(CO) and $\delta(C_{carb.})$ move to low field on increasing the electron density in the antibonding orbitals of the π-acceptor ligand (CO or NO) {thus $[Ni(CO)_4]$ has CO at 191.2 p.p.m.,[42,43] whereas $[Ni(CO)_3L^{Et}]$ has CO at 199.1 p.p.m. and $C_{carb.}$ at 214.4 p.p.m., and $[Ni(CO)_2(L^{Et})_2]$ has CO at 205.4 p.p.m. and $C_{carb.}$ at 223.4 p.p.m.}; (*ii*) δ(CO) shifts to lower field compared with analogous PPh_3 complexes (see, for example, refs. 42, 43), presumably because of the higher σ donor : π acceptor ratio of L^R {*e.g.* $[Fe(CO)_4(PPh_3)]$ has CO at 213.4 p.p.m., whereas $[Fe(CO)_4L^{Me}]$ has CO at 217.2 p.p.m., *trans*-$[Fe(CO)_3(PPh_3)_2]$ at 214.3 p.p.m., *trans*-$[Fe(CO)_3(L^{Me})_2]$ at 225.9 p.p.m., $[Ni(CO)_2(PPh_3)_2]$ at 199.4 p.p.m., and $[Ni(CO)_2(L^{Et})_2]$ at 205.4 p.p.m.}; (*iii*) increasing the metal oxidation state causes a high-field shift of $C_{carb.}$, and the more electronegative the anionic substituents the greater is the high-field shift [and a related observation is the increase in $\nu(CN_2)$] {*e.g.* $[Ni(CO)_2(L^{Et})_2]$ has $C_{carb.}$ at 223.4 p.p.m., $[NiCl_2(L^{Me})_2]$ at 194.5 p.p.m., and $[NiI_2(L^{Me})_2]$ at 208.8 p.p.m.}. Also of some interest are the data obtained for $[Co(CO)(L^{Et})_2(NO)]$ (13); ^{13}C n.m.r. information for cobalt complexes is rare and that for (13) represents the first reported for a carbenecobalt complex. The value of δ(CO) of 221.3 p.p.m. is unexceptional, considering trend (*i*) *i.e.* $[Co_2(CO)_8]$ has δ(CO) at 202.5 p.p.m. and $[Co(CO)_4]^-$ at 211.2 p.p.m.[42,43] In the tetrahedral isoelectronic d^{10} bis(carbene) series $[Fe(L^{Me})_2(NO)_2]$ (2), $[Co(CO)(L^{Et})_2(NO)]$ (13), and $[Ni(CO)_2(L^{Et})_2]$ (19) the values of $\delta(C_{carb.})$ are comparable (231.2, 228.4, and 223.4 p.p.m.), but show a distinct upfield shift on increasing the formal oxidation state of the metal (decreasing the number of NO ligands). Whether this is a genuine example of trend (*iii*), or merely connected with the differences in π-acceptor ability of the NO and CO ligands, affecting the electron deficiency of $C_{carb.}$, or is a composite of both cannot, at the moment, be unequivocally established. Variable-low-temperature ^{13}C n.m.r. studies have been used to obtain quantitative information for the *cis* $\rightleftharpoons$ *trans* isomerisation equilibrium of $[Fe_2(CO)_3(\eta\text{-}C_5H_5)_2\{P(OEt)_3\}]$[19] and $[Fe_2(CO)_3(\eta\text{-}C_5H_5)_2(CNR)]$.[44] A similar study was initiated on $[Fe_2(CO)_3(\eta\text{-}C_5H_5)_2L^{Et}]$, which, unlike the other complexes, clearly showed both isomers, by virtue of four singlets observed for the C_5H_5 ring carbons at 30 °C, but the insolubility and decomposition on warming prevented accumulation of data, and indeed the signals assigned to CO and C_{carb} were very weak and poorly resolved.

Difficulties were also encountered for $[Ru_3(CO)_{11}L^{Et}]$ (10) where two isomers may be present:



The spectrum at 35 °C shows two signals only, attributable to 11 carbonyl-carbon and one carbene-carbon atoms, thus indicating in solution a non-rigid system, or, less likely, accidental equivalence of the carbonyl-carbon atoms. The complex $[Ru_3(CO)_{12}]$ has been shown[45] to exhibit a single signal at 199.7 p.p.m., but another report[43,46] suggests two signals of equal intensity, at 188.7 and 198.8 p.p.m. In $[Ru_3(CO)_{12}]$ it has been assumed[45] that scrambling of the CO ligands over the trinuclear metal skeleton occurs *via* an asymmetric 2CO- or symmetric 3CO-bridged species or a simple CO(ax) $\rightleftharpoons$ CO(eq) equilibrium *via* a twist mechanism around an individual Ru atom. The latter mechanism does not necessitate the transfer of CO groups from one metal atom to another and is therefore unlikely to be operative in (10), whereas the former (which may also involve a bridging L^{Et} fragment) appears much more likely, because of the equivalence of all the 11 CO groups. On cooling complex (10) (<10 °C) in perdeuteriotoluene precipitation occurred and halogenated solvents caused decomposition; therefore low-temperature spectroscopic information is not available.

EXPERIMENTAL

General Procedures.—All the reactions were carried out under an atmosphere of dry dinitrogen or argon. Hydrocarbon and ether solvents were dried over sodium wire and distilled before use and chlorinated solvents were distilled from P_4O_{10}. Analyses were carried out in our microanalytical laboratory by Mr. and Mrs. A. G. Olney and for very air-sensitive materials by the A. Bernhardt Laboratory, West Germany.

Carbon-13 n.m.r. spectra were obtained by Mr. T. M. Sivérns on a Jeol PFT-100 Fourier-transform spectrometer. Infrared spectra (250—4 000 cm^{-1}) were routinely examined as dilute Nujol mulls using a Perkin-Elmer 457 grating spectrometer and solution spectra using a Perkin-Elmer 257 spectrometer with the × 10 expanded scale for accurate wavenumber measurements. Spectra were calibrated against polystyrene film (1 801 or 1 601 cm^{-1})

---

[41] Part 4, D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1982.

[42] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135 and refs. therein.

[43] L. J. Todd and J. R. Wilkinson, *J. Organometallic Chem.*, 1974, **77**, 1 and refs. therein.

[44] J. A. S. Howell, T. W. Matheson, and M. J. Mays, *J.C.S. Chem. Comm.*, 1975, 865.

[45] A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1042.

[46] J. R. Wilkinson, A. R. Garber, and L. J. Todd, unpublished work.

and frequencies quoted as $\bar{\nu}_{max.}$/cm^{-1}. Melting points were determined in evacuated sealed tubes and are uncorrected. The electron-rich olefins were prepared by literature methods [47] from the relevant diamine. Other starting materials were prepared by standard literature procedures,[48] $[Fe(CO)_5]$ and $[Ni(CO)_4]$ were used as purchased, and a gift of $[Ru_3(CO)_{12}]$ from Professor F. G. A. Stone is gratefully acknowledged.

$[Fe(CO)_4L^R]$ (R = Me *or* Et).—To a solution of $[Fe(CO)_5]$ (0.98 g, 5.0 mmol) in hexane (15 cm^3) was added bi(1,3-diethylimidazolidin-2-ylidene) (0.63 g, 2.5 mmol) and the mixture was heated (65 °C, 1 h) to form a yellow solution and a dark oil. The mixture was cooled (-20 °C, 24 h) and filtered. Volatiles were removed *in vacuo*. The yellow liquid residue was dissolved in pentane (5 cm^3) and refiltered. The solution was 'seeded' by cooling (-78 °C) and allowed to crystallise (-25 °C, 7 d) to deposit yellow crystals of *tetracarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)-*iron*(0) (1.0 g, 70%) which melted below -10 °C to a yellow liquid.

$[Fe(CO)L^{Me}(NO)_2]$.—To a solution of $[Fe(CO)_2(NO)_2]$ (0.35 g, 2.0 mmol) in hexane (10 cm^3) was added bi(1,3-dimethylimidazolidin-2-ylidene) (0.21 g, 1.2 mmol) and the mixture was heated gently (65 °C, 1 h) to form a dark solution. The mixture was cooled and the volatiles were removed. The residue was extracted with pentane (5 cm^3), filtered, and cooled (-30 °C, 48 h) to afford red-brown needles of *carbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*dinitrosyliron*($-$II) (0.22 g, 45%).

$[Fe(L^{Me})_2(NO)_2]$.—To a solution of $[Fe(CO)_2(NO)_2]$ (0.35 g, 2.0 mmol) in $C_6H_{11}Me$ (10 cm^3) was added $L^{Me}{}_2$ (0.50 g, 2.5 mmol) and the mixture was heated (100 °C, 2 h). A brown-purple precipitate formed and was removed by filtration, washed with OEt_2, dried, and recrystallised from CH_2Cl_2–OEt_2 (-30 °C, 48 h) to afford small purple crystals of *bis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*dinitrosyliron*($-$II) (0.37g, 60%).

trans-$[Fe(CO)_3(L^{Me})_2]$.—A mixture of $[Fe(CO)_5]$ (1.96 g, 10.0 mmol) and $L^{Me}{}_2$ (2.94 g, 15.0 mmol) was slowly heated (3 h) in decalin to 180 °C (12 h). A dark oil formed initially, but slowly disappeared on continued heating. The pale yellow solution became golden-yellow and on cooling deposited a bright yellow microcrystalline precipitate of trans-*tricarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)-*iron*(0) (3.20 g, 95%). This complex may also be obtained (but in lower yield, *ca.* 50%) by heating the olefin with $[Fe(CO)_3(nbd)]$ (nbd = norbornadiene) in xylene (140 °C, 6 h).

$[Fe_2(CO)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2L^R]$ (R = Me *or* Et).—A mixture of $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (0.25 g, 0.70 mmol) and $L^{Me}{}_2$ (0.14 g, 0.70 mmol) in xylene (10 cm^3) was heated under reflux (140 °C, 6 h). The initial orange-brown solution became an intense green and on cooling (25 °C) dark green crystals formed. The crystals were removed by filtration, washed with diethyl ether (2 × 5 cm^3), and dried *in vacuo* to afford *di*-μ-*carbonyl-carbonylbis*(η-*cyclopentadienyl*)(1,3-*dimethylimidazolidin*-2-*ylidene*)*di-iron*(Fe–Fe) (0.23 g, 80%).

trans-$[Fe(CO)_3L^{Me}(PR_3)]$.—(*i*) (R = Ph). To a solution of $[Fe(CO)_4L^{Me}]$ (0.12 g, 0.45 mmol) in $C_6H_{11}Me$ (10 cm^3) was added triphenylphosphine (0.12 g, 0.45 mmol) and the mixture was heated (100 °C, 3 h). On cooling the reaction mixture (20 °C), bright yellow microcrystals of trans-*tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*iron*(0) (0.20 g, 90%) precipitated.

(*ii*) (R = Et). To a solution of $[Fe(CO)_4L^{Me}]$ (0.12 g, 0.45 mmol) in hexane (10 cm^3) was added triethylphosphine (0.12 g, 1.0 mmol) and the mixture was irradiated (25 °C, 6 h). The solution was then filtered and cooled (-25 °C, 12 h) to afford cream crystals of trans-*tricarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*iron*(0) (0.13 g, 80%).

$[Fe(CO)_2I_2(L^{Me})_2]$.—To a stirred solution of *trans*-$[Fe(CO)_3(L^{Me})_2]$ (0.34 g, 1.0 mmol) in CH_2Cl_2 (5 cm^3) cooled to 0 °C was added dropwise a solution of I_2 (0.25 g, 1.0 mmol) in CH_2Cl_2 (10 cm^3) over 1 h. The initial yellow colour of the solution became green and finally brown-red on completion of I_2 addition. The solution was cooled (-25 °C, 24 h) and filtered. Addition of OEt_2 (*ca.* 10 cm^3) and further cooling (-25 °C, 48 h) caused formation of small brown crystals of *dicarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*di-iodoiron*(II) (0.37 g, 65%), which were removed by filtration, washed with diethyl ether (3 × 5 cm^3), and dried *in vacuo*.

$[Ru_3(CO)_{11}L^{Et}]$.—To a solution of $[Ru_3(CO)_{12}]$ (0.50 g, 0.78 mmol) in hexane (20 cm^3) was added $L^{Et}{}_2$ (0.30 g, 1.2 mmol) and the mixture was heated (60 °C, 0.5 h). The solution became dark red and was cooled (-25 °C) to afford a mixture of red and orange crystals. The solvent was removed and the residue extracted with OEt_2–C_6H_6 (1 : 1, 4 cm^3) and filtered, to leave unchanged orange $[Ru_3(CO)_{12}]$. Hexane (5 cm^3) was added to the filtrate which on cooling (-30 °C, 72 h) afforded deep crimson-red crystals of *undecacarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)-triangulo-*triruthenium*(0) (0.15 g, 25%).

$[Co(CO)_2L^{Me}(NO)]$.—To a solution of $[Co(CO)_3(NO)]$ (0.35 g, 2.0 mmol) in $C_6H_{11}Me$ (10 cm^3) was added $L^{Me}{}_2$ (0.20 g, 1.0 mmol) and the mixture was slowly heated (80 °C, 1 h) and then at 100 °C (1 h). The dark scarlet solution was cooled and filtered, and volatiles removed *in vacuo*. The resulting red oil was dissolved in pentane (10 cm^3), filtered, and slowly cooled to -50 °C (2 h) to form scarlet crystals. The solvent was removed *via* a syringe and the product dried *in vacuo* (-30 °C, 4 h) to afford *dicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*nitrosylcobalt*($-$I) (0.39 g, 80%) as a low-melting-point, deep scarlet, crystalline solid.

$[Co(CO)(L^R)_2(NO)]$ (R = Me *or* Et).—To a solution of $[Co(CO)_3(NO)]$ (0.35 g, 2.0 mmol) in $C_6H_{11}Me$ (10 cm^3) was added $L^{Et}{}_2$ (0.75 g, 3.0 mmol) and the mixture was heated under reflux (100 °C, 3 h). On cooling, red-brown crystalline platelets of *carbonylbis*(1,3-*diethylimidazolidin*-2-*ylidene*)*nitrosylcobalt*($-$I) (0.67 g, 90%) slowly precipitated. The solution was then cooled (-25 °C, 12 h), the product removed by filtration, washed with cold (0 °C) pentane (4 × 5 cm^3), and dried *in vacuo*.

$[Co(CO)L^{Et}(NO)(PPh_3)]$.—The complex $[Co(CO)_3(NO)]$ (0.32 g, 1.8 mmol) and $L^{Et}{}_2$ (0.12 g, 1.0 mmol) were heated (80 °C) in $C_6H_{11}Me$ (15 cm^3) for 3 h. The solution was cooled and filtered. Triphenylphosphine (0.26 g, 1.0 mmol) was added to the solution (8 cm^3) and the mixture was heated under reflux (100 °C, 2 h). Cooling at 20 °C overnight resulted in the formation of brown-red platelets which were removed by filtration, washed with cold pentane (-20 °C), dried, and recrystallised from C_6H_6–C_5H_{12} (3 : 20) (20 °C, 48 h) to afford red-brown crystals of *carbonyl*-(1,3-*diethylimidazolidin*-2-*ylidene*)*nitrosyl*(*triphenylphosphine*)*cobalt*($-$I) (0.30 g, 60%).

---

[47] H. E. Winberg, *Chem. Abs.*, 1966, **64**, 15854h.

[48] R. B. King, 'Organometallic Syntheses,' Academic Press, New York, 1965, vol. 1.

$[\mathrm{Mn(CO)_2(\eta\text{-}C_5H_4Me)L^{Me}}]$.—A solution of $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_4Me)}]$ (0.25 g, 1.14 mmol) and $\mathrm{L^{Me}_2}$ in decalin (5 $\mathrm{cm^3}$) was heated (180 °C, 3 h) and then irradiated (25 °C, 8 h). Cooling the resulting solution (−30 °C, 72 h) caused precipitation of a small quantity of dark oil. The supernatant liquid was removed and the oil washed with EtOH (2 $\mathrm{cm^3}$) to leave a few small yellow crystals of *dicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(η-*methylcyclopentadienyl*)*manganese*(I), characterised by i.r. spectroscopy only.

fac-$[\mathrm{MnBr(CO)_3(L^{Me})_2}]$.—A mixture of $[\mathrm{MnBr(CO)_3(PPh_3)_2}]$ (0.58 g, 0.78 mmol) and $\mathrm{L^{Me}_2}$ (0.24 g, 1.3 mmol) was heated in toluene (20 $\mathrm{cm^3}$, 110 °C, 30 min). The solution became pale yellow and clear, and after cooling (25 °C) was filtered. The volume of toluene was reduced (10 $\mathrm{cm^3}$), hexane was added (5 $\mathrm{cm^3}$), and the mixture cooled (−20 °C, 72 h) to afford a very small quantity of a pale yellow powder, identified by i.r. and ^{1}H n.m.r. spectroscopy as fac-*bromotricarbonylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*manganese*(I).

$[\mathrm{Ni(CO)_3L^R}]$ (R = Me *or* Et).—To a solution of $[\mathrm{Ni(CO)_4}]$ (2.81 g, 16.4 mmol) in hexane (20 $\mathrm{cm^3}$) was added $\mathrm{L^{Et}_2}$ (2.27 g, 9 mmol) and the mixture was heated slowly to 60 °C over 4 h, and then for another 3 h. The reaction mixture was cooled (20 °C), filtered, and cooled (−45 °C, 8 h) to afford white crystals. The supernatant was removed by use of a syringe and again cooled (−70 °C, 12 h) to give more solid. The solvent was removed, and the crystalline solids were combined and recrystallised from pentane (5 $\mathrm{cm^3}$, −45 °C, 15 h) to give *tricarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)*nickel*(0) (3.8 g, 85%) as white crystals which melted to a colourless liquid above −10 °C.

$[\mathrm{Ni(CO)_2(L^R)_2}]$ (R = Me *or* Et).—The complex $[\mathrm{Ni(CO)_4}]$ (1.71 g, 10.0 mmol) and $\mathrm{L^{Et}_2}$ (3.2 g, 12.7 mmol) in $\mathrm{C_6H_{11}Me}$ (15 $\mathrm{cm^3}$) were slowly heated over 6 h to 70 °C and then refluxed (100 °C, 4 h). The solution became orange-yellow and cooling (−20 °C, 72 h) afforded a pale yellow microcrystalline solid which was recrystallised from $\mathrm{OEt_2\text{–}C_6H_{14}}$ (2 : 1, 30 $\mathrm{cm^3}$) to give pale yellow crystals of *dicarbonylbis*(1,3-*diethylimidazolidin*-2-*ylidene*)*nickel*(0) (3.3 g, 90%).

$[\mathrm{Ni(CO)_2L^{Me}(PR_3)}]$ (R = Ph *or* $\mathrm{C_6H_{11}}$).—To a solution of $[\mathrm{Ni(CO)_3L^{Me}}]$ (0.48 g, 2.0 mmol) in hexane (10 $\mathrm{cm^3}$) was slowly added $\mathrm{PPh_3}$ (0.65 g, 2.5 mmol). Immediate evolution of carbon monoxide occurred and a yellow microcrystalline precipitate formed. The mixture was stirred (25 °C, 1 h) and the solid was removed by filtration, washed with pentane–diethyl ether (4 : 1, 3 × 5 $\mathrm{cm^3}$) then pentane (2 × 5 $\mathrm{cm^3}$), and dried *in vacuo* to afford *dicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*nickel*(0) (0.90 g, 95%) as pale yellow microcrystals. Similarly prepared was *dicarbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*tricyclohexylphosphine*)*nickel*(0).

$[\mathrm{NiCl_2(L^{Me})_2}]$.—To a solution of $[\mathrm{Ni(CO)_2(L^{Me})_2}]$ (0.31 g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (10 $\mathrm{cm^3}$) cooled to −78 °C was added dropwise a solution of $\mathrm{Cl_2}$ (0.07 g, 1.0 mmol) in $\mathrm{CCl_4}$ over 30 min. Rapid evolution of carbon monoxide occurred and the solution became greenish yellow. The mixture was then allowed to warm slowly to room temperature, whereupon the colour became yellow-orange. The solution was filtered and flotation of $\mathrm{OEt_2}$ on the $\mathrm{CH_2Cl_2}$ solution caused formation of orange-yellow crystals of *dichlorobis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*nickel*(II) (0.29 g, 90%) which were washed with $\mathrm{OEt_2}$ (3 × 5 $\mathrm{cm^3}$) and dried *in vacuo*.

trans-$[\mathrm{NiCl_2(L^{CH_2Ph})_2}]$.—To a suspension of dichlorobis(triphenylphosphine)nickel(II) (0.66 g, 1.0 mmol) in tetrahydrofuran (20 $\mathrm{cm^3}$) was added bi(1,3-dibenzylimidazolidin-2-ylidene) (0.75 g, 1.5 mmol) and the mixture was slowly heated to 65 °C. After 1 h at this temperature the mixture was filtered while hot, the residue washed with $\mathrm{OEt_2}$ (3 × 5 $\mathrm{cm^3}$), cold (0 °C) $\mathrm{CH_2Cl_2}$ (3 × 5 $\mathrm{cm^3}$), and then $\mathrm{OEt_2}$ (3 × 5 $\mathrm{cm^3}$), and dried to afford orange trans-*dichlorobis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nickel*(II) (0.47 g, 75%).

$[\mathrm{NiI_2(L^{Me})_2}]$.—To a solution of $[\mathrm{Ni(CO)_2(L^{Me})_2}]$ (0.31 g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (10 $\mathrm{cm^3}$) was added dropwise (1 h) $\mathrm{I_2}$ (0.25 g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (5 $\mathrm{cm^3}$). The resulting red-brown solution was filtered and $\mathrm{OEt_2}$ (10 $\mathrm{cm^3}$) added. Cooling (−25 °C, 48 h) afforded dark red crystals of *bis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*di-iodonickel*(II) (0.46 g, 90%).

$[\mathrm{NiI_2(L^{Me})(PPh_3)}]$.—To a solution of $[\mathrm{Ni(CO)_2L^{Me}(PPh_3)}]$ (10.47 g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (10 $\mathrm{cm^3}$) was added dropwise (1 h) a solution of $\mathrm{I_2}$ (0.25 g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (5 $\mathrm{cm^3}$). The resulting red-brown solution was filtered and $\mathrm{OEt_2}$ (10 $\mathrm{cm^3}$) added. Cooling (−25 °C, 48 h) afforded dark red-brown crystals of (1,3-*dimethylimidazolidin*-2-*ylidene*)-*di-iodo*(*triphenylphosphine*)*nickel*(II) (0.60 g, 90%).

$[\mathrm{Ni(L^{Me})_2(NO_3)_2}]$.—To a rapidly stirred solution of $[\mathrm{NiI_2(L^{Me})_2}]$ (0.51 g, 1.0 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) was added portionwise (0.5 h) $\mathrm{Ag[NO_3]}$ (0.35 g, 2.0 mmol). The pale yellow precipitate of AgI was removed by filtration and flotation of $\mathrm{OEt_2}$ on to the $\mathrm{CH_2Cl_2}$ filtrate afforded yellow crystals of *bis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*dinitratonickel*(II) (0.36 g, 95%).

Reaction between $[\mathrm{Ni(CO)_3L^{Et}}]$ *and* $[\mathrm{Ni(\eta\text{-}C_5H_5)_2}]$.—To a solution of $[\mathrm{Ni(CO)_3L^{Et}}]$ (0.50 g, 1.86 mmol) in benzene (10 $\mathrm{cm^3}$) was added $[\mathrm{Ni(\eta\text{-}C_5H_5)_2}]$ (0.28 g, 1.50 mmol) and the mixture was heated (80 °C, 3 h) to form a deep red-brown solution. The reaction mixture was cooled (25 °C) and the solvent was removed *in vacuo*. The residue was extracted with $\mathrm{OEt_2\text{–}C_6H_5Me}$ (1 : 1, 3 × 10 $\mathrm{cm^3}$) and cooled (−30 °C, 48 h) to afford a small quantity of dark red-brown crystals which were recrystallised from $\mathrm{OEt_2\text{–}C_6H_5Me}$ (−30 °C) to give μ-*carbonyl*-μ-(1,3-*diethylimidazolidin*-2-*ylidene*)-*bis*(η-*cyclopentadienyl*)*dinickel*(I) (0.15 g, 25%).

[7/670 *Received*, 22nd *April*, 1977]