# Reaction of Amines with Nickel, Palladium, and Platinum Complexes Containing Isocyanide and Fluorocarbon Ligands to yield Monocarbene Complexes

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Reaction between the nickel(II) species $[Ni \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_2(CNR)_2]$ (R = Bu$^t$ or Pr$^i$) and dimethylamine, diethylamine, t-butylamine, pyrrolidine, or morpholine affords monocarbene complexes $[Ni \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_2 (CNR)\{C(NHR)NR'_2\}]$; the structures were established by i.r. and n.m.r. spectroscopy. Analogous reactions occurred with $[Ni \cdot CF_2 \cdot CF:CF \cdot CF_2(CNBu^t)_2]$, $[M \cdot C(CF_3)_2O \cdot C(CF_3)_2O(CNR)_2]$ (M = Ni, Pd, or Pt; R = Bu$^t$ or Pr$^i$), $[Pd \cdot C(CF_3):C(CF_3) \cdot C(CF_3):C(CF_3)(CNBu^t)_2]$, and $[Pd \cdot C(CF_3)_2 \cdot C(CN)_2(CNBu^t)_2]$ to give the corresponding monocarbene complexes.

FOLLOWING the observation [1] that alcohols and primary amines (HY) react with the Pt$^{II}$ complexes cis-[PtX$_2$-(PEt$_3$)(CNPh)] (X = Cl or Br) to give carbene complexes [2-4] cis-[PtX$_2$(PEt$_3$){C(NHPh)Y}], it has been found that the susceptibility of co-ordinated isocyanides to nucleophilic attack is governed by a delicate balance of steric and electronic effects both in the substrate and in the nucleophile. Whereas the cationic isocyanide complex of rhodium(I) [Rh(CNBu$^t$)$_4$]$^+$ reacts [5] with a variety of amines to give carbene complexes as a result of cis-addition to one isocyanide ligand, it is reported [6] that [Ir(CNMe)$_4$]$^+$ does not react with hydrazine. In contrast, the complexes [M(CNMe)$_4$]$^{2+}$ (M = Ni, Pd, or Pt) all react [7] with methylamine to give the tetracarbene complexes [M{C(NHMe)$_2$}$_4$]$^{2+}$. In trans-[Pt(PR$_3$)$_2$-(CNR)$_2$]$^{2+}$ where two of the isocyanide ligands have been replaced by phosphines, nucleophilic attack by HY

(Y = NHR, OR, or SR) leads to 1,2-cis-addition on only one isocyanide ligand.[8] In the case of complexes of the type cis- and trans-[MX$_2$(CNR)$_2$] (M = Pd or Pt), small variations can have a considerable effect upon the nature of the product. For example, the cis- or trans-complexes (M = Pd, R = Bu$^t$ or p-ClC$_6$H$_4$; X = Cl, Br, or I) react [9] to give cis- or trans-[MX$_2$(CNR){C(NHR)Y}], in which one isocyanide is attacked; whereas, the cis-complexes (M = Pd, R = p-Z-C$_6$H$_4$; Z = MeO, Me, H, or NO$_2$; X = Cl) react [10,11] with a variety of nucleophiles to give cis-[MX$_2${C(NHR)Y}$_2$] in which both isocyanide ligands are attacked.

These observations, together with the discovery of isocyanide complexes of nickel and palladium having fluorocarbon groups as ligands,[12,13] suggested that compounds such as $[Ni \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot CF_2(CNR)_2]$ would

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[12] M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 2828.

[13] H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 3472.

similarly react with amines. Moreover, monocarbene complexes of Ni$^{II}$ have not been hitherto reported, due presumably to the fact that few compounds of the type [NiX$_2$(CNR)$_2$] are known. Therefore it seemed that iso-cyanide(fluorocarbon)nickel compounds might serve as useful precursors to carbene–nickel complexes. This proved to be the case, and the work was extended to include Pd$^{II}$ and Pt$^{II}$ complexes containing both co-ordinated isocyanide and a fluorocarbon ring system.

were in accord with 1 : 1 addition of the amine to one isocyanide ligand. The i.r. spectrum showed bands at 3358, 2189, and 1549 cm$^{-1}$, which were assigned to v(NH), v(NC), and v(N$\overset{|}{=}$C$\overset{}{=}$N), respectively. Bands characteristic of the nickelaoctafluorocyclopentane ring were also present; the presence of this ring was confirmed by the $^{19}$F n.m.r. spectrum (Table 2).
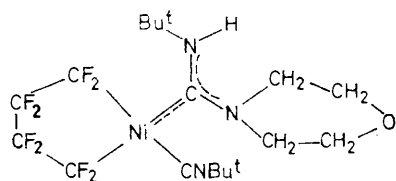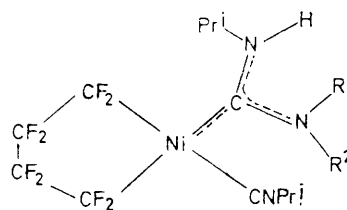
The $^1$H n.m.r. spectrum contained distinct resonances
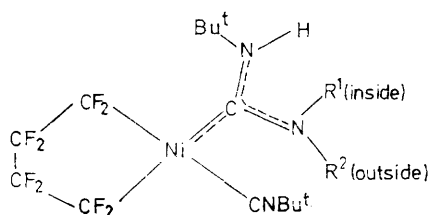


(I, R$^1$ = R$^2$ = Me)
(II, R$^1$ = R$^2$ = Et)
(III, R$^1$ = H, R$^2$ = Bu$^t$)
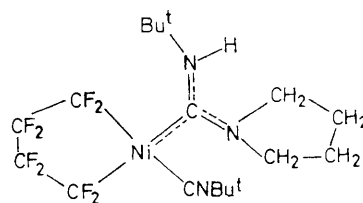
(IV)

(V)

(VI, R$^1$ = R$^2$ = Et)
(VII, R$^1$ = R$^2$ = Me)
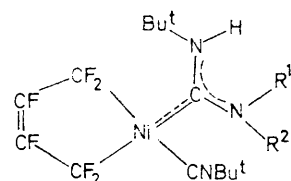
(VIII, R$^1$ = R$^2$ = Me)
(IX, R$^1$ = R$^2$ = Et)
(X, R$^1$ = $^t$Bu, R$^2$ = H)
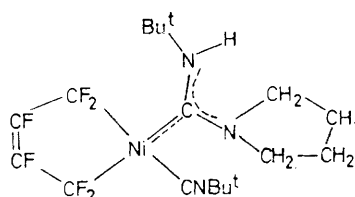
(XI)

The new compounds described were characterised by elemental analysis (Table 1), and i.r. and n.m.r. spectroscopy (Table 2).

The nickelaoctafluorocyclopentane [Ni·CF$_2$·CF$_2$·CF$_2$·CF$_2$(CNBu$^t$)$_2$], the stereochemistry of which is determined by the chelating nature of the fluorocarbon ligand, reacts within a few minutes with neat dimethylamine to give the stable, crystalline complex (I) in near quantitative yield. Elemental analysis and the appearance of a parent ion in the mass spectrum

for the two types of Bu$^t$N groups, an N$H$ resonance, and two broad singlets of equal intensity, each corresponding to three protons at $\tau$ 6·14 and 7·07.

These two resonances may be attributed to the presence in the carbene ligand of two $N$-methyl environments, which arise through the presence of a high barrier to rotation about the C$\overset{}{=}$NMe$_2$ bond. In the complex [Fe(CO)$_4${C(OEt)NMe$_2$}] the free energy enthalpies of rotation about the C$\overset{}{=}$N and C$\overset{}{=}$O bonds are ca. 21 and 6 kcal mol$^{-1}$ respectively.[14] The carbene ligand present in (I) has previously been observed in four other complexes, trans-[PdX$_2$(CNBu$^t$){C(NMe$_2$)NHBu$^t$}] (X = Cl, Br, or I) [9] and [Rh(CNBu$^t$)$_3${C(NMe$_2$)NHBu$^t$}]$^+$BF$_4^-$,[5] for

[14] E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Müller, and E. Winkler, Chem. Ber., 1972, 105, 162.
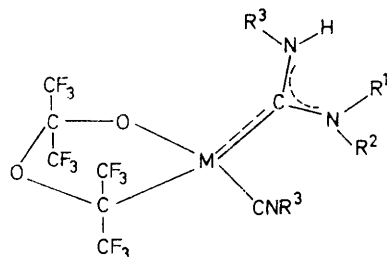
(XII, M = Ni, R$^1$ = R$^2$ = Et, R$^3$ = Bu$^t$ )
(XIII, M = Ni, R$^1$ = R$^2$ = Et, R$^3$ = Pr$^i$ )
(XV, M = Pd, R$^1$ = R$^2$ = Me, R$^3$ = Bu$^t$.)
(XVI, M = Pd, R$^1$ = R$^2$ = Et , R$^3$ = Bu$^t$ )
(XVII, M = Pd, R$^1$ = R$^2$ = Me, R$^3$ = C$_6$H$_{11}$)
(XVIII, M = Pd, R$^1$ = R$^2$ = Et, R$^3$ = C$_6$H$_{11}$)
(XXII, M = Pt , R$^1$ = R$^2$ = Me, R$^3$ = Bu$^t$ )
(XXIII, M = Pt, R$^1$ = R$^2$ = Et, R$^3$ = Bu$^t$ )
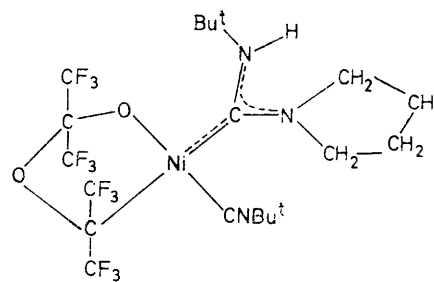
(XIV)
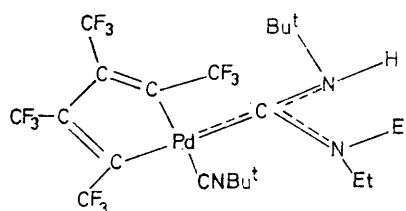
(XIX)
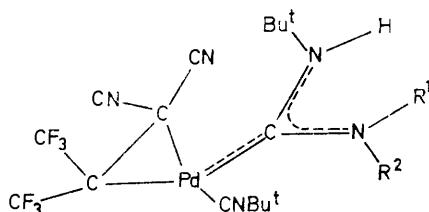
(XX, R$^1$ = R$^2$ = Me)
(XXI, R$^1$ = R$^2$ = Et)

## TABLE 1

Analytical $^a$ and physical data for the complexes

| Compound | M.p./°C | Yield (%) | C | H | N | $M^b$ |
|---|---|---|---|---|---|---|
| (I) | 151—152 | 88 | 40·8 (40·8) | 5·4 (5·3) | 8·7 (8·9) | 469 (469) |
| (II) | 138—139 | 92 | 43·4 (43·4) | 5·9 (5·8) | 8·2 (8·4) | 497 (497) |
| (III) | 147—148 | 62 | 43·5 (43·4) | 5·8 (5·8) | 8·1 (8·4) | 497 (497) |
| (IV) | 166—168 | 84 | 43·9 (43·6) | 5·4 (5·4) | 8·5 (8·5) | 495 (495) |
| (V) | 174—175 | 76 | 42·5 (42·2) | 5·4 (5·3) | 8·4 (8·4) | 512 (512) |
| (VI) | 125—127 | 94 | 40·8 (40·8) | 5·3 (5·3) | 8·6 (8·9) | 469 (469) |
| (VII) | 154—156 | 87 | 38·1 (38·0) | 5·1 (4·8) | 9·6 (9·5) | |
| (VIII) | 150—152 | 64 | 44·4 (44·4) | 5·8 (5·8) | 9·6 (9·7) | 431 (431) |
| (IX) | 148—150 | 76 | 46·8 (47·0) | 6·3 (6·3) | 9·1 (9·1) | 459 (459) |
| (X) | 95—98 | 46 | 47·2 (47·0) | 6·4 (6·3) | 9·4 (9·1) | 459 (459) |
| (XI) | 156—158 | 73 | 46·9 (47·2) | 6·0 (5·9) | 9·2 (9·2) | 457 (457) |
| (XII) | 141—142 | 62 | 37·9 (38·1) | 4·7 (4·6) | 6·6 (6·7) | |
| (XIII) | 147—149 | 71 | 35·8 (35·9) | 3·9 (4·2) | 6·8 (7·0) | |
| (XIV) | 160 dec. | 66 | 38·1 (38·2) | 4·4 (4·3) | 7·2 (6·7) | |
| (XV) | 100 dec. | 67 | 33·1 (33·3) | 3·8 (3·9) | 6·4 (6·5) | |
| (XVI) | 159—160 dec. | 89 | 35·8 (35·4) | 4·1 (4·3) | 6·1 (6·2) | |
| (XVII) | 172—174 | 57 | 37·6 (37·7) | 4·2 (4·2) | 6·0 (6·0) | |
| (XVIII) | 169—172 dec. | 73 | 39·4 (39·5) | 4·4 (4·6) | 5·6 (5·8) | |
| (XIX) $^c$ | 149—151 | 41 | 39·3 (39·5) | 4·5 (4·4) | 6·4 (6·3) | |
| (XX) | 147—148 | 41 | 40·6 (40·6) | 4·7 (4·7) | 13·2 (13·1) | |
| (XXI) $^d$ | 145—147 | 78 | 43·1 (42·9) | 5·5 (5·2) | 12·8 (12·5) | |
| (XXII) | 180—181 | 63 | 29·7 (29·3) | 3·5 (3·4) | 5·4 (5·7) | |
| (XXIII) | 172—174 | 66 | 31·2 (31·4) | 3·8 (3·8) | 5·3 (5·5) | |

$^a$ Calculated values given in parentheses. $^b$ From mass spectra, based on $^{58}$Ni isotope. $^c$ Found: F, 34·2. Reqd.: 34·0%.
$^d$ Found: F, 20·3. Reqd.: 20·4%.

which very similar spectroscopic properties were reported. Although two isomeric configurations are possible for this carbene ligand, in which the Bu$^t$ group be thermodynamically the more stable. The stereochemical stability of (I) suggests that it has the illustrated, *i.e.* thermodynamically stable, configuration.

TABLE 2

I.r.,$^a$ $^1$H,$^b$ and $^{19}$F $^c$ n.m.r. data for the complexes

| Compound | ν(NH) | ν(NC) | ν(NCN) | Chemical shifts |
|---|---|---|---|---|
| (I) | 3358w | 2189s | 1549s | $^1$H at 3·74s (N*H*), 6·14s (NC*H*₃), 7·07s (NC*H*₃), 8·32s (N*Bu*$^t$), and 8·52s (N*Bu*$^t$); $^{19}$F at 104·0m (α-C*F*₂), 108·7m (α-C*F*₂), and 138·4m (β-C*F*₂) |
| (II) | 3374w | 2190s | 1539s | $^1$H at 3·68s (N*H*), 5·05m [NC*H*$_x$H$_y$CH₃, *J*(H$_x$H$_y$) 14·0 Hz, *J*(CH₃H$_x$) 7·0 Hz], 5·90m [NCH$_x$H$_y$CH₃, *J*(H$_x$H$_y$) 14·0 Hz, *J*(CH₃H$_y$) 7·0 Hz], 6·58q [NC*H*₂CH₃, *J*(HH) 7·0 Hz] 8·28s (N*Bu*$^t$), 8·45s (N*Bu*$^t$), 8·68t [NCH₂C*H*₃, *J*(HH) 7·0 Hz], and 8·92t [NCH₂C*H*₃, *J*(HH) 7·0 Hz]; $^{19}$F at 104·1m (α-C*F*₂), 109·3m (α-C*F*₂), and 138·9m (β-C*F*₂) |
| (III) | 3438m, 3380m | 2191s | 1546s | $^1$H at 8·40s (N*Bu*$^t$) and 8·48s (N*Bu*$^t$); $^{19}$F at 100·0m (α-C*F*₂), 106·5m (α-C*F*₂), and 136·1m (β-C*F*₂) |
| (IV) | 3354m | 2188s | 1553m | $^1$H at 3·74s (N*H*), 5·70m (NC*H*₂), 6·72m (C*H*₂), 8·31s (N*Bu*$^t$), and 8·51s (N*Bu*$^t$); $^{19}$F at 104·6m (α-C*F*₂), 109·4m (α-C*F*₂), and 138·8m (β-C*F*₂) |
| (V) | 3375w | 2192s | 1547s | $^1$H at 3·32s (N*H*), 5·45—6·45 complex m (NC*H*₂ and OC*H*₂), 8·30s (N*Bu*$^t$), and 8·48s (N*Bu*$^t$); $^{19}$F at 103·8m (α-C*F*₂), 108·1m (α-C*F*₂), and 141·0m (β-C*F*₂) |
| (VI) | 3371m | 2197s | 1553s | $^1$H at 3·28s (N*H*), 4·95m, 5·85m, 6·64m [C*H*(CH₃)₂ and NC*H*₂], and 8·56m [CH(C*H*₃)₂ and NCH₂C*H*₃]; $^{19}$F at 106·9m (α-C*F*₂), 110·8m (α-C*F*₂), and 139·6m (β-C*F*₂) |
| (VII) | 3360m | 2195s | 1561s | $^1$H at 3·94m [N*H* and C*H*(CH₃)₂, *J*(HH) 6·5 Hz], 6·35s (NC*H*₃), 7·20s (NC*H*₃), 8·59d [CH(C*H*₃)₂, *J*(HH) 6·5 Hz], and 8·73m [CH(C*H*₃)₂]; $^{19}$F at 106·7m (α-C*F*₂), 109·8m (α-C*F*₂), and 138·2m (β-C*F*₂) |
| (VIII) | 3358m | 2183s | 1554s | $^1$H at 3·78s (N*H*), 6·05s (NC*H*₃), 7·10s (NC*H*₃), 8·32s (N*Bu*$^t$), and 8·57s (N*Bu*$^t$); $^{19}$F at 90·8m (α-C*F*₂), 95·5m (α-C*F*₂), 148·7m (β-C*F*), and 149·6m (β-C*F*) |
| (IX) | 3361w | 2181s | 1548s | $^1$H at 3·78s (N*H*), 5·00m [NC*H*$_x$H$_y$CH₃, *J*(H$_y$H$_x$) 14·0 Hz, *J*(CH₃H$_x$) 7·0 Hz], 6·00m [NCH$_x$H$_y$CH₃, *J*(H$_x$H$_y$) 14·0 Hz, *J*(CH₃H$_y$) 7·0 Hz], 6·58q (NC*H*₂CH₃), 8·28s (N*Bu*$^t$), 8·48s (N*Bu*$^t$), 8·70t [NCH₂C*H*₃, *J*(HH) 7·0 Hz], and 8·92t [NCH₂C*H*₃, *J*(HH) 7·0 Hz]; $^{19}$F at 91·0m (α-C*F*₂), 96·1m (α-C*F*₂), 148·6m (β-C*F*), and 150·1m (β-C*F*) |
| (X) | 3364w | 2195s | 1537s | $^1$H at 8·47s (N*Bu*$^t$) and 8·62s (N*Bu*$^t$); $^{19}$F at 90·9m (α-C*F*₂), 94·2m (α-C*F*₂), 148·8m (β-C*F*), and 149·9m (β-C*F*) |
| (XI) | 3350m | 2182s | 1549s | $^1$H at 3·78s (N*H*), 5·52m (NC*H*₂), 6·75m (C*H*₂), 8·32s (N*Bu*$^t$), and 8·52s (N*Bu*$^t$); $^{19}$F at 91·3m (α-C*F*₂), 92·7m (α-C*F*₂), 148·8m (β-C*F*), and 150·1m (β-C*F*) |
| (XII) | 3390s | 2200s | 1541s | $^1$H at 3·71s (N*H*), 4·94m (NC*H*₂CH₃), 6·51m (NCH₂C*H*₃), 8·14s (N*Bu*$^t$), 8·24t [NCH₂C*H*₃, *J*(HH) 7·0 Hz], 8·57s (N*Bu*$^t$), and 8·88t [NCH₂C*H*₃, *J*(HH) 7·0 Hz]; $^{19}$F at 65·6 septet [α-C(C*F*₃)₂, *J*(FF) 4·0 Hz], and 80·4m [β-C(C*F*₃)₂] |
| (XIII) | 3380m | 2202s | 1553s | $^1$H at 4·24m [C*H*(CH₃)₂], 4·97m (N*H*), 5·47m (NC*H*₂), 6·16m [C*H*(CH₃)₂], 6·82m (NC*H*₂), 8·66m [CH(C*H*₃)₂ and NCH₂C*H*₃], and 8·92t [NCH₂C*H*₃, *J*(HH) 7·0 Hz]; $^{19}$F at 65·4 septet [α-C(C*F*₃)₂, *J*(FF) 4·0 Hz], and 80·1m [β-C(C*F*₃)₂] |
| (XIV) | 3363m | 2200s | 1549s | $^1$H at 5·22m (NC*H*₂), 6·68m (C*H*₂), 8·18s (N*Bu*$^t$), and 8·58s (N*Bu*$^t$); $^{19}$F at 65·9m [α-C(C*F*₃)₂], and 80·7m [β-C(C*F*₃)₂] |
| (XV) | 3380m | 2221s | 1553s | $^1$H at 3·54s (N*H*), 6·21s (NC*H*₃), 6·94s (NC*H*₃), 8·36s (N*Bu*$^t$), and 8·51s (N*Bu*$^t$); $^{19}$F at 66·7 septet [α-C(C*F*₃)₂, *J*(FF) 4·0 Hz], and 80·7m [β-C(C*F*₃)₂] |
| (XVI) | 3380m | 2222s | 1543s | $^1$H at 4·35s (N*H*), 5·76m (NC*H*₂CH₃), 6·75m (NCH₂C*H*₃), 8·40s (N*Bu*$^t$), 8·60s (N*Bu*$^t$), 8·71t [NCH₂C*H*₃, *J*(HH) 7·0 Hz], and 8·87t [NCH₂C*H*₃, *J*(HH) 7·0 Hz]; $^{19}$F at 66·8 septet [α-C(C*F*₃)₂, *J*(FF) 4·0 Hz], and 80·6m [β-C(C*F*₃)₂] |
| (XVII) | 3380m | 2221s | 1572s | $^1$H at 4·68m (N*H*), 5·20m (NC*H*), 5·50m (NC*H*), 6·40s (NC*H*₃), 7·12s (NC*H*₃), and 8·0—9·0 complex m (C*H*₂C*H*₂C*H*₂); $^{19}$F at 66·7 septet [α-C(C*F*₃)₂, *J*(FF) 3·5 Hz], and 80·9 septet [β-C(C*F*₃)₂, *J*(FF) 3·5 Hz] |
| (XVIII) | 3375m | 2223s | 1560s | $^1$H at 4·65m (N*H*), 5·44m, 5·99m, 6·78m, 8·0—9·0 complex m; $^{19}$F at 66·7m [α-C(C*F*₃)₂], and 80·8m [β-C(C*F*₃)₂] |
| (XIX) | 3390m | 2213s | 1540s | $^1$H at 3·68s (N*H*), 5·66m (NC*H*₂CH₃), 6·46m (NCH₂C*H*₃), 8·44s (N*Bu*$^t$), 8·47s (N*Bu*$^t$), 8·74t [NCH₂C*H*₃, *J*(HH) 7·0 Hz], and 8·96t [NCH₂C*H*₃, *J*(HH) 7·0 Hz]; $^{19}$F at 53·2q [α-C(C*F*₃), *J*(FF) 14·7 Hz], 55·8m [α-C(C*F*₃)], and 57·0m [β-C(C*F*₃)] |
| (XX) | 3340m | 2192s | 1542s | $^1$H at 3·25s (N*H*), 6·39s (NC*H*₃), 6·92s (NC*H*₃), and 8·47s (N*Bu*$^t$); $^{19}$F at 55·3s (C*F*₃) |
| (XXI) | 3340m | 2192s | 1538s | $^1$H at 4·16s (N*H*), 5·80m (NC*H*₂CH₃), 6·23m (NCH₂C*H*₃), 8·55s (N*Bu*$^t$), and 8·78m (NCH₂C*H*₃); $^{19}$F at 55·4s (C*F*₃) |
| (XXII) | 3400m | 2211s | 1553s | $^1$H at 3·39s (N*H*), 6·23s (NC*H*₃), 6·88s (NC*H*₃), 8·36s (N*Bu*$^t$), and 8·54s (N*Bu*$^t$); $^{19}$F at 67·5t of m [α-C(C*F*₃)₂, *J*(PtF) 83·0 Hz], and 80·5m [β-C(C*F*₃)₂] |
| (XXIII) | 3400m | 2211s | 1550s | $^1$H at 3·22s (N*H*), 5·69m (NC*H*₂CH₃), 6·42m (NCH₂C*H*₃), 8·36s (N*Bu*$^t$), 8·54s (N*Bu*$^t$), and 8·77m (NCH₂C*H*₃); $^{19}$F at 67·5t of septets [α-C(C*F*₃)₂, *J*(FF) 4·0 Hz, *J*(PtF) 82·0 Hz], and 80·4m [β-C(C*F*₃)₂] |

$^a$ In cm$^{-1}$, in Nujol. $^b$ Measured in (CD₃)₂CO except for (VII), (XIII), (XIV), (XVI), (XVII), (XVIII), and (XXI) which were measured in CDCl₃. $^c$ P.p.m. relative to CFCl₃, measured in (CH₃)₂CO for (I)—(VI) and (VIII)—(XI); in CH₂Cl₂ for (VII), (XII), and (XV)—(XXIII); and in (C₂H₅)₂O for (XIII).

occupies an 'inside' or 'outside' position, consideration of molecular models would suggest that the latter would

$^{15}$ D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, L. J. Manojlović-Muir, and K. W. Muir, *J. Organometallic Chem.*, 1972, **44**, C59.

An *X*-ray crystal structure determination $^{15}$ of *cis*-[PtCl₂(PEt₃){C(NPhCH₂)₂}] shows that the carbene N·C·N plane is perpendicular to the PtCl₂ plane, and it is suggested that (I) has a similar configuration, in which π-bonding is predominantly in the N·C·N moiety.

Diethylamine reacted similarly with

[Ni·CF$_2$·CF$_2$·CF$_2$·CF$_2$(CNBu$^t$)$_2$] to give (II) containing the carbene ligand {C(NHBu$^t$)NEt$_2$}. Although the $^1$H n.m.r. spectrum of (II) exhibited the expected two Bu$^t$N resonances and one NH resonance, the signals arising from the two N-ethyl groups were unexpectedly complex. The ' outside ' N-ethyl group appeared as a quartet (CH$_2$) and triplet (CH$_3$) at τ 6·55 and 8·93 [J(HH) = 7·0 Hz] respectively. For the ' inside ' group the methyl resonance appeared as a triplet at τ 8·70 (J = 7·0 Hz), but the methylene protons formed two six line multiplets centred at τ 5·02 and 5·98. The intensities of the lines in these multiplets were in the ratio 1 : 3 : 4 : 4 : 3 : 1, whereas in a binomial sextet the ratio would be 1 : 5 : 10 : 10 : 5 : 1. A comparison of the corresponding 60 and 100 MHz $^1$H n.m.r. spectra confirmed that the multiplets were separate signals. In decoupling experiments, double irradiation of the ' inside ' methyl triplet caused both multiplets to collapse to doublets (J = 14·0 Hz), and double irradiation of one multiplet caused the other to collapse to a quartet (J = 7·0 Hz). Thus the two multiplets are coupled to each other and to the ' inside ' methyl triplet. The existence of these multiplets can be explained if it is assumed that the ' inside ' methylene group is subjected to steric interaction with the ' inside ' NH atom of the carbene ligand. This prevents free rotation about the N·CH$_2$ bond, rendering the methylene protons (H$_x$,H$_y$) magnetically non-equivalent. The coupling constant between geminal methylene protons is usually ca. 12—15 Hz. In the case of (II), J$_{gem}$(HH) was found to be 14·0 Hz exactly twice the value of J(CH$_3$–H$_x$) and J(CH$_3$–H$_y$); a combination of these two couplings produces a 1 : 3 : 4 : 4 : 3 : 1 multiplet. The $^1$H n.m.r. spectrum of (II) was unchanged at 55 °C, indicating a moderate barrier to rotation.

The corresponding reaction between

[Ni·CF$_2$·CF$_2$·CF$_2$·CF$_2$(CNBu$^t$)$_2$] and t-butylamine gave crystalline (III) with the expected spectroscopic characteristics. The $^1$H n.m.r. spectrum showed only two resonances at τ 8·40 and 8·48, indicating the illustrated symmetrical structure, in which both t-butyl groups in the carbene ligand occupy ' outside ' positions. This would arise if cis-addition of t-butylamine to the isocyanide had occurred. Careful examination of the $^1$H spectrum indicated the possible presence of a second, minor isomer for which two signals, due to ' inside ' and ' outside ' Bu$^t$N groups, in addition to a Bu$^t$NC signal, were observed.

Complex (III) was less stable in solution than (I) or (II), and the corresponding reaction with the primary amine methylamine produced an oil from which it was not possible to isolate a stable carbene complex.

The cyclic secondary amines, pyrrolidine and morpholine reacted straightforwardly to produce the stable carbene complexes (IV) and (V), with similar spectroscopic properties (Table 2) to those of (I), (II), and (III). The $^1$H n.m.r. spectra exhibited the expected NH and

Bu$^t$N resonances, but the signals arising from the methylene groups were very complex and could not be simplified by decoupling experiments.

Dimethylamine and diethylamine reacted with

[Ni·CF$_2$·CF$_2$·CF$_2$·CF$_2$(CNPr$^i$)$_2$] to form (VII) and (VI) in high yield. The i.r. and $^{19}$F n.m.r. spectra were similar to those of (I) and (II). In (VI) however, although the $^1$H n.m.r. spectrum showed similar patterns for the ' outside ' and ' inside ' N-ethyl resonances of the carbene ligand, a complete analysis was not possible because the multiplets were superimposed on the two Me$_2$CH septets.

The nickelahexafluorocyclopenta-3-ene complex

[Ni·CF$_2$·CF:CF·CF$_2$(CNBu$^t$)$_2$] [12] also underwent similar reactions with primary and secondary amines to form the mono-carbene complexes (VIII)—(XI) with spectroscopic properties very similar to those of (I)—(V), except that the i.r. spectra showed a band in the region 1747—1751 cm$^{-1}$, due to the uncomplexed double bond of the fluorocarbon ring, confirming that the reaction with amine did not involve attack at this point of the molecule. The $^1$H n.m.r. spectrum of the {C(NHBu$^t$)-NEt$_2$} complex (IX) showed the same multiplet pattern for the ' inside ' N-ethyl group as observed in the spectrum of (II).

It was of interest to ascertain whether the above reactions with amines also occurred with other fluorocarbon–metal systems containing isocyanide ligands.

Reaction of the complex [Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O-(CNBu$^t$)$_2$] [12] with diethylamine or pyrrolidine afforded the stable, crystalline complexes (XII) and (XIV), and in addition diethylamine also reacted smoothly with

[Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNPr$^i$)$_2$] [16] to afford (XIII). The extension of these reactions to the corresponding palladium [13] and platinum [17] systems gave stable complexes (XV—XVIII) and (XXII—XXIII), respectively. These compounds showed i.r. and $^1$H n.m.r. spectra characteristic of a co-ordinated carbene. The $^{19}$F n.m.r. spectra showed a typical pattern (Table 2) characteristic of the ring system M·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O, confirming that the reaction with amine involved attack only at an isocyanide ligand.

The isocyanide stretching frequencies in the i.r. spectrum of, for example [Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNBu$^t$)$_2$], occur at 2228 and 2215 cm$^{-1}$. As expected, the complex

(XII)   [Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNBu$^t$){C(NHBu$^t$)NEt$_2$}] shows only one isocyanide stretching band, interestingly at lower frequency, indicating a higher degree of back-bonding in the remaining isocyanide ligand of the carbene complex. This implies that the carbene ligands are relatively poorer π-acceptors, a possible consequence of the geometry of the complexes, i.e. the carbene plane is

[16] C. H. Davies, Ph.D. Thesis, University of Bristol, 1973.

[17] J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, J.C.S. Dalton, 1973, 381.

perpendicular to the molecular plane (see below). Increased back-bonding to the remaining isocyanide ligand would be expected to decrease the susceptibility to nucleophilic attack, probably explaining why only monocarbene complexes are formed in these reactions.

Reaction of the complexes [M·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O-(CNR)$_2$] (M = Ni, Pd, or Pt) with amine could in principle lead to two isomeric complexes since isocyanide ligands are present cis and trans to the oxygen atom $\alpha$ to the metal. For the compounds cis-[PdX$_2$(CNPh)-(PPh$_3$)] (X = Cl or Br) the reactivity sequence Cl > Br towards amine has been explained [18] by assuming that the higher electronegativity of chlorine increased the electrophilicity of the isocyanide trans to that halogen. A similar argument would suggest that for the complexes [M·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNR)$_2$] nucleophilic attack would occur preferentially at the isocyanide ligand trans to the oxygen atom. However, an X-ray crystallographic study [19] carried out on complex (XVI) revealed that the carbene ligand {C(NEt$_2$)NHBu$^t$} is trans to the $\alpha$-C(CF$_3$)$_2$ group. The carbene N·C·N plane is perpendicular to the plane of the five-membered ring, and the carbene t-butyl group occupies an ' outside ' position.

Preferential attack of the amine on the isocyanide ligand trans to the C(CF$_3$)$_2$ group may be due to the steric effect of this group making adduct formation cis to it, and trans to the oxygen atom, more difficult.

In the reaction of [Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNBu$^t$)$_2$] with dimethylamine a lemon-yellow crystalline complex (XXIV) was obtained, there being no evidence for the formation of a carbene complex. Elemental analysis indicated the structure [Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNBu$^t$)-(NHMe$_2$)], and this was supported by the i.r. spectrum which showed bands due to NH (3293 cm$^{-1}$) and NC (2210 cm$^{-1}$), and the complete absence of any bands in the region 2210—1472 cm$^{-1}$. The $^{19}$F n.m.r. spectrum was almost identical with that of the starting complex, and the $^1$H n.m.r. spectrum showed two resonances at $\tau$ 7·55 (6H) and 8·40 (9H), suggesting the presence of coordinated dimethylamine and isocyanide. There was some evidence for similar reactions with other amines, but these were difficult to reproduce. The formation of (XXIV) could involve either displacement of the carbene ligand by excess of amine or direct displacement of isocyanide by amine.

In addition to the above reactions, it was found that the metallocyclopentadiene [Pd·C(CF$_3$):C(CF$_3$)·C(CF$_3$):C-(CF$_3$)(CNBu$^t$)$_2$] [20] reacted with an excess of diethylamine to afford the carbene complex (XIX). The metallocyclopropane [Pd·C(CN)$_2$·C(CF$_3$)$_2$(CNBu$^t$)$_2$] [13] also reacted with dimethyl- or diethyl-amine to give the monocarbene complexes (XX) and (XXI).

Attempts to extend these reactions to other nucleo-

philes (MeOH or MeSH) were unsuccessful when using [Ni·CF$_2$·CF$_2$·CF$_2$·CF$_2$(CNBu$^t$)$_2$] or [Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O-(CNBu$^t$)$_2$] as model compounds.

## EXPERIMENTAL

$^1$H and $^{19}$F N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100·0 and 94·1 MHz, respectively; chemical shifts are relative to Me$_4$Si ($\tau$ 10·0) and CCl$_3$F (0·0 p.p.m.). I.r. spectra were measured on a Perkin-Elmer 257 spectrophotometer as Nujol or hexachlorobutadiene mulls. Mass spectra were measured on an A.E.I. MS 902 spectrometer operating at 70 eV. All experiments and purification steps were carried out in an atmosphere of dry, oxygen-free nitrogen. The starting materials were prepared by the published methods [12,13,17,20] except for those noted below, which were obtained by a simple extension of these methods. (a) Reaction of [Pd-(CNC$_6$H$_{11}$)$_2$] (0·32 g, 1·0 mmol) with hexafluoroacetone (0·65 g, 4·0 mmol) in diethyl ether (20 ml) gave, after 3 days at room temperature, on addition of hexane, white crystals of [Pd·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNC$_6$H$_{11}$)$_2$] (0·48 g, 72%) m.p. 116° (Found: C, 36·4; H, 3·3; N, 4·1. C$_{20}$H$_{22}$F$_{12}$N$_2$O$_2$Pd requires C, 36·5; H, 3·4; N, 4·3%); $^1$H n.m.r. resonances (CDCl$_3$) at $\tau$ 6·12 (m, 2H, CH) and 8·40 (m, 22H, CH$_2$); $^{19}$F n.m.r. resonances (Et$_2$O) at 66·9 p.p.m. [septet, 6F, $\alpha$-C(CF$_3$)$_2$, J(FF) 4·0 Hz] and 80·7 [septet, 6F, $\beta$-C(CF$_3$)$_2$, J(FF) 4·0 Hz].

(b) Addition of Bu$^t$NC (0·15 g, 1·8 mmol) to a stirred solution of [Pt·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(1,5-C$_8$H$_{12}$)] [17] (0·56 g, 0·9 mmol) in diethyl ether (25 ml) gave, on addition of hexane, white crystals of [Pt·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O(CNBu$^t$)$_2$] (0·50 g, 81%), m.p. 178—180° (Found: C, 27·3; H, 2·6; N, 3·9. C$_{16}$H$_{18}$F$_{12}$O$_2$N$_2$Pt requires C, 27·7; H, 2·6; N, 4·0%), v(NC) (Nujol) at 2251s and 2222s cm$^{-1}$; $^1$H n.m.r. (CDCl$_3$), $\tau$ 8·45 (s, 9H, CNBu$^t$) and 8·54 (s, 9H, CNBu$^t$); $^{19}$F n.m.r. resonances (CDCl$_3$) at 67·9 p.p.m. [septet, 6F, $\alpha$-C(CF$_3$)$_2$, J(FF) 4·0 Hz, J(PtF) 90·0 Hz] and 81·1 [septet, 6F, $\beta$-C(CF$_3$)$_2$, J(FF) 4·0 Hz].

Synthesis of Complex (I).—The complex [Ni·CF$_2$·CF$_2$·CF$_2$·CF$_2$(CNBu$^t$)$_2$] (0·12 g, 0·28 mmol) was stirred in neat dimethylamine (10 ml) at 0 °C for 15 min. An excess of amine was removed in vacuo and the residue crystallised from toluene–hexane to give crystals of (I) (0·12 g, 88%) with the properties listed in Tables 1 and 2. The same general procedure was followed for the preparation of related complexes.

Reaction of Dimethylamine with [Ni·C(CF$_3$)$_2$O·C(CF$_3$)$_2$O-(CNBu$^t$)$_2$].—The complex (0·11 g, 0·20 mmol) was stirred in neat dimethylamine (2 ml) at 0 °C for 2 h. After an excess of amine had been removed in vacuo, the residue was recrystallised from toluene–hexane to give lemon-yellow crystals of (XXIV) (0·08 g, 78%), m.p. 144—146° (Found: C, 30·4; H, 3·2; N, 5·4. C$_{13}$H$_{16}$F$_{12}$N$_2$NiO$_2$ requires C, 30·1; H, 3·1; N, 5·4%), v$_{max.}$ (Nujol and hexachlorobutadiene) at 3293w, 3002w, 2927w, 2855w, 2210s, 1472w, 1377w, 1303w, 1284m, 1262m, 1233m, 1206s, 1190s, 1157s, 1109w, 1080m, 1028m, 964m, 932m, 896w, 754w, 724m, and 704m cm$^{-1}$;

[18] B. Crociani, T. Boschi, M. Nicolini, and U. Belluco, Inorg. Chem., 1972, 11, 1292.

[19] A. Modinos and P. Woodward, unpublished work.
[20] S. K. Shakshooki, Ph.D. Thesis, Bristol University, 1971.

$^1$H n.m.r. resonances ([$^2$H$_6$]acetone) at $\tau$ 7·55 (s, 6H, N$Me_2$) and 8·40 (s, 9H, s, $Bu^tN$); $^{19}$F n.m.r. resonances (acetone) at 66·6 p.p.m. [septet, 6F, $\alpha$-C(CF$_3$)$_2$, $J$(FF) 4·0 Hz] and 81·3 [septet, 6F, $\beta$-C(CF$_3$)$_2$, $J$(FF) 4·0 Hz].