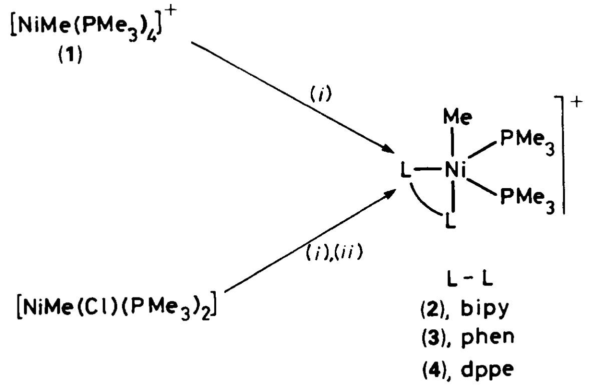
Synthesis of some Cationic 16- and 18-Electron Nickel Alkyl Phosphine Complexes containing Bidentate Ligands: Ligand-dependent Square-planar, Trigonal-bipyramidal, and Square-pyramidal Co-ordination Geometries, their Reactions with CO and Alkynes, and the Crystal Structure of $[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$†

Manfred Bochmann* and Ian Hawkins
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ
Michael B. Hursthouse and Richard L. Short
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Treatment of $[NiMe(PMe_3)_4]BF_4$ (**1**) with chelating ligands L–L gives the complexes $[NiMe(PMe_3)_2(L\text{–}L)]BF_4$ which may be rigid, with a trigonal-bipyramidal 18-electron structure [L–L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)], or show fluxional behaviour [L–L = 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(dimethylphosphino)ethane (dmpe)]. The latter two complexes are in equilibrium with square-planar $[NiMe(PMe_3)(L\text{–}L)]BF_4$. Treatment of (**1**) with excess of dmpe leads to complete substitution of PMe_3 to give square-pyramidal $[NiMe(dmpe)_2]BF_4$. In $[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$ (**9**) the co-ordination of a fourth PMe_3 ligand to give a five-co-ordinate complex analogous to (**1**) is precluded for steric reasons. The crystal structure of (**9**) shows the metal centre in a tetrahedrally distorted square-planar environment, with P–Ni–P and P–Ni–C angles of 135.5(2) and 157.8(7)°, respectively. While $[NiMe(PMe_3)_2(dmpe)]BF_4$ and $[NiMe(dmpe)_2]BF_4$ react with CO to give stable nickel acyl complexes, the dppe complex $[Ni(COMe)(PMe_3)(dppe)]BF_4$ is only observed at low temperature. Treatment of (**1**) with 2 equivalents of PPh_3 or with an excess of bipy, phen, or dppe leads to reductive elimination and formation of zerovalent nickel complexes. Similarly, PhC≡CPh induces the reductive methyl migration in (**1**) from nickel to PMe_3 *via* spectroscopically observable ylidic intermediates to give $[Ni(C_2Ph_2)(PMe_3)_2]$ and $[PMe_4]BF_4$.

Whereas the chemistry of neutral nickel alkyl complexes has been comprehensively studied,[1] examples of cationic nickel alkyl complexes are relatively few and include the square-planar perhalogenophenyl cations $[Ni(C_6X_5)L_3]^+$,[2] alkyl cations of terdentate ligands, *e.g.* $[NiMe\{PPh(C_2H_4PPh_2)_2\}]^+$,[3] the rigid trigonal-bipyramidal complexes $[NiR\{N(CH_2CH_2EPh_2)_3\}]^+$ (E = P or As, R = Me or CH_2Ph),[4] and $[NiMe(PMe_3)_4]^+$ (**1**) which is fluxional in solution but trigonal bipyramidal at low temperature and in the solid state.[5] We have recently described[6] the reactions of (**1**) with CO as part of our interest in the chemistry of cationic transition metal alkyl complexes[7] and report here the synthesis of four- and five-co-ordinate nickel alkyl cations with bidentate N- and P-donor ligands and the dependence of their stability on the ligand π-donor and π-acceptor properties.



Scheme 1. (*i*) L–L, (*ii*) $TlBF_4$

Results and Discussion

The five-co-ordinate complexes $[NiMe(PMe_3)_2(L\text{–}L)]BF_4$ [L–L = 2,2′-bipyridyl (bipy) (**2**), 1,10-phenanthroline (phen) (**3**), or 1,2-bis(diphenylphosphino)ethane (dppe) (**4**)] can be prepared either by ligand displacement from $[NiMe(PMe_3)_4]BF_4$ (**1**) or directly from $[NiMe(Cl)(PMe_3)_2]$, $TlBF_4$, and L–L in tetrahydrafuran (thf), acetone, or methanol (Scheme 1) in near-quantitative yield as air-sensitive, thermally stable brown (**2**), maroon (**3**), or orange (**4**) crystalline solids.

Attempts to prepare the bis(dimethylphosphino)ethane (dmpe) analogue of (**4**) led to a mixture of products, the expected $[NiMe(PMe_3)_2(dmpe)]BF_4$ (**6**), isolated as orange crystals, and a yellow microcrystalline salt, $[NiMe(PMe_3)(dmpe)]BF_4$ (**7**). The two products could be separated by fractional crystallisation. Pure (**6**) is obtained by recrystallising the mixture in the presence of excess of PMe_3.

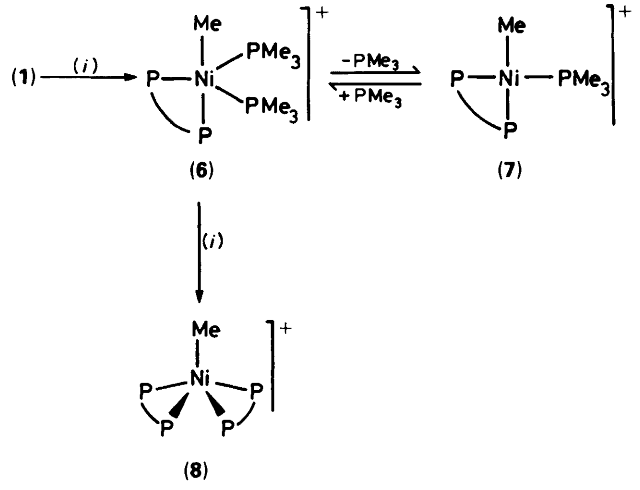
The remaining trimethylphosphine ligands in complexes (**6**) and (**7**) can be completely displaced by treatment with excess of dmpe to give the red crystalline complex $[NiMe(dmpe)_2]BF_4$ (**8**) (Scheme 2); (**8**) can also be prepared directly from $[NiMe(Cl)(PMe_3)_2]$, 2 equivalents of dmpe, and $TlBF_4$.

No product was isolated on treating complex (**1**) with 1 equivalent of bis(diphenylphosphino)methane (dppm); brown oils resulted instead, even after metathesis with $NaBPh_4$. The ^{31}P n.m.r. spectrum confirmed the formation of a mixture which could not be separated.

---

† Tris(trimethylphosphine)(trimethylsilylmethyl)nickel(II) tetrafluoroborate.

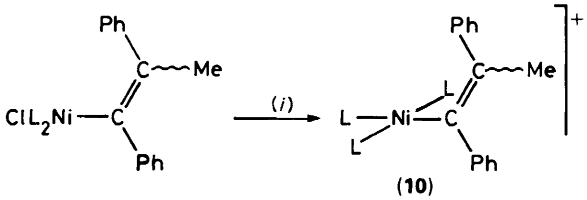
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.



Scheme 2. (i) dmpe

In contrast to the reaction of $[NiMe(Cl)(PMe_3)_2]$ with PMe_3 in the presence of $TlBF_4$ which gives the 18-electron complex (1), the analogous reaction with the more bulky $[Ni(CH_2SiMe_3)Cl(PMe_3)]$[8] produces the 16-electron species $[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$ (9). Spectroscopic data suggested a distorted square-planar structure, which was subsequently confirmed by an *X*-ray structure determination (see below). Solutions of (9) containing excess of PMe_3 gave no indication for an interaction of the nickel centre with a fourth phosphine ligand but, surprisingly, showed the presence of small amounts of the methyl complex (1), suggesting that the trimethylsilyl group in (9) may be susceptible to nucleophilic attack, possibly by adventitious water [equation (1)]. Hydrolytic cleavage of silicon–carbon bonds of trimethylsilylmethyl derivatives under relatively mild conditions has been observed for a number of acyl, iminoacyl, carbyne, and alkynyl complexes.[9] Cationic 16-electron nickel alkyl complexes are less stable than 18-electron species with which they tend to form an equilibrium [*e.g.* (6) $\rightleftharpoons$ (7)]. The failure of (9) to add a fourth PMe_3 ligand and give a trigonal-bipyramidal 18-electron structure is no doubt due to the steric hindrance by the trimethylsilylmethyl group. Cationic nickel alkyl complexes differ in this respect from palladium analogues where square-planar co-ordination is generally preferred, even in the absence of steric restrictions, such as in $[PdMe(PMe_3)_3]^+$.[10] However, if the nickel centre carries unsaturated σ ligands such as acyl or vinyl groups, it too adopts a square-planar geometry. For example, treatment of the vinyl complex *trans*-$[Ni\{C(Ph){=}C\text{-}MePh\}Cl(PMe_3)_2]$ (a 44:56 mixture of *E*:*Z* isomers)[11] with PMe_3 and $TlBF_4$ in thf generates the nickel vinyl cation (10) as a very soluble red oil (mixture of *E* and *Z* isomers). Like $[Ni(\sigma\text{-}COMe)(PMe_3)_3]^+$,[6] (10) has a square-planar structure [equation (2)]. In the absence of strong steric interactions, there is no evidence for structural distortion.

$$[Ni(CH_2SiMe_3)(PMe_3)_3]^+ + H_2O \xrightarrow{PMe_3} [NiMe(PMe_3)_4]^+ + SiMe_3(OH) \quad (1)$$

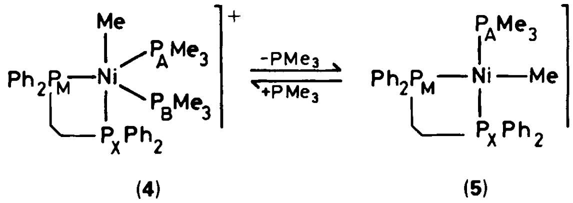


(10) (2)

L = PMe_3; (*i*) PMe_3, $TlBF_4$, thf

Phosphorus-31 *N.M.R. Spectroscopy*.—The structures of the complex cations are assigned on the basis of low-temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra (Table 1). The complexes (2) and (3) show temperature-independent singlets at δ_P −27.3 and −26.2 p.p.m., respectively, and although a square-planar geometry with an apical methyl ligand cannot be ruled out, a comparison with the structure of (4) (below) suggests that a trigonal-bipyramidal co-ordination geometry with two equivalent equatorial PMe_3 ligands is more likely.

The ^{31}P n.m.r. spectra of the dppe complex (4) were found to be more complex. The room temperature spectrum, consisting of a sharp singlet at δ −28 and a broad absorption at δ +70 p.p.m. corresponding to PMe_3 and dppe, respectively, evolves into a complex pattern on cooling which is fully resolved at −90 °C. Nine different values of $^2J_{PP}$ are observed, which suggests that two species are present, one displaying an ABMX-type spectrum, while the other gives rise to an AMX pattern. Apparently, partial dissociation of a PMe_3 ligand occurs to give a four-co-ordinate 16-electron cation (5) [equation (3)]. The doublet of doublets displayed by the PMe_3 ligand in (5) shows a typically large *trans*- and a small *cis*-coupling constant $^2J_{PP}$ of 256 and 36.6 Hz, respectively,[12] confirming the square-planar geometry of the cation.



(4) (5) (3)

The ABMX spectrum of (4) shows that all four ligand P atoms are non-equivalent. Examination of the $^2J_{pp}$ values shows two distinct ranges, small *cis* coupling (23, 27, and 48 Hz) and intermediate values for bond angles close to 120° (127, 145, and 155 Hz), as found in the equatorial plane of a trigonal bipyramid. The values for the coupling constants agree well with those found for related nickel, palladium, and platinum phosphine complexes.[12] The non-equivalence of the two PMe_3 ligands at low temperature and the observation of an ABMX instead of an A_2MX pattern is best explained by the non-planar conformation of the puckered Ni(dppe) five-membered ring which brings the sterically demanding phenyl groups of the equatorially co-ordinated dppe phosphorus closer to one PMe_3 ligand than to the other. At −90 °C the rate of interconversion of the possible ring conformations is apparently slow enough to appear frozen out on the n.m.r. time-scale. This assumption is supported by spectra run at −80 °C which are not fully resolved.

The dmpe complex (6) displays an A_2MX spectral pattern, suggesting a structure very similar to (4). Both PMe_3 ligands are equivalent and at −70 °C give rise to a doublet-of-doublets pattern which shows a small 6 Hz splitting; this is most probably due to second-order effects since it is not expected that a preferential conformation of the sterically undemanding dmpe ligand could be frozen out at this temperature. The coincidental equivalence of the *cis* coupling constants $^2J_{AX} = {}^2J_{MX}$ (35.4 Hz) simplifies the spectrum. A computer simulation confirmed this assignment.

The four-co-ordinate cation (7) possesses a structure analogous to (5).

By contrast, the complex $[NiMe(dmpe)_2]BF_4$ (8) gives rise to an unexpectedly simple ^{31}P n.m.r. spectrum, consisting of a singlet which could not be resolved on cooling down to −90 °C. Since the ligand-exchange processes of related nickel com-

Table 1. Proton and ^{31}P n.m.r. data for cationic nickel complexes

Complex	^1H N.m.r.[a]	^{31}P-{^1H} N.m.r.[b]
(**2**) $[NiMe(PMe_3)_2(bipy)]BF_4$	-0.26 (s, 3 H, Ni–Me), 1.07 (d, 18 H, J_{PH} 6, PMe_3), 7.7—9.0 (m, 8 H, bipy)	-27.3 (s)
(**3**) $[NiMe(PMe_3)_2(phen)]BF_4$	-0.05 (s, 3 H, Ni–Me), 1.05 (d, 18 H, J_{PH} 6, PMe_3), 8.2—9.3 (m, 8 H, phen)	-26.2 (s)
(**4**) $[NiMe(PMe_3)_2(dppe)]BF_4$	0.43 (s, 3 H, Ni–Me), 1.07 (d, 18 H, J_{PH} 6, PMe_3), 1.4—1.6 (m, 4 H, C_2H_4), 7.57 (m, 20 H, Ph)	-28.1 (td, P_AMe_3, J_{AB} 127, J_{AM} 145, J_{AX} 27), -18.0 (td, P_BMe_3, J_{AB} 127, J_{BM} 155, J_{BX} 48), 46.8 [ddd, P_MPh_2 (equatorial), J_{AM} 145, J_{BM} 155, J_{MX} 23], 72.1 (ddd, P_XPh_2, J_{AX} 27, J_{BX} 48, J_{XM} 23)[c]
(**5**) $[NiMe(PMe_3)(dppe)]BF_4$		-8.31 (dd, P_AMe_3, J_{AM} 36.6, J_{AX} 256), 53.0 (dd, P_MPh_2, J_{AM} 36.6, J_{MX} 22), 65.2 (dd, P_XPh_2, J_{AX} 256, J_{MX} 22)
(**6**) $[NiMe(PMe_3)_2(dmpe)]BF_4$	-0.04 (m, 3 H, Ni–Me), 1.34 (s, 18 H, PMe_3), 1.47 (s, 12 H, PMe_2), 1.4—1.6 (m, 4 H, C_2H_4)	-23.3 (dd, P_AMe_3, J_{AM} 148, J_{AX} 35), 39.5 [dd, P_MMe_2 (equatorial), J_{AM} 148, J_{MX} 35], 46.1 (dd, P_XMe_2, $J_{AX} = J_{MX}$ 35)
(**7**) $[NiMe(PMe_3)(dmpe)]BF_4$	0.0 (m, 3 H, Ni–Me), 1.40 (s, 9 H, PMe_3), 1.4—1.6 (m, 4 H, C_2H_4), 1.62 (s, 12 H, PMe_2)	-8.7 (dd, P_AMe_3, J_{AM} 35, J_{AX} 271), 33.6 (dd, P_MMe_2, J_{AM} 35, J_{MX} 24), 46.1 (dd, P_XMe_2, J_{AX} 271, J_{MX} 24)
(**8**) $[NiMe(dmpe)_2]BF_4$	-0.12 (m, br, 3 H, Ni–Me), 1.5 (s, 24 H, PMe_2), 1.8—2.1 (m, 8 H, C_2H_4)	23.3 (s)
(**9**) $[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$	0.22 (s, 9 H, $SiMe_3$), 0.31 (s, 2 H, CH_2Si), 1.47 (s, br, 27 H, PMe_3)	-15.4 (t, P_AMe_3, J_{AB} 41.5), -11.9 (d, P_BMe_3)
(**10**) $[Ni\{C(Ph)C(Me)Ph\}(PMe_3)_3]BF_4$		(*Z*)-isomer[d], -19.6 (t, J_{AB} 39), -10.7 (d); (*E*)-isomer, -16.3 (t, J_{AB} 39), -13.9 (d)
(**12**) $[Ni(COMe)(PMe_3)(dmpe)]BF_4$	1.36 (s, 9 H, PMe_3), 1.47 (s, 12 H, PMe_2), 1.6—2.1 (m, 4 H, C_2H_4), 2.50 (s, br, 3 H, COMe)	
(**13**) $[Ni(COMe)(dmpe)_2]BF_4$	1.49 (d, br, 24 H, J_{PH} 3, PMe_2), 1.6—2.1 (m, 8 H, C_2H_4), 2.54 (qnt, 3 H, J_{PH} 7, COMe)	

[a] $[^2H_6]$Acetone solution, 60 MHz, 35 °C; s = singlet, d = doublet, t = triplet, qnt = quintet, m = multiplet, and br = broad; J = in Hz. [b] $[^2H_6]$Acetone solution, 40.3 MHz, -70 °C unless stated otherwise; J in Hz. [c] At -90 °C. [d] Assigned on the basis of the relative abundance of this isomer in the starting material (see text).

plexes such as (**1**), (**6**), and (**7**) are frozen out below -70 °C, it is unlikely that (**8**) remains fluxional under these conditions, and the spectrum is therefore consistent only with a square-pyramidal geometry with an axial methyl ligand. The equivalence of all four P atoms suggests that the NiP_2C_2 five-membered rings remain conformationally flexible on the n.m.r. time-scale at low temperature. Complete planarity of both chelate rings is unlikely; the twisted conformation of five-membered dmpe chelate rings in the solid state has been demonstrated for example in the cases of $[Ni(C_2H_4)(PPh_3)(dmpe)]$[13] and $[RhCl(CH_2Cl)(dmpe)_2]Cl$,[14] although in solution all dmpe-phosphorus nuclei were found to be magnetically equivalent.

Miller and Caulton[15] have proposed that the energy barrier for the rearrangement from a trigonal bipyramid to a square pyramid for a series of bis(chelate) complexes $[M(CO)(L–L)_2]^+$ (M = Rh or Ir) depends on both the ring size and the steric requirements of the chelate ligand, decreasing in the order dppp > dppe > dppm [dppp = 1,3-bis(diphenylphosphino)propane]. The $[M(CO)(dppe)_2]^+$ complexes are trigonal bipyramidal, whereas the dppm analogues are square pyramidal.[15] Similarly, Karsch[16] has shown that the $CH_2(PMe_2)_2$ (dmpm) ligand with its small bite angle favours square-pyramidal co-ordination in $[Co(PMe_3)(dmpm)_2]^+$ and $[Ni(PMe_3)(dmpm)_2]^{2+}$. Square-pyramidal co-ordination is more commonly found with complexes of tridentate ligands and was confirmed by *X*-ray diffraction for $[Ni(tppme)(SeO_4)]$ [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane],[17] which has a rather distorted structure, and for $[Ni(bdma)(pdma)]^{2+}$ [bdma = bis(2-dimethylarsinophenyl)methylarsine and pdma = *o*-phenylenebis(dimethylarsine)];[18] its occurrence in the dmpe complex (**8**) is under these circumstances unexpected.

The low-temperature ^{31}P n.m.r. spectrum of $[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$ (**9**) consists of the expected AB_2 triplet-doublet pattern (Table 1), albeit distorted due to second-order effects, with the central peak of the triplet and the high-frequency line of the doublet split into doublets (J = 8 Hz).

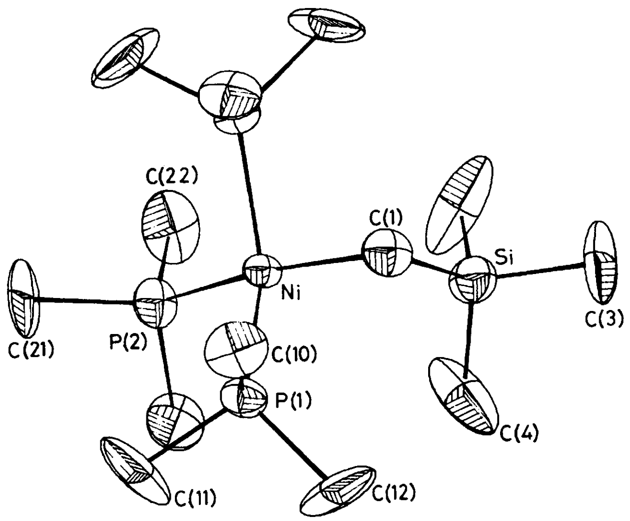


Figure 1. Structure of $[Ni(CH_2SiMe_3)(PMe_3)_3]^+$, showing the atomic numbering scheme. Ellipsoids correspond to 50% probability

Crystal Structure of $[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$ (**9**).—The structure of $[Ni(CH_2SiMe_3)(PMe_3)_3]^+$ shows the metal centre in a sterically congested tetrahedrally distorted square-planar ligand environment (Figure 1). Bond lengths and angles and fractional atomic co-ordinates are collected in Tables 2 and 3, respectively. The structure of (**9**) provides an interesting comparison with the neutral analogue [Ni-

Table 2. Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex (**9**)

C(1)–Ni	1.920(22)	P(1)–Ni	2.188(5)
P(2)–Ni	2.190(7)	Si–C(1)	1.957(24)
C(3)–Si	1.946(30)	C(4)–Si	1.775(16)
C(10)–P(1)	1.861(14)	C(11)–P(1)	1.820(15)
C(12)–P(1)	1.841(15)	C(21)–P(2)	1.868(27)
C(22)–P(2)	1.837(15)		
P(1)–Ni–C(1)	88.6(4)	P(2)–Ni–C(1)	157.8(7)
P(2)–Ni–P(1)	99.6(2)	Si–C(1)–Ni	102.0(10)
C(3)–Si–C(1)	103.5(17)	C(4)–Si–C(1)	116.0(7)
C(4)–Si–C(3)	109.7(11)	C(4)–Si–C(4)	101.9(12)
C(10)–P(1)–Ni	105.0(5)	C(11)–P(1)–Ni	122.6(7)
C(11)–P(1)–C(10)	99.6(8)	C(12)–P(1)–Ni	122.2(6)
C(12)–P(1)–C(10)	102.3(8)	C(12)–P(1)–C(11)	101.2(9)
P(1)–Ni–P(1)	135.5(2)	C(21)–P(2)–Ni	121.8(11)
C(22)–P(2)–Ni	112.5(6)	C(22)–P(2)–C(21)	104.6(9)
C(22)–P(2)–C(22)	97.9(11)		

Table 3. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for complex (**9**)

Atom	*x*	*y*	*z*
Ni	2 517(3)	2 500	3 717(1)
C(1)	681(25)	2 500	3 316(9)
Si	1 513(9)	2 500	2 632(2)
C(3)	−315(51)	2 500	2 210(18)
C(4)	2 700(19)	3 809(17)	2 472(6)
P(1)	1 937(4)	4 422(4)	3 965(1)
C(10)	176(15)	4 233(14)	4 356(5)
C(11)	3 126(22)	5 315(17)	4 404(7)
C(12)	1 368(24)	5 676(14)	3 520(6)
P(2)	4 983(6)	2 500	3 881(2)
C(21)	5 730(34)	2 500	4 540(13)
C(22)	5 999(16)	1 185(16)	3 573(6)
B(1)	2 461(24)	2 500	731(8)
F(1)	3 979(23)	2 500	555(8)
F(2)	3 013(38)	2 500	1 222(9)
F(3)	1 304(84)	2 500	363(23)
F(4)	1 008(35)	2 500	959(21)
F(5)	1 518(29)	3 507(20)	584(10)
F(6)	2 353(36)	3 416(27)	1 107(10)
F(7)	2 183(49)	3 799(11)	661(17)
F(8)	2 206(56)	1 800(37)	284(10)

$(CH_2SiMe_3)Cl(PMe_3)_2]$ (**11**).[8] Substitution of Cl by PMe_3 significantly increases the distortion towards a tetrahedral geometry. The bulky CH_2SiMe_3 group is oriented away from the PMe_3 ligands, with the Ni–C–Si plane bisecting the P–Ni–P angle. The P–Ni–P angle between the *trans* PMe_3 ligands is reduced from an average of 164 in (**11**) to only 135.5(2) in (**9**), and the P(*trans*)–Ni–C angle of 157.8 in (**9**) compares to a C–Ni–Cl angle of 173° in (**11**).* There is a slight shortening of the Ni–C bond of complex (**9**) [1.920(22) compared to 1.95(2) Å in (**11**)] and a significant lengthening of the CH_2–Si distance [1.957(24) *vs* 1.85(1) Å] on creating a cationic complex. The Ni–C bond distance is shorter than those observed in other cationic nickel alkyls, *viz.* (**1**) (2.034 Å)[5b] and $[NiMe\{N(CH_2CH_2PPh_2)_3\}]^+$(2.02 Å).[4]

Reactions with π-Acceptor Ligands.—Treatment of thf solutions of the dmpe complexes (**6**) and (**8**) with excess CO at room temperature induces a colour change from deep orange to yellow, and the orange acyl complexes $[Ni(COMe)(PMe_3)(dmpe)]BF_4$ (**12**) and $[Ni(COMe)(dmpe)_2]BF_4$ (**13**) precipitate in quantitative yield [equation (4)]. The complexes show acyl

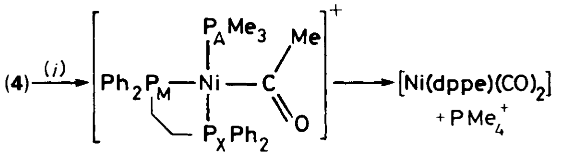
$$(\mathbf{6})\text{ or }(\mathbf{8}) + CO \longrightarrow [Ni(COMe)L(dmpe)]BF_4 \qquad (4)$$

$$(\mathbf{12})\ L = PMe_3$$

$$(\mathbf{13})\ L = dmpe$$

C–O stretching frequencies at 1 625 and 1 620 cm^{-1}, respectively, considerably lower than the 1 700 cm^{-1} observed for $[Ni(COMe)(PMe_3)_3]BF_4$.[6] They are stable towards excess of CO. Neither cation gave well resolved ^{31}P n.m.r. spectra, in part due to the poor solubility at low temperatures. At 25 °C (**13**) shows a singlet at δ 13.1 p.p.m. which broadens on cooling but remains unresolved even at −90 °C (in acetone or methanol), preventing unequivocal determination of the solution structure. Similar difficulties were encountered for (**12**), although by analogy to $[Ni(COMe)(PMe_3)_3]^+$ [6] a square-planar structure is highly likely.

When a stoicheiometric quantity of CO is added to an acetone solution of the dppe complex (**4**) at low temperature in an n.m.r. tube, resolved spectra are obtained at −90 °C, and although several species are present, the major component gives an AMX spectrum in agreement with the formation of a square-planar acyl complex $[Ni(COMe)(PMe_3)(dppe)]BF_4$ [δ 76.9, dd, P_XPh_2, J_{AX} = 154, J_{MX} = 21; 66.0, dd, P_MPh_2, J_{AM} = 27, J_{MX} = 21; 16.6 p.p.m., dd, P_AMe_3, J_{AX} = 154, J_{AM} = 27 Hz). Unlike (**12**) and (**13**), this complex proved to be thermally unstable. The n.m.r. signals disappear on warming, to be replaced by a singlet at δ +25 p.p.m., characteristic of PMe_4^+, and suggest the decomposition of the intermediate acyl complex *via* a pathway involving decarbonylation and reductive migration of an alkyl cation from the metal centre to a trialkylphosphine ligand (Scheme 3). The resulting zerovalent nickel dicarbonyl complex, $[Ni(dppe)(CO)_2]$, was identified by i.r. spectroscopy [ν(CO) 2 005 and 1 945 cm^{-1}] by comparison with literature data.[1a]



Scheme 3. (*i*) CO, −90 °C

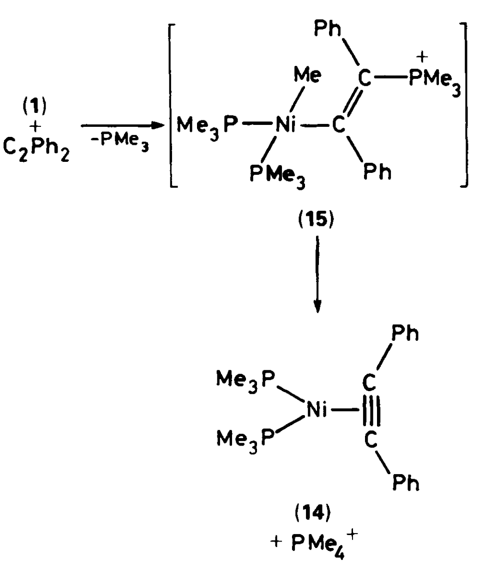
Similarly facile CO-induced reductive elimination reactions are observed for a number of cationic nickel alkyls. The reaction of the bipy and phen complexes (**2**) and (**3**) with excess or stoicheiometric amounts of CO at room temperature leads to the rapid formation of $[PMe_4]BF_4$ and $[Ni(CO)_2(L–L)]$ [L–L = bipy, ν(CO) 1 982 and 1 915 cm^{-1}; L–L = phen, ν(CO) 1 980 and 1 907 cm^{-1}].[1a] Surprisingly, even the sterically hindered complex (**9**) proved to be unstable towards CO and decomposed to $[Ni(PMe_3)_2(CO)_2]$ and $[PMe_3(CH_2SiMe_3)]BF_4$ (δ_P + 29.6 p.p.m., acetone). The reaction of the acyl complexes $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$[8] and $[Ni(COPh)Cl(PMe_3)_2]$ [prepared by the addition of PhCOCl to a mixture of bis(cyclo-octa-1,5-diene)nickel and PMe_3] with PMe_3 and $TlBF_4$ gave similar results [equation (5); R = Ph or CH_2SiMe_3,

$$[RCO–NiL_2Cl] + L + TlBF_4 \longrightarrow [NiL_3(CO)] + [PRMe_3]BF_4 + TlCl \qquad (5)$$

L = PMe_3]. In the latter case an unstable yellow crystalline solid could be isolated by the rapid removal of the thf solvent. Although the i.r. spectrum showed a band at 1 630 cm^{-1}, satisfactory analyses were not obtained. The solid slowly lost

---

* By comparison, steric hindrance in *trans*-$[Ni(CH_2SiMe_3)_2(PMe_3)_2]$ too, is less pronounced, as indicated by the P–Ni–P and C–Ni–C angles of 146.9(3) and 170(1)°, respectively.[17]



Scheme 4.

CO, and recrystallisation attempts at −15 °C led to decomposition, with formation of $[PMe_3Ph]BF_4$ (δ_P + 21.0 p.p.m. acetone). Whereas the addition of excess of dmpe to (**1**) results in the complete substitution of all PMe_3 ligands, leaving the nickel–methyl bond intact, analogous cations $[NiMe(L\text{–}L)_2]^+$ with less strongly electron-donating ligands cannot be isolated (L–L = bipy, phen, or dppe). Once again, reductive elimination of $PMe_4{}^+$ occurs instead to give zerovalent nickel complexes [equation (6)]. Conversely, these zerovalent nickel complexes fail to give cationic nickel alkyl complexes by oxidative addition of MeI or $[OMe_3]BF_4$.

$$[NiMe(PMe_3)_2(L\text{–}L)]^+ + L\text{–}L \longrightarrow [Ni(L\text{–}L)_2] + PMe_4{}^+ + PMe_3 \quad (6)$$

Triphenylphosphine is particularly effective in inducing the elimination process. The addition of only 2 equivalents of PPh_3 to solutions of $[NiMe(PMe_3)_4]BF_4$ (**1**) leads to the immediate formation of $[PMe_4]BF_4$ and the precipitation of orange crystalline $[Ni(PMe_3)_2(PPh_3)_2]$. The PPh_3-induced migration of aryl ligands from nickel to phosphine has previously been exploited in the catalytic formation of tetra-arylphosphonium salts from aryl halides and PPh_3 in the presence of *trans*-$[NiPh(Br)(PPh_3)_2]$.[19]

Neutral nickel alkyl complexes *trans*-$[NiR(Cl)(PMe_3)_2]$ are known to react with alkynes to give nickel vinyl complexes[11,20] (*e.g.* with diphenylacetylene) or alkyne trimerisation products.[11] Although cationic nickel vinyl complexes are stable, *viz.* (**10**) above, the methyl complex (**1**) in methanol fails to insert phenylacetylene into the nickel–carbon bond, giving instead $[PMe_4]BF_4$ and an air-sensitive petroleum-soluble product, $[Ni(C_2Ph_2)(PMe_3)_2]$ (**14**) (Scheme 4). The latter was prepared independently by Pörschke *et al.*[21] from $[Ni(C_2H_4)(PMe_3)_2]$ *via* ligand exchange.

The reaction of complex (**1**) with diphenylacetylene in methanol was followed by ^{31}P n.m.r. spectroscopy by heating samples in an n.m.r. tube to 60 °C for 15-min intervals before cooling them to −90 °C in the spectrometer to observe the spectrum. Initially, only the doublet–quartet structure of (**1**) was seen. This collapsed as the reaction proceeded and signals due to (**14**) appeared (δ_P −11.9 p.p.m.) ($[PMe_4]BF_4$ can only be detected at room temperature due to its insolubility in methanol at lower temperatures). During the course of the reaction an intermediate species (**15**) was observed which displayed an AMX spectrum (Figure 2), indicative of three PMe_3 ligands in different environments (δ −18.5, dd, ^2J 29.3 and 9.7; −15.3, dd, ^2J 29.3 and 7.0; +21.0 p.p.m., dd, ^2J 9.7 and 7.0 Hz).

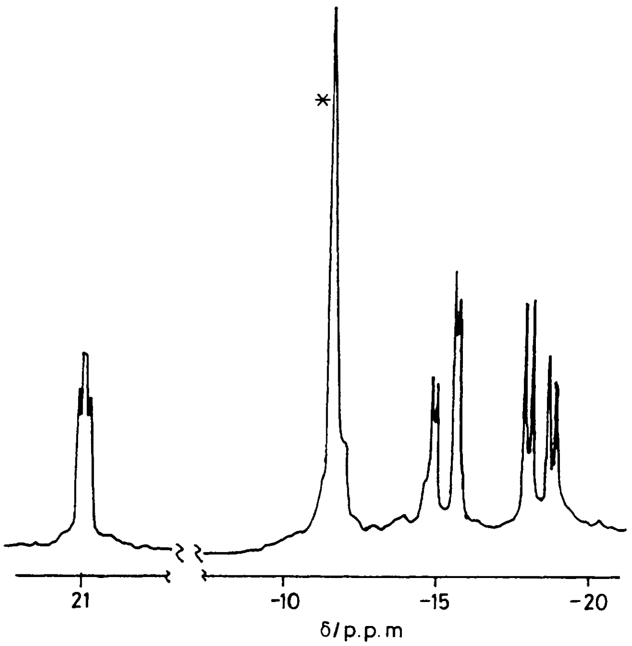


Figure 2. Low-temperature (−90 °C) $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of intermediate (**15**) formed during the reaction of $[NiMe(PMe_3)_4]^+$ with diphenylacetylene (solvent methanol). The signal due to $[Ni(C_2Ph_2)(PMe_3)_2]$ is marked by an asterisk

Phosphorus-phosphorus coupling constants of about 30 Hz suggest approximately right angles between the PMe_3 ligands. The large positive shift of one PMe_3 ligand to δ +21.0 p.p.m. is comparable to that of the $PMe_4{}^+$ ion (δ 25.7 p.p.m.); it is also reminiscent of the C-bound PMe_3 in the labile ylidic nickel acyclopropane complex $[Ni\{CPh(PMe_3)CHR\}Cl(PMe_3)]$ (R = $COCH_2Ph$)[22] (δ 14.7 p.p.m.), and of the methylenephosphorane complex $[NiPh(Ph_2PCHCPhO)(CH_2PMe_3)]$ (δ 20.8 p.p.m.).[23] The similarity is further underlined by the low values of the P–P coupling constants in these cases. Although solution i.r. spectroscopy of the reaction showed no conclusive evidence of a π-bonded diphenylacetylene other than that of (**14**), it seems reasonable to assume that the reaction proceeds *via* the replacement of one PMe_3 ligand in complex (**1**) by diphenylacetylene, followed by the reversible attack of PMe_3 on the co-ordinated C_2Ph_2 ligand to give an ylidic intermediate such as (**15**) which decomposes to give $PMe_4{}^+$ and the nickel (0) complex (**14**) (Scheme 4).

The reaction of complex (**1**) with PhC≡CH or $MeO_2CC{\equiv}CCO_2Me$ in thf or MeOH led to dark brown solutions from which no nickel-containing species could be isolated. The alkyne trimerisation products $C_6H_3Ph_3$ and $C_6(CO_2Me)_6$ were identified after acid hydrolysis, most probably formed under the catalytic influence of zerovalent nickel species formed *in situ*; nickel(0) complexes are known to catalyse alkyne trimerisations.[24]

Conclusion

The results indicate that cationic nickel alkyl complexes can be isolated only for certain combinations of ligands and require for their stabilisation at least two strongly electron-donating phosphine ligands. The formation of five-co-ordinate 18-electron complexes of trigonal-bipyramidal structure is favoured, although alternative co-ordination geometries may be adopted, as in the cases of the square-pyramidal $[NiMe(dmpe)_2]^+$ and

Table 4. Analytical and physical data for cationic nickel complexes

Complex	M.p. (°C)	Colour	Analysis (%)[a] C	H
(2)	94[b]	Brown	43.6 (43.0)	6.2 (6.1)
(3)	118[b]	Maroon	46.0 (46.3)	5.9 (5.9)
(4)	91–92	Orange	55.7 (55.7)	6.5 (6.5)
(6)	109	Orange	33.6 (33.7)	8.0 (8.0)
(7)	116	Yellow	31.0 (31.1)	7.3 (7.3)
(8)	125[b]	Scarlet	34.0 (34.2)	7.7 (7.7)
(9)	94	Brown	33.8 (33.9)	8.3 (8.3)
(12)	128[b]	Yellow	31.7 (31.8)	6.7 (6.8)
(13)	130[b]	Yellow-orange	34.4 (34.7)	7.2 (7.2)

[a] Required values are given in parentheses. [b] With decomposition.

the sterically congested complex $[Ni(CH_2SiMe_3)(PMe_3)_3]^+$ with its tetrahedrally distorted square-planar structure. The preferred decomposition pathway in these systems is the reductive migration of the alkyl ligands from nickel to a PMe_3 ligand. This process is readily induced if the electron density of the metal centre is lowered by the co-ordination of a range of π-acceptor ligands and, in contrast to the behaviour of analogous neutral complexes, dominates over the insertion of unsaturated substrates into the nickel–carbon σ bond.

Experimental

All operations were carried out under inert gas using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium–benzophenone [diethyl ether, thf, light-petroleum (b.p. 40—60 °C)] or sodium (toluene). Acetone was pre-dried over anhydrous K_2CO_3, distilled onto and stored over 4A molecular sieve, and redistilled before use. Perkin-Elmer 684 (i.r.) and JEOL PMX-60 (^1H) and FX-100 (^1H and ^{31}P n.m.r.) spectrometers were used. The compounds $[NiMe(PMe_3)_4]BF_4$[6] and $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$[8] were prepared as described; dppe, dmpe, and diphenylacetylene were used as purchased, 2,2′-bipyridyl and 1,10-phenanthroline were purified by vacuum sublimation. Melting points were determined in sealed capillaries under nitrogen and are uncorrected. Elemental analyses for the new compounds are given in Table 4.

General Procedure for the Syntheses of Complexes (**2**)—(**7**).—*Method* (*a*). To a solution of $[NiMe(Cl)(PMe_3)_2]$ (*ca.* 0.5 g) in thf (20 cm^3) at room temperature was added 1 equivalent of the appropriate bidentate ligand. The mixture was then added to a suspension of 1 equivalent of $TlBF_4$ in thf (10 cm^3) and stirred for 10 min. After filtration to remove TlCl the solution was concentrated and left to crystallise. The products were obtained in near-quantitative yield and recrystallised from thf or acetone.

Method (*b*). To a solution of $[NiMe(PMe_3)_4]BF_4$ (**1**) (*ca.* 0.5 g) in thf (20 cm^3) was added 1 equivalent of bidentate ligand. The volatiles were removed *in vacuo* to leave the product in quantitative yield, followed by recrystallisation from thf or acetone. Complex (**7**) was contaminated with (**6**) and obtained pure by manual separation.

$[NiMe(dmpe)_2]BF_4$ (**8**).—To a solution of $[NiMe(PMe_3)_2(dmpe)]BF_4$ (**6**) (0.6 g, 1.31 mmol) in thf (30 cm^3) was added dmpe (0.25 cm^3, 1.5 mmol). The colour deepened from yellow-orange to orange-red. The solution was stirred for 2 h at room temperature, concentrated and cooled to −20 °C to obtain scarlet crystals of complex (**8**) (0.5 g, 1.08 mmol, 83%).

$[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$ (**9**).—To a solution of $TlBF_4$ (0.506 g, 1.74 mmol) in thf (20 cm^3) was added a solution of $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$ (0.580 g, 1.74 mmol) and PMe_3 (0.36 cm^3, 3.48 mmol). After stirring for 1 h at room temperature, the mixture was filtered to remove TlCl, concentrated, and left to crystallise at −15 °C to obtain brown cubes of complex (**9**) (0.64 g, 1.3 mmol, 75%).

$[Ni(COMe)(PMe_3)(dmpe)]BF_4$ (**12**).—Passing CO gas through a solution of complex (**6**) (0.150 g, 0.3 mmol) in thf (10 cm^3) led to a colour change from orange to yellow, and a yellow precipitate of analytically pure (**12**) was collected in near-quantitative yield. The compound is poorly soluble, and satisfactory n.m.r. spectra were not obtained, ν(CO) 1 625 vs cm^{-1} (Nujol).

$[Ni(COMe)(dmpe)_2]BF_4$ (**13**).—A solution of complex (**8**) (0.2 g, 0.44 mmol) in thf (10 cm^3) was treated with CO at room temperature for 1 min. The yellow-orange precipitate was isolated by filtration in near-quantitative yield. Recrystallisation gave orange crystals of (**13**), ν(CO) 1 620 cm^{-1} (Nujol).

Reactions of Complex (**1**).—*With* PPh_3. To a solution of complex (**1**) (0.653 g, 1.42 mmol) in thf was added PPh_3 (0.742 g, 2.84 mmol). The brown solution discoloured quickly, leaving an orange precipitate which was recrystallised from toluene to give orange crystals of $[Ni(PMe_3)_2(PPh_3)_2]$ (0.788 g, 1.16 mmol, 82%), m.p. 93—95 °C (Found: C, 68.9; H, 6.7. $C_{42}H_{48}NiP_4$ requires C, 68.6; H, 6.6%).

With diphenylacetylene. Diphenylacetylene (0.2 g, 1.1 mmol) was added to a solution of complex (**1**) (0.5 g, 1.08 mmol) in methanol (10 cm^3). The mixture lightened in colour. The reaction was completed by warming to 50 °C for 45 min. Removal of volatiles, extraction of the residue with light petroleum followed by filtration gave a yellow filtrate and an off-white residue of $[PMe_4]BF_4$. The filtrate was concentrated and left to crystallise at −15 °C to give yellow crystals of $[Ni(C_2Ph_2)(PMe_3)_2]$ (0.26 g, 0.67 mmol, 61%). ν(C≡C) 1 800 cm^{-1} (Nujol) (lit.,[21] 1 802 cm^{-1}). The reactions of (**1**) with excess of bipy, phen, and dppe were carried out in an analogous manner.

$[Ni(COPh)Cl(PMe_3)_2]$.—To a mixture of bis(cyclo-octa-1,5-diene)nickel (2.50 g, 9.1 mmol) and PMe_3 (1.38 g, 18.2 mmol) in toluene (50 cm^3) cooled to −78 °C was added dropwise a solution of freshly distilled PhCOCl (9.1 mmol) in toluene (15 cm^3). The mixture was allowed to warm to room temperature over 3 h and changed colour to orange. Filtration through Kieselguhr, concentration of the filtrate, and crystallisation at −15 °C gave the product as orange crystals (1.76 g, 0.5 mmol, 55%), ν(CO) 1 620 cm^{-1} (Nujol) (Found: C, 44.4; H, 6.5; Cl, 10.3. $C_{13}H_{23}ClNiOP_2$ requires C, 44.4; H, 6.6; Cl, 10.1%), δ_H (C_6D_6) 1.05 (18 H, s, PMe_3) and 7.20 (5 H, m, Ph). Stirring thf solutions of $[Ni(COPh)Cl(PMe_3)_2]$ at room temperature for 24 h with periodic flushing with N_2 led to a colour change from orange to yellow due to decarbonylation, and $[NiPh(Cl)(PMe_3)_2]$ was isolated as yellow needles in low yield.

X-*Ray Crystallography.*—Crystallographic measurements were made on a crystal of approximate dimensions 0.2 × 0.22 × 0.24 mm, sealed under nitrogen in a thin-walled glass capillary using an Enraf-Nonius CAD4 diffractometer operating in the ω—2θ scan mode with graphite-monochromated Mo-K_α radiation [λ(Mo-K_α) = 0.71 069 Å], following previously detailed procedures.[25] The structure was solved *via* the heavy-atom method and refined by least squares, with non-hydrogen atoms anisotropic and hydrogens, inserted in idealised positions and refined as components of rigid groups, isotropic.

Crystal data. $[C_{13}H_{38}NiP_3Si][BF_4]$, M_r = 460.95, orthorhombic, $a = 8.701(2)$, $b = 10.537(2)$, $c = 26.573(2)$ Å, $U = 2\,436.3$ Å^3, space group *Pcmn* (alternative setting of *Pnma*, no. 62), $Z = 4$, $D_c = 1.26$ g cm^{-3}, μ(Mo-K_α) = 10.0 cm^{-1}, $F(000) = 976$.

Data collection. $T = 294$ K, $1.5 \leqslant \theta \leqslant 25°$, $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 31$. 2 267 Unique reflections measured, 1 194 observed [$F_o > 3\sigma(F_o)$], empirical absorption corrections,[26] maximum and minimum transmission 1.0 and 0.95.

Structure solution and refinement. Patterson method and difference synthesis; refinement *via* full-matrix least-squares with non-hydrogen atoms anisotropic and hydrogens inserted in idealised positions with group U_{iso} values and rigid constraints. After refinement in the centrosymmetric space group *Pcmn*, a number of atoms showed strong displacements perpendicular to the mirror plane, and attempts were made to refine in the non-centrosymmetric space group $Pc2_1n$. This was not successful; the indications for mirror symmetry were always present, and we presume that the higher-symmetry space group is correct and is satisfied by systematic disorder of an approximately symmetrical molecule. Accordingly the results presented herein are based on the higher-symmetry model. The disorder of the cation and of the BF_4^- anion are almost certainly the reason for the unusually high *R* values, *R* 0.093, *R'* 0.077 (139 parameters, unit weights). The BF_4^- group was modelled with the B atom on the mirror plane and eight partially occupied F positions with constraints applied to the B–F positions.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We are grateful to the University of East Anglia for support (to I. H.) and to the S.E.R.C. for the provision of *X*-ray facilities, and thank Dr. I. J. Colquhoun for his assistance with the ^{31}P n.m.r. experiments.

References

1 (*a*) P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1974; (*b*) P. W. Jolly, in 'Comprehensive Organometallic Chemistry', eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 37.

2 M. Wada, *Inorg. Chem.*, 1975, **14**, 1415; M. Wada and K. Ogura, *ibid.*, 1976, **15**, 2346; F. Caballero and P. Royo, *J. Organomet. Chem.*, 1977, **137**, 229; M. Anton, J. M. Coronas, G. Muller, J. Sales, and M. Secco, *Inorg. Chim. Acta*, 1979, **36**, 173.

3 C. Mealli, M. Peruzzini, and P. Stoppioni, *J. Organomet. Chem.*, 1980, **192**, 437.

4 L. Sacconi, P. Dapporto, P. Stoppioni, P. Innocenti, and C. Benelli, *Inorg. Chem.*, 1977, **16**, 1669; P. Stoppioni, P. Dapporto, and L. Sacconi, *ibid.*, 1978, **17**, 718.

5 (*a*) H. F. Klein, H. H. Karsch, and W. Buchner, *Chem. Ber.*, 1974, **107**, 537; (*b*) A. Gleizes, A. Kerkeni, M. Dartiguenave, and H. F. Klein, *Inorg. Chem.*, 1981, **20**, 2372.

6 M. Bochmann, I. Hawkins, M. B. Hursthouse, and R. L. Short, *J. Organomet. Chem.*, 1987, **332**, 361.

7 M. Bochmann and L. M. Wilson, *J. Chem. Soc., Chem. Commun.*, 1986, 1610; M. Bochmann, L. M. Wilson, M. B. Hursthouse, and R. L. Short, *Organometallics*, 1987, **6**, 2556; M. Bochmann, L. M. Wilson, M. B. Hursthouse, and M. Motevalli, *ibid.*, 1988, **7**, 1148; M. Bochmann, A. J. Jaggar, L. M. Wilson, M. B. Hursthouse, and M. Motevalli, *Polyhedron*, 1989, **8**, 1838.

8 E. Carmona, F. González, M. Poveda, J. L. Atwood, and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1980, 2108.

9 S. R. Allen, M. Green, A. G. Orpen, and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 826; E. Carmona, L. Sánchez, J. M. Marín, M. L. Proveda, J. L. Atwood, R. D. Priester, and R. D. Rogers, *J. Am. Chem. Soc.*, 1984, **106**, 3214; P. Legzdins, S. J. Rettig, and L. Sánchez, *Organometallics*, 1988, **7**, 2394; A. Höhn, H. Otto, M. Dziallas, and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1987, 852.

10 H. Werner and W. Bertleff, *J. Chem. Res.*, 1978, (*S*) 201; (*M*) 2720.

11 M. Bochmann, I. Hawkins, and M. P. Sloan, *J. Organomet. Chem.*, 1987, **332**, 371.

12 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229; D. L. DuBois and A. Miedaner, *Inorg. Chem.*, 1987, **25**, 4642; *J. Am. Chem. Soc.*, 1987, **109**, 113; G. K. Anderson and G. J. Lumetta, *Inorg. Chem.*, 1987, **26**, 1518.

13 K. R. Pörschke, R. Mynott, C. Krüger, and M. J. Romao, *Z. Naturforsch., Teil B*, 1984, **39**, 1076.

14 T. B. Marder, W. C. Fultz, J. C. Calabrese, R. L. Harlow, and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1543.

15 J. J. Miller and K. G. Caulton, *J. Am. Chem. Soc.*, 1975, **97**, 1067.

16 H. H. Karsch, *Chem. Ber.*, 1983, **116**, 1643.

17 E. Carmona, M. Paneque, M. L. Poveda, R. D. Rogers, and J. L. Atwood, *Polyhedron*, 1984, **3**, 317.

18 B. Bosnich, R. S. Nyholm, P. J. Pauling, and M. L. Tobe, *J. Am. Chem. Soc.*, 1968, **90**, 4741.

19 E. Cassar and M. Foa, *J. Organomet. Chem.*, 1974, **74**, 75.

20 H. F. Klein and L. Reitzel, *Chem. Ber.*, 1988, **121**, 1115.

21 K. R. Pörschke, R. Mynott, K. Angermund, and C. Krüger, *Z. Naturforsch., Teil B*, 1985, **40**, 199.

22 E. Carmona, E. Gutiérrez-Puebla, A. Monge, J. M. Marín, M. Paneque, and M. L. Poveda, *Organometallics*, 1984, **3**, 1438; *ibid.*, 1989, **8**, 967.

23 K. A. Ostoja Starzewski and J. Witte, *Angew. Chem.*, 1985, **97**, 610.

24 W. Reppe and W. J. Schweckendiek, *Liebigs Ann. Chem.*, 1948, **560**, 104; W. Reppe, N. v. Kutepow, and A. Magin, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 727; J. J. Eisch, J. E. Galle, A. A. Avadi, and M. P. Boleslawski, *J. Organomet. Chem.*, 1986, **312**, 399.

25 R. A. Jones, M. B. Hursthouse, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

26 A. C. T. North, D. C. Philips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

Received 11*th July* 1989; *Paper* 9/02928A