Journal of Organometallic Chemistry, 332 (1987) 361–370
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The acetyltris(trimethylphosphine)nickel cation: synthesis, carbonylation reactions, and the crystal and molecular structure of $[\{Ni(PMe_3)_4\}BF_4 \cdot Ni_4(CO)_6(PMe_3)_4]$

Manfred Bochmann*, **Ian Hawkins**,

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ (Great Britain)

Michael B. Hursthouse and Richard L. Short

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS (Great Britain)

(Received March 6th, 1987)

Abstract

Carbonylation of $[NiMe(PMe_3)_4]BF_4$ (**1**) under controlled conditions, or alternatively, treatment of $Ni(COMe)Cl(PMe_3)_2$ with PMe_3 and $TlBF_4$, gives the cationic nickel acetyl complex $[Ni(COMe)(PMe_3)_3]BF_4$ (**2**). Further reaction of **2** with CO in THF generates spectroscopically detectable unstable cationic acylcarbonyl species, which decompose to $[PMe_4]BF_4$ and $Ni(CO)_2(PMe_3)_2$. Carbonylation of **1** in dichloromethane gives **2** and the Ni^I/Ni^0 compound $[\{Ni(PMe_3)_4\}BF_4 \cdot Ni_4(CO)_6(PMe_3)_4]$ (**4**), whose crystal structure was determined. Crystals of **4** are cubic, space group $F\bar{4}3m$, with a 19.011(4) Å, $Z = 4$. The structure has been refined to R and R_w values of 0.0795 and 0.069, respectively, for 320 observed/356 measured reflections. The structure consists of tetrahedral Ni_4 units with edge-bridging CO and terminal PMe_3 ligands, BF_4^- anions and $[Ni(PMe_3)_4]^+$ cations arranged in a linear manner along the body diagonal of the unit cell.

Introduction

The crucial role which transition metal alkyl complexes play in stoichiometric and, above all, catalytic processes depends on the ability of metal–carbon bonds to react with a wide range of organic molecules [1]. While the reactivity of metal–alkyl bonds in neutral complexes is well-studied, we became interested in the reactions of cationic alkylmetal complexes in the expectation that a positive charge would result in an increased polarity of the metal–carbon bond, improve their propensity towards insertion reactions (i.e. increase the mobility of the alkyl group), and/or alter the course of the reaction since the position of labile ligand sites and the

0022-328X/87/$03.50

preferred complex geometry may differ in cationic and neutral complexes. A good model compound for testing structural and reactivity changes should be relatively free of steric constraints, undergo facile ligand exchange, and have several coordination geometries available, and we therefore chose to study methyltrimethylphosphine nickel complexes, which fulfil these criteria. We report here the reactions of the stereochemically non-rigid methyltetrakis(trimethylphosphine)nickel cation [2] with carbon monoxide.

Results and disccusion

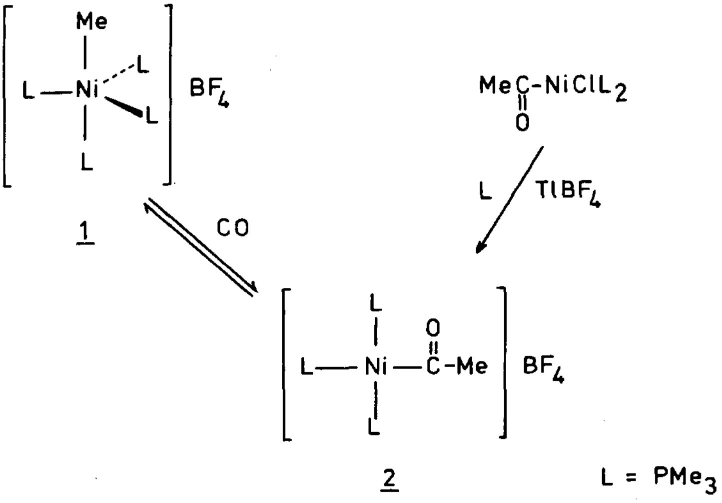
Treatment of a mixture of $NiMeCl(PMe_3)_2$ ($Me = CH_3$) [3] with two equivalents of trimethylphosphine in tetrahydrofuran or acetone with thallium(I) tetrafluoroborate affords $[NiMe(PMe_3)_4]BF_4$ (**1**) as orange-red crystals. For most reactions freshly prepared solutions of **1** were used directly after the removal of the TlCl precipitate.

On brief exposure to a stream of carbon monoxide at 0 to 10 °C dilute solutions (< 0.3 molar) of **1** quickly become opaque, and the acetylnickel complex $[Ni(COMe)(PMe_3)_3]BF_4$ (**2**) separates as an orange microcrystalline solid which can be recrystallised from acetone or THF to give dark orange to brown rhombic plates. The reaction of more concentrated solutions of **1** leads mainly to brown decomposition products. Alternatively, **2** can be prepared from $Ni(COMe)Cl(PMe_3)_2$ [4a], PMe_3, and $TlBF_4$ in acetone if the reaction is followed by quick work-up at 0 °C to avoid decarbonylation (Scheme 1).

We note that previous attempts to prepare tetraphenylborate and chloride analogues of **2**, either via acylation of $Ni(PMe_3)_4$ or carbonylation of $[NiMe(PMe_3)_4]BPh_4$, or from $Ni(COMe)Cl(PMe_3)_2$, have been unsuccessful [4].

The carbonylation is reversible, and dissolution of **2** in THF by warming to 50–60 °C leads to the regeneration of **1**.

The acyl group in solid **2** gives an infrared band at 1700 cm^{-1} (1715 cm^{-1} in



Scheme 1

THF or dichloromethane solution), a shift of 65 cm^{-1} to higher wavenumbers compared with that for $Ni(COMe)Cl(PMe_3)_2$ as a result of reduced metal-to-acyl back bonding in the cation **2**.

Compound **2** is fluxional on the NMR time scale. At 25 °C the ^1H NMR spectrum in acetone-d_6 shows only one singlet, at δ 1.5 ppm, for the PMe_3 ligands. On cooling to -50 °C the acetyl group appears at δ 2.47 ppm as a quartet, coupling to three apparently equal phosphine ligands (^4J(P–H) 1.95 Hz). There is no change on further cooling. The square-planar structure of **2** is confirmed by the ^{31}P NMR spectrum at -90 °C in acetone which shows an A_2B pattern with a doublet at δ -11.6 ppm and a triplet at -22.2 ppm (^2J(P–P) 22 Hz). In methanol or dichloromethane solvents the doublet-triplet structure was not resolved at -95 °C.

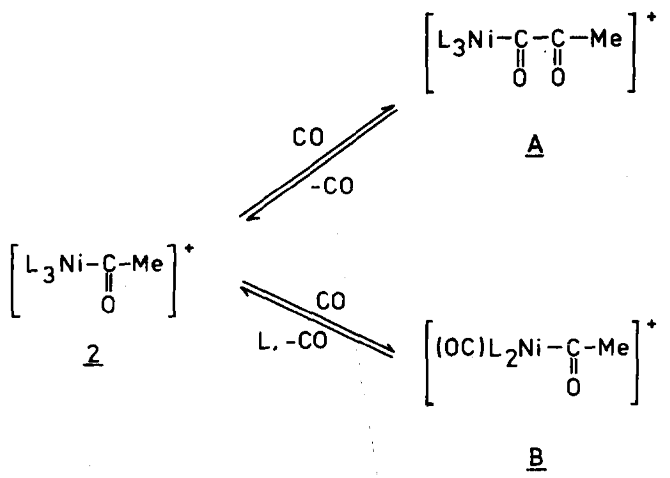
Only two other cationic acylnickel complexes have, to our knowledge, been prepared previously, the compounds $[\{E(CH_2CH_2PPh_2)_3\}NiCOMe]BF_4$ (E = N, As), in which the 18-electron count and the trigonal-bipyramidal structure are dictated by the tetradentate ligands [5]. It appears that in the absence of such constraints cationic nickel(II) complexes carrying at least one π-acceptor ligand, such as an acyl group, prefer a square-planar 16-electron structure, while a pentacoordinate geometry is adopted only if all ligands are strong electron donors, as in **1**. No adduct formation between **2** and excess PMe_3 is detectable. This behaviour of nickel(II) is in interesting contrast to cobalt(I) complexes which form an isoelectronic series of 18-electron compounds, e.g. $CoMe(PMe_3)_4$, $CoMe(CO)(PMe_3)_3$, $Co(COMe)(CO)_2(PMe_3)_2$ and $Co(COMe)(CO)_4$, all of which exhibit trigonal-bipyramidal geometry irrespective of the donor or acceptor capacity of the ligands [6].

Further carbonylation of $[Ni(COMe)(PMe_3)_3]BF_4$

Exposure of **1** to carbon monoxide at higher temperature and for longer periods can lead to several products; the outcome of the reaction is influenced by the solvent.

Bubbling carbon monoxide through THF solutions of **1** for 20 to 30 s at 15–20 °C, followed by standing at -10 °C, leads to the precipitation of an orange-yellow compound **3** as fine, sometimes flake-like, crystals. The IR spectrum of solid **3** closely resembles that of **2**, except for the surprising appearance of two major bands in the ν(C=O) region, at 1700 and 1655 cm^{-1} (accompanied by a weak band at 1600 cm^{-1} which is also present in the spectrum of **2**) and by a signal of terminally coordinated CO at 2020 cm^{-1}. Unfortunately, **3** proved to be unstable in solution, and attempted recrystallisations afforded mainly $Ni(CO)_2(PMe_3)_2$ and $[PMe_4]BF_4$. Attempts to generate **3** in situ for ^{31}P NMR spectroscopy by adding CO to NMR samples of **2** in THF at 0 °C leads to a collapse of the A_2B pattern to a singlet at -15.1 ppm which is not resolved at -95 °C. Apparently ligand exchange processes are greatly accelerated in the presence of CO; the generation of free PMe_3 is not observed.

The carbonylation reaction can be monitored by ^{13}C NMR spectroscopy by injecting 3–4 equivalents of ^{13}CO (99% ^{13}C label) into an NMR sample of **1** in THF at 0 °C. Three peaks are observed in the region of carbonyl-C, a broadened signal at δ 242 ppm, a sharp singlet at δ 167.2 ppm, and a quartet at δ 203 ppm due to $Ni(CO)(PMe_3)_3$, a decomposition product (J(P–C) 8.3 Hz). After prolonged reaction, a fourth signal appears at δ 173.2 ppm.



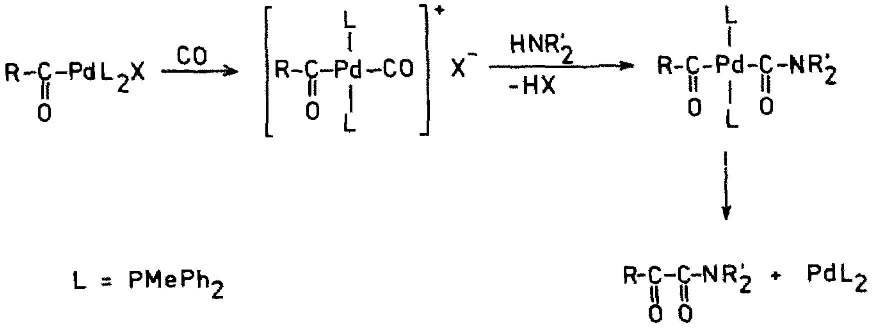
Scheme 2

Treatment of 3 with an excess of diethylamine in THF gives diethyl acetamide as the major product together with a minor amount of diethylpyruvamide, $MeCOCONEt_2$, identified by GC-MS and comparison with an authentic sample.

These findings allow two explanations, as outlined in Scheme 2. While the IR data in the region of 1700 to 1600 cm^{-1} are reminiscent of the formation of a pyruvyl group, as found in $Pd(COCOMe)Cl(PMePh_2)_2$ (ν(CO) 1710, 1690, 1640 cm^{-1}) [7] and $Mn(COCOMe)(CO)_5$ (ν(CO) 1708, 1636, 1597 cm^{-1}) [8], the formation of such a C(O)–C(O)–Me linkage via double CO insertion into a metal–carbon bond (Scheme 2, structure **A**) is a thermodynamically unfavourable process [8] and to our knowledge has not been observed before.

Alternatively, the bands at 1655 and 2020 cm^{-1} can be ascribed to the formation of a carbonyl species such as $[Ni(COMe)(PMe_3)_2(CO)]^+$ (**B**) which probably co-precipitates with **2** under the carbonylation conditions. It has been demonstrated that a palladium analogue of **B** is involved in the stoichiometric and catalytic synthesis of α-ketoamides which is known to involve nucleophilic attack on coordinated CO in an intermediate cationic complex (Scheme 3), rather than double CO insertion into a Pd–Me bond followed by nucleophilic attack and reductive elimination [9,10].

The observed formation of diethylpyruvamide from **3** does little to distinguish between structures **A** and **B** (cf. [7]), and while the ^{13}C NMR data clearly indicate the presence of a metal-acyl species at δ 242 ppm (12.7 ppm upfield from the comparable $Ni(COMe)Cl(PMe_3)_2$), the assignment of the second signal at δ 167.1 ppm is less certain. Clearer evidence, however, is obtained by monitoring the decomposition of fresh dichloromethane solutions of **3** by IR spectroscopy (Fig. 1). The two acyl bands appear at 1715 and 1670 cm^{-1}, shifted slightly with respect to the solid sample. Of these two bands, only the intensity of the latter decreases with time, while the former does not change in position, shape, or intensity and is identical to the acyl band of **2**. The loss of the 1670 cm^{-1} band is accompanied by (i) a decrease of the band at 2040 cm^{-1}, (ii) an increase in the intensity of a sharp band at 2075 cm^{-1}, and (iii) an increase in the absorption of $Ni(CO)_2(PMe_3)_2$, the end-product of decomposition, at 1925 and 1990 cm^{-1}.



Scheme 3

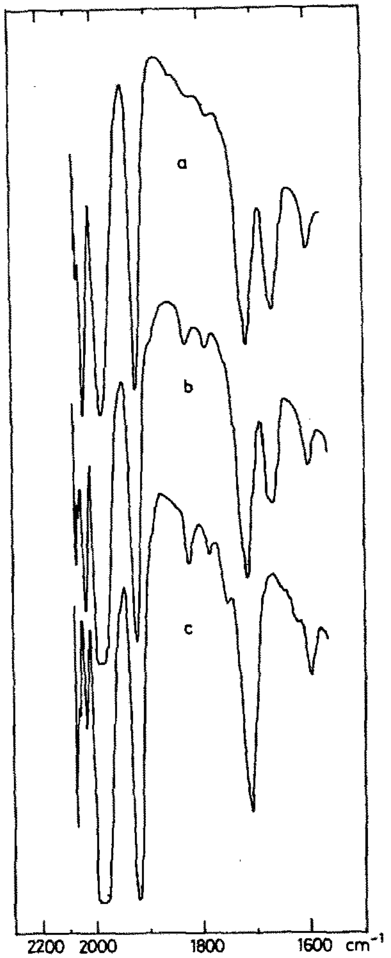
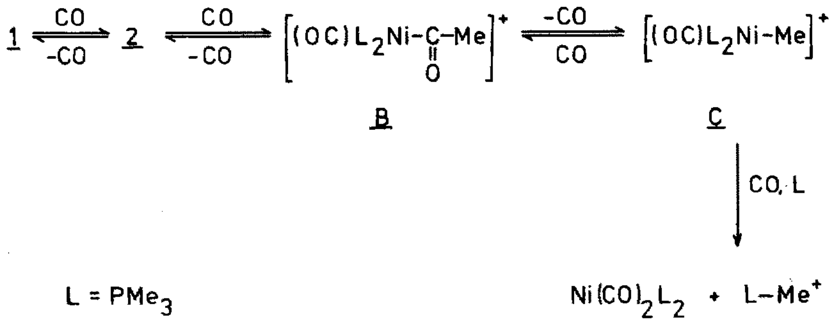


Fig. 1. IR spectral changes of fresh dichloromethane solutions of 3 at 20 °C in the absence of an excess of CO; (a) after 2 min; (b) after 5 min; (c) after 15 min.



Scheme 4

Although the assignments have to remain tentative, we believe the results are best explained by the reaction sequence outlined in Scheme 4. Complex **2** reacts partially with CO to form intermediate **B**, which is characterised by IR bands at 2040 and 1670 cm^{-1} and co-precipitates with **2** from THF solutions to give mixed-crystalline **3**. In solution, **B** undergoes decarbonylation to give the intermediate **C**, indicated by the IR band at 2075 cm^{-1} and the ^{13}C NMR signal at δ 173.2 ppm [11*]. *C* is apparently unstable, and undergoes reductive methyl group migration from nickel to trimethylphosphine, resulting in $Ni(CO)_2(PMe_3)_2$ and $[PMe_4]BF_4$ as final products.

Synthesis and crystal structure of $[\{Ni(PMe_3)_4\}BF_4 \cdot Ni_4(CO)_6(PMe_3)_4]$ (4)

While the reaction of $Ni(COMe)Cl(PMe_3)_2$ with PMe_3 and $TlBF_4$ in acetone gives pure **2**, a similar mixture in dichloromethane affords a variety of carbonyl containing species, though **2** is still the main product. Besides **2**, an orange-red product is obtained, which on recrystallisation from acetone gives a mixture of $[PMe_4]BF_4$ and red prisms (**4**) which contain BF_4^- and are characterised in the IR spectrum by strong bands at 1780 and 1715 cm^{-1}, typical for bridging carbonyl ligands.

The structure of **4** was determined by X-ray crystallography (Fig. 2). Compound **4** is the unusual product of co-crystallisation of the nickel(I) complex $[Ni(PMe_3)_4]BF_4$ with the tetrahedral nickel cluster $Ni_4(\mu\text{-}CO)_6(PMe_3)_4$. The three components of **4** are linearly arranged in the unit cell with no close intermolecular contacts. The cluster consists of a regular Ni_4 tetrahedron with a CO group bridging each of the six edges and a terminal PMe_3 ligand coordinated to each nickel atom along each of the four three-fold axes. Important bond distances and angles and fractional atomic coordinates are collected in Tables 1, 2 and 3. The Ni–Ni bonds are 2.476(6) Å, ca. 0.03 Å shorter than those in the related cluster $Ni_4(\mu\text{-}CO)_6[P(CH_2CH_2CN)_3]_4$ (**5**) (2.508(4) Å) [12], the only previous example of this cluster type. The Ni–P bond lengths of 2.179(9) Å are equal within experimental error to those in **5**, but the Ni–C bonds are shorter (1.80(2) Å compared with 1.85(2)–1.92(2) Å). The structure of the $[Ni(PMe_3)_4]^+$ cation has been previously determined in the BPh_4^- salt [13], in

---

* This and other references marked with asterisks indicate notes occurring in the list of references.

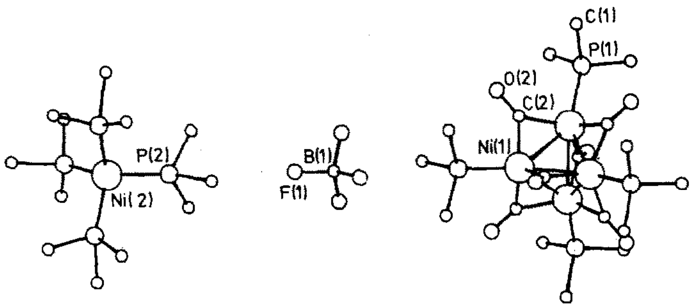


Fig. 2. Molecular structure of [{Ni(PMe$_3$)$_4$)BF$_4$·Ni$_4$(CO)$_6$(PMe$_3$)$_4$] (4).

Table 1

Bond lengths (Å) in [{Ni(PMe$_3$)$_4$}·BF$_4$·Ni$_4$(CO)$_6$(PMe$_3$)$_4$]

P(1)–Ni(1)	2.179(9)	C(2)–Ni(1)	1.797(20)
Ni(1)–Ni(1a)	2.476(6)	C(1)–P(1)	1.735(18)
H(11)–C(1)	0.958(19)	H(22)–C(1)	0.991(12)
O(2)–C(2)	1.300(25)		
P(2)–Ni(2)	2.237(10)	C(3)–P(2)	1.751(27)
H(31)–C(3)	1.020(29)	H(32)–C(3)	0.994(20)
B(1)–F(1)	1.377(16)		

Symmetry operator: (a) $-x$, y, $-z$

Table 2

Bond angles (deg) in [{Ni(PMe$_3$)$_4$}·BF$_4$·Ni$_4$(CO)$_6$(PMe$_3$)$_4$] [a]

C(2)–Ni(1)–P(1)	98.3(6)	C(2)–Ni(1)–C(2b)	118.0(4)
C(1)–P(1)–Ni(1)	115.9(8)	C(1)–P(1)–C(1b)	102.4(9)
H(12)–C(1)–P(1)	108.8(11)	H(11)–C(1)–P(1)	110.8(15)
H(12)–C(1)–H(12b)	106.9(18)	H(12)–C(1)–H(11)	110.7(12)
Ni(1)–C(2)–Ni(1c)	87.1(12)	O(2)–C(2)–Ni(1)	136.4(5)
C(3)–P(2)–Ni(2)	121.8(11)	C(3)–P(2)–C(3d)	94.8(14)
H(31)–C(3)–P(2)	112.6(21)	H(32)–C(3)–P(2)	115.2(17)
H(32)–C(3)–H(31)	110.4(20)	H(32)–C(3)–H(32b)	91.1(23)

Symmetry operators: (b) y, x, z; (c) x, $-y$, $-z$; (d) y, z, x.

[a] P–Ni–P and F–B–F angles are 109.5° by symmetry.

Table 3

Fractional atomic coordinates ($\times 10^4$) for **4**

Atom	x	y	z
Ni(1)	460(1)	460(1)	460(1)
P(1)	1122(2)	1122(2)	1122(2)
C(1)	1687(6)	1687(6)	681(10)
C(2)	1145(13)	0	0
O(2)	1829(9)	0	0
Ni(2)	5000	5000	5000
P(2)	4321(2)	4321(2)	4321(2)
C(3)	3721(10)	3721(10)	4680(15)
B(1)	2500	2500	2500
F(1)	2900(5)	2900(5)	2900(5)

which there are Ni–P bond distances of 2.111(3)–2.221(3) Å and P–Ni–P angles of 104.6(1)–111.0(1)°, compared with values of 2.237(10) Å and 109.5° for **4**. Other bond distances and angles are as expected.

Conclusions

Under carefully controlled conditions $[NiMe(PMe_3)_4]BF_4$ (**1**) reacts with carbon monoxide in THF or acetone to give a stable nickel acyl complex, $[Ni(COMe)(PMe_3)_3]BF_4$ (**2**), a square-planar 16-electron species whose formation points to electronic rather than steric control of the coordination geometry. The same complex is obtained from $Ni(COMe)Cl(PMe_3)_2$, PMe_3 and $TlBF_4$. Ligand exchange of PMe_3 in **2** for CO generates a number of labile species and induces the reductive elimination of Ni–Me groups to give $[PMe_4]BF_4$ and zerovalent nickel carbonyl complexes. A "double CO insertion" process is unlikely to be involved. The solvent influences the decomposition process, and a product of co-crystallisation, $[\{Ni(PMe_3)_4\}BF_4 \cdot Ni_4(\mu\text{-}CO)_6(PMe_3)_4]$ (**4**), can be isolated from dichloromethane.

Experimental

All operations were carried out under inert gas using vacuum line techniques. Solvents were distilled under nitrogen from sodium-benzophenone (diethyl ether, THF, petrol); acetone was pre-dried over K_2CO_3, distilled onto and stored over 4Å molecular sieve and re-distilled prior to use. Perkin–Elmer 684 (IR) and Jeol FX-100 (^1H, ^{13}C, ^{31}P NMR) spectrometers were used. For GC-MS experiments, a Kratos MS 25 mass spectrometer was connected to a 25 m OV-1 capillary gas chromatography column. The compounds $NiMeCl(PMe_3)_2$ and $Ni(COMe)Cl(PMe_3)_2$ were prepared according to the literature [3,4a]. $TlBF_4$ was made from thallium(I) acetate and aqueous HBF_4, diethylpyruvamide from pyruvyl chloride [14] and diethylamine.

Methyltetrakis(trimethylphosphine)nickel tetrafluoroborate (1)

$NiMeCl(PMe_3)_2$ (550 mg, 2.1 mmol) is dissolved in 20 ml THF. Trimethylphosphine (0.4 ml, 4 mmol) is added, to give a deep red-brown solution which is added to a suspension of powdered $TlBF_4$ (540 mg, 2.1 mmol) in 20 ml THF. The mixture is stirred for 10 min at room temperature, and the pale-yellow precipitate of TlCl filtered off to give a bright-orange solution of **1**. The spectroscopic properties of the nickel cation are identical to those of the known tetraphenylborate salt [2].

Acetyltris(trimethylphosphine)nickel tetrafluoroborate (2)

(a) By carbonylation of $[NiMe(PMe_3)_4]BF_4$. A solution of **1** (2 mmol) in 60 ml THF is cooled in an ice bath and CO is bubbled through for 15–20 s. Fine orange needles separate and are collected and recrystallised from acetone as orange-brown rhombic plates (670 mg, 1.6 mmol, 80%), dec. 95°C. IR (Nujol mull, KBr plates): 1700(vs), 1600(w), 1310(m), 1297(m), 1290(m), 1095(s), 1055(vs), 1035(sh), 970(sh), 945(s), 925(sh), 852(w), 735(s), 730(m), 670(m), 565(m), 527(m) cm^{-1}. ^1H NMR (−50°C, acetone-d_6, relative to $SiMe_4$): δ 2.47 (q, $COCH_3$, $^4J(P\text{–}H)$ 1.95 Hz); 1.45, 1.25 ppm (m, PMe_3). ^{31}P NMR (−90°C, acetone, relative to external 85% aqueous H_3PO_4): δ −11.6 (d, $^2J(P\text{–}P)$ 22 Hz), −22.2 ppm (t). Analysis Found: C, 31.67, H, 7.18. $C_{11}H_{30}BF_4NiP_3O$ calc.: C, 31.70, H, 7.20%.

(b) From $Ni(COMe)Cl(PMe_3)_2$. $Ni(COMe)Cl(PMe_3)_2$ (330 mg, 1.15 mmol) in 30 ml acetone is treated with PMe_3 (0.2 ml, 2 mmol) and a solution of $TlBF_4$ (350 mg, 1.2 mmol) in 10 ml acetone. The mixture is stirred for 15 min, filtered, concentrated at 0 °C, and left to crystallise at −15 °C.

Treatment of 1 with excess CO

A freshly prepared solution of **1** (1.4 mmol) in 40 ml THF is treated with a stream of CO for 40–60 s at 15 °C. The fine-crystalline orange precipitate (**3**) is filtered off, washed with diethyl ether, and dried briefly in vacuo. IR (Nujol mull, KBr plates): 2050(sh), 2020(m), 1700(vs), 1655(s), 1600(w), 1310(m), 1298(m), 1290(m), 1095(s), 1050(vs), 1035(sh), 970(sh), 945(vs), 925(sh), 850(w), 738(m), 730(m), 670(m), 565(m), 526(m) cm^{-1}. Attempted recrystallisations were unsuccessful. Treatment of a freshly prepared sample with 20 equivalents of diethylamine at room temperature for 18 h gave a solution containing > 90% *N,N*-diethylacetamide and minor quantities of *N,N*-diethylpyruvamide, identified by GC-MS and comparison with an authentic sample.

Preparation of $[\{Ni(PMe_3)_4\}BF_4 \cdot Ni_4(CO)_6(PMe_3)_4]$ (4)

A solution of $Ni(COMe)Cl(PMe_3)_2$ (4.30 mg, 1.48 mmol) in 30 ml dichloromethane is treated with PMe_3 (2 mmol) and $TlBF_4$ (440 mg, 1.5 mmol) for 30 min at room temperature. The brown colour changes to orange. Concentration and addition of diethyl ether precipitates red-orange **2**, which is filtered off. The filtrate is kept at 5 °C to give a mixture of finely divided pale-yellow $[PMe_4]BF_4$ and red prisms of **4**, which are picked out manually; dec. 105–110 °C. IR (Nujol mull, KBr plates): 1780(vs), 1718(s), 1590(w), 1365(m), 1305(m), 1290(sh), 1284(m), 1220(m), 1093(s), 1050(vs), 1035(m), 960(vs), 945(s), 738(m), 725(m), 675(m), 665(m), 530(sh), 520(s), 390(m) cm^{-1}.

Crystallography

Crystallographic measurements were made using an Enraf–Nonius CAD4 diffractometer and graphite monochromated Mo-K_α radiation (λ(Mo-K_α) = 0.71069 Å) at room temperature (295 ± 2 K) followed procedures previously outlined in detail [15]. A crystal of **4** was sealed under argon in a thin-walled glass capillary. Data were recorded for a crystal of the size 0.6 × 0.5 × 0.3 mm using an $\omega/2\theta$ scan mode for $1.5 \leqslant \theta \leqslant 25°$ within the octant $+h$, $+k$, $+l$ giving 1663 measured, 356 unique and 320 observed ($I > 1.5\sigma(I)$) reflections.

Crystal data. $C_{30}H_{72}BF_4Ni_5O_6P_8$, $M = 1156.896$, cubic, space group $F\bar{4}3m$, a 19.011(4) Å, V 6870 $Å^3$, $Z = 4$, D_{calc} 1.118 g cm^{-3}, μ(Mo-K_α) 15.722 cm^{-1}.

The structure was solved by Patterson methods and refined by full matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms being included at calculated positions with one overall isotropic thermal parameter. The function minimised was $\Sigma\omega|F_0 - F_c|^2$ with weight ω given by $\omega = 1/[\sigma^2(F_0) + g(F_0)^2]$ with $g = 0.0002$ giving acceptable agreement analysis. Final R $(= \Sigma\Delta F/\Sigma F_0)$ and R' $(= \Sigma\omega^{1/2}|\Delta F|/\Sigma\omega^{1/2}F_0)$ values were 0.0795 and 0.0687, respectively, for a total of 36 parameters. Final atomic coordinates are given in Table 3. Neutral atom scattering factors, including corrections for anomalous dispersion, were based on data from ref. 16. All calculations were made using the SHELX programme [17] on a VAX 11/750 computer. Tables of thermal parameters and F_0/F_c values are available from the authors.

Acknowledgements

We are grateful to Dr. I. Colquhoun for assistance with the variable temperature NMR spectra, and to the S.E.R.C. for provision of X-ray facilities.

References

1 G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon Press 1982.

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

3 H.F. Klein, and H.H. Karsch, Chem. Ber., 105 (1972) 2628.

4 (a) H.F. Klein, and H.H. Karsch, Chem. Ber., 109 (1976) 2524; (b) ibid., 109 (1976) 2515.

5 P. Stoppioni, P. Dapporto, and L. Sacconi, Inorg. Chem., 17 (1978) 718.

6 H.F. Klein, and H.H. Karsch, Chem. Ber., 108 (1975) 944.

7 F. Ozawa, T. Sugimoto, T. Yamamoto, and A. Yamamoto, Organometallics, 3 (1984) 692.

8 C.P. Casey, C.A. Bunnell, and J.C. Calabrese, J. Am. Chem. Soc., 98 (1976) 1166.

9 J.T. Chen, and A. Sen, J. Am. Chem. Soc., 106 (1984) 1506.

10 F. Ozawa, T. Sugimoto, Y. Yuasa, M. Santra, T. Yamamoto, and A. Yamamoto, Organometallics, 3 (1984) 683.

11 The ^{13}C NMR and IR data for C are similar to those in $[PtMeL_2(CO)]^+$ ($L = PMe_2Ph$, ^{13}C: δ 177.6 ppm; $L = AsMe_3$, ^{13}C: δ 178.7 ppm, $\nu(CO)$ 2085 cm^{-1}). M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers, and J.E.H. Ward, J. Am. Chem. Soc. 95 (1973) 8574.

12 M.J. Bennet, F.A. Cotton, and B.H.C. Winquist, J. Am. Chem. Soc., 89 (1967) 5366.

13 A. Gleizes, M. Dartiguenave, Y. Dartiguenave, J. Galy, and H.F. Klein, J. Am. Chem. Soc., 99 (1977) 5187.

14 H.C.J. Ottenhijm and J.H. de Man, Org. Synth., 61 (1983) 1.

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

16 International Tables for X-ray Crystallography, The Kynoch Press, Birmingham 1974, vol. 4.

17 SHELX76, G.M. Sheldrick, University of Cambridge, U.K., 1976.