CLUSTER CHEMISTRY

XIII *. SYNTHESIS AND REACTIONS OF SOME IRON-NICKEL CLUSTERS: CRYSTAL AND MOLECULAR STRUCTURE OF [Ni(PMe₃)₂⁻(η-C₅H₅)][Fe₂Ni(μ₃-C₂Ph₂)(CO)₆(η-C₅H₅)]

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Summary

Reactions between $[(\eta\text{-}C_5H_5)Ni]_2Fe_2(CO)_6(\mu_4\text{-}C_2Ph_2)$ and PR_3 (R = Me or OMe) afford $[Ni(PR_3)_2(\eta\text{-}C_5H_5)][(\eta\text{-}C_5H_5)NiFe_2(CO)_6(\mu_3\text{-}C_2Ph_2)]$, which has been characterised by a single-crystal X-ray study. The cation has distorted trigonal geometry, with Ni–C(cp) 2.113 Å (mean), Ni–P 2.151, 2.163 Å, and P–Ni–P 98.9°. The anion contains an Fe_2Ni triangle, to which are attached 6 CO ligands (to Fe) and the C_5H_5 group (to Ni); the C_2Ph_2 moiety is attached via two σ bonds (to one Fe and the Ni) and a π bond (to the second Fe), with the C–C bond parallel to the Fe–Ni bond. Significant bond lengths include: Fe–Fe 2.506(1), Fe–Ni 2.453, 2.474(1), C–C 1.383(7) Å. The formation of the square pyramidal Fe_2NiC_2 core in the complex anion by formal addition of Ph^- to $(\eta\text{-}C_5H_5)NiFe_2(CO)_6(C_2Ph)$ (containing a trigonal bipyramidal Fe_2NiC_2 core) is discussed.

Introduction

There has been much recent interest in heterometallic cluster complexes containing alkyne, $Fe(CO)_3$ and $Ni(\eta\text{-}C_5H_5)$ moieties. These interesting compounds are found with $FeNi_2$, Fe_2Ni and Fe_2Ni_2 cores, the first examples being described over twenty years ago [2]. They are formed in reactions between the alkyne, iron carbonyls [$Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$] and nickelocene or $[Ni(CO)(\eta\text{-}C_5H_5)]_2$, or more conveniently, between iron carbonyls and the preformed $[Ni(\eta\text{-}C_5H_5)]_2(\mu\text{-}RC{\equiv}CR')$ complex [3–7]. These reactions are exceedingly complex, as indicated by the report that nineteen products were obtained from $[Ni(\eta\text{-}C_5H_5)]_2(\mu\text{-}HC_2Bu^t)$

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and $Fe_3(CO)_{12}$ [4]. Italian workers have described these complexes in considerable detail, and mixed-metal clusters of types I [5], II [4], III [6,7], IV [7] and V [7] have been reported; the first three have been characterised by X-ray studies. In the course of experiments designed to determine the nature of complexes of type III, which were commenced before the publication of the structural study referred to above, we discovered an unusual cluster degradation reaction which afforded a further example of an Fe_2Ni cluster. This paper describes this work, and amplifies a preliminary communication [8].
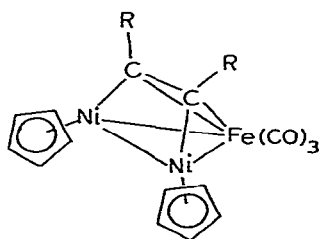
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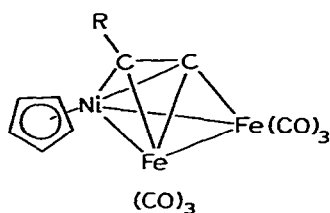
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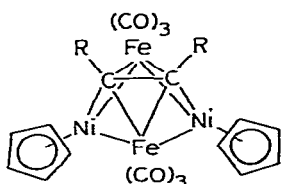
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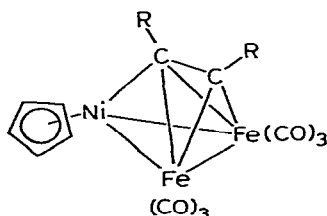
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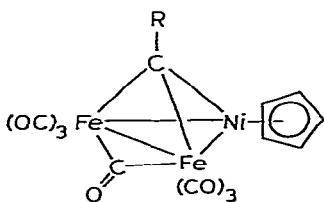
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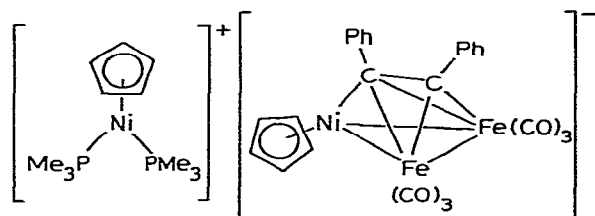
(VI)

Experimental

General experimental details are similar to those described in previous papers of this series. Reactions were carried out in dried solvents under nitrogen; thin-layer chromatography was on plates (20 × 20 cm) coated with Kieselgel G.

Stepwise syntheses of $[Ni(\eta\text{-}C_5H_5)]_2(\mu\text{-}C_2Ph_2)$, $[Ni(\eta\text{-}C_5H_5)]_2[Fe(CO)_3](\mu_3\text{-}C_2Ph_2)$ and $[Ni(\eta\text{-}C_5H_5)]_2[Fe(CO)_3]_2(\mu_4\text{-}C_2Ph_2)$
    (a) $[Ni(\eta\text{-}C_5H_5)]_2(\mu\text{-}C_2Ph_2)$. A mixture of $Ni(\eta\text{-}C_5H_5)_2$ (4.0 g, 21.2 mmol) and

C_2Ph_2 (2.0 g, 11.2 mmol) was heated in refluxing benzene (50 ml) for 20 h. Work-up by column chromatography (alumina) gave the product as the major fraction eluted with light petroleum/benzene mixtures: dark green crystals. m.p. 140°C (lit. [2] 149–150°C), yield 2.18 g, 24%. ^{1}H NMR: δ(CDCl$_3$) 5.37s (C$_5$H$_5$), 7.3–7.8m (Ph) ppm.

(b) *[Ni(η-C$_5$H$_5$)]$_2$[Fe(CO)$_3$](µ$_3$-C$_2$Ph$_2$).* A mixture of [Ni(η-C$_5$H$_5$)]$_2$(µ-C$_2$Ph$_2$) (76 mg, 0.2 mmol) and Fe$_2$(CO)$_9$ (100 mg, 0.3 mmol) was heated in refluxing benzene for 16 h. TLC of the filtered and concentrated reaction mixture afforded the FeNi$_2$ cluster (I, R = Ph) as the major product: light green crystals, dec. 198°C (lit. [2], 198–199°C); IR: v(CO) 2030 vs, 1979 s, 1963 m cm^{-1}; ^{1}H NMR: δ(CDCl$_3$) 4.71s. (C$_5$H$_5$), 6.95–7.38m (Ph) ppm.

(c) *[Ni(η-C$_5$H$_5$)]$_2$[Fe(CO)$_3$]$_2$(µ$_4$-C$_2$Ph$_2$).* After 18 h heating in refluxing benzene (25 ml), a mixture of the FeNi$_2$ cluster (50 mg, 0.1 mmol) and Fe$_2$(CO)$_9$ (44 mg, 0.12 mmol) was separated by TLC (developed in 3/1 light petroleum/benzene) to give the dark blue Fe$_2$Ni$_2$ cluster (III, R = Ph) (50%) and unreacted FeNi$_2$ cluster (33%). The former had m.p. 180°C (lit. [2] 180°C); IR: v(CO) 2010 s, 1973 s cm^{-1}; ^{1}H NMR: δ(CDCl$_3$) 4.80s (C$_5$H$_5$), 7.18–7.68m (Ph) ppm.

Reactions of [Ni(η-C$_5$H$_5$)]$_2$[Fe(CO)$_3$]$_2$(µ$_4$-C$_2$Ph$_2$)

(a) *With PMe$_3$.* Trimethylphosphine (5.3 mg. 0.07 mmol) was condensed into a solution of the Fe$_2$Ni$_2$ cluster (43 mg, 0.06 mmol) dissolved in light petroleum and contained in a Carius tube. Reaction occurred readily at room temperature, affording a dark brown precipitate. Recrystallisation (CH$_2$Cl$_2$/Et$_2$O) afforded brown crystals of [Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)][(Ni(η-C$_5$H$_5$))(Fe(CO)$_3$)$_2$(µ$_3$-C$_2$Ph$_2$)] (VI) (44 mg, 85%), dec. > 150°C. (Found: C, 50.20; H, 4.45; C$_{36}$H$_{38}$Fe$_2$Ni$_2$O$_6$P$_2$ calcd.: C, 50.35; H, 4.43%). IR (CH$_2$Cl$_2$): v(CO) 2022 vvw, 2003 s, 1957 vs, 1911 s cm^{-1}. ^{1}H NMR: δ[(CD$_3$)$_2$CO] 1.63t, J(HP) 10.0 Hz (PMe$_3$), 4.64s (C$_5$H$_5$), 5.63s (C$_5$H$_5$), 6.82–7.58m (Ph) ppm.

(b) *With P(OMe)$_3$.* A similar reaction between trimethyl phosphite (15 mg, 0.12 mmol) and the Fe$_2$Ni$_2$ cluster (40 mg, 0.056 mmol) in light petroleum required heating at 60°C for 14 h to give brown [Ni(P(OMe)$_3$)$_2$(η-C$_5$H$_5$)][(Ni(η-C$_5$H$_5$))(Fe(CO)$_3$)$_2$(µ$_3$-C$_2$Ph$_2$)] (VII) (45 mg, 84%), dec. > 200°C. (Found: C, 44.1; H, 3.8; C$_{36}$H$_{38}$Fe$_2$Ni$_2$O$_{12}$P calcd.: C, 45.3; H, 4.0%). IR (CH$_2$Cl$_2$): v(CO) 2023 vvw, 2005 s, 1959 vs, 1914 s cm^{-1}. ^{1}H NMR: δ[(CD$_3$)$_2$CO] 3.85t, J(HP) 6.8 Hz [P(OMe)$_3$], 4.67s (C$_5$H$_5$), 5.87s (C$_5$H$_5$), 6.8–7.6m (Ph) ppm.

Reaction between VI and HPF$_6$ · OEt$_2$

A solution of complex VI (25.5 mg, 0.03 mmol) in CH$_2$Cl$_2$ (4 ml) was treated with HPF$_6$ · OEt$_2$ (6.6 mg, 0.03 mmol) at room temperature. Removal of solvent (10^{-2} mmHg) gave a brown residue, which was extracted with light petroleum, and dried to give pink [Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (VIII) (7.0 mg, 56%). (Found: C, 30.5; H, 5.2; C$_{11}$H$_{23}$F$_6$NiP$_3$ calcd.: C, 31.4; H, 5.5%). ^{1}H NMR: δ[(CD$_3$)$_2$CO] 1.63t, J(HP) 10.2 Hz (PMe$_3$), 5.57s (C$_5$H$_5$) ppm. The compound slowly turns green in air.

X-ray structure determination

Black, irregularly shaped crystals of [Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)][(Ni(η-C$_5$H$_5$))(Fe(CO)$_3$)$_2$(µ$_3$-C$_2$Ph$_2$)] were obtained from acetone. Preliminary rotation and Weissenberg photographs showed them to be orthorhombic, with space group *Pbca*.

A needle-shaped crystal, 0.36 × 0.34 × 0.36 mm, was mounted about c and attached to a glass fibre with epoxy resin. The cell constants were obtained from axial reflexions by $\omega(h00,0k0)$ and $\mu(00l)$ scans on a Stoe Weissenberg diffractometer using Mo-K_α radiation and a graphite monochromator.

Crystal Data. $C_{36}H_{38}Fe_2Ni_2O_6P_2$, F.W. = 857.72, orthorhombic, space group *Pbca* (No. 61). Cell constants (at 21°C): a 15.275(2), b 20.325(2), c 24.264(3) Å; $Z = 8$, D_c 1.51 g cm^{-3}; $F(000) = 3296$; μ(Mo-K_α) 18.32 cm^{-1}; λ 0.71069 Å.

Intensity data were collected for levels $hk0$ to $hk20$ in the range $0° < 2\theta < 50°$ using ω scan technique. Lorentz, polarisation and absorption corrections were applied to give 3813 unique reflexions with $I > 2.5\sigma(I)$. The transmission factors varied between 0.51 and 0.58.

Structure solution and refinement. The iron and nickel atoms were located by direct methods using the SHELX system of programs [20]. All the remaining non-hydrogen atoms were located in successive difference Fourier syntheses. All hydrogen atom positions were calculated using standard geometries (C–H 0.965 Å). The structure was refined by block-matrix least-square techniques with anisotropic
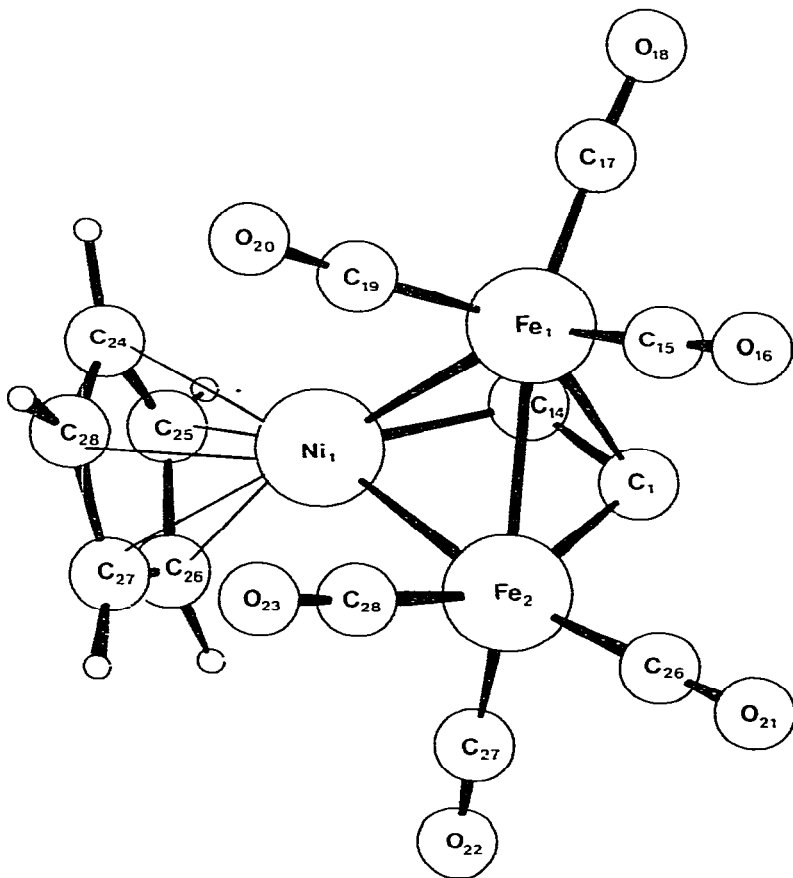

Fig. 1. PLUTO plot (ref. 22) of the complex anion $[\{(\eta\text{-}C_5H_5)Ni\}Fe_2(CO)_6(\mu_3\text{-}C_2Ph_2)]^-$ in VI, showing atom numbering.
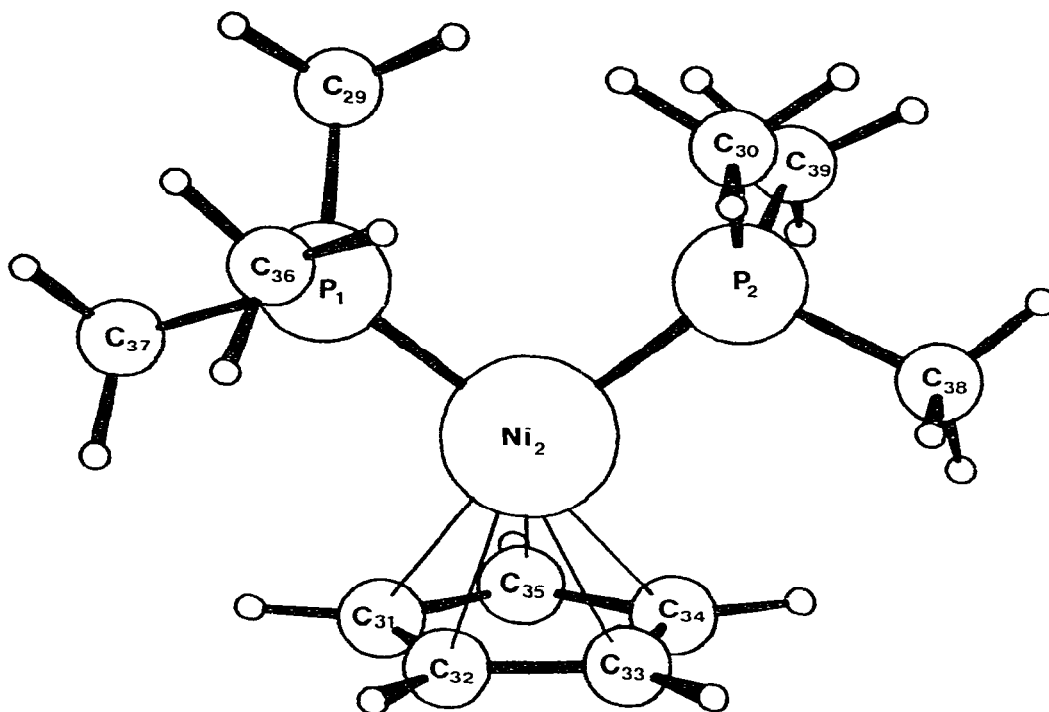
Fig. 2. PLUTO plot of the cation $[Ni(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ in VI, showing atom numbering.

thermal parameters for all non-hydrogen atoms. A weighting scheme was used which converged to $w = 2.4898/[\sigma^2(F) + 0.00001F^2]$. The final residuals were $R = 4.85\%$, $R_w = 4.04\%$ for 3780 reflexions. The final electron-density difference synthesis showed no peak > 0.7 eÅ^{-3} except in the immediate neighbourhood of Ni(2). All scattering factors were taken from reference [10]. Non-hydrogen atomic fractional coordinates are listed in Table 1; significant bond distances and angles are given in Tables 2 and 3, respectively. Figures 1 and 2 show geometries and atom numbering schemes for the cation and anion, respectively. A list of the final observed and calculated structure factors is available from the authors.

Results and discussion

The tetranuclear mixed-metal complex $Fe_2Ni_2(\mu_4\text{-}C_2Ph_2)(CO)_6(\eta\text{-}C_5H_5)_2$ (III, R = Ph) is obtained directly from reactions between $Fe_2(CO)_9$, $Ni(\eta\text{-}C_5H_5)_2$ and C_2Ph_2, or from preformed $FeNi_2(\mu_3\text{-}C_2Ph_2)(CO)_3(\eta\text{-}C_5H_5)$ and $Fe_2(CO)_9$. It reacts readily with PMe_3 or $P(OMe)_3$ to give black complexes which are insoluble in non-polar solvents, and which were characterised as the bis-adducts $Fe_2Ni_2(C_2Ph_2)(CO)_6(PR_3)_2(\eta\text{-}C_5H_5)_2$ (VI, R = Me; VII, R = OMe) by micro-analyses, spectroscopic data and finally by a single-crystal X-ray study of VI. That these complexes were not simple substitution products resulting from displacement of CO by the tertiary phosphine or phosphite was originally suggested by their complex $v(CO)$ spectra, and the ^1H NMR spectra, which revealed that the two C_5H_5

TABLE 1

FRACTIONAL ATOM COORDINATES FOR NON-HYDROGEN ATOMS IN $[Ni(PMe_3)_2(\eta\text{-}C_5H_5)][Fe_2Ni(\mu_3\text{-}C_2Ph_2)(CO)_6(\eta\text{-}C_5H_5)]$ (Fe, $Ni \times 10^5$, all others $\times 10^4$)

	x/a	y/b	z/c
Fe(1)	13447(5)	−1594(4)	38220(3)
Ni(1)	14345(5)	9979(4)	41027(2)
Fe(2)	18957(6)	6911(4)	31596(3)
C(1)	2628(4)	163(2)	3660(2)
C(3)	4001(4)	−44(3)	3133(2)
C(4)	4744(4)	−394(4)	3014(2)
C(5)	4911(4)	−972(4)	3292(3)
C(6)	4329(5)	−1182(3)	3690(2)
C(7)	3584(4)	−822(3)	3817(2)
C(2)	3405(4)	−241(3)	3538(2)
C(14)	2331(3)	343(2)	4177(2)
C(8)	2277(4)	146(3)	5197(2)
C(9)	2756(3)	301(2)	4719(2)
C(10)	3637(4)	441(3)	4783(2)
C(11)	4013(4)	451(3)	5311(3)
C(12)	3518(4)	306(3)	5764(2)
C(13)	2649(4)	152(3)	5714(2)
C(15)	1337(4)	−790(4)	4318(2)
O(16)	1353(4)	−1234(3)	4614(2)
C(17)	1274(4)	−693(3)	3247(2)
O(18)	1237(3)	−1048(2)	2885(2)
C(19)	258(5)	86(3)	3891(3)
O(20)	−496(3)	216(3)	3915(2)
C(21)	1492(9)	1618(5)	4808(4)
C(22)	1758(7)	1954(5)	4349(7)
C(23)	1023(15)	1989(5)	4003(4)
C(24)	402(8)	1659(7)	4261(8)
C(25)	673(11)	1434(5)	4747(6)
C(26)	2597(5)	1380(3)	3107(2)
O(21)	3089(4)	1813(3)	3087(2)
C(27)	2176(4)	327(3)	2518(2)
O(22)	2339(3)	87(3)	2097(2)
C(28)	845(5)	989(3)	2950(2)
O(23)	154(3)	1156(3)	2813(2)
Ni(2)	20481(5)	23418(4)	12960(3)
P(1)	1376(1)	2985(1)	1858(1)
C(29)	997(5)	3728(3)	1553(3)
P(2)	921(1)	1873(1)	925(1)
C(30)	533(4)	1188(3)	1332(2)
C(31)	3301(6)	2491(8)	1602(5)
C(32)	3266(5)	2773(5)	1048(6)
C(33)	3071(5)	2278(6)	705(3)
C(34)	3014(5)	1691(5)	1029(5)
C(35)	3186(6)	1808(8)	1546(5)
C(36)	446(5)	2688(3)	2220(3)
C(37)	2028(6)	3294(4)	2416(3)
C(38)	−50(4)	2328(4)	776(3)
C(39)	1153(5)	1506(3)	250(2)

TABLE 2

SIGNIFICANT BOND LENGTHS (Å) FOR [Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)][Fe$_2$Ni(μ$_3$-C$_2$Ph$_2$)(CO)$_6$(η-C$_5$H$_5$)]

(a) Anion			(b) Cation	
Metal core			*PMe$_3$ groups*	
Fe(1)–Fe(2)	2.506(1)		Ni(2)–P(1)	2.151(2)
Fe(1)–Ni(1)	2.453(1)		Ni(2)–P(2)	2.163(2)
Fe(2)–Ni(1)	2.474(1)		P–Me	range 1.775–1.833(8), mean 1.795
Cyclopentadienyl group			*Cyclopentadienyl group*	
Ni(1)–C(21)	2.128(10)	C(21)–C(22) 1.37(2)	Ni(2)–C(31)	2.075(10)
Ni(1)–C(22)	2.091(11)	C(22)–C(23) 1.40(2)	Ni(2)–C(32)	2.142(9)
Ni(1)–C(23)	2.124(12)	C(23)–C(24) 1.32(2)	Ni(2)–C(33)	2.126(8)
Ni(1)–C(24)	2.107(14)	C(24)–C(25) 1.33(2)	Ni(2)–C(34)	2.085(9)
Ni(1)–C(25)	2.142(15)	C(25)–C(21) 1.31(2)	Ni(2)–C(35)	2.137(12)
Alkyne group				
Fe(1)–C(1)	2.104(6)			
Fe(1)–C(14)	2.014(5)			
Fe(2)–C(1)	1.970(5)			
Ni(1)–C(14)	1.918(5)			
C(1)–C(14)	1.383(7)			
Carbonyl groups				
Fe–C	range 1.742–1.790(8), mean 1.768			
C–O	range 1.138–1.183(9), mean 1.158			

TABLE 3

SIGNIFICANT BOND ANGLES (DEGREES) FOR [Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)][Fe$_2$Ni(μ_3-C$_2$Ph$_2$)(CO)$_6$(η-C$_5$H$_5$)]

(a) Anion		(b) Cation	
Metal core		*PMe$_3$ groups*	
Fe(2)–Fe(1)–Ni(1)	59.9	P(1)–Ni(2)–P(2)	98.7(1)
Fe(2)–Ni(1)–Fe(1)	61.1		
Ni(1)–Fe(2)–Fe(1)	59.0	Ni(2)–P(1)–C(29)	114.0(2)
		Ni(2)–P(1)–C(36)	119.3(2)
Alkyne group		Ni(2)–P(1)–C(37)	115.3(3)
Fe(2)–Fe(1)–C(1)	49.7(1)	Ni(2)–P(2)–C(30)	111.9(2)
Ni(1)–Fe(1)–C(1)	72.6(1)	Ni(2)–P(2)–C(38)	121.2(2)
Ni(1)–Fe(1)–C(14)	49.7(1)	Ni(2)–P(2)–C(39)	113.4(2)
Fe(2)–Fe(1)–C(14)	70.9(1)		
C(1)–Fe(1)–C(14)	39.2(2)	C(29)–P(1)–C(36)	103.5(3)
Fe(1)–Ni(1)–C(14)	53.2(2)	C(29)–P(1)–C(37)	101.4(4)
Fe(2)–Ni(1)–C(14)	73.1(2)	C(36)–P(1)–C(37)	101.0(4)
Fe(1)–Fe(2)–C(1)	54.5(2)	C(30)–P(2)–C(38)	103.7(3)
Ni(1)–Fe(2)–C(1)	74.3(1)	C(30)–P(2)–C(39)	103.8(3)
Fe(1)–C(1)–Fe(2)	75.8(2)	C(38)–P(2)–C(39)	101.0(3)
Fe(1)–C(1)–C(14)	66.9(3)		
Fe(2)–C(1)–C(14)	103.2(4)		
C(2)–C(1)–C(14)	126.5(5)		
Fe(1)–C(14)–Ni(1)	77.2(2)		
Fe(1)–C(14)–C(1)	73.9(3)		
Ni(1)–C(14)–C(1)	109.5(4)		
Fe(1)–C(14)–C(9)	133.2(4)		
Ni(1)–C(14)–C(9)	116.1(4)		
C(1)–C(14)–C(9)	130.6(5)		

groups were inequivalent. No mass spectra could be obtained. Although a possible explanation of these anomalies was that two CO's on the one iron atom had been substituted, there was no obvious explanation for this unusual reaction to occur (both iron atoms being equivalent), so a single-crystal X-ray diffraction study was undertaken.

The structure of VI was found to consist of [Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)]$^+$ cations and [Fe$_2$Ni(μ_3-C$_2$Ph$_2$)(CO)$_6$(η-C$_5$H$_5$)]$^-$ anions; no unusual interionic contacts less than normal Van der Waals separations were found. The structure of the cation is illustrated in Fig. 1, and that of the anion in Fig. 2.

The [Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)]$^+$ cation. This appears to be the first occasion on which a cation of the [Ni(PR$_3$)$_2$(η-C$_5$H$_5$)]$^+$ series has been structurally characterised, although examples of salts containing these cations have been known for fifteen years [11]. Three groups described such compounds independently, and many other examples are now know.

As expected, the cation has C_{2v} symmetry, the nickel atom being bonded to the two tertiary phosphines, with Ni–P 2.151, 2.163(2) Å, and to the cyclopentadienyl group (Ni–C 2.075–2.142(10), mean 2.113 Å). The C$_5$ ring is not a regular pentagon (C–C, 1.305–1.461(23) Å), the bond lengths suggesting some contribution from the ene-allyl form. Coordination about the metal atom is distorted trigonal, with

P(1)–Ni–P(2) 98.9°; and P–Ni–Cp 131.3, 129.8°; the distortion arises from the presence of the large C_5 ligand. An alternative description of a five-coordinate nickel(II) cation with distorted trigonal bipyramidal stereochemistry may also be used. The Ni–P distances are slightly longer than those normally found for nickel(II) derivatives, e.g. 2.138(2) or 2.145(4) Å for Ni–P in $NiR(PPh_3)(\eta\text{-}C_5H_5)$ (R = Ph [12] and C_6F_5 [13], respectively), while the Ni–C(Cp) distances may be compared with values of 2.139 and 2.144 Å in these two complexes; in $Ni(\eta\text{-}C_5H_5)_2$, the average Ni–C distance is 2.185 Å [14].

The $[Fe_2Ni(\mu_3\text{-}C_2Ph_2)(CO)_6(\eta\text{-}C_5H_5)]^-$ anion. The anion consists of an Fe_2Ni triangle, all three metal atoms interacting with the C_2Ph_2 moiety in a $(2\sigma + \pi)$ fashion. The coordination of each iron atom is completed by three CO groups (mean Fe–C, 1.768 Å), and of the nickel atom by an η^5-cyclopentadienyl group (mean Ni–C, 2.118 Å; not significantly different from those in the cation). The alkyne C–C bond is 1.383(7) Å and longer than those found in I (1.34(2) Å) [5] or II (1.284(14) Å) [4].

The Fe–Fe distance (2.506(1) Å) may be compared with those found in $Fe_2Ni(CO)_6(\mu_3\text{-}C_2Bu^t)(\eta\text{-}C_5H_5)$ (2.610(3) Å) [4] $Fe_3(CO)_7(\mu_3\text{-}C_2Ph)(\eta\text{-}C_5H_5)$ (2.524(1) Å) [15] and $Fe_3(CO)_9(\mu_3\text{-}C_2Ph_2)$ (2.579(11) Å) [16] which are similarly bridged by the alkyne C–C bond. The two Fe–Ni distances, not unexpectedly, are significantly different: that parallel to the alkyne C–C bond is the longer, at 2.474(1) Å, while that bridged by C(14) is 2.453(1) Å. The latter may be compared with values of 2.381, 2.388(5) Å for the similar bonds in I [5]. Comparison with II shows that while the alkyne-bridged Ni–Fe bond is ca. 0.1 Å shorter in II, the other metal–metal bonds are both ca. 0.1 Å longer, resulting in similar overall sizes for the Fe_2Ni cores.

The major feature of interest in the difference in mode of attachment of the alkyne to the Fe_2Ni cluster in complexes II and VI. Complex II is one of a growing number of compounds containing small ligands CX attached in an $\eta^2\text{-}(\mu_3\text{-}C,\mu_2\text{-}X)$ mode to a triangular M_3 cluster. Other examples are CO (in $Nb_3(CO)_7(\eta\text{-}C_5H_5)_3$) [17], $CNBu^t$ (in $Fe_3(CO)_9(CNBu^t)$) [18], NCPr (in $Fe_3(CO)_9(NCPr)$) [19] and $C\equiv CR^-$ (in $Fe_3(C\equiv CPh)(CO)_7(\eta\text{-}C_5H_5)$ and $Ru_3(C\equiv CR)(\mu\text{-}PPh_2)(CO)_8$) [15,20]. In these, the C–X bond is above the M_3 triangle and orthogonally bridges one of the metal–metal bonds. The alkyne moiety in VI, on the other hand, is oriented so that the C–C bond lies above but parallel to a metal–metal bond. A similar arrangement is found in I.

An alternative, and perhaps more helpful, way of considering the structures of II and the variety of other similar complexes is to formulate them as electron-precise trigonal bipyramidal M_3CX clusters. Addition of a 2e donor, i.e. an electron pair, should then result in opening of the n atom *closo* polyhedron to one based on the $(n + 1)$ atom *closo* polyhedron. In these cases $n = 5$, so we should expect the formation of a polyhedron based on the octahedron, but since there are only five skeletal atoms, one apex will be missing: the resulting structure will thus be a square pyramid. It can be seen that VI, which results from formal addition of Ph^- to II, is indeed a distorted square pyramid, with a square face comprised of atoms $\overline{C(1)\text{-}C(14)\text{-}Ni(1)\text{-}Fe(2)}$. We have recently reported the related reaction of H^- with $Fe_3(CO)_9(\mu_3\text{-}CNBu^t)$ to give $[HFe_3(CO)_9(CNBu^t)]^-$ [18] and it would not be surprising to find similar additions of H^- or R^- to II would afford analogues of the anion in VI.
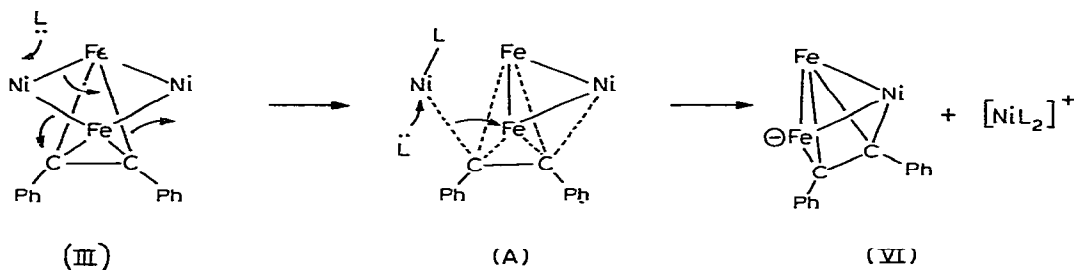
SCHEME 1. Cyclopentadienyl and carbonyl ligands omitted.

Speculation regarding the course of the reactions of tertiary phosphines or phosphites with III (R = Ph) that give VI and VII is of limited value. One may consider attack of the 2e donor ligand at the open Fe_2Ni_2 face of III to give an intermediate such as A (Scheme 1). Further addition of PR_3 results in heterolytic cleavage of the remaining Ni–C bond, as found in the reaction between $NiX(PR_3)(\eta\text{-}C_5H_5)$ (X = halide) and excess phosphine [21], generating the 18e $[Ni(PR_3)_2(\eta\text{-}C_5H_5)]^+$ cation and the cluster anion. Rearrangement of A, in which the Fe_2NiC_2 part of the cluster approximates to a trigonal bipyramid, to the square pyramidal anion found in VI, is a result of accommodating the "excess" electron density remaining after loss of the cation.

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