Reactivity of Bis(diphenylphosphino)methane in Cationic Octahedral Iron(II) Derivatives. X-Ray Structure of mer-[FeCl{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₃]PF₆ †

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Treatment of the cationic complexes $[FeL(dppm)(CNPh)_3]^{n+}$ [L = CNPh, n = 2, (1a); L = PPh₃, n = 2, (1b); L = I⁻, n = 1, (1c); L = Cl⁻, n = 1, (1d)] (dppm = Ph₂PCH₂PPh₂) with KOH gives the corresponding deprotonated species $[FeL\{(Ph_2P)_2CH\}(CNPh)_3]^{(n-1)+}$ (2a)—(2d). Complexes (2a) and (2d) react with [AuCl(tht)] (tht = tetrahydrothiophene) affording the bimetallic complexes $[FeL\{(Ph_2P)_2CH(AuCl)\}(CNPh)_3]^{(n-1)+}$ (3a) and (3d). Reaction of (2c) with 0.5 equivalent of [Au(tht)₂]PF₆ gives the trimetallic compound $[\{FeI[(Ph_2P)_2CH](CNPh)_3\}_2Au]PF_6$ (4), and with [Au(PPh₃)(tht)]PF₆ gives mer-$[FeI\{(Ph_2P)_2CH(AuPPh_3)\}(CNPh)_3]PF_6$ (5c). The analogous mer-$[FeCl\{(Ph_2P)_2CH(AuPPh_3)\}(CNPh)_3]PF_6$ (5d) is obtained by reaction of (1d) with 1 equivalent of [AuCl(PPh₃)] in the presence of KOH. Addition of 2 equivalents of [AuCl(PPh₃)] to a dichloromethane solution of (1a), (1c), (1d), or [Fe(dppm)(CNC₆H₄Me-4)₄][PF₆]₂ (1e) in the presence of an excess of KOH affords $[FeL\{(Ph_2P)_2C(AuPPh_3)_2\}(CNR)_3]^{n+}$ (6a) and (6c)—(6e). The structure of complex (6d) has been determined by X-ray analyses, showing a short Au–Au contact.

Bis(diphenylphosphino)methane (dppm) has played an important role in co-ordination and organometallic chemistry.[1] Its ability to act as a chelate or unidentate ligand in mononuclear complexes and as a bridge in binuclear complexes as well as its reactivity in these species have contributed to that interest. The anionic derivative bis(diphenylphosphino)methanide has also received considerable attention. Derivatives were first obtained by reaction of (Ph₂P)₂CH⁻Li⁺ with a number of compounds of Ni, Pd, and Pt.[2-5] Deprotonation reactions of co-ordinated dppm with strong bases was revealed as an easier method for obtaining the methanide derivatives; in this way chelated[6,7] and bridged[8,9] complexes were prepared.

In this paper we describe the synthesis of octahedral iron(II) bis(diphenylphosphino)methanide derivatives of general formula $[FeL\{(Ph_2P)_2CH\}(CNPh)_3]^{n+}$ (L = Cl⁻, I⁻, PPh₃, or CNPh; n = 0 or 1). By reaction of these complexes with gold(I) species, new hetero-di- and -tri-metallic compounds in which the methanide acts as a tridentate ligand have been obtained. We also describe a previously unreported aspect of the reactivity of the dppm ligand; that is the substitution of the two hydrogens of the central carbon atom by two Au(PPh₃) units. Thus we have prepared complexes of general formula $[FeL\{(Ph_2P)_2C(AuPPh_3)_2\}(CNR)_3]^{n+}$ (L = Cl⁻, I⁻, or CNR; R = Ph or C₆H₄Me-4; n = 1 or 2). A preliminary account of some of this work has been published.[10]

Results and Discussion

Treatment of the cationic complexes [Fe(dppm)(CNPh)₄]-[ClO₄]₂ (1a), mer-[Fe(PPh₃)(dppm)(CNPh)₃][ClO₄]₂ (1b), mer-[FeI(dppm)(CNPh)₃]I (1c), or mer-[FeCl(dppm)-(CNPh)₃]PF₆ (1d)[11] with an excess of KOH in CH₂Cl₂ resulted in the formation of [Fe{(Ph₂P)₂CH}(CNPh)₄]ClO₄ (2a), mer-[Fe(PPh₃){(Ph₂P)₂CH}(CNPh)₃]ClO₄ (2b), mer-[FeI{(Ph₂P)₂CH}(CNPh)₃] (2c), or mer-[FeCl{(Ph₂P)₂CH}-(CNPh)₃] (2d) respectively (see Scheme).

As expected, the deprotonation reactions occurred with

maintenance of the isocyanide arrangement of the parent compounds. In accordance with this, the i.r. spectra in the v(C–N) region for compounds (2) gave a similar pattern to those of the parent complexes but at lower frequencies (≈ 25 cm⁻¹) (see Table 1). Other spectroscopic and analytical data for these species are given in Tables 1 and 2. Compounds (2) are moderately stable to air but readily afforded the parent compounds when treated with weak acids.

It has been shown that compounds with the (Ph₂P)₂CH ligand react easily with organic electrophiles[12-14] and also with metallic species.[15] However, compound (2a) or (2c) did not react with MeI, and with Me₃O⁺SbCl₆⁻ only the protonated compounds (1a) and (1c) were recovered.

Fortunately, reactions of compounds (2) with gold(I) complexes allowed us to obtain a number of heterometallic species in which (Ph₂P)₂CH acts as a tridentate ligand. Thus when (2a) or (2d) was treated with [AuCl(tht)] (tht = tetrahydrothiophene) in CH₂Cl₂ the compounds [Fe{(Ph₂P)₂CH(AuCl)}-(CNPh)₄]ClO₄ (3a) and mer-[FeCl{(Ph₂P)₂CH(AuCl)}-(CNPh)₃] (3d) were readily obtained (see Scheme). The proton bonded to the central carbon atom in the diphosphine appeared as a triplet at δ 5.16 [(3a)] and 4.37 [(3d)] in the ¹H n.m.r. spectra, and the i.r. spectra for the v(C–N) region were typical for cis-tetrakis(isocyanide) and mer-isocyanide derivatives (see Tables 1 and 2).

It is interesting that when the reaction with [AuCl(tht)] was carried out with (2c) a complex mixture of four compounds was detected by ³¹P-{¹H} n.m.r. spectroscopy, one of them being (3d) and the others probably species resulting from the metathesis of the Cl and I atoms in their two possible positions in the molecule (bonded to gold or to iron).

Attempts to deprotonate (3a) and (3d) with KOH afforded
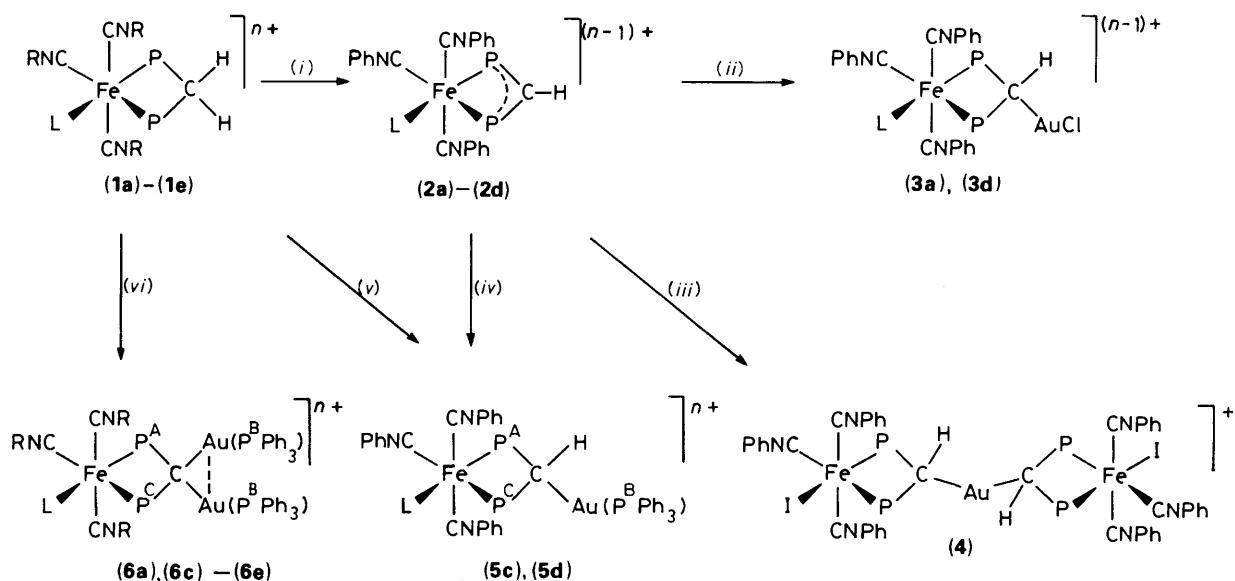
Scheme. (*i*) R = Ph, excess of KOH, CH_2Cl_2; (*ii*) [AuCl(tht)] (1 equiv.), CH_2Cl_2; (*iii*) L = I⁻, [Au(tht)₂]PF₆ (0.5 equiv.), thf; (*iv*) [Au(PPh₃)-(tht)]PF₆ (1 equiv.), thf; (*v*) R = Ph, [AuCl(PPh₃)] (1 equiv.), excess of KOH, CH_2Cl_2; (*vi*) [AuCl(PPh₃)] (2 equiv.), excess of KOH, CH_2Cl_2

Table 1. Analytical,[a] conductivity,[b] and i.r.[c] data

| | Compound | Analysis/% | | | Λ_M | I.r./cm⁻¹ |
		C	H	N		
(2a)	[Fe{(Ph₂P)₂CH}(CNPh)₄]ClO₄	65.8 (66.9)	4.3 (4.3)	6.8 (5.9)	131	2 180w, 2 138s, 2 120(sh)
(2b)	mer-[Fe(PPh₃){(Ph₂P)₂CH}(CNPh)₃]ClO₄	68.6 (69.2)	4.8 (4.6)	4.4 (3.8)	120	2 158w, 2 115s
(2c)	mer-[FeI{(Ph₂P)₂CH}(CNPh)₃]	64.3 (63.1)	4.3 (4.1)	4.6 (4.8)		2 150w, 2 102s
(2d)	mer-[FeCl{(Ph₂P)₂CH}(CNPh)₃]	69.2 (70.4)	4.5 (4.6)	5.1 (5.3)		2 158w, 2 110s, 2 090(sh)
(3a)	[Fe{(Ph₂P)₂CH(AuCl)}(CNPh)₄]ClO₄	52.3 (53.7)	3.7 (3.4)	4.4 (4.7)	121	2 193m, 2 152s
(3d)	[FeCl{(Ph₂P)₂CH(AuCl)}(CNPh)₃]	53.9 (54.3)	3.5 (3.5)	4.1 (4.1)		2 172w, 2 132s
(4)	[{FeI[(Ph₂P)₂CH](CNPh)₃}₂Au]PF₆	52.1 (52.7)	3.6 (3.4)	3.9 (4.0)	109	2 160w, 2 123s
(5c)	mer-[FeI{(Ph₂P)₂CH(AuPPh₃)}(CNPh)₃]PF₆	51.1 (51.9)	3.3 (3.4)	2.5 (2.8)	122	2 160w, 2 120s
(5d)	mer-[FeCl{(Ph₂P)₂CH(AuPPh₃)}(CNPh)₃]PF₆	55.0 (55.3)	3.5 (3.6)	3.1 (3.0)	117	2 170w, 2 130s
(6a)	[Fe{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₄][PF₆]₂	51.2 (52.9)	3.5 (3.5)	2.6 (2.7)	233	2 187m, 2 145s
(6c)	mer-[FeI{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₃]BPh₄	59.0 (60.2)	3.8 (4.0)	1.8 (1.9)	120	2 157m, 2 115s
(6d)	mer-[FeCl{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₃]PF₆	53.0 (53.3)	3.5 (3.5)	2.2 (2.2)	124	2 165m, 2 125s
(6e)	[Fe{(Ph₂P)₂C(AuPPh₃)₂}(CNC₆H₄Me-4)₄][PF₆]₂	51.9 (52.7)	3.6 (3.6)	2.5 (2.6)	240	2 190m, 2 145s

[a]Calculated values are in parentheses. [b] The values (ohm⁻¹ cm² mol⁻¹) were obtained in acetone solutions (5 × 10⁻⁴ mol dm⁻³). [c] Spectra recorded as CH_2Cl_2 solutions, except for (4) and (5c) in thf solutions.

Table 2. Hydrogen-1 and ³¹P-{¹H} n.m.r. data

Compound	³¹P-{¹H}[a]	J(PP)/Hz	¹H[b] PPCH	J(PH)/Hz
(2a)	−8.9 (s)		2.45 (t)	4.7
(2b)	52.5 (m), −1.8 (m), −9.6 (m)			
(2c)	16.3 (d), −18.8 (d)	46		
(3a)	18.4 (s)		5.16 (t)	12
(3d)	47.3 (d), 9.7 (d)	71	4.37 (t)	14
(4)	52.2 (d), 10.1 (d)	74	4.53 (t)	13
(5c)	Pᴬ 48.5 (dd), Pᴮ 38.7 (t), Pᶜ 6.0 (dd)	J(PᴬPᶜ) = 66, J(PᴬPᴮ) = J(PᴮPᶜ) = 11		
(5d)	Pᴬ 45.0 (dd), Pᴮ 38.9 (t), Pᶜ 8.5 (dd)	J(PᴬPᶜ) = 71, J(PᴬPᴮ) = J(PᴮPᶜ) = 10		
(6a)	35.7 (t), 27.8 (t)	8		
(6c)	Pᴬ 60.0 (dt), Pᴮ 35.7 (t), Pᶜ 19.1 (dt)	J(PᴬPᶜ) = 64, J(PᴬPᴮ) = J(PᴮPᶜ) = 9		
(6d)	Pᴬ 56.5 (dt), Pᴮ 35.7 (t), Pᶜ 20.7 (dt)	J(PᴬPᶜ) = 69, J(PᴬPᴮ) = J(PᴮPᶜ) = 9		
(6e)	35.5 (t), 28.4 (t)	8		

[a] In CH_2Cl_2 as solvent; chemical shifts are positive at higher frequencies relative to 85% H₃PO₄. The positions of Pᴬ, Pᴮ, and Pᶜ are shown in the Scheme. [b] In CDCl₃ as solvent; chemical shifts (δ) relative to SiMe₄.

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the starting compounds (2a) and (2d) in addition to metallic gold as a black precipitate.

Another heterometallic derivative, mer-[{FeI[(Ph₂P)₂CH]-

(CNPh)₃}₂Au]PF₆ (4), was obtained by reaction of (2c) with [Au(tht)₂]PF₆ in a molar ratio of 2:1 in tetrahydrofuran (thf) as solvent. As shown in the Scheme, complex (4) possesses a
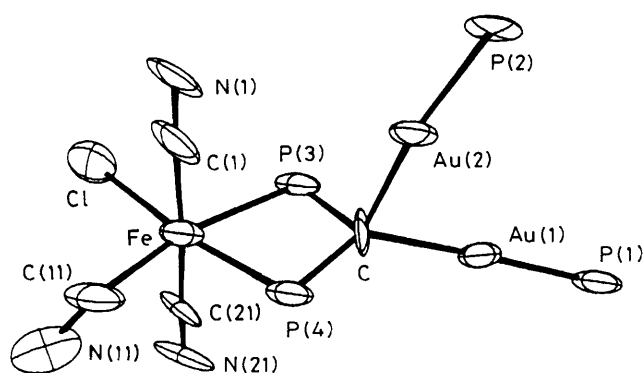
Figure. Structure of the cation mer-[FeCl{(Ph₂P)₂C(AuPPh₃)₂}-(CNPh)₃]⁺ showing the atomic labelling scheme. All phenyl groups have been omitted for clarity

Table 3. Selected interatomic distances (Å) and angles (°) of complex (6d)

Au(1)–Au(2)	2.891(4)	C(11)–N(11)	1.10(10)
Fe–Cl	2.38(2)	C(21)–N(21)	1.13(9)
Fe–C(1)	1.84(7)	P(3)–C	1.67(4)
Fe–C(11)	1.87(7)	P(4)–C	1.79(5)
Fe–C(21)	1.90(7)	C–Au(1)	2.09(3)
Fe–P(3)	2.23(2)	C–Au(2)	2.22(5)
Fe–P(4)	2.27(2)	Au(1)–P(1)	2.25(2)
C(1)–N(1)	1.19(10)	Au(2)–P(2)	2.27(2)
Cl–Fe–C(1)	87.7(25)	C(21)–Fe–P(4)	92.6(17)
Cl–Fe–C(11)	95.6(29)	P(3)–Fe–P(4)	69.8(8)
Cl–Fe–C(21)	86.8(23)	Fe–P(3)–C	98.9(17)
Cl–Fe–P(3)	169.9(8)	Fe–P(4)–C	93.9(15)
Cl–Fe–P(4)	100.1(8)	P(3)–C–P(4)	95.9(21)
C(1)–Fe–C(11)	94.7(31)	P(3)–C–Au(1)	129.5(22)
C(1)–Fe–C(21)	174.3(34)	P(3)–C–Au(2)	112.4(25)
C(1)–Fe–P(3)	92.6(24)	P(4)–C–Au(1)	125.3(23)
C(1)–Fe–P(4)	87.3(18)	P(4)–C–Au(2)	107.7(19)
C(11)–Fe–C(21)	87.0(31)	Au(1)–C–Au(2)	84.1(15)
C(11)–Fe–P(3)	94.5(29)	C–Au(1)–P(1)	177.4(14)
C(11)–Fe–P(4)	164.2(28)	C–Au(2)–P(2)	171.9(10)
C(21)–Fe–P(3)	92.7(22)	C–P(3)–P(4)–Fe	−167.29

gold atom bonded to the central carbon atom of two (Ph₂P)₂CH units. A similar situation has been described recently for the cation [{Au(C₆F₅)₂[(Ph₂P)₂CH]}₂Au]⁺.[15] Spectroscopic data show that the two units mer-FeI{(Ph₂P)₂-CH}(CNPh)₃ are equivalent (Tables 1 and 2).

When the reaction of (2c) was carried out with [Au(PPh₃)-(tht)]PF₆ {obtained in situ from [AuCl(PPh₃)], TlPF₆, and tht in thf as solvent} the cationic complex mer-[FeI{(Ph₂P)₂CH-(AuPPh₃)}(CNPh)₃]PF₆ (5c) was obtained. The analogous complex mer-[FeCl{(Ph₂P)₂CH(AuPPh₃)}(CNPh)₃]PF₆ (5d) was synthesized by treating (1d) directly with [AuCl(PPh₃)] in a 1:1 molar ratio in the presence of an excess of KOH in CH₂Cl₂ (see Scheme).

Compounds (5) show a characteristic pattern of signals in their ³¹P-{¹H} n.m.r. spectra consisting of two doublets of doublets due to the two phosphorus atoms of the diphosphine, and a triplet for the phosphorus atom in the Au(PPh₃) group (see Table 2).

The substitution of the two protons of the dppm by two Au(PPh₃) units was easily achieved by reaction of the complexes [Fe(dppm)(CNPh)₄][PF₆]₂ (1a′), mer-[FeI(dppm)-(CNPh)₃]I (1c), mer-[FeCl(dppm)(CNPh)₃]PF₆ (1d), or [Fe(dppm)(CNC₆H₄Me-4)₄][PF₆]₂ (1e) with 2 equivalents of [AuCl(PPh₃)] in the presence of an excess of KOH in CH₂Cl₂ (see Scheme).

The complexes mer-[FeCl{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₃]-

PF₆ (6d) and mer-[FeI{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₃]BPh₄ (6c), this last obtained after interchanging the anion with NaBPh₄) gave ³¹P-{¹H} n.m.r. spectra consisting of two doublets of triplets for the two phosphorus atoms in the diphosphine and a pseudo-triplet for the two equivalent phosphorus atoms of the Au(PPh₃) groups, whereas the tetrakis(isocyanide) derivatives [Fe{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₄][PF₆]₂ (6a) and [Fe{(Ph₂P)₂C(AuPPh₃)₂}(CNC₆H₄Me-4)₄][PF₆]₂ (6e) gave two triplets for the two types of phosphorus in the molecule.

Compounds having two gold atoms bonded to the same carbon atom usually present a gold–gold interaction.[16,17] In order to study this feature in compounds (6) an X-ray diffraction study of (6d) was undertaken. The structure of the cation is shown in the Figure. Selected bond lengths and interbond angles are given in Table 3. Iron is at the centre of a distorted cationic octahedron. Three vertices are occupied by three phenyl isocyanide molecules in a mer arrangement. Another vertex is occupied by a chlorine, cis to the three phenyl isocyanides. The last two vertices are occupied by the phosphorus atoms of the diphosphine. The two phosphorus atoms of the diphosphine and the two gold atoms form a very distorted tetrahedron around the central carbon atom (C). As expected, an interaction exists between the two gold atoms; thus the Au–Au distance [2.891(4) Å] is close to the interatomic separation in metallic gold (2.884 Å), similar to that found in the derivative [{Au[(Ph₂P)₂CH]}₂] [2.888(3) Å],[18] and a little longer than in the three-centre two-electron system [Fe(C₅H₅)-{C₅H₄(AuPPh₃)₂}]⁺ [16] (2.77 Å).

The bond lengths P(3)–C (1.67 Å) and P(4)–C (1.79 Å) are shorter than those commonly associated with the dppm ligand (1.84 Å) and similar to those found in (Ph₂P)₂CH derivatives,[5,6] suggesting significant double-bond character. The Au(2) atom deviates much more (1.92 Å) from the plane determined by atoms P(3), P(4), and C than does the Au(1) atom (0.86 Å). In this context, the bond length Au(2)–C (2.22 Å) is longer than Au(1)–C (2.09 Å).

Other bond lengths and interbond angles of the molecule are not very significant and are of the order normally found (see Table 3).

Experimental

All reactions were carried out under a dry oxygen-free argon atmosphere, with solvents dried and distilled under argon prior to use. I.r. spectra were obtained on a Perkin-Elmer 298 spectrophotometer, n.m.r. spectra (¹H and proton-decoupled ³¹P) on a Varian FT-80. Compounds (1) were obtained as described previously.[11]

[Fe{(Ph₂P)₂CH}(CNPh)₄]ClO₄ (2a).—To a solution of [Fe(dppm)(CNPh)₄][ClO₄]₂ (1a) (0.23 g, 0.22 mmol) in CH₂Cl₂ (30 cm³) an excess of KOH (1 g, 17.5 mmol) was added. After stirring for 15 min, the solution was filtered under an argon atmosphere. The solvent was then removed in vacuo and a yellow oily precipitate was obtained. The residue was washed and stirred with diethyl ether (20 cm³) until a yellow solid corresponding to (2a) was obtained. The product can be re-crystallized from pyridine–diethyl ether (0.19 g, 91%).

mer-[Fe(PPh₃){(Ph₂P)₂CH}(CNPh)₃]ClO₄ (2b).—This was similarly prepared from mer-[Fe(PPh₃)(dppm)(CNPh)₃]-[ClO₄]₂ (1b) (0.33 g, 0.27 mmol) and KOH (2 g, 35 mmol). Yield 0.24 g (80%).

mer-[FeI{(Ph₂P)₂CH}(CNPh)₃] (2c).—This was similarly prepared from mer-[FeI(dppm)(CNPh)₃]I (1c) (0.3 g, 0.3 mmol) and KOH (2 g, 35 mmol). In this case 4 h of stirring were necessary for complete reaction. Yield 0.25 g (95%).

Table 4. Final atomic co-ordinates (× 10³; × 10⁴ for Au and Fe) for mer-[FeCl{(Ph₂P)₂C(AuPPh₃)₂}(CNPh)₃]PF₆

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Au(1)	1 810(2)	1 917(2)	122(3)	C(313)	413(3)	219(3)	−101(5)
Au(2)	2 558(2)	3 360(2)	1 230(3)	C(314)	476(3)	259(3)	−52(5)
P(1)	88(1)	160(1)	−146(21)	C(315)	504(3)	276(3)	71(5)
C(101)	88(1)	53(2)	−220(46)	C(316)	470(3)	253(3)	145(5)
C(102)	77(2)	30(2)	−344(46)	P(4)	265(1)	227(1)	312(2)
C(103)	82(2)	−50(2)	−401(46)	C(401)	207(2)	155(3)	323(4)
C(104)	98(2)	−108(2)	−334(46)	C(402)	221(2)	134(3)	433(4)
C(105)	110(2)	−85(2)	−210(46)	C(403)	172(2)	90(3)	455(4)
C(106)	105(2)	−4(2)	−153(46)	C(404)	110(2)	67(3)	369(4)
C(111)	2(2)	175(3)	−98(48)	C(405)	96(2)	88(3)	260(4)
C(112)	−8(2)	241(3)	−6(48)	C(406)	145(2)	132(3)	237(4)
C(113)	−73(2)	255(3)	29(48)	C(411)	223(3)	321(2)	381(5)
C(114)	−128(2)	203(3)	−28(48)	C(412)	157(3)	343(2)	313(5)
C(115)	−118(2)	138(3)	−120(48)	C(413)	116(3)	410(2)	360(5)
C(116)	−53(2)	124(3)	−155(48)	C(414)	142(3)	456(2)	475(5)
C(121)	72(4)	216(3)	−260(41)	C(415)	209(3)	434(2)	543(5)
C(122)	7(4)	227(3)	−340(41)	C(416)	249(3)	367(2)	496(5)
C(123)	6(4)	264(3)	−432(4)	Fe	3 843(5)	2 009(5)	3 729(10)
C(124)	68(4)	289(3)	−444(4)	C(1)	395(3)	307(4)	389(6)
C(125)	133(4)	278(3)	−364(4)	N(1)	401(3)	375(3)	396(6)
C(126)	135(4)	241(3)	−272(4)	C(2)	409(2)	454(2)	416(5)
P(2)	233(1)	451(1)	61(2)	C(3)	428(2)	484(2)	330(5)
C(201)	150(2)	450(3)	−52(4)	C(4)	433(2)	566(2)	349(5)
C(202)	94(2)	416(3)	−32(4)	C(5)	419(2)	618(2)	453(5)
C(203)	27(2)	415(3)	−110(4)	C(6)	400(2)	588(2)	538(5)
C(204)	15(2)	449(3)	−208(4)	C(7)	395(2)	506(2)	520(5)
C(205)	71(2)	484(3)	−227(4)	C(11)	481(4)	170(4)	378(8)
C(206)	139(2)	484(3)	−149(4)	N(11)	534(4)	140(3)	370(6)
C(211)	301(2)	474(4)	−5(5)	C(12)	594(2)	87(3)	345(4)
C(212)	335(2)	545(4)	29(5)	C(13)	604(2)	6(3)	341(4)
C(213)	388(2)	554(4)	−26(5)	C(14)	665(2)	−37(3)	310(4)
C(214)	407(2)	491(4)	−115(5)	C(15)	715(2)	1(3)	282(4)
C(215)	373(2)	420(4)	−149(5)	C(16)	705(2)	82(3)	285(4)
C(216)	320(2)	411(4)	−94(5)	C(17)	644(2)	125(3)	317(4)
C(221)	215(2)	540(2)	178(4)	C(21)	372(3)	94(4)	372(6)
C(222)	232(2)	533(2)	297(4)	N(21)	367(3)	29(3)	358(6)
C(223)	218(2)	598(2)	387(4)	C(22)	361(3)	−47(2)	353(5)
C(224)	187(2)	669(2)	359(4)	C(23)	418(3)	−103(2)	340(5)
C(225)	171(2)	676(2)	240(4)	C(24)	409(3)	−184(2)	320(5)
C(226)	185(2)	611(2)	150(4)	C(25)	342(3)	−209(2)	314(5)
C	268(2)	215(3)	159(4)	C(26)	284(3)	−153(2)	327(5)
P(3)	353(1)	177(1)	174(2)	C(27)	294(3)	−72(2)	347(5)
C(301)	356(2)	70(2)	113(5)	Cl	396(1)	230(1)	583(2)
C(302)	423(2)	32(2)	102(5)	P	233(1)	687(1)	758(3)
C(303)	428(2)	−50(2)	51(5)	F(1)	219(3)	656(3)	862(5)
C(304)	367(2)	−93(2)	12(5)	F(2)	266(3)	619(3)	731(5)
C(305)	301(2)	−55(2)	24(5)	F(3)	223(3)	762(3)	810(4)
C(306)	295(2)	27(2)	74(5)	F(4)	293(3)	698(3)	800(5)
C(311)	407(3)	213(3)	97(5)	F(5)	243(5)	715(3)	646(6)
C(312)	378(3)	196(3)	−26(5)	F(6)	171(1)	684(2)	720(3)

mer-[FeCl{(Ph₂P)₂CH}(CNPh)₃] (2d).—This was similarly prepared from mer-[FeCl(dppm)(CNPh)₃]PF₆ (1d) (0.18 g, 0.19 mmol) and KOH (2 g, 35 mmol). In this case 3 h of stirring were necessary for complete reaction. Yield 0.13 g (87%).

[Fe{(Ph₂P)CH(AuCl)}(CNPh)₄]ClO₄ (3a).—A solution of complex (2a) (0.091 g, 0.095 mmol) in CH₂Cl₂ (30 cm³) was added dropwise to a solution of [AuCl(tht)] (0.031 g, 0.096 mmol) in CH₂Cl₂ (10 cm³). The resultant mixture was stirred for 10 min, then filtered and the solvent evaporated to dryness until a yellow oily precipitate appeared. The residue was washed and stirred with diethyl ether (30 cm³) until a yellow solid was obtained. The product can be recrystallized from dichloromethane–diethyl ether. Yield 0.1 g (89%).

mer-[FeCl{(Ph₂P)₂CH(AuCl)}(CNPh)₃] (3d).—This was simi-

larly prepared from complex (2d) (0.044 g, 0.054 mmol) and [AuCl(tht)] (0.018 g, 0.056 mmol). Yield 0.035 g (64%).

[{FeI[(Ph₂P)₂CH](CNPh)₃}₂Au]PF₆ (4).—A solution of [Au(tht)₂]PF₆ in thf, prepared from [AuCl(tht)] (0.0317 g, 0.1 mmol), TlPF₆ (0.0347 g, 0.1 mmol), and tht (0.042 g, 0.5 mmol) in thf (10 cm³), was added dropwise (over 1 h) to a stirred solution of mer-[FeI{(Ph₂P)₂CH}(CNPh)₃] (2c) (0.176 g, 0.2 mmol) in thf (20 cm³). The solution was then filtered and the solvent evaporated to dryness. The remaining oil was washed with light petroleum (b.p. 60—80 °C) (20 cm³) until a brown solid was obtained (0.16 g, 77%).

mer-[FeI{(Ph₂P)₂CH(AuPPh₃)}(CNPh)₃]PF₆ (5c).—To a stirred solution of [Au(PPh₃)(tht)]PF₆ in thf, prepared from [AuCl(PPh₃)] (0.05 g, 0.1 mmol), TlPF₆ (0.035 g, 0.1 mmol), tht

(0.042 g, 0.5 mmol), and thf (10 cm^3), a solution of *mer*-[FeI{(Ph$_2$P)$_2$CH}(CNPh)$_3$] (**2c**) (0.088 g, 0.1 mmol) in thf (20 cm^3) was added dropwise over 1 h. The solution was then filtered and the solvent evaporated to dryness. The residue was washed with light petroleum (20 cm^3) until a brown solid was obtained (0.11 g, 74%).

mer-[FeCl{(Ph$_2$P)$_2$CH(AuPPh$_3$)}(CNPh)$_3$]PF$_6$ (**5d**).—To a solution of *mer*-[FeCl(dppm)(CNPh)$_3$]PF$_6$ (0.93 g, 0.1 mmol) and [AuCl(PPh$_3$)] (0.05 g, 0.1 mmol) in CH$_2$Cl$_2$ (20 cm^3), an excess of KOH (2 g, 35 mmol) was added. The mixture was stirred for 45 min. Then the solution was filtered and the solvent evaporated to dryness. The resulting oil was washed with light petroleum (20 cm^3) until an orange solid was obtained (0.1 g, 67%).

[Fe{(Ph$_2$P)$_2$C(AuPPh$_3$)$_2$}(CNPh)$_4$][PF$_6$]$_2$ (**6a**).—This was similarly prepared from [Fe(dppm)(CNPh)$_4$][PF$_6$]$_2$ (**1a'**) (0.08 g, 0.07 mmol), [AuCl(PPh$_3$)] (0.07 g, 0.14 mmol), and an excess of KOH (2 g, 35 mmol). Yield 0.133 g (92%).

mer-[FeI{(Ph$_2$P)$_2$C(AuPPh$_3$)$_2$}(CNPh)$_3$]BPh$_4$ (**6c**).—To a solution of *mer*-[FeI(dppm)(CNPh)$_3$]I (**1c**) (0.1 g, 0.1 mmol) and [AuCl(PPh$_3$)] (0.1 g, 0.2 mmol) in CH$_2$Cl$_2$ (30 cm^3), an excess of KOH (2 g, 35 mmol) was added. The resulting mixture was stirred for 30 min. Then the solution was filtered and NaBPh$_4$ (0.035 g, 0.1 mmol) and ethanol (10 cm^3) added. The mixture was stirred for 1 h. Then the solvent was evaporated to dryness. After extraction with CH$_2$Cl$_2$ (30 cm^3) the solution was filtered and the solvent evaporated to dryness. The resulting oil was washed with diethyl ether (20 cm^3) until a brown solid was obtained. Yield 0.33 g (78%).

mer-[FeCl{(Ph$_2$P)$_2$C(AuPPh$_3$)$_2$}(CNPh)$_3$]PF$_6$ (**6d**).—To a solution of *mer*-[FeCl(dppm)(CNPh)$_3$]PF$_6$ (**1d**) (0.2 g, 0.21 mmol) and [AuCl(PPh$_3$)] (0.21 g, 0.42 mmol) in CH$_2$Cl$_2$ (30 cm^3), an excess of KOH (2 g, 35 mmol) was added. After stirring for 3 h, the solution was filtered, diethyl ether (20 cm^3) was added, and an orange solid corresponding to (**6d**) was obtained. The product can be recrystallized from dichloromethane–diethyl ether. Yield 0.33 g (85%).

[Fe{(Ph$_2$P)$_2$C(AuPPh$_3$)$_2$}(CNC$_6$H$_4$Me-4)$_4$]PF$_6$ (**6e**).—This was similarly prepared from [Fe(dppm)(CNC$_6$H$_4$Me-4)$_4$]-[PF$_6$]$_2$ (**1e**) (0.1 g, 0.083 mmol), [AuCl(PPh$_3$)] (0.084 g, 0.168 mmol), and KOH (2 g, 35 mmol). Yield 0.15 g (85%).

X-Ray Structure Determination of Complex (**6d**).—*Crystal data.* C$_{82}$H$_{65}$Au$_2$ClF$_6$FeN$_3$P$_5$, M = 1 846.5, triclinic, space group $P\bar{1}$, a = 19.325(4), b = 17.430(4), c = 11.906(3) Å, α = 105.03(3), β = 104.62(3), γ = 82.95(3)°, U = 3 741(2) Å^3, Z = 2, D_c = 1.639 g cm^{-3} $F(000)$ = 1 816, λ(Mo-K_α) = 0.710 69 Å, μ = 4.4 mm^{-1}, 288 K, orange tablet, 0.1 × 0.1 × 0.07 mm.

Data collection and reduction. Phillips PW-1100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation, ω-scan technique, scan width 1.2°, and scan speed 0.03° s^{-1}; 7 400 reflections measured (2 ⩽ θ ⩽ 25°), 2 661 assumed as observed with I = 2.5σ(I). Lorentz-polarization and empirical absorption corrections were made. Cell constants determined

from 25 reflections (4 ⩽ θ ⩽ 12°), refined by least-squares method.

Structure solution and refinement. Patterson methods, followed by full-matrix least-squares refinements.[19] Function minimized $\Sigma w(F_o - F_c)^2$, where $w = [\sigma(F_o)^2 + 0.0010(F_o)^2]^{-1}$. Values of f, f', and f'' were taken from ref. 20. In order to reduce the number of refined parameters, phenyl groups were refined with planarity, bond angles and lengths constrained, and an overall anisotropic thermal parameter was used for all atoms of the same phenyl group. The high equivalent thermal parameters for the F atoms of PF$_6$ indicate a disorder which was not determined. Final R and R' values were 0.078 and 0.076. Maximum peak in final difference synthesis 0.4 e Å^{-3}, maximum shift/e.s.d. 0.3 in U_{13} of F(4). Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

References

1 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 124.
2 K. Issleib and H. P. Abicht, *J. Prakt. Chem.*, 1970, **312**, 456.
3 K. Issleib, H. P. Abicht, and H. Winkelmann, *Z. Anorg. Allg. Chem.*, 1972, **388**, 89.
4 H. Schmidbaur and J. R. Mandl, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 640.
5 J. M. Bassett, J. R. Maudl, and H. Schmidbaur, *Chem. Ber.*, 1980, **113**, 1145.
6 J. Browning, G. W. Bushned, and K. R. Dixon, *J. Organomet. Chem.*, 1980, **198**, C11.
7 J. Al-Jibori and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 286.
8 G. M. Dawkins, M. Green, J. C. Jeffery, Clemens Sambale, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 499.
9 M. P. Brown, A. Yavari, Lj. Manojlovic-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1983, **256**, C19.
10 V. Riera and J. Ruiz, *J. Organomet. Chem.*, 1986, **310**, C36.
11 V. Riera, J. Ruiz, and F. Mayor, *J. Organomet. Chem.*, 1984, **276**, 47.
12 J. Al-Jibori and B. L. Shaw, *Inorg. Chim. Acta*, 1983, **74**, 235.
13 J. Al-Jibori, M. Hall, A. T. Hutton, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 863.
14 J. Al-Jibori and B. L. Shaw, *J. Organomet. Chem.*, 1984, **272**, 213.
15 R. Usón, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 839.
16 G. Wilkinson, F. G. A. Stone, and E. W. Abel (eds.), 'Comprehensive Organometallic Chemistry,' Pergamon, Oxford, 1982, vol. 2, p. 779.
17 J. Vicente, M. T. Chicote, J. A. Caynelas, J. Fernández-Baeza, P. G. Jones, G. M. Sheldrick, and P. Espinet, *J. Chem. Soc., Dalton Trans.*, 1985, 1163.
18 C. E. Briant, K. P. Hall, and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **229**, C5.
19 G. M. Sheldrick, SHELX 76, A Computer Program for Crystal Structure Determination, University of Cambridge, 1976.
20 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, pp. 99, 100, and 149.