

Bimetallic Systems. Part 21.¹ Synthesis of Vinylidene- and Phenylene-bridged Complexes of Dinickel(II), Nickel(II)–Palladium(II), and Nickel(II)–Platinum(II) containing Ph₂PCH₂PPh₂ (dppm): Crystal Structures of [(SCN)Ni(μ-dppm)₂(μ-C=CH₂)Ni(NCS)] and [ClPd(μ-dppm)₂(μ-C=CCl₂)NiCl] †

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Treatment of toluene solutions of [Ni(cod)₂] (cod = cyclo-octa-1,5-diene) and Ph₂PCH₂PPh₂ (dppm) (1 : 1.5 mol ratio) with Cl₂C=CH₂ gives the vinylidene-bridged 'A-frame' complex [ClNi(μ-dppm)₂(μ-C=CH₂)NiCl] (**1a**). A better route to (**1a**) involves the combination of [Ni(cod)₂], dppm, and *trans*-[NiCl(CCl=CH₂)(PPh₃)₂] (1 : 2 : 1 mol ratio) in benzene. Treatment of (**1a**) with LiBr, NaI, or KCNS in acetone gives the corresponding dibromide, di-iodide, or di-isothiocyanate complexes (**1b**), (**1c**), or (**1d**). Phenylene- and substituted phenylene-bridged A-frames of the type [XNi(μ-dppm)₂(μ-C₆H₃R)NiX] [X = Cl, R = H (**2a**); X = Br, R = H (**2b**); X = Cl, R = Me (**3**); X = Cl, R = OH (**4**)] have been synthesised similarly, using *trans*-[NiX(C₆H₃RX)(PPh₃)₂]. By treating these substituted vinyl or aryl nickel complexes with [Pd(PPh₃)₄] and dppm, heterobimetallic A-frame complexes of the types [ClPd(μ-dppm)₂(μ-C=CR₂)NiCl] [R = H (**5a**), R = Cl (**5b**)] and [XPd(μ-dppm)₂(μ-C₆H₃R)NiX] [X = Cl, R = H (**6a**); X = Br, R = H (**6b**)] have been obtained. By using [Pt(PPh₃)₄], dppm, and the appropriate nickel complex, [ClPt(μ-dppm)₂(μ-C=CCl₂)NiCl] (**5c**), was obtained but attempts to effect analogous reactions with other nickel complexes gave dinickel A-frames as the only bimetallic products. Hydrogen-1, ³¹P-{¹H}, and ¹H-{³¹P} n.m.r. and i.r. data are given and the crystal structures of [(SCN)Ni(μ-dppm)₂(μ-C=CH₂)Ni(NCS)] (**1d**) and [ClPd(μ-dppm)₂(μ-C=CCl₂)NiCl] (**5b**) have been determined. Crystals of (**1d**) are monoclinic, space group *P2₁/n* (*P2₁/c*, no. 14), *a* = 1 275.7(2), *b* = 1 508.6(3), *c* = 2 636.6(5) pm, β = 99.75(1)°, and *Z* = 4; final *R*' = 0.0481. Crystals of (**5b**) are tetragonal, space group *P4₂,2,2*, *a* = 1 418.3(2), *c* = 2 814.5(3) pm, *Z* = 4; final *R*' = 0.0517.

In contrast to the many and varied complexes of platinum and palladium containing the moiety M¹(μ-dppm)M² (M¹, M² = Pt or Pd; dppm = Ph₂PCH₂PPh₂),^{2–4} there are very few such complexes of nickel. The known dinickel complexes of this type are [Ni₂(μ-CNMe)(CNMe)₃(μ-dppm)₂][PF₆],⁵ containing a metal–metal bond, and the binuclear [Ni₂(NCS)₄(μ-dppm)₂] of uncertain structure.⁶ Recently, we synthesised a limited range of Ni^{II}Hg^{II} and Ni^{II}Au^I heterobimetallics of type [(RC≡C)₂Ni(μ-dppm)₂HgCl₂] and [(RC≡C)₂Ni(μ-dppm)₂Au]Cl.⁷ These complexes are very labile but we reasoned that the incorporation of an additional, strongly bridging group (X) might give much less labile bimetallic systems containing at least one nickel atom. In this paper systematic syntheses of stable complexes containing the moiety Ni(μ-dppm)₂(μ-X)M, where M = Ni, Pd, or Pt and X = vinylidene or substituted vinylidene, or phenylene or substituted phenylene are reported.

Results and Discussion

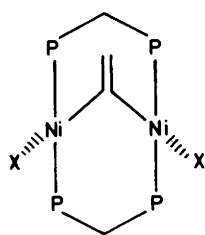
Balch *et al.*⁸ have used two-centre, three-fragment, oxidative-addition reactions of ICH₂I or *o*-C₆H₄I₂ with [Pd₂(dppm)₃] to generate 'A-frames' of the type [Pd₂I₂(μ-dppm)₂(μ-X)] (X = -CH₂- or *o*-C₆H₄). We have now done a similar synthesis, reacting [Ni(cod)₂] (cod = cyclo-octa-1,5-diene), dppm, and Cl₂C=CH₂ together at -30 °C, giving the dinickel (A-frame)

complex [ClNi(μ-dppm)₂(μ-C=CH₂)NiCl] (**1a**), albeit in poor yield (38%); preparative details are in the Experimental section. A much better synthesis was to treat *trans*-[NiCl(CCl=CH₂)(PPh₃)₂] with dppm and [Ni(cod)₂] at *ca.* 20 °C for 10 min, after which the red-purple dinickel complex (**1a**) was isolated in 74% yield. The formulation follows from (i) the elemental analysis (C, H, and Cl, Table 1), (ii) the i.r. spectrum, which showed a weak band at *ca.* 1 580 cm⁻¹ [ν(C=C)], and a strong band at 314 cm⁻¹ [ν(Ni-Cl)], and (iii) the ³¹P-{¹H}, ¹H, and ¹H-{³¹P} n.m.r. spectra (data in Table 2). In particular, the ³¹P-{¹H} spectrum showed a singlet, temperature-invariant resonance due to the bridging dppm groups; the ¹H-{³¹P} spectrum showed an AX pattern due to the dppm methylenes and a singlet due to the C=CH₂ protons. In the ¹H spectrum each of the AX hydrogens gave a 1:4:6:4:1 quintet pattern due to virtual coupling to all four phosphorus nuclei; similarly, the vinylidene protons gave rise to a virtually coupled 1:4:6:4:1 quintet (Table 2). The dinickel complex (**1a**) is stable in dichloromethane solution (the ³¹P-{¹H} n.m.r. spectrum remained unchanged over 72 h at 20 °C). It is surprisingly stable thermally, melting with decomposition above 200 °C. The chloride ligands are readily replaced by bromide, iodide, or thiocyanate, by treatment with LiBr, NaI, or KSCN respectively in acetone solution, to give (**1b**), (**1c**), or (**1d**) respectively; preparative details are in the Experimental section and characterising data in Tables 1 and 2. The crystal structure of the di-isothiocyanate has been determined (see below).

Various attempts to replace the chloride ligands in (**1a**) with acetylides failed. Treatment with Hg(C≡CPh)₂ at 60 °C in ethanol caused no reaction, neither did treatment with NaOMe-HC≡CPh-MeOH and treatment with LiC≡CPh-tetrahydrofuran (thf) caused decomposition. Treatment with TlPF₆-

† Bis-μ-[bis(diphenylphosphino)methane]-μ-vinylidene-bis[isothiocyanatonickel(II)] and -1,2-dichloro-μ-dichlorovinylidene-nickel(II)-palladium(II) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

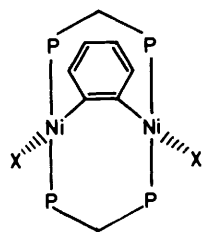


(1a) X = Cl

(1b) X = Br

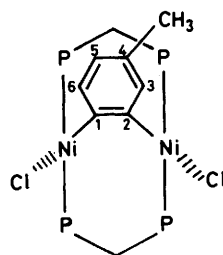
(1c) X = I

(1d) X = NCS

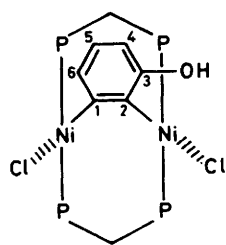


(2a) X = Cl

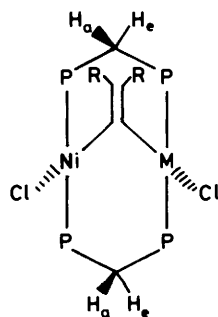
(2b) X = Br



(3)



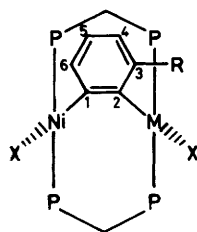
(4)



(5a) M = Pd, R = H

(5b) M = Pd, R = Cl

(5c) M = Pt, R = Cl



(6a) R = H, X = Cl, M = Pd

(6b) R = H, X = Br, M = Pd

(6c) R = OH, X = Cl, M = Pd

NEt₃-HC≡CPh in dichloromethane-acetone gave no nickel acetylide derivative but a cationic product, possibly [Ni₂(Me₂-CO)₂(μ-dppm)₂(μ-C≡CH₂)] [PF₆]₂, was formed but could not be isolated pure. It is surprising that dinickel acetylides could not be made since there are many examples of stable nickel acetylide complexes of the type *trans*-[Ni(C≡CR)₂(PR'₃)₂].^{9,10} On treatment of (1a) with an excess of *p*-tolylmagnesium bromide no replacement of Cl by *p*-tolyl was detected and only the dibromide (1b) was isolated from the reaction mixture. Treatment of the dichloride (1a) with methylmagnesium bromide, phenylmagnesium bromide, phenyl-lithium, or *n*-butyl-lithium caused extensive decomposition to dark, unidentified, products. Similarly, attempts to protonate the vinylidene group in (1a) by treatment with HBF₄·Et₂O, or to methylate it by treatment with Me₃OBf₄, gave dark, tarry products.

We then attempted to extend this synthesis by using bridging phenylene groups instead of the vinylidene group. The required mononuclear nickel intermediates were made by an extension of the method reported for *trans*-[NiCl(CCl=CH₂)(PPh₃)₂],¹¹ which we used for the syntheses described above.

Treatment of a mixture of nickel(II) tetrafluoroborate, PPh₃, and 1,2-dichloro- or 1,2-dibromo-benzene with NaBH₄ in ethanol gave *trans*-[NiX(C₆H₄X)(PPh₃)₂] (X = Cl or Br) in ca. 50% yields. A similar reaction using 1,2-dichloro-4-methylbenzene gave, as might be expected, a mixture of two isomers of *trans*-[NiCl(C₆H₃ClMe)(PPh₃)₂] (based on micro-analytical and n.m.r. evidence), depending on which of the two chlorines in 1,2-dichloro-4-methylbenzene had been replaced by nickel. When this mixture was recrystallised from dichloromethane-ethanol, a single isomer was obtained in 22% yield; characterising data are in Tables 1 and 2. We do not know whether in this product the C₆H₃ClMe group is 2-chloro-4-methyl or 2-chloro-5-methyl but for subsequent syntheses of dinickel complexes, it does not matter. Treatment of nickel(II) tetrafluoroborate, PPh₃, and 2,3-dichlorophenol with NaBH₄ in ethanol gave *trans*-[NiCl{C₆H₃Cl(OH)}(PPh₃)₂] in 20% yield, as a single isomer; characterising data are in Tables 1 and 2 and preparative details in the Experimental section. It seems likely that, for steric reasons, the nickel would replace the chlorine in the 3-position of 2,3-dichlorophenol much faster than the chlorine in the 2-position and that the product is therefore *trans*-chloro(2-chloro-3-hydroxyphenyl)bis(triphenylphosphine)nickel(II).

Treatment of a benzene solution of [Ni(cod)₂] and dppm

Table 1. Microanalytical^a and i.r. data^b (cm⁻¹)

Complex	Analysis (%)			ν(M-X)	Other
	C	H	Halogen		
(1a)	63.1 (63.5)	4.7 (4.7)	7.2 (7.2)	314m	
(1b)	58.3 (58.4)	4.3 (4.4)	14.3 (14.9)	225m	
(1c)·0.5CH ₂ Cl ₂	51.6 (52.2)	4.0 (3.9)	20.5 (21.0) ^c		
(1d)	63.15 (63.1)	4.55 (4.5)	2.55 (2.7) ^d		2 095s [ν(NCS)]
(2a)	65.3 (65.1)	4.65 (4.65)	6.6 (6.9)		
(2b)	60.1 (60.0)	4.4 (4.7)	14.4 (14.3)		
(3)	65.35 (65.4)	4.75 (4.8)	6.65 (6.8)		
(4)	63.9 (64.1)	4.6 (4.6)	7.3 (6.9)		3 510w [ν(O-H)]
(5a)	60.7 (60.6)	4.4 (4.5)	7.0 (6.9)	274, 310	
(5b)	56.85 (56.8)	4.3 (4.0)	11.9 (12.9)	280, 314	
(5c)	52.0 (52.5)	3.7 (3.7)	11.2 (11.9)	282, 312	
(6b)	57.3 (57.5)	4.1 (4.1)	13.5 (13.7)		
(6c)					3 520w [ν(O-H)]
[NiCl(C ₆ H ₃ ClMe)(PPh ₃) ₂]	67.3 (67.6)	5.2 (4.6)	9.0 (9.5)	353m	
[NiCl{C ₆ H ₃ Cl(OH)}(PPh ₃) ₂]	69.2 (69.7)	4.0 (4.9)	9.8 (9.5)	358m	3 500w [ν(O-H)]

^a Calculated values in parentheses. ^b Nujol mulls. ^c Iodine analysis. ^d Nitrogen analysis.

Table 2. N.m.r. spectroscopic data

Compound	³¹ P N.m.r. (δ/p.p.m.) ^a	¹ H and ¹ H- ³¹ P n.m.r. (δ/p.p.m.) ^b
(1a)	19.3 (s)	4.36 [2 H, -C=CH ₂ , J(PH) = 4.0], 3.13 and 2.23 [4 H, PCH _A H _X P, J(H _A H _X) = 12.9, J(PH) = 5.6 and 3.5 respectively]
(1b)	21.3 (s)	4.40 [2 H, μ-C=CH ₂ , J(PH) = 4.6], 3.19 and 2.25 [4 H, PCH _A H _X P, J(H _A H _X) = 13.0, J(PH) = 5.6 and 3.6 respectively] ^c
(1c)	25.3 (s)	4.47 [2 H, μ-C=CH ₂ , J(PH) = 4.4], 3.28 and 2.40 [4 H, PCH _A H _X P, J(H _A H _X) = 13.3, J(PH) = 5.6 and 3.5 respectively]
(1d)	23.5 (s)	4.26 [2 H, μ-C=CH ₂ , J(PH) = 4.6], 3.06 and 2.26 [4 H, PCH _A H _X P, J(H _A H _X) = 13.2, J(PH) = 5.8 and 3.6 respectively]
(2a)	5.0 (s)	5.92 and 5.42 [4 H, AA'XX', C ₆ H ₄ , N = 5.5 ^d], 2.17 and 1.13 [4 H, PCH _A H _X P, J(H _A H _X) = 12.1, J(PH) = 4.2 and 5.5 respectively]
(2b)	6.25 (s)	5.99 and 5.65 (AA'BB', C ₆ H ₄), 2.14 and 1.24 [4 H, PCH _A H _X P, J(H _A H _X) = 12.2, J(PH) = 4.4 and 5.1 respectively]
(3)	4.98, 4.78 (AA'BB') ^e	5.78 and 5.34 [H ⁶ and H ⁵ , J(H ⁶ H ⁵) = 7.5], 5.03 (H ³), 2.12 and 1.13 [4 H, PCH _A H _X P, J(H _A H _X) = 12.1, J(PH) = 4.1 and 6.0 respectively], 1.50 (CH ₃)
(4)	2.79, 2.56 (AA'BB')	5.94 [H ⁵ , J(H ⁵ H ^{4,6}) = 7.5], 5.66 and 5.23 (H ⁴ , H ⁶), 4.6 (OH), 2.25 and 1.55 [4 H, PCH _A H _X P, J(H _A H _X) = 12.3, J(PH) = 4.3 and 6.3 respectively]
(5a) ^g	^e 18.6 and 15.3 [AA'BB', ² J(AA') = 379, ² J(BB') = 285, ² J(AB) = 87, ⁴ J(AB') = -3.8]	4.89 and 4.70 [2 H, μ-C=CH ₂ H _X , J(H _A H _X) = 4.5 ^h], 3.32 and 2.41 [4 H, PCH _A H _X P, J(H _A H _X) = 13.0, J(PH) = 5.5 and 3.4 respectively]
(5b) ^g	11.3 and 8.3 [AA'BB', ² J(AA') = 441, ² J(BB') = 334, ² J(AB) = 55, ⁴ J(AB') = -4.8]	3.26 and 2.72 [4 H, PCH _A H _X P, J(H _A H _X) = 12.9, J(PH) = 5.4 and 3.6 ⁱ]
(5c)	^e 8.2 [P(Ni), ² J(PtP) = 177], 7.3 [P(Pt), ¹ J(PtP) = 3 081, N = 35 ^d]	3.42 and 2.72 [4 H, PCH _A H _X P, J(H _A H _X) = 13.1, J(PH) = 5.6 and 3.3 respectively, ⁱ J(PtH) = 34.0 ^j]
(6a) ^k	8.3, 6.3 (AA'BB')	6.14 and 5.92 [H ^{4,5} , J(H-H _{ortho}) = 7.2, J(H-H _{meta}) = 1.3], 5.73 and 5.15 [H ^{3,6} , J(H-H _{ortho}) = 7.2, J(H-H _{meta}) = 1.3], 2.33 and 1.46 [PCH _A H _X P, J(H _A H _X) = 12.2, J(PH) = 4.2 and 5.3 respectively] ^l
(6b)	8.5, 6.9 (AA'BB'), N = 59 ^d	5.89 [H ⁵ , ³ J(H ⁵ H ^{4,6}) 7.5], 5.76 and 4.98 [H ⁴ and H ⁶], 4.64 (OH), 2.41 and 1.68 [4 H, PCH _A H _X P, J(H _A H _X) = 12.2, J(PH) = 4.0 and 5.5 respectively]
(6c)	6.4, 3.9 (AA'BB'), N = 45 ^d	6.63 and 5.92 [H ⁶ and H ⁴ , J(H-H _{ortho}) = 7.4, J(H-H _{meta}) = 1.4], 6.25 [H ⁵ , J(H-H _{ortho}) = 7.4] See Results and Discussion
[NiCl{C ₆ H ₃ Cl(OH)}(PPh ₃) ₂]	21.8	
[NiCl(C ₆ H ₃ ClMe)(PPh ₃) ₂]	21.3	

^a ³¹P-¹H N.m.r. spectra at 40.3 MHz in CH₂Cl₂-CD₂Cl₂ for compounds (1a)–(1d), (2a), (2b), (4), and the two mononuclear compounds. Compounds (3), (6a)–(6c), (5a)–(5c) were measured at 162 MHz. ^b Hydrogen-1 and ¹H-³¹P n.m.r. spectra measured at 400 MHz, unless stated otherwise. Values of J(PH) are virtual couplings, see Results and Discussion. The two dpmm methylene hydrogens H_A and H_X have not been assigned as pseudo-equatorial or pseudo-axial, except for compound (5c), see Results and Discussion. ^c Recorded at 100 MHz in CD₂Cl₂. ^d N = |²J(AX) + ⁴J(AX')|. ^e At 162 MHz. ^f The substituted bridging arene groups are numbered from Ni (C¹) such that M (Ni or Pd) is at C². ^g The coupling constants for the ³¹P-¹H n.m.r. spectrum were obtained by computer simulation using PANIC. ^h Complex multiplets observed in the ¹H n.m.r. spectrum due to coupling with P_A and P_B were not resolved. ⁱ Couplings to P_A and P_B were not resolved. ^j Platinum-195 coupling was observed to the high-field portion of the methylene region only. ^k Contaminated with (2a), see Results and Discussion.

(1:2 mol ratio) with 1 mol equiv. of *trans*-[NiCl(C₆H₄Cl-2)-(PPh₃)₂] gave, after 3 h at 20 °C, a 20% yield of the desired phenylene-bridged dinickel complex [ClNi(μ-dppm)₂(μ-C₆H₄)NiCl]. The formulation follows from the elemental analysis (C, H, and Cl) and particularly from the n.m.r. data. The ³¹P-¹H n.m.r. resonance was a singlet and the ¹H pattern of the phenylene protons was of the AA'XX' type and at a much higher field than the normal arene region, as has been noted previously for [Pd₂I₂(μ-dppm)₂(μ-C₆H₄)].⁸ The dpmm methylene protons also resonated at unusually high field, giving an AX pattern in the ¹H-³¹P spectrum (data in Table 2). In the ¹H n.m.r. spectrum the resonances due to the methylene protons are each split into a 1:4:6:4:1 quintet due to virtual coupling to all four P nuclei, with the apparent coupling constants, J(P-H), *i.e.* separation between adjacent peaks, given in Table 2.

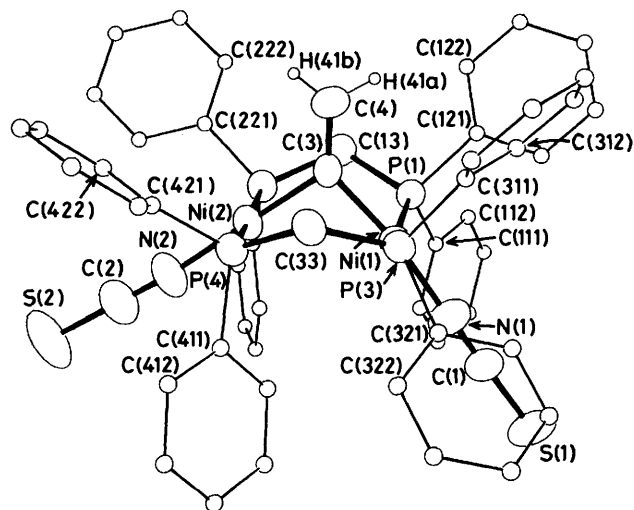
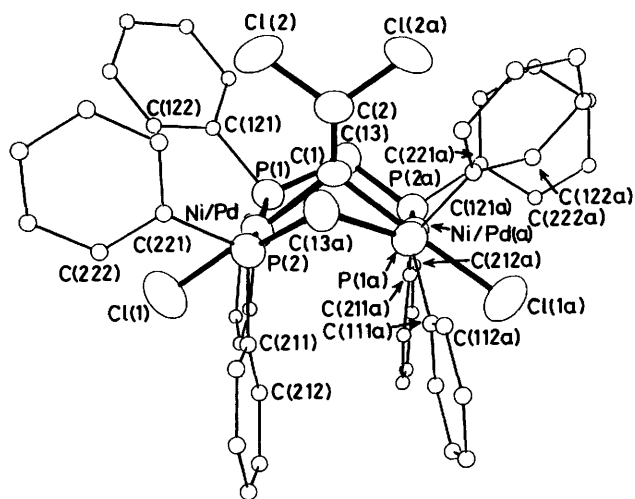
Treatment of a mixture of [Ni(cod)₂] and dpmm with *trans*-[NiCl(C₆H₃ClMe)(PPh₃)₂] or with *trans*-[NiCl{C₆H₃Cl(OH)}(PPh₃)₂] gave, respectively, the 4-methylphenylene and the 3-hydroxyphenylene dinickel complexes (3) and (4). These

formulations follow from the microanalytical and i.r. data (Table 1); the phenolic compound (4) showed an i.r. absorption band at 3 510 cm⁻¹ due to ν(O-H); and the ³¹P-¹H n.m.r. spectrum of (3) was of the AA'BB' type at 162 MHz. The ¹H n.m.r. patterns for the dpmm protons of both (3) and (4) were similar to those of (2a) and (2b) and the phenylene protons gave essentially first-order patterns at 162 MHz; data for these protons and for the Me protons in (3) and the OH proton in (4) are given in Table 2.

Our success in synthesising dinickel complexes led us to investigate whether the use of Pd⁰ or Pt⁰ in place of Ni⁰ would enable us to synthesise analogous nickel-palladium and nickel-platinum complexes. Treatment of a 1:2 mol ratio of [Pd(PPh₃)₄] and dpmm with [NiCl(CCl=CH₂)(PPh₃)₂] (1 mol equiv.) in benzene at *ca.* 80 °C for 30 min gave a moderate yield (24%) of [ClPd(μ-dppm)₂(μ-C=CH₂)NiCl] (5a). Although the microanalytical data were good (Table 1) the ³¹P-¹H n.m.r. spectrum showed that the product was contaminated with a few percent of the dinickel complex (1a), which we could not

Table 3. Selected interatomic distances (pm) and angles ($^{\circ}$) for complex (**1d**) with estimated standard deviations (e.s.d.s) in parentheses

Ni(2)–Ni(1)	284.0(4)	N(2)–Ni(2)	189.7(7)	N(1)–Ni(1)	187.6(7)	N(2)–C(2)	115.4(9)
P(1)–Ni(1)	219.4(3)	C(3)–Ni(2)	188.5(7)	C(3)–Ni(1)	187.1(7)	C(4)–C(3)	113.4(9)
P(3)–Ni(1)	220.0(3)	N(1)–C(1)	117.5(8)	P(2)–Ni(2)	219.9(3)	C(1)–S(1)	160.2(8)
				P(4)–Ni(2)	219.4(30)	C(2)–S(2)	162.8(8)
P(1)–Ni(1)–Ni(2)	93.4	C(3)–Ni(2)–Ni(1)	40.7(1)	C(3)–Ni(1)–P(1)	85.9(2)	C(2)–N(2)–Ni(2)	173.8(5)
P(3)–Ni(1)–Ni(2)	95.1	C(3)–Ni(2)–P(2)	87.9(2)	C(3)–Ni(1)–P(3)	85.4(2)	Ni(2)–C(3)–Ni(1)	98.3(3)
P(3)–Ni(1)–P(1)	155.3(1)	C(3)–Ni(2)–P(4)	88.0(2)	C(3)–Ni(1)–N(1)	171.5(2)	C(4)–C(3)–Ni(1)	133.9(4)
N(1)–Ni(1)–Ni(2)	130.5(1)	C(3)–Ni(2)–N(2)	178.5(2)	P(4)–Ni(2)–P(2)	173.1(1)	C(4)–C(3)–Ni(2)	127.8(5)
N(1)–Ni(1)–P(1)	95.9(2)	N(1)–C(1)–S(1)	178.7(5)	N(2)–Ni(2)–P(2)	93.5(2)	P(2)–C(13)–P(1)	112.1(4)
N(1)–Ni(1)–P(3)	96.2(2)	C(1)–N(1)–Ni(1)	178.9(4)	N(2)–Ni(2)–P(4)	90.5(2)	P(4)–C(33)–P(3)	112.1(3)
C(3)–Ni(1)–Ni(2)	41.0(1)	N(2)–C(2)–S(2)	179.3(5)				

**Figure 1.** Crystal structure of $[(\text{SCN})\text{Ni}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{Ni}(\text{NCS})]$ (**1d**). The non-phenyl atoms have been drawn with 30% probability ellipsoids**Figure 2.** Crystal structure of $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CCl}_2)\text{NiCl}]$ (**5b**). The non-phenyl atoms have been drawn with 30% probability ellipsoids

remove. However, by heating a mixture of $[\text{Pd}\{\text{PhCH}=\text{C}(\text{O})\text{CH}=\text{CHPh}\}_2]$, dppm, and $[\text{NiCl}(\text{CCl}=\text{CCl}_2)(\text{PPh}_3)_2]$ in benzene for 2 min, we obtained $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CCl}_2)\text{NiCl}]$ (**5b**) in 29% yield, which was free from binuclear nickel complexes. Both (**5a**) and (**5b**) showed well defined AA'BB'

Table 4. Selected interatomic distances (pm) and angles ($^{\circ}$) for complex (**5b**) with e.s.d.s in parentheses*

P(1)–Pd(1)	227.9(4)	C(13)–P(1a)	183.6(9)
P(2)–Pd(1)	225.2(4)	C(13)–P(2)	184.9(10)
Cl(1)–Pd(1)	230.3(4)	C(2)–Cl(2)	174.8(9)
C(1)–Pd(1)	193.7(8)	C(2)–C(1)	129.0(14)
Pd(1)–Pd(1a)	309.1(4)		
P(1)–Pd(1)–Pd(1a)	91.1(2)	C(13a)–P(1)–Pd(1)	114.7(3)
P(2)–Pd(1)–Pd(1a)	87.3(2)	C(13)–P(2)–Pd(1)	116.2(4)
P(2)–Pd(1)–P(1)	169.8(1)	C(2)–C(1)–Pd(1)	127.1(3)
Cl(1)–Pd(1)–P(1)	94.5(2)	Pd(1a)–C(1)–Pd(1)	105.8(5)
Cl(1)–Pd(1)–P(2)	92.6(2)	C(1)–C(2)–Cl(2)	124.8(4)
C(1)–Pd(1)–Pd(1a)	37.1(1)	Cl(2a)–C(2)–Cl(2)	110.3(4)
C(1)–Pd(1)–P(1)	85.8(2)	P(1a)–C(13)–P(2)	111.1(5)
C(1)–Pd(1)–P(2)	86.8(2)		
C(1)–Pd(1)–Cl(1)	177.8(2)		

* Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): (a) y, x, –z.

$^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra, which were fully analysed (see Table 2) but we do not know which resonances are associated with which P nuclei. The dppm methylene resonances showed similar ^1H and $^1\text{H}\{-^31\text{P}\}$ patterns to those of the dinickel complexes discussed above.

Mixed nickel–platinum complexes were much more difficult to make, thus, under all conditions tried $[\text{Pt}(\text{PPh}_3)_4]$, dppm, and $[\text{NiCl}(\text{CCl}=\text{CH}_2)(\text{PPh}_3)_2]$ in 1:2:1 mol ratio gave in good yield the dinickel complex (**1a**) as the only nickel-containing product. However, treatment of $[\text{NiCl}(\text{CCl}=\text{CCl}_2)(\text{PPh}_3)_2]$ with $[\text{Pt}(\text{PPh}_3)_4]$ and dppm gave the desired nickel–platinum complex $[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CCl}_2)\text{NiCl}]$ (**5c**), albeit in 12% yield; characterising microanalytical and i.r. data are in Table 1 and n.m.r. data in Table 2. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum at 162 MHz was of the AA'XX' + AA'MXX' type ($M = ^{195}\text{Pt}$). In the $^1\text{H}\{-^31\text{P}\}$ n.m.r. spectrum only one of the $\text{PCH}_2\text{H}_2\text{P}$ protons was coupled to platinum, $^3J(\text{Pt}-\text{H}) = 34.0$ Hz, and this was clearly H_e , with the torsion angle $\text{Pt}-\text{P}-\text{C}-\text{H}$ ca. 180° for the reasons we have discussed previously;¹² H_e thus resonates at higher field than H_a , in this case.

Some heterobimetallics with bridging phenylene groups were also prepared. On heating a mixture of $[\text{Pd}(\text{PPh}_3)_4]$, dppm, and $[\text{NiBr}(\text{C}_6\text{H}_4\text{Br}-2)(\text{PPh}_3)_2]$ in benzene the required complex $[\text{BrPd}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_4)\text{NiBr}]$ (**6b**) was formed and isolated in 54% yield; preparative details are in the Experimental section and characterising data in Tables 1 and 2. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum at 162 MHz was of the AA'BB' type. The four non-equivalent phenylene protons gave a well defined AMPX pattern at 400 MHz, with both *ortho* (7.2 Hz) and *meta* (1.3 Hz) couplings well resolved (see Table 2 for data). However, treatment of $[\text{NiCl}(\text{C}_6\text{H}_4\text{Cl}-2)(\text{PPh}_3)_2]$ with $[\text{Pd}(\text{PPh}_3)_4]$ and

dppm probably gave the required product (**6a**) but this was contaminated with the dinickel complex (**2a**), which we could not remove. The impure heterobimetallic complex (**6a**) was thus only characterised by its AA'BB' ^{31}P - $\{^1\text{H}\}$ n.m.r. pattern (Table 2).

We have also treated the phenolic nickel complex $[\text{NiCl}\{\text{C}_6\text{H}_3\text{Cl}(\text{OH})\}(\text{PPh}_3)_2]$ with $[\text{Pd}(\text{PPh}_3)_4]$ and dppm and obtained a product, which we formulate as $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_3\text{OH})\text{NiCl}]$ (**6c**); details are in the Experimental section. The product contained ca. 10% of the dinickel complex (**4**), which we could not remove, but the spectroscopic data suggest that ca. 90% of the product was the desired nickel-palladium complex (**6c**): the product showed a sharp band at $3\ 520\ \text{cm}^{-1}$ in its i.r. spectrum due to $\nu(\text{O}-\text{H})$ and showed the expected type of AA'BB' ^{31}P - $\{^1\text{H}\}$ n.m.r. pattern (Table 2). The ^1H and ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra showed patterns typical of three adjacent phenylene hydrogens, an O-H resonance and resonances due to H_c and H_a of the two dppms in the A-frame (Table 2). It seems more likely that the nickel in (**6c**) is *meta* to the OH group, for the reasons discussed above, and that the palladium is therefore *ortho* to the OH group.

*Crystal Structures of $[(\text{SCN})\text{Ni}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{Ni}(\text{NCS})]$ (**1d**) and $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CCl}_2)\text{NiCl}]$ (**5b**).—*Crystals of (**1d**) and (**5b**) were grown by diffusion of di-isopropyl ether into 1,2-dichloroethane solutions. Both crystallised without solvent of crystallisation. The structure of the dinickel di-isothiocyanate complex (**1d**) is shown in Figure 1, with selected data in Table 3, and the nickel-palladium complex (**5b**) is shown in Figure 2, with data in Table 4. In both structures the metal centres are linked by two *trans*-dppm bridges, giving eight-membered $\text{Ni}_2\text{Pd}_2\text{M}$ [$\text{M} = \text{Ni}$ (**1d**), $\text{M} = \text{Pd}$ (**5b**)] rings. The $\text{M}\cdots\text{M}$ separations in both complexes are longer than would be expected for M-M bonding. The structure of (**5b**) is disordered, with equal populations of $\text{Pd}\cdots\text{Ni}$ and $\text{Ni}\cdots\text{Pd}$ molecules, so that the bond lengths in Table 4 are all averages of Pd-X and Ni-X. This presumably arises because the environments of Ni and Pd are closely similar, this being borne out by the ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum, in which all four P nuclei have very similar chemical shifts. However, in the structure of (**1d**) the two Ni environments are not identical. While square-planar geometry pertains around Ni(1), that around Ni(2) is distorted, the P-Ni-P angle being 155° . As the ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum of (**1d**) is a singlet down to -60°C this distortion is presumably either due to crystal packing forces or to the geometric demands of the N-C-S and bridging vinylidene moieties.

Experimental

The complexes $[\text{Ni}(\text{cod})_2]$,¹³ $[\text{NiCl}(\text{CCl}=\text{CR}_2)(\text{PPh}_3)_2]$,¹¹ and $[\text{PdCl}(\text{CCl}=\text{CR}_2)(\text{PPh}_3)_2]$ ¹⁴ were prepared by literature methods or modifications thereof. General methods and instrumentation used were as described in earlier publications from this laboratory.¹⁵

$[\text{ClNi}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{NiCl}]$ (**1a**).—*Method (i)*. A solution of $[\text{Ni}(\text{cod})_2]$ (0.27 g, 1.0 mmol) in toluene ($20\ \text{cm}^3$) was treated with dppm (0.576 g, 1.5 mmol) and the resultant mixture was stirred for 10 min under argon. The solution was then cooled to -30°C and $\text{Cl}_2\text{C}=\text{CH}_2$ (1.0 g, 10.3 mmol) was added with stirring. The solution was allowed to warm up to room temperature over 30 min and then evaporated to ca. $10\ \text{cm}^3$; this gave the required product (0.37 g, 38%).

Method (ii). A solution of $[\text{Ni}(\text{cod})_2]$ (0.27 g, 1.0 mmol) in benzene ($15\ \text{cm}^3$) was treated with dppm (0.77 g, 2.0 mmol). The resultant solution was stirred for 10 min, then treated with $[\text{NiCl}(\text{CCl}=\text{CH}_2)(\text{PPh}_3)_2]$ (0.67 g, 1.0 mmol) and the mixture

stirred for 45 min at ca. 20°C . This gave the required product, as purple-red microcrystals, which were filtered off (0.73 g, 74%).

$[\text{Ni}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{NiCl}]$ (**1c**).— $[\text{ClNi}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{NiCl}]$ (0.25 g, 0.27 mmol) was added to a solution of sodium iodide (0.41 g) in acetone ($20\ \text{cm}^3$). The mixture was stirred for ca. 2 min and then evaporated to dryness under reduced pressure. The required product was extracted into dichloromethane and formed deep purple microcrystals from dichloromethane-methylcyclohexane. Yield 0.24 g (82%).

$[\text{BrNi}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{NiBr}]$ (**1b**) was similarly prepared, in 79% yield, as red microcrystals.

$[(\text{SCN})\text{Ni}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{Ni}(\text{NCS})]$ (**1d**) was similarly prepared, in 86% yield, as orange microcrystals.

$[\text{ClNi}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_4)\text{NiCl}]$ (**2a**).— $[\text{NiCl}(\text{C}_6\text{H}_4\text{Cl}-2)(\text{PPh}_3)_2]$ (0.73 g, 1.0 mmol) was added with stirring to a solution of $[\text{Ni}(\text{cod})_2]$ (0.27 g, 1.0 mmol) and dppm (0.77 g, 2.0 mmol) in benzene ($15\ \text{cm}^3$). After 3 h the precipitate was filtered off, washed with benzene and diethyl ether, and recrystallised from dichloromethane-ethanol to give the required product as light brown microcrystals (0.20 g, 20%).

$[\text{BrNi}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_4)\text{NiBr}]$ (**2b**) was prepared similarly, using $[\text{NiBr}(\text{C}_6\text{H}_4\text{Br}-2)(\text{PPh}_3)_2]$, in 24% yield as a yellow solid.

$[\text{ClNi}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_3\text{Me}-4)\text{NiCl}]$ (**3**) was prepared similarly from $[\text{NiCl}(\text{C}_6\text{H}_3\text{ClMe})(\text{PPh}_3)_2]$, in 18% yield as a yellow solid.

$[\text{ClNi}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_3\text{OH}-3)\text{NiCl}]$ (**4**) was prepared similarly using $[\text{NiCl}\{\text{C}_6\text{H}_3\text{Cl}(\text{OH})\}(\text{PPh}_3)_2]$ in 20% yield as a brown solid.

$[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)\text{NiCl}]$ (**5a**).—*trans*- $[\text{NiCl}(\text{CCl}=\text{CH}_2)(\text{PPh}_3)_2]$ (0.238 g, 0.35 mmol) was added to a solution prepared by treating $[\text{Pd}(\text{PPh}_3)_4]$ (0.400 g, 0.366 mmol) in benzene ($15\ \text{cm}^3$) with dppm (0.280 g, 0.732 mmol). The resultant mixture was stirred for 3 h and then evaporated to dryness. The residue was triturated with diethyl ether and then methanol, to give the required product, as red microcrystals (0.087 g, 24%).

$[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CCl}_2)\text{NiCl}]$ (**5b**).— $[\text{NiCl}(\text{CCl}=\text{CCl}_2)(\text{PPh}_3)_2]$ (0.260 g, 0.35 mmol) was added to a solution, prepared from $[\text{Pd}\{\text{PhCH}=\text{CHC}(\text{O})\text{CH}=\text{CHPh}\}_2]$ (0.210 g, 0.366 mmol) and dppm (0.280 g, 0.728 mmol) in benzene ($10\ \text{cm}^3$). The mixture was then heated to boiling for 2 min, cooled, and the orange precipitate collected. This, when recrystallised from dichloromethane-methanol, gave the required product (0.11 g, 29%).

$[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-C}=\text{CCl}_2)\text{NiCl}]$ (**5c**).— $[\text{NiCl}(\text{CCl}=\text{CCl}_2)(\text{PPh}_3)_2]$ (0.135 g, 0.18 mmol) was added to a solution prepared from $[\text{Pt}(\text{PPh}_3)_4]$ and dppm (0.137 g, 0.355 mmol) in benzene ($8\ \text{cm}^3$). The resultant solution was heated under reflux for 2 h, after which the precipitate was collected and recrystallised from dichloromethane-methanol, to give the required product (0.026 g, 12%).

$[\text{BrPd}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_4)\text{NiBr}]$ (**6b**).— $[\text{NiBr}(\text{C}_6\text{H}_4\text{Br}-2)(\text{PPh}_3)_2]$ (0.41 g, 0.5 mmol) was added to a solution prepared from $[\text{Pd}(\text{PPh}_3)_4]$ (0.58 g, 0.05 mmol) and dppm (0.39 g, 1.0 mmol) in benzene (cm^3). The mixture was then refluxed for 1 h, cooled, and the resultant orange crystals of the required product isolated (0.30 g, 54%).

$[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_4)\text{NiCl}]$ (**6a**) was prepared similarly, using $[\text{NiCl}(\text{C}_6\text{H}_4\text{Cl}-2)(\text{PPh}_3)_2]$, but was contaminated with $[\text{Ni}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_4)]$.

$[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C}_6\text{H}_3\text{OH}-3)\text{NiCl}]$ (**6c**) was prepared similarly, using $[\text{NiCl}\{\text{C}_6\text{H}_3\text{Cl}(\text{OH})\}(\text{PPh}_3)_2]$, in ca. 17% yield, but was contaminated with some of the dinickel compounds (see Results and Discussion and Table 2).

[NiCl(C₆H₃ClMe)(PPh₃)₂].—A solution of sodium tetrahydroborate (0.075 g, 2.0 mmol) in ethanol (10 cm³) was added dropwise to a stirred solution of [Ni(OH₂)₆][BF₄]₂ (0.34 g, 1.0 mmol), PPh₃ (0.79 g, 3.0 mmol), and 1,2-dichloro-4-methylbenzene (0.81 g, 5.0 mmol) in ethanol (40 cm³) at 20 °C. The mixture was then stirred for 2 h, after which the resultant orange precipitate was isolated, washed with 1% hydrochloric acid, water (3 cm³), and ethanol (3 cm³) and then dried. It formed orange microcrystals from dichloromethane–ethanol. Yield 0.16 g, 21.5%.

[NiCl{C₆H₃Cl(OH)}(PPh₃)₂] was prepared analogously but at 50 °C. It formed yellow microcrystals from dichloromethane–ethanol. Yield 20%.

X-Ray Studies.—All crystallographic measurements were made using a Nicolet P3/F diffractometer operating in the ω – 2θ scan mode using graphite-monochromated Mo- K_{α} radiation ($\lambda = 71.069$ pm) following a procedure described elsewhere in detail.¹⁶ Both data sets were corrected for absorption empirically, once their structures had been determined.¹⁷ Both structures were determined by standard heavy-atom methods and refined by full-matrix least-squares methods using the SHELX program system.¹⁸

Compound (5b) was found to be positioned on a crystallographic two-fold axis running along the C=C vector of the bridging dichlorovinylidene group. This produces unique metal atom sites between which the two metal atoms are 50:50 disordered. The site was therefore refined as a palladium atom with an occupancy factor of 0.804 (equivalent to 0.5Pd + 0.5Ni). The refinement was much the same for both compounds

with all non-hydrogen atoms assigned anisotropic thermal parameters and all hydrogen atoms included in calculated positions [except the vinylidene hydrogens in (1d), which were located experimentally] and refined with an overall isotropic thermal parameter assigned to each ligand. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement for both compounds to obtain satisfactory agreement analysis, and $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $R' = \Sigma w(|F_o| - |F_c|) / \Sigma|F_o|$.

Crystal data for [(SCN)Ni(μ -dppm)₂(μ -C=CH₂)Ni(NCS)] (1d). C₅₄H₄₆N₂Ni₂P₄S₂, $M = 1028.41$, monoclinic, space group $P2_1/n$ ($P2_1/c$, no. 14), $a = 1275.7(2)$, $b = 1508.6(3)$, $c = 2636.6(5)$ pm, $\beta = 99.75(1)^\circ$, $U = 5.001$ nm³, $Z = 4$, $D_c = 1.37$ g cm⁻³, $\mu(\text{Mo-}K_{\alpha}) = 5.83$ cm⁻¹, $F(000) = 2016$, $T = 290$ K.

Data collection. Scans running from 0.9° below $K_{\alpha 1}$ to 0.9° above $K_{\alpha 2}$, scan speeds 2.0–29.3° min⁻¹, $4.0 \leq 2\theta \leq 45.0^\circ$. 6063 Unique data, 5194 observed [$I > 2.0\sigma(I)$].

Structure refinement. Number of parameters = 490, weighting factor $g = 0.0009$, $R = 0.0416$, $R' = 0.0481$.

Crystal data for [ClPd(μ -dppm)₂(μ -C=CCl₂)NiCl] (5b). C₅₂H₄₄Cl₄Ni₂P₄Pd, $M = 1099.22$, tetragonal, space group $P4_22$, $a = 1418.3(2)$, $c = 2814.5(3)$ pm, $U = 5.661$ nm³, $Z = 4$, $D_c = 1.30$ g cm⁻³, $\mu(\text{Mo-}K_{\alpha}) = 4.53$ cm⁻¹, $F(000) = 1116$, $T = 290$ K.

Data collection. Parameters as above. 3847 Unique data, 3457 observed [$I > 2.0\sigma(I)$].

Structure refinement. Number of parameters = 240, weighting factor $g = 0.0008$, $R = 0.0500$, $R' = 0.0517$.

Lists of final co-ordinates for compound (1d) are in Table 5, and for compound (5b) in Table 6.

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for (1d) with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Ni(1)	5 565.0(4)	2 388.1(4)	3 926.9(2)	C(222)	8 613(3)	2 101(2)	2 502(1)
Ni(2)	5 467.0(4)	1 642.4(4)	2 930.9(2)	C(223)	9 081(3)	2 171(2)	2 063(1)
P(1)	7 300(1)	2 254(1)	4 117.0(4)	C(224)	8 752(3)	1 615(2)	1 643(1)
P(2)	7 177(1)	1 337(1)	3 085(1)	C(225)	7 956(3)	989(2)	1 663(1)
P(3)	4 054(1)	3 115(1)	3 737.7(4)	C(226)	7 487(3)	919(2)	2 103(1)
P(4)	3 813(1)	2 096(1)	2 734.5(4)	C(311)	4 229(2)	4 290(1)	3 885(1)
S(1)	4 886(1)	1 162(1)	5 458(1)	C(312)	5 145(2)	4 563(1)	4 215(1)
C(1)	5 116(4)	1 568(4)	4 926(2)	C(313)	5 254(2)	5 444(1)	4 375(1)
N(1)	5 278(3)	1 881(3)	4 539(2)	C(314)	4 448(2)	6 053(1)	4 205(1)
S(2)	4 529(2)	-932(1)	1 976(1)	C(315)	3 533(2)	5 781(1)	3 875(1)
C(2)	4 859(4)	-61(4)	2 332(2)	C(316)	3 423(2)	4 899(1)	3 715(1)
N(2)	5 103(3)	555(3)	2 584(2)	C(321)	3 006(2)	2 852(2)	4 107(1)
C(3)	5 792(4)	2 731(3)	3 272(2)	C(322)	2 011(2)	2 508(2)	3 900(1)
C(4)	6 083(5)	3 488(4)	3 074(2)	C(323)	1 280(2)	2 308(2)	4 221(1)
C(111)	7 885(2)	1 449(2)	4 597(1)	C(324)	1 546(2)	2 454(2)	4 750(1)
C(112)	8 908(2)	1 585(2)	4 870(1)	C(325)	2 541(1)	2 798(2)	4 957(1)
C(113)	9 365(2)	960(2)	5 231(1)	C(326)	3 271(2)	2 998(2)	4 635(1)
C(114)	8 800(2)	200(2)	5 318(1)	C(33)	3 446(4)	3 090(3)	3 059(2)
C(115)	7 777(2)	64(2)	5 045(1)	C(411)	2 905(2)	1 269(2)	2 902(1)
C(116)	7 320(2)	688(2)	4 684(1)	C(412)	1 928(2)	1 068(2)	2 599(1)
C(121)	7 874(3)	3 302(2)	4 377(1)	C(413)	1 259(2)	443(2)	2 768(1)
C(122)	8 548(3)	3 822(2)	4 135(1)	C(414)	1 567(2)	17(2)	3 239(1)
C(123)	8 912(3)	4 635(2)	4 348(1)	C(415)	2 544(2)	217(2)	3 542(1)
C(124)	8 602(3)	4 928(2)	4 802(1)	C(416)	3 213(2)	843(2)	3 374(1)
C(125)	7 928(3)	4 408(2)	5 044(1)	C(421)	3 380(3)	2 382(2)	2 066(1)
C(126)	7 564(3)	3 595(2)	4 831(1)	C(422)	4 027(3)	2 165(2)	1 707(1)
C(13)	7 969(4)	2 041(4)	3 567(2)	C(423)	3 718(3)	2 397(2)	1 192(1)
C(211)	7 544(3)	222(2)	3 299(1)	C(424)	2 762(3)	2 845(2)	1 034(1)
C(212)	6 827(3)	-285(2)	3 521(1)	C(425)	2 114(3)	3 061(2)	1 393(1)
C(213)	7 111(3)	-1 134(2)	3 705(1)	C(426)	2 424(3)	2 830(2)	1 909(1)
C(214)	8 111(3)	-1 474(2)	3 668(1)	H(41a)	6 246(39)	4 008(36)	3 278(20)
C(215)	8 828(3)	-967(2)	3 446(1)	H(41b)	6 276(40)	3 514(36)	2 765(21)
C(216)	8 544(3)	-119(2)	3 261(1)				
C(221)	7 816(3)	1 475(2)	2 522(1)				

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for (5b) with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Pd(1)	3 425(1)	2 320(1)	382.8(3)	C(124)	5 342(4)	4 165(4)	1 884(2)
P(1)	2 823(2)	3 254(1)	968(1)	C(125)	4 579(4)	4 776(4)	1 834(2)
P(2)	4 202(1)	1 611(2)	-217(1)	C(126)	3 797(4)	4 503(4)	1 567(2)
Cl(1)	3 449(2)	979(2)	844(1)	C(13)	4 374(6)	2 321(6)	-760(3)
Cl(2)	4 054(2)	5 137(2)	-333(1)	C(211)	3 657(4)	553(4)	-443(2)
C(1)	3 455(5)	3 455(5)	0*	C(212)	2 782(4)	273(4)	-266(2)
C(2)	4 098(5)	4 098(5)	0*	C(213)	2 353(4)	-543(4)	-438(2)
C(111)	1 921(4)	2 825(4)	1 376(2)	C(214)	2 799(4)	-1 081(4)	-787(2)
C(112)	1 700(4)	3 340(4)	1 783(2)	C(215)	3 674(4)	-801(4)	-964(2)
C(113)	1 012(4)	3 010(4)	2 096(2)	C(216)	4 103(4)	16(4)	-792(2)
C(114)	546(4)	2 164(4)	2 002(2)	C(221)	5 393(3)	1 253(5)	-63(2)
C(115)	767(4)	1 649(4)	1 595(2)	C(222)	6 181(3)	1 798(5)	-175(2)
C(116)	1 454(4)	1 979(4)	1 282(2)	C(223)	7 071(3)	1 530(5)	-12(2)
C(121)	3 779(4)	3 619(4)	1 350(2)	C(224)	7 172(3)	717(5)	263(2)
C(122)	4 543(4)	3 008(4)	1 400(2)	C(225)	6 384(3)	172(5)	375(2)
C(123)	5 324(4)	3 281(4)	1 668(2)	C(226)	5 494(3)	441(5)	212(2)

* Co-ordinate fixed by special position.

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References

- Part 20, A. Blagg, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, preceding paper.
- K. A. Azam, A. A. Frew, B. R. Lloyd, L. Manojlovic-Muir, K. W. Muir, and R. J. Puddephatt, *Organometallics*, 1985, **4**, 1400 and refs. therein.
- P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 889.
- C-L. Lee, B. Besenyi, B. R. James, D. A. Nelson, and M. A. Lilga, *J. Chem. Soc., Chem. Commun.*, 1985, 1175.
- D. L. DeLaet, D. R. Powell, and C. P. Kubiak, *Organometallics*, 1985, **4**, 954.
- C. Ercolani, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chim. Acta*, 1973, **7**, 413.
- X. L. R. Fontaine, S. J. Higgins, C. R. Langrick, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1987, 777.
- A. L. Balch, C. T. Hunt, C-L. Lee, M. M. Olmstead, and J. P. Farr, *J. Am. Chem. Soc.*, 1981, **103**, 3764.
- J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1960, 1718.
- 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, London, 1982.
- J. Caravajal, G. Muller, J. Sales, X. Solans, and C. Miravittles, *Organometallics*, 1984, **3**, 996.
- D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 859.
- F. Guerrieri and G. Salerno, *J. Organomet. Chem.*, 1976, **114**, 339.
- P. Fitton and J. E. McKeon, *J. Chem. Soc., Chem. Commun.*, 1986, 4.
- S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.
- A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.
- N. Walker and P. Stewart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- G. M. Sheldrick, SHELX 76, Program System for X-Ray Structure Determinations, University of Cambridge, 1976.

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