Complexes of Functional Phosphines. Part 11.* β-Ketophosphine Complexes of Nickel, Palladium, and Platinum. Crystal Structures of *trans*-[$NiX_2(HL)_2$] [X = Cl or I, HL = $Ph_2PCH_2C(O)Ph$]†

Pierre Braunstein, Dominique Matt, and Dominique Nobel
Laboratoire de Chimie de Coordination, Associé au C.N.R.S. (U.A. 416), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France
Fadila Balegroune, Salah-Eddine Bouaoud, and Daniel Grandjean
Laboratoire de Cristallochimie, Associé au C.N.R.S. (U.A. 254), Université de Rennes I, Avenue du Général Leclerc, F-35042 Rennes Cédex, France
Jean Fischer
Laboratoire de Cristallochimie et de Chimie Structurale, Associé au C.N.R.S. (U.A. 424), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France

The synthesis and spectroscopic properties (^{1}H and ^{31}P n.m.r., i.r.) of complexes containing the β-ketophosphine $Ph_2PCH_2C(O)Ph$ (HL) are described. In [$NiX_2(HL)_2$] [X = Cl (**1**), Br, or I (**3**)], [$PdCl_2(HL)_2$] (**4**), [$PtCl_2(HL)_2$] (**5**), and [{$PdCl(\mu$-Cl)(HL)}$_2$] (**6**), HL behaves as a *P*-bonded monodentate ligand whereas in the cationic complexes [$Pd(HL)_2$][BF_4]$_2$ and [{Pd(μ-Cl)(HL)}$_2$][CF_3SO_3]$_2$ it acts as a *P,O* chelate. The crystal structures of (**1**) and (**3**) have been determined using single-crystal *X*-ray diffraction methods. Compound (**1**) crystallises in space group $P2_1/n$, with a = 10.079(3), b = 11.510(3), c = 15.411(3) Å, β = 93.42(2)°, and Z = 2. Compound (**3**) crystallises in space group $P2_1/c$, with a = 9.283(1), b = 10.261(1), c = 19.318(1) Å, β = 96.20(1)°, and Z = 2. The structures have been refined to R 0.050 (R' 0.060) for (**1**) and to R 0.032 (R' 0.041) for (**3**). The geometries of these complexes are essentially identical although the ν(CO) frequencies of these complexes are significantly different [1 662 cm^{-1} for (**1**) and 1 620 cm^{-1} for (**3**)]; the nickel atom occupies a centre of symmetry and has thus a square-planar environment. Although the ketone group is bent towards the nickel atom, no significant Ni–O bonding interaction occurs, as deduced from the Ni–O distances [3.230(4) Å in (**1**) and 3.231(1) Å in (**3**)]. In refluxing toluene (**1**), (**4**), or (**5**) lead to the phosphine–phosphinite complexes *cis*-[MCl_2{$Ph_2PCHC(Ph)OPPh_2$}] (M = Ni, Pd, or Pt). Treatment of (**1**), (**4**), or (**5**) with base gives the enolato-complexes *cis*-[M{$Ph_2PCHC(O)Ph$}$_2$] (M = Ni, Pd, or Pt). Reaction of (**6**) with NaH affords the binuclear complex [{Pd(μ-Cl)[$Ph_2PCHC(O)Ph$]}$_2$]. The latter reacts with PPh_3 to give *cis*-[PdCl{$Ph_2PCHC(O)Ph$}(PPh_3)], and with $Ph_2PCH_2CH_2PPh_2$–$TlPF_6$ to give [Pd{$Ph_2PCHC(O)$-Ph}($Ph_2PCH_2CH_2PPh_2$)]PF_6. The P–O coupling products [$NiCl_2${[$Ph_2PCHC(Ph)O$]$_2$PR}] (R = Cl or Ph) are obtained by reaction of the complex [Ni{$Ph_2PCHC(O)Ph$}$_2$] with PCl_3 and $PPhCl_2$ respectively, and shown to have a five-co-ordinate structure. The square-planar *P,P,P* complex [NiCl{[$Ph_2PCHC(Ph)O$]$_2$PPh}]PF_6 results from reaction of [$NiCl_2${[$Ph_2PCHC(Ph)O$]$_2$PPh}] with $TlPF_6$.

We report here some complexes containing the β-ketophosphine $Ph_2PCH_2C(O)Ph$ (HL) or the corresponding phosphine–enolate $Ph_2PCHC(O)Ph^-$ (L^-). Our interest for such phosphines lies (*i*) in their ability to form unsymmetrical *P,O* chelates, a class of ligands which were shown to be of catalytic relevance, leading in particular to very selective reactions;[1] and (*ii*) in the possibility of preparing dinuclear complexes containing the P–C bridging unit and corresponding to the C-bound enolate form.[2] We recently published evidence of the intrinsic reactivity of the chelating L^- ligand, illustrating its ambidentate behaviour.[3,4] Thus, when co-ordinated to palladium, L^- reacts smoothly with organic isocyanates to form phosphine–amides *via* a C–C coupling reaction involving the carbon atom in the α-position to the phosphorus atom, whereas with PPh_2Cl the phosphine–phosphinite ligand $Ph_2PCHC(Ph)OPPh_2$ is formed, resulting from a P–O coupling reaction with the enolate oxygen. We describe now some new aspects of the reactivity of nickel, palladium, and platinum complexes containing HL or L^-. We also report a comparative *X*-ray study of *trans*-[$NiCl_2(HL)_2$] and *trans*-[$NiI_2(HL)_2$], undertaken in order to elucidate the reasons for their different i.r. spectroscopic properties.

Results and Discussion

Complexes with Monodentate HL.—Addition of $Ph_2PCH_2C(O)Ph$ (HL) to a solution of $NiCl_2{\cdot}6H_2O$ in ethanol resulted in the precipitation of the red-violet complex *trans*-[$NiCl_2(HL)_2$] (**1**). In its i.r. (KBr) spectrum, the ν(C=O) stretching frequency appears at 1 662 cm^{-1} indicating an unco-ordinated ketone group (Table 1). Complex (**1**) is practically insoluble in methanol or ethanol. Dissolution in CD_2Cl_2 leads to decomposition of the complex (formation of a green precipi-

---

* Part 10 is ref. 4.

† *trans*-Dichloro- and di-iodo-bis(diphenylphosphinomethyl phenyl ketone-*P*)nickel(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Comparison of selected i.r.[a] (cm^{-1}) and n.m.r. [δ/p.p.m., J/Hz] data

	I.r.	^{1}H N.m.r.[b]			
Compound	ν(C=O) or ν(C⋯C) + ν(C⋯O)	PCH_2	PCH	$^2J(PH)$	^{31}P N.m.r.[c]
HL $Ph_2PCH_2C(O)Ph$	1 670	3.80		0.0	−17.1
(1) $[NiCl_2(HL)_2]$	1 662				
(2) $[NiBr_2(HL)_2]$	1 612				
(3) $[NiI_2(HL)_2]$	1 620				
(4) $[PdCl_2(HL)_2]$ *cis*	1 677, 1 671[d]	4.42		11.2	22.6
trans		4.37		^{2+4}J 7.9	13.4
(5) $[PtCl_2(HL)_2]$	1 670	4.36		10.9	4.3 [J(PtP) 3 794]
(6) $[\{PdCl(\mu\text{-}Cl)(HL)\}_2]$	1 674	4.36		11.8	24.9
(7) $[NiCl_2\{Ph_2PCHC(Ph)OPPh_2\}]$	1 602		5.72	2.5	2.0, 126.6 [J(PP) 106]
(8) $[PdCl_2\{Ph_2PCHC(Ph)OPPh_2\}]$	1 600		5.97	2.0, 6.0	4.2, 129.5 [J(PP) 6]
(9) $[PtCl_2\{Ph_2PCHC(Ph)OPPh_2\}]$	1 598		6.02	2.6, 3.7 [^3J(PtH) 66]	−14.5 [J(PtP) 3 386], 99.8 [J(PtP) 4 040, J(PP) 24]
(10) $[Pd\{Ph_2PCH_2C(O)Ph\}_2][BF_4]_2$	1 558	5.10		12.5	46.2
(11) $[\{Pd(\mu\text{-}Cl)[Ph_2PCH_2C(O)Ph]\}_2]$-$[CF_3SO_3]_2$	1 545	5.13		12.7	45.1
(12) $[Ni\{Ph_2PCHC(O)Ph\}_2]$	1 515		4.55	0.0	28.2
(13) $[Pd\{Ph_2PCHC(O)Ph\}_2]$	1 513		4.75	2.1	37.7
(14) $[Pt\{Ph_2PCHC(O)Ph\}_2]$	1 517		4.82	5.2 [^3J(PtH) 28.7]	12.9 [J(PtP) 3 520]
(15) $[\{Pd(\mu\text{-}Cl)[Ph_2PCHC(O)Ph]\}_2]$	1 514		4.42	5.3	41.3
(17) $[PdCl\{Ph_2PCHC(O)Ph\}(PPh_3)]$	1 512		4.45	2.4, 5.7	28.8, 45.7 [J(PP) 8]
(18) $[Pd\{Ph_2PCHC(O)Ph\}(Ph_2PCH_2$-$CH_2PPh_2)]PF_6$	1 511	2.56, 2.82	4.84	^{2+4}J(PH) 4.8	38.1, 53.7, 56.1 [J(PP) 362, 14, 28]
(19) $[NiCl_2\{[Ph_2PCHC(Ph)O]_2PCl\}]$	1 597		6.01	^4J 3.0, ^{2+4}J 6.0	−3.7, 83.9 [J(PP) 132]
(20) $[NiCl_2\{[Ph_2PCHC(Ph)O]_2PPh\}]$	1 600		5.86	^4J 2.5, ^{2+4}J 5.0	2.2, 117.0 [J(PP) 87]
(21) $[NiCl\{[Ph_2PCHC(Ph)O]_2PPh\}]PF_6$	1 594		6.02	^4J 1.6, ^{2+4}J 6.6	1.6, 163.3 [J(PP) 96]

[a] Recorded as KBr disc. [b] Spectra recorded in $CDCl_3$, except those of **(9)**, **(10)**, **(11)**, and **(12)** in CD_2Cl_2, of **(13)** in C_6D_6, and of **(19)** in [$^2H_8$]toluene. [c] Spectra recorded in $CDCl_3$, except those of **(9)**, **(12)**, and **(13)** in CH_2Cl_2–C_6D_6, of **(10)** in CH_2Cl_2–CD_2Cl_2, of **(11)** and **(19)** in CH_2Cl_2–[$^2H_8$]toluene, and of **(15)** in thf–C_6D_6. [d] Observed ν(CO) in mixtures of *cis*- and *trans*-**(4)**.

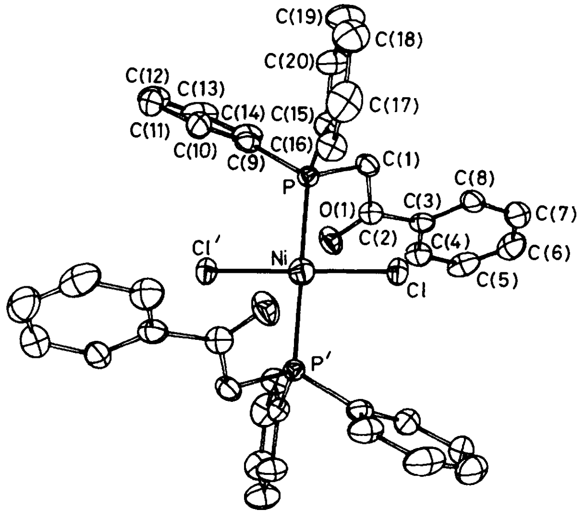


Figure 1. Perspective drawing of $[NiCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ **(1)**

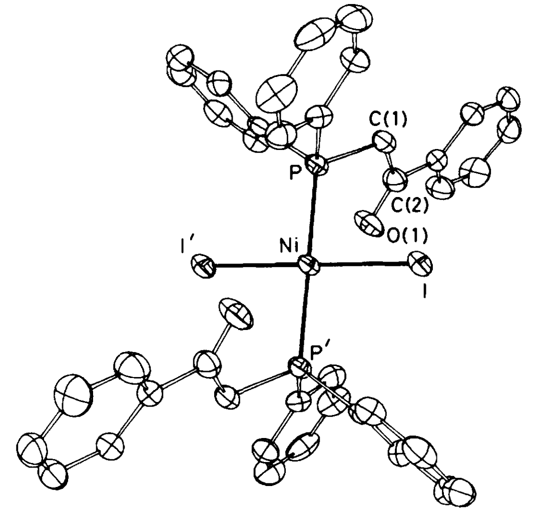


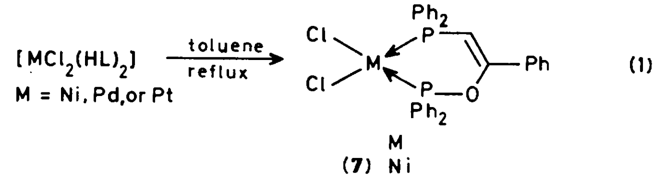
Figure 2. Perspective drawing of $[NiI_2\{Ph_2PCH_2C(O)Ph\}_2]$ **(3)**

tate) and the ^{1}H and ^{31}P n.m.r. spectra of the solution only showed the presence of free (HL) and broad peaks. This strongly suggests the existence, in solution, of an equilibrium between a square-planar $[NiCl_2(HL)_2]$ form and a tetrahedral (paramagnetic) one, the latter dissociating easily into unstable $NiCl_2(HL)$ and free phosphine.[5] Interestingly, in the i.r. (Nujol mull) spectra of the bromo **(2)** and iodo **(3)** analogues, we observed lower ν(C=O) stretching frequencies than in complex **(1)** [1 612 cm^{-1} for **(2)** and 1 620 cm^{-1} for **(3)**]. *A priori* one would consider this to be related to a direct nickel–oxygen interaction rather than to a halogen-induced through-bond perturbation of the monodentate ligand. Indeed, in the related complex $[NiBr_2\{Ph_2PCH_2C(O)OEt\}_2]$ no abnormal lowering of the ν(CO) frequency is observed when comparing its value (1 706 cm^{-1}) with that of the free phosphine ester $Ph_2PCH_2C(O)OEt$ (1 720 cm^{-1}).[6]

This largely motivated a comparative *X*-ray diffraction study of (**1**) and (**3**). It was found that, in both complexes, the nickel atom occupies the centre of symmetry of the molecule and has thus a square-planar environment with the two phosphorus atoms occupying *trans* positions (Figures 1 and 2). Although the oxygen atoms of (**1**) and (**3**) are bent towards the nickel atom, a nickel–oxygen bonding interaction seems unlikely in view of the long Ni–O distances [3.230(4) Å in (**1**) and 3.231(1) Å in (**3**)]. This pseudo-octahedral geometry probably minimises the repulsion forces within the molecule and optimizes the packing in the crystal lattice. As the C(2)–O(1) distances are very similar in (**1**) and (**3**), a tentative explanation for the *ca.* 50 cm^{-1} difference between the corresponding ν(CO) frequencies was sought in the differences in the O(1)–C(2)–C(3)–C(4) torsion angles. Although their values are significantly different, 14.1(1) and 8.9(1)° for (**1**) and (**3**) respectively, the smaller angle being associated with a better electron delocalization between the carbonyl function and the phenyl ring and therefore with a lower ν(CO) frequency, this may however not be sufficient to account for the large i.r. shift observed. The bond lengths in both structures are unexceptional and some selected values are given in Table 2.

The reaction of two mol equiv. of HL with $[PdCl_2(PhCN)_2]$ or $[PdCl_2(SEt_2)_2]$ in solvents such as chloroform, dichloromethane, or tetrahydrofuran (thf) afforded mixtures of *cis*- and *trans*-$[PdCl_2(HL)_2]$ (**4**). As described in a previous paper,[4] attempts to separate these isomers were unsuccessful because of rapid equilibrium resulting in a *ca.* 1:1 ratio (from ^1H n.m.r. integration). This contrasts with the situation observed with the ligand $Ph_2PCH_2C(O)OEt$, for which the complex *trans*-$[PdCl_2\{Ph_2PCH_2C(O)OEt\}_2]$ could be isolated pure.[6] The PCH_2 protons of the *cis* isomer are characterised by the presence of a doublet at δ 4.42 p.p.m. [$^2J(PH)$ = 11.2 Hz] in the ^1H n.m.r. spectrum, whereas in the *trans* isomer they appear as a virtual triplet typical for *trans*-RCH_2P–Pd–PCH_2R arrangements. Only one isomer, *cis*-$[PtCl_2(HL)_2]$ (**5**), was obtained by reacting two mol equiv. of HL with $[PtCl_2(PhCN)_2]$. A strong ν(CO) absorption band appears at 1 670 cm^{-1} in its i.r. (KBr) spectrum, in keeping with an unco-ordinated ketone group. The presence of a doublet with Pt satellites in the ^1H n.m.r. spectrum at δ 4.36 p.p.m. [$^3J(PtH)$ = 21 Hz] for the PCH_2 protons indicates a *cis* configuration of the ligands.

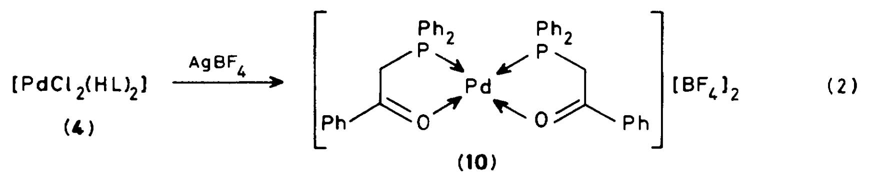
When $[PdCl_2(PhCN)_2]$ was treated with only one mol equiv. of HL, the brick-red dimer $[\{PdCl(\mu\text{-}Cl)[Ph_2PCH_2C(O)Ph]\}_2]$ (**6**) was formed quantitatively. Characterising analytical, i.r. and n.m.r. data are given in the Experimental section and in Table 1. Addition of PPh_3 to (**6**) afforded a mixture of *cis*- and *trans*-$[PdCl_2(HL)_2]$ (**4**) and *trans*-$[PdCl_2(PPh_3)_2]$, as shown by ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectroscopy. No complex of formula $[PdCl_2(HL)(PPh_3)]$ could be isolated, in agreement with studies of Nelson and co-workers[7] who showed that only $[PdCl_2(PR_3)_2]$ and $[PdCl_2(PR'_3)_2]$ complexes are usually isolated from solutions containing mixed phosphine complexes of the type $[PdCl_2(PR_3)(PR'_3)]$. We recently found that upon refluxing for 4 h a toluene solution of (**4**), the phosphine–phosphinite complex *cis*-$[\overline{PdCl_2\{Ph_2PCHC(Ph)OPPh_2}\}]$ (**8**) was formed.[4] The corresponding complexes *cis*-$[\overline{MCl_2\{Ph_2PCHC(Ph)OPPh_2}\}]$ [M = Ni (**7**) or Pt (**9**)] could be obtained similarly by heating a toluene suspension of $[NiCl_2(HL)_2]$ (4 h) or $[PtCl_2(HL)_2]$ (24 h), respectively [equation (1)]. Only in the case of Ni and Pd was the yield nearly quantitative, that of (**9**) being *ca.* 40%. Comparative spectroscopic and analytical data for (**7**)—(**9**) are given in Table 1. Note that the rather large value of the $^2J(PP)$ coupling constant (106 Hz) found for (**7**) is in agreement with values reported for other *cis*-$[NiCl_2(P\text{–}P)]$ (P–P = bidentate diphosphine ligand) complexes.[8] The first step in the reaction of equation (1) is likely to be the formation of $CH_2C(O)Ph^-$ by thermal cleavage of the P–C bond. This base would then deprotonate the $Ph_2PCH_2C(O)Ph$ ligand, yielding $Ph_2PCH\text{-}C(O)Ph^-$ which could then couple with the previously generated PPh_2 fragment to give the co-ordinated phosphine–phosphinite ligand, in a manner similar to that observed previously with PPh_2Cl.[3a] Note that prolonged heating of free HL left this phosphine unmodified, suggesting that the P–C bond is activated by co-ordination of the ligand.



M
(**7**) Ni
(**8**) Pd
(**9**) Pt

Complexes with chelating $Ph_2PCH_2C(O)Ph$ *or* $Ph_2PCHC(O)Ph^-$. The complexes $[PdCl_2(HL)_2]$ (**4**) and $[\{PdCl(\mu\text{-}Cl)(HL)\}_2]$ (**6**) were treated with silver salts to give the cationic complexes (**10**) and (**11**), respectively [equations (2) and (3)].

Both complexes show a doublet PCH_2 pattern in their ^1H n.m.r. spectra. This is in keeping with a *cis* structure for (**10**). The



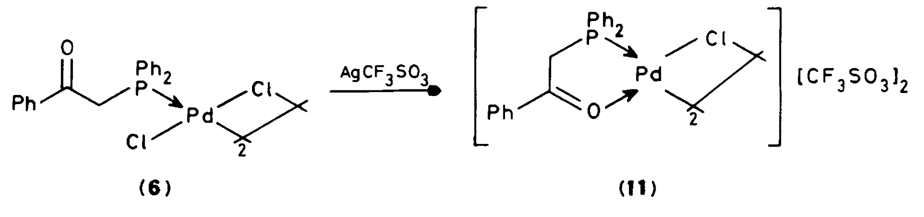
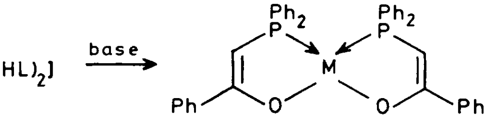


Table 2. Selected interatomic distances (Å) and angles (°) for $[NiX_2(HL)_2]$ [X = Cl (**1**) or I (**3**)]

	(**1**)	(**3**)
Ni–P	2.245(1)	2.234(1)
Ni–O(1)	3.230(4)	3.231(1)
Ni–X	2.162(1)	2.510(1)
P–C(1)	1.828(4)	1.834(7)
C(1)–C(2)	1.537(6)	1.516(9)
C(2)–C(3)	1.481(5)	1.468(9)
C(2)–C(1)	1.205(4)	1.208(7)
P–C(9)	1.812(4)	1.382(7)
P–C(15)	1.816(3)	1.815(6)
X–Ni–P	87.43(3)	87.89(4)
P–C(1)–C(2)	111.7(2)	113.8(5)
C(1)–C(2)–O(1)	119.0(3)	121.3(7)
O(1)–C(2)–C(3)	121.5(3)	121.2(6)

ν(C=O) values of 1 558 and 1 545 cm^{-1} for (**10**) and (**11**) respectively unambiguously establish co-ordination of the ketone group to the palladium centre. We were unable to identify a product of formula $[PdCl\{Ph_2PCH_2C(O)Ph\}(PPh_3)]^+$ formed by reacting (**11**) with PPh_3. As shown by $^{31}P-\{^1H\}$ n.m.r., this reaction led to a mixture of products.

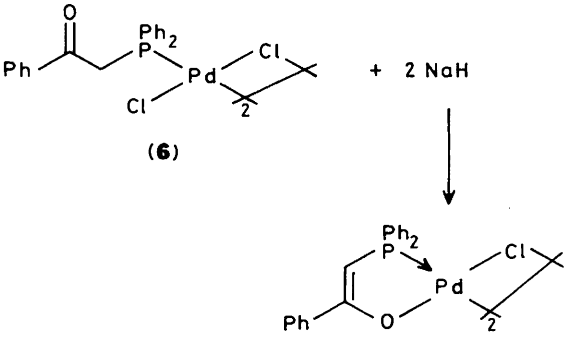
The chelating $Ph_2PCHC(O)Ph^-$ ligand can easily be generated from complexes (**1**)—(**6**). Thus, treatment of *trans*-$[NiCl_2(HL)_2]$, *cis*- and *trans*-$[PdCl_2(HL)_2]$, or *cis*-$[PtCl_2(HL)_2]$ with base [NaOEt–EtOH for (**1**) and (**5**); NaH–thf for (**4**)] afforded the *cis*-$[M\{Ph_2PCHC(O)Ph\}_2]$ complexes (**12**)—(**14**) in high yield [equation (4)].



(4)

M	
(**1**) Ni	(**12**)
(**4**) Pd	(**13**)
(**5**) Pt	(**14**)

For each of these complexes, the *cis* configuration is inferred from the presence in the ^1H n.m.r. spectrum of a doublet [or a singlet in the case of (**12**)] for the PCH protons [with Pt satellites in the case of (**14**), $^3J(PtH)$ = 28.7 Hz] and confirmed by the solid-state structure of (**12**), independently prepared by reacting the ylide $Ph_3PCHC(O)Ph$ with $[Ni(cod)_2]$ (cod = cyclo-octa-1,5-diene) in the presence of $AsPh_3$.[9] A *cis* structure was also observed in, *e.g.* the related $[Pd\{Ph_2PCHC(O)CF_3\}_2]$ complex[10] and this contrasts with the situation found for the $[M\{Bu^t_2PCHC(O)Ph\}_2]$ (M = Ni, Pd, or Pt) complexes which were shown to have a *trans* configuration (virtual triplet for the PCH protons)[11] owing to the steric bulk of the phosphorus substituents. Each of the complexes (**12**)—(**14**) showed a strong absorption band at *ca.* 1 515 cm^{-1}, attributable to ν(C⋯C) + ν(C⋯O) (Table 1). Interestingly, complex (**12**) could also be obtained quantitatively by reacting $[Ni(cod)_2]$ with two mol equiv. of HL [equation (5)]. This reaction probably occurs with protonation of the co-ordinated cod ligand, as in the reaction of equation (6), reported by Peuckert and Keim[12] in which the COOH proton of the phosphine acid $Ph_2PCH_2C(O)OH$ is transferred onto cod, resulting in the formation of a nickel *P,O* chelate complex. Note that our attempts to prepare the related complex $[Ni\{Ph_2PCHC(O)Ph\}(C_8H_{13})]$ [equation (7)] by addition of one mol equiv. of HL to $[Ni(cod)_2]$ only led to (**12**) in 50% yield with respect to nickel. Protonation of complex (**12**) in thf with dilute HCl instantaneously gave a red-violet solution from which crystals of (**1**) could be obtained. Upon standing, this solution decomposes with formation of a green insoluble precipitate.

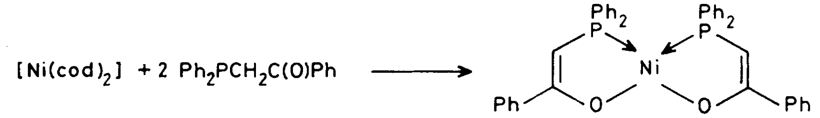


(**6**)

(8)

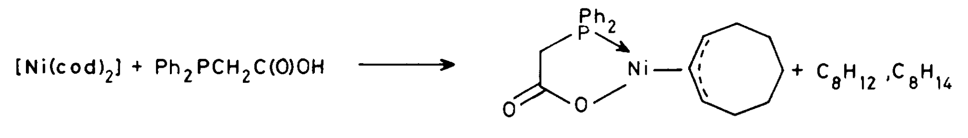
(**15**)

Reacting *clean* NaH (two mol equiv.) with (**6**) afforded complex (**15**) in high yield [equation (8)]. Analytical and spectroscopic characterisation is given in the Experimental section and in Table 1. The chelating nature of the anionic ligand thus formed was shown by a strong absorption band at

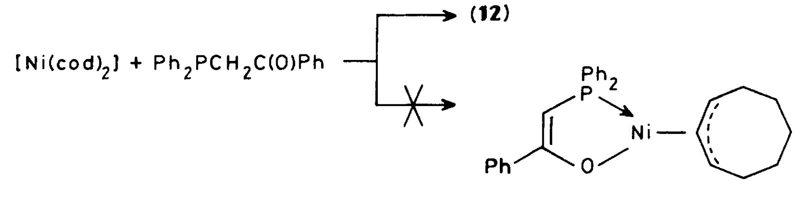


(**12**)

(5)

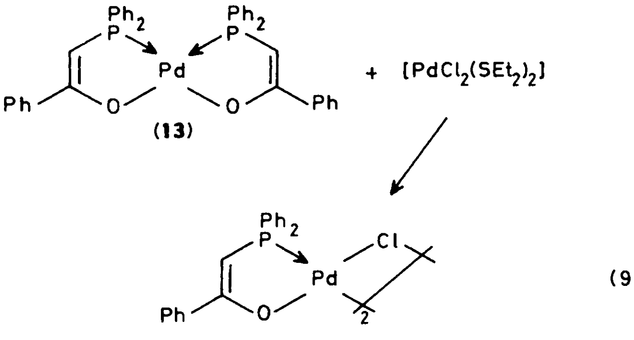


(6)



(7)

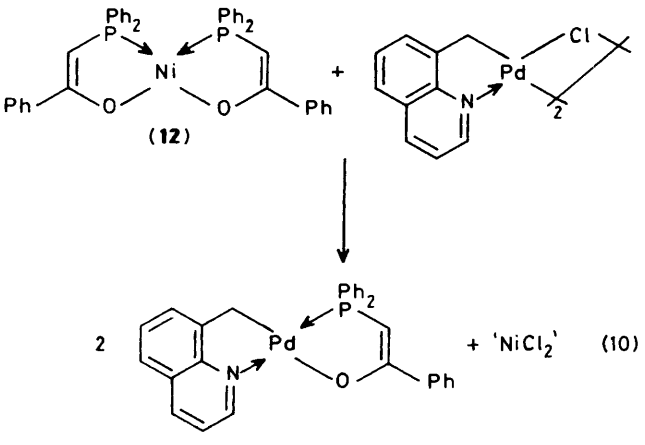
1 514 cm^{-1} in the i.r. spectrum of (**15**). This complex also results from the reaction shown in equation (9) (^{1}H and ^{31}P n.m.r. evidence) where easy transfer of the $Ph_2PCHC(O)Ph^-$ ligand from one metal to another occurs, a behaviour which appears to be a general feature. Thus, when complex (**12**) was treated with the cyclopalladated dimer [{Pd(μ-Cl)(mquin)}$_2$] (Hmquin = 8-methylquinoline), transmetallation of the three-electron donor *P,O* ligand occurred yielding *quantitatively* complex (**16**) [equation (10)].



(**13**)

(**15**)

(9)

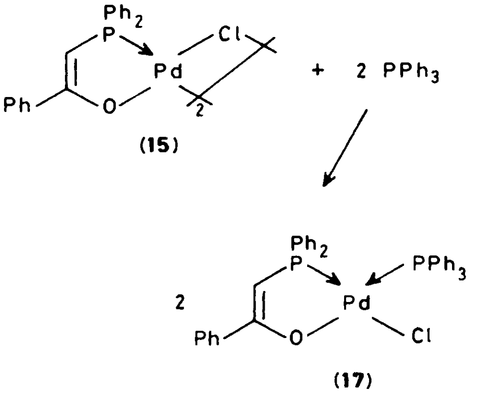


(**12**)

(**16**)

(10)

The expected bridge cleavage reaction occurred when (**15**) was treated with PPh_3, leading to complex (**17**) [equation (11)].

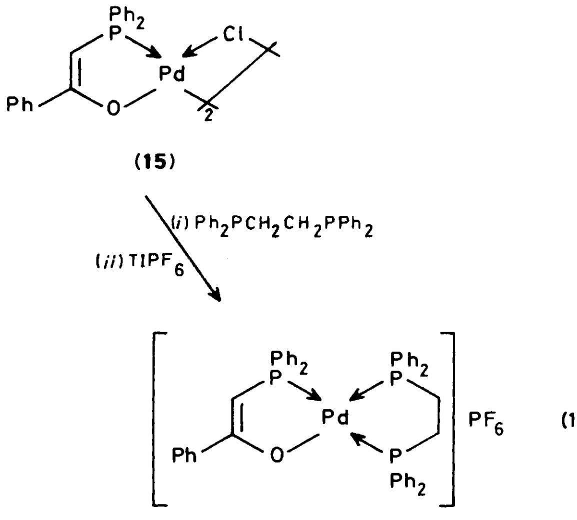


(**15**)

(**17**)

(11)

In the ^{1}H n.m.r. spectrum of (**17**) the PCH proton appears as a doublet of doublets owing to coupling to the two phosphorus atoms [*J*(PH) = 2.4 and 5.7 Hz]. The existence of a ^2J(PP) coupling constant of 8 Hz is in agreement with phosphorus atoms occupying *cis* positions.



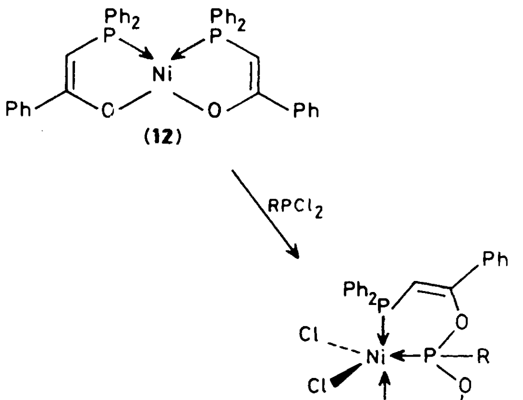
(**15**)

(**18**)

(12)

The cationic complex (**18**) was obtained by the reaction sequence shown in equation (12). The presence of a strong ν(C⋯O) + ν(C⋯C) absorption band at 1 511 cm^{-1} indicates that the *P,O* chelating ligand in (**18**) is maintained in this reaction. In the ^{1}H n.m.r. spectrum the PCH proton appears as a pseudo quintet (actually a doublet of virtual triplets) at δ 4.84 p.p.m. and the two non-equivalent P–CH$_2$ groups as two complex multiplets owing to spin–spin coupling between each of them with the phosphorus atoms and the adjacent CH$_2$ protons (A_2B_2MXY spin system). The ^{31}P-{^{1}H} n.m.r. spectrum displays an ABM pattern with δ_A 38.1, δ_B 53.7, and δ_M 56.1 p.p.m. Only the signals due to the phosphorus atom *trans* to the oxygen atom could be attributed unambiguously on the basis of the observed ^2J(PP) *cis* coupling constants [signal at 56.1 p.p.m., ^2J(PP) = 14 and 28 Hz].

Previous reactivity studies on co-ordinated L$^-$ have shown the nucleophilic character of the enolate oxygen towards the P–Cl bond of PPh_2Cl, leading to P–O coupling products.[3a] The presence of two such enolate ligands in (**12**)—(**14**) led us to envisage the possibility of a double coupling reaction.[3b] Thus, reaction of (**12**) with PCl_3 or $PPhCl_2$ led to the complexes (**19**) and (**20**) respectively [equation (13)].



(**12**)

(**19**) R = Cl

(**20**) R = Ph

(13)

The i.r. (KBr) spectra of (**19**) and (**20**) are each characterised by two strong absorption bands at *ca.* 1 600 and 1 570 cm^{-1} due

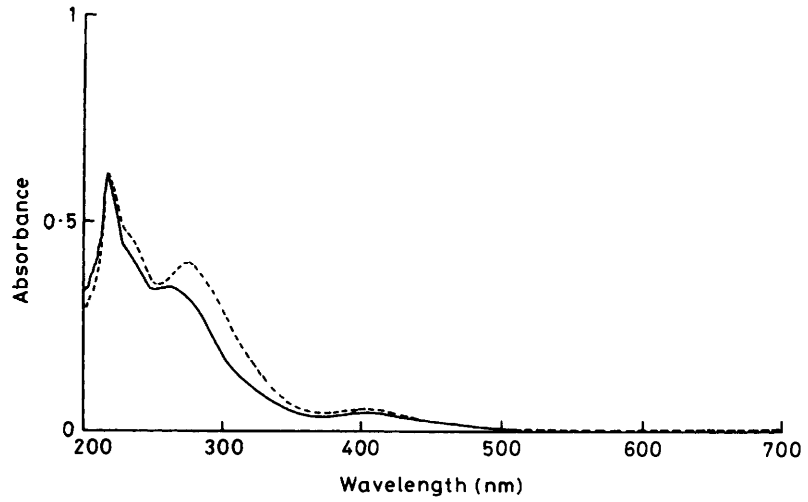
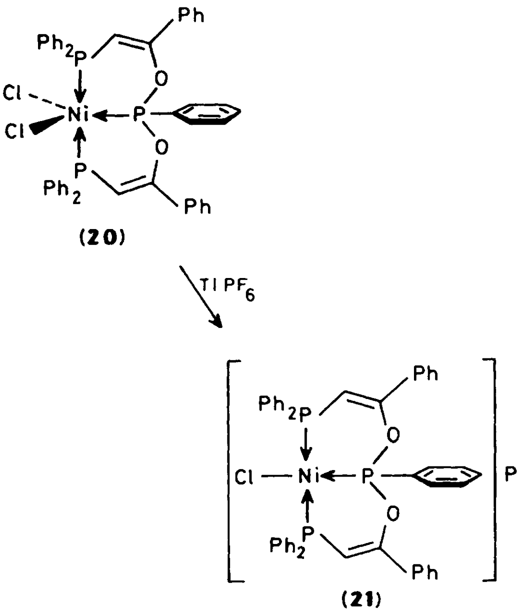


Figure 3. U.v.–visible spectra of 1.05 × 10^{-4} mol dm^{-3} $[NiCl_2\{[Ph_2PCHC(Ph)O]_2PPh\}]$ (**20**) (——) and 1.10 × 10^{-4} mol dm^{-3} $[NiCl\{[Ph_2PCHC(Ph)O]_2PPh\}]PF_6$ (**21**) (– – –)



(14)

to the P–O–C=C–P linkages. The *trans* arrangement of the Ph_2PCH groups in (**19**) and (**20**) was deduced from the presence in their ^1H n.m.r. spectrum of a pseudo quadruplet (actually a doublet of virtual triplets) at δ 6.01 and 5.86 p.p.m. respectively, for the PCH protons. In the ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**19**), the two types of phosphorus atoms appear respectively as a doublet at δ −3.7 p.p.m. for the *trans* P atoms and as a triplet at δ 83.9 p.p.m. for the chlorophosphite P; the *J*(PP) coupling constant of 132 Hz unambiguously establishes the co-ordination of all three phosphorus atoms [*cf.* the value of 106 Hz for (**7**)]. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**20**) displays a similar pattern (see Table 1). Treatment of (**19**) with NH_4PF_6 in CH_2Cl_2 left the complex unchanged, thus confirming its neutral nature. As could be seen on molecular models, an ideal trigonal-bipyramidal structure for (**19**) and (**20**) implies a strain of the chelating moieties of the *P,P,P* ligand because of the C=C(Ph) double bonds. It is noteworthy that the visible spectra of (**19**) and (**20**) in CH_2Cl_2, both showing two ligand-field bands [at 385 (ε 1 516) and 308 (sh) nm for (**19**) and at 403 (ε 3 882 dm^3 mol^{-1} cm^{-1}) and 310 (sh) nm for (**20**)] are in agreement with the general pattern observed for the spectra of diamagnetic five-co-ordinated complexes of Ni^{II} with trigonal-bipyramidal structures.[13]

Abstraction of a chloride ligand from (**20**) yielded the diamagnetic complex (**21**) [equation (14)]. As found for (**20**), the ^1H and ^{31}P-$\{^1H\}$ n.m.r. data for (**21**) also indicate co-ordination of all three P atoms (see Table 1) and the observation of a single absorption band at 405 nm (Figure 3) is in agreement with the expected C_{2v} local symmetry about the Ni centre.

In conclusion, we would like to emphasize (*i*) that a range of transition-metal complexes with a co-ordinated β-phosphinoketonate are directly accessible in high yield from the corresponding neutral functional phosphine and (*ii*) that new polydentate phosphorus ligands may easily be obtained from such complexes. Multihalide substitution reactions of halogenophosphines by transition-metal co-ordinated nucleophilic ligands have been only little exploited to date,[14] and such template condensation reactions are expected to find more synthetic applications in the future.

Experimental

All reactions were performed in Schlenk-type flasks under argon. All solvents were purified and dried by conventional methods and stored under argon. The ligand $Ph_2PCH_2C(O)Ph$ and the complexes $[PdCl_2(HL)_2]$ (**4**), $[PdCl_2\{Ph_2PCHC(Ph)OPPh_2\}]$ (**8**), and $[Pd\{Ph_2PCHC(O)Ph\}(mquin)]$ (**16**) were prepared according to procedures reported previously.[4] The complexes $[PdCl_2(PhCN)_2]$ and $[PtCl_2(PhCN)_2]$ were prepared according to literature methods.[15] The ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra were recorded at 200 and 81 MHz, respectively, on a FT Bruker WP-200 SY instrument. The u.v. spectra were recorded on a Shimadzu UV260 spectrophotometer, the molar absorption coefficient being given in dm^3 mol^{-1} cm^{-1}.

Preparations.—*trans*-$[NiCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ (**1**). A mixture of $NiCl_2{\cdot}6H_2O$ (0.399 g, 1.68 mmol) and $Ph_2PCH_2C(O)Ph$ (1.02 g, 3.36 mmol) was stirred in EtOH (20 cm^3). A red precipitate was formed rapidly. After stirring for 1 h, the suspension was filtered. The precipitate was washed with cold EtOH (3 × 10 cm^3) and dried *in vacuo* (yield 0.960 g, 77%), m.p. 164 °C [Found: C, 64.90; H, 4.65. Calc. for $C_{40}H_{34}Cl_2NiO_2P_2$ (*M* = 738.28): C, 65.10; H, 4.65%]; i.r. (KBr): 1 662s cm^{-1} [ν(C=O)]. Complex (**1**) is sparingly soluble in all common solvents. Crystals of (**1**), suitable for *X*-ray analysis, were obtained from a toluene–pentane solution of complex (**12**) in the presence of HCl.

trans-[NiBr$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (**2**). To a stirred suspension of NiBr$_2$·3H$_2$O (0.272 g, 1.00 mmol) in EtOH (10 cm^3) was added a solution of Ph$_2$PCH$_2$C(O)Ph (0.604 g, 2.0 mmol) in EtOH (10 cm^3). After vigorously stirring for 1 h, the suspension was filtered. The collected brown product was washed with EtOH and recrystallised from CH$_2$Cl$_2$–pentane affording yellow-brown needles of (**2**) (yield 0.490 g, 90%), m.p. 193 °C [Found: C, 55.75; H, 4.15. Calc. for $C_{40}H_{34}Br_2NiO_2P_2$·0.5CH$_2$Cl$_2$ (*M* = 869.65): C, 55.95; H, 4.05%]; i.r. (KBr): 1 612s [ν(C=O)], 1 593s, 1 572s cm^{-1}. All ^{1}H n.m.r. signals were broad (see Results and Discussion section).

trans-[NiI$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (**3**). Complex (**2**) (0.200 g, 0.24 mmol) and NaI (0.300 g, 2.00 mmol) were reacted in acetone (20 cm^3). Instantaneously the solution turned red. After stirring for 0.25 h, the solvent was removed *in vacuo*. The red residue was dissolved in CH$_2$Cl$_2$ and the solution was filtered. Addition of pentane afforded red crystals of (**3**) (yield 0.197 g, 94%), m.p. 208 °C [Found: C, 45.60; H, 3.30. Calc. for $C_{40}H_{34}I_2NiO_2P_2$ (*M* = 921.18): C, 52.15; H, 3.70%]; i.r. (KBr or Nujol): 1 620s [ν(C=O)], 1 590s, 1 571s cm^{-1}. ^{1}H N.m.r. signals were broad (see Results and Discussion section).

cis-[PtCl$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (**5**). [PtCl$_2$(PhCN)$_2$] (0.944 g, 2.00 mmol) and Ph$_2$PCH$_2$C(O)Ph (1.216 g, 4.00 mmol) were reacted in toluene (15 cm^3). After stirring for 4 h, the solution was filtered and the white precipitate was washed with pentane. The product was recrystallised from CH$_2$Cl$_2$–pentane (yield 1.70 g, 98%), m.p. 239 °C [Found: C, 54.90; H, 3.80. Calc. for $C_{40}H_{34}Cl_2O_2P_2Pt$ (*M* = 874.66): C, 54.95; H, 3.90%]; i.r. (KBr): ν(C=O) 1 670s cm^{-1}; ^{1}H n.m.r. (CDCl$_3$): δ 4.36 [d with Pt satellites, 4 H, PCH$_2$, ^{2}J(PH) 10.9, ^{3}J(PtH) 21 Hz], 7.10—7.86 (30 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (CDCl$_3$): δ 4.3 [s with Pt satellites, *J*(PtP) 3 794 Hz].

[{PdCl(μ-Cl)[Ph$_2$PCH$_2$C(O)Ph]}$_2$] (**6**). [PdCl$_2$(PhCN)$_2$] (0.390 g, 1.00 mmol) and Ph$_2$PCH$_2$C(O)Ph (0.304 g, 1.0 mmol) were reacted in a mixture of toluene (15 cm^3) and CH$_2$Cl$_2$ (15 cm^3). After stirring for 1 h, the solution was filtered. Concentration of the filtrate and addition of pentane afforded orange crystals of (**6**) (yield 0.425 g, 81%), m.p. 232—240 °C (decomp.) [Found: C, 46.95; H, 3.20. Calc. for $C_{40}H_{34}Cl_4O_2P_2Pd_2$·CH$_2Cl_2$ (*M* = 1 048.21): C, 47.00; H, 3.45%]; i.r. (KBr): ν(C=O) 1 674s cm^{-1}; ^{1}H n.m.r. (CDCl$_3$): δ 4.36 [d, 2 H, CH$_2$, ^{2}J(PH) 11.8 Hz], 7.31—7.87 (15 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (CDCl$_3$): δ 24.9.

cis-[MCl$_2${Ph$_2$PCHC(Ph)OPPh$_2$}] [M = Ni (**7**), Pd (**8**), *or* Pt (**9**)]. These complexes were prepared by refluxing for 4 h a toluene solution containing the corresponding [MCl$_2$(HL)$_2$] complex, as detailed for M = Pd.[4] Complexes (**7**) and (**9**) were identified by comparison with authentic samples prepared by a different method.[16]

cis-[Pd{Ph$_2$PCH$_2$C(O)Ph}$_2$][BF$_4$]$_2$ (**10**). Complex (**4**) (0.200 g, 0.25 mmol) and AgBF$_4$ (0.100 g, 0.51 mmol) were reacted in CH$_2$Cl$_2$ (10 cm^3). After stirring for 2 h, the solution was filtered through Celite. Addition of pentane afforded yellow crystals of (**10**) (yield 0.190 g, 86%), m.p. 170—185 °C (decomp.) [Found: C, 54.20; H, 3.80. Calc. for $C_{40}H_{34}B_2F_8O_2P_2Pd$ (*M* = 888.7): C, 54.05; H, 3.85%]; i.r. (CH$_2$Cl$_2$): ν(C=O) 1 558s cm^{-1}; ^{1}H n.m.r. (CD$_2$Cl$_2$): δ 5.10 [d, 4 H, PCH$_2$, ^{2}J(PH) 12.5 Hz], 7.26—8.20 (30 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (CH$_2$Cl$_2$–CD$_2$Cl$_2$): δ 46.2.

[{Pd(μ-Cl)[Ph$_2$PCH$_2$C(O)Ph]}$_2$][CF$_3$SO$_3$]$_2$ (**11**). Complex (**6**) (0.200 g, 0.19 mmol) and AgCF$_3$SO$_3$ (0.107 g, 0.40 mmol) were reacted in CH$_2$Cl$_2$ (15 cm^3). After stirring for 1 h, the solution was filtered through Celite. Addition of a toluene (10%)—pentane mixture afforded mustard yellow crystals of (**11**) (yield 0.193 g, 85%), m.p. 170—200 °C (decomp.) [Found: C, 46.10; H, 3.30. Calc. for $C_{42}H_{34}Cl_2F_6O_8P_2Pd_2S_2$·C$_6H_5$Me (*M* = 1 282.6): C, 45.90; H, 3.30%]; i.r. (Nujol): ν(C=O) 1 545s cm^{-1}; ^{1}H n.m.r. (CD$_2$Cl$_2$): δ 5.13 [d, 2 H, PCH$_2$, ^{2}J(PH) 12.7 Hz], 7.30—8.17 (15 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (CH$_2$Cl$_2$–[^{2}H$_8$]toluene): δ 45.1.

cis-[Ni{Ph$_2$PCHC(O)Ph}$_2$] (**12**). A solution of NaOEt in EtOH (prepared from 0.2 g Na and 15 cm^3 EtOH) was slowly added to a stirred suspension of [NiCl$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (1.90 g, 2.57 mmol) in EtOH (15 cm^3). An orange powder precipitated immediately. After stirring for 1 h, the mixture was concentrated and filtered. The precipitate was first washed with cold EtOH and then recrystallised from toluene–CH$_2$Cl$_2$–pentane (yield 1.627 g, 95%), m.p. 239 °C [Found: C, 72.25; H, 4.95. Calc. for $C_{40}H_{32}NiO_2P_2$ (*M* = 665.36): C, 72.20; H, 4.85%]; i.r. (KBr): ν(C$\cdots$O) + ν(C$\cdots$C) 1 515s cm^{-1}; ^{1}H n.m.r. (CD$_2$Cl$_2$): δ 4.55 (s, 2 H, PCH), 7.04—7.85 (30 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (C$_6$D$_6$–CH$_2$Cl$_2$): δ 28.2.

cis-[Pd{Ph$_2$PCHC(O)Ph}$_2$] (**13**). Complex (**4**) (0.393 g, 0.50 mmol) was reacted with NaH (two-fold excess) in thf (40 cm^3). After stirring overnight, the mixture was filtered and the solvent removed *in vacuo*. Recrystallisation from CH$_2$Cl$_2$–pentane afforded yellow crystals of (**13**) (yield 0.328 g, 92%), m.p. 215 °C (decomp.) [Found: C, 66.15; H, 4.55. Calc. for $C_{40}H_{32}O_2P_2Pd$ (*M* = 713.05): C, 67.40; H, 4.50%]; i.r. (KBr): 1 513s, 1 484s cm^{-1}; ^{1}H n.m.r. (C$_6$D$_6$): δ 4.75 [d, 2 H, PCH, ^{2}J(PH) 2.1 Hz], 6.74—8.39 (30 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (CH$_2$Cl$_2$–C$_6$D$_6$): δ 37.7.

cis-[Pt{Ph$_2$PCHC(O)Ph}$_2$] (**14**). A solution of NaOEt in EtOH (prepared from 0.2 g Na and 15 cm^3 EtOH) was slowly added to a stirred suspension of [PtCl$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (0.865 g, 0.99 mmol) in EtOH (20 cm^3). After stirring for 1 h, the reaction mixture was concentrated and filtered. The white precipitate was washed with EtOH and then recrystallised from CH$_2$Cl$_2$–pentane (yield 0.750 g, 94%), m.p. > 260 °C [Found: C, 58.30; H, 3.90. Calc. for $C_{40}H_{32}O_2P_2Pt$ (*M* = 801.74): C, 59.95; H, 4.00%]; i.r. (KBr): ν(C$\cdots$O) + ν(C$\cdots$C) 1 517s cm^{-1}; ^{1}H n.m.r. (CDCl$_3$): δ 4.82 [d with Pt satellites, PCH, 2 H, ^{2}J(PH) 5.2, ^{3}J(PtH) 28.7 Hz], 6.95—8.03 (30 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (CDCl$_3$): δ 12.9 [s with Pt satellites, *J*(PtP) 3 520 Hz].

[{Pd(μ-Cl)[Ph$_2$PCHC(O)Ph]}$_2$] (**15**). Complex (**6**) (0.500 g, 0.51 mmol) and NaH (0.025 g, 1.04 mmol) were reacted in thf (100 cm^3). After stirring overnight, the solution was filtered and the solvent removed *in vacuo*. The residue was then dissolved in CH$_2$Cl$_2$ (200 cm^3) and the solution was filtered. Addition of pentane to the filtrate afforded (**15**) as an orange powder (yield 0.395 g, 87%), m.p. 207—220 °C (decomp.) [Found: C, 52.40; H, 3.45. Calc. for $C_{40}H_{32}Cl_2O_2P_2Pd_2$ (*M* = 890.4): C, 53.95; H, 3.60%]; i.r. (KBr): ν(C$\cdots$O) + ν(C$\cdots$C) 1 514s cm^{-1}; ^{1}H n.m.r. (CDCl$_3$): δ 4.42 [d, 1 H, PCH, ^{2}J(PH) 5.3 Hz], 7.13—7.89 (15 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (thf–C$_6$D$_6$): δ 41.3.

cis-[PdCl{Ph$_2$PCHC(O)Ph}(PPh$_3$)] (**17**). To a stirred suspension of complex (**15**) (0.075 g, 0.08 mmol) in thf (10 cm^3) was dropwise added a solution of PPh$_3$ (0.044 g, 0.17 mmol) in thf (10 cm^3). After stirring for 15 min, pentane was added, affording yellow crystals of (**17**) which were recrystallised from CH$_2$Cl$_2$–pentane (yield 0.107 g, 90%), m.p. 207 °C [Found: C, 59.40; H, 4.20. Calc. for $C_{38}H_{31}ClOP_2Pd$·CH$_2$Cl$_2$ (*M* = 792.4): C, 59.10; H, 4.20%]; i.r. (KBr): ν(C$\cdots$O) + ν(C$\cdots$C) 1 512s cm^{-1}; ^{1}H n.m.r. (CDCl$_3$): 4.45 [dd, 1 H, PCH, *J*(PH) 2.4 and 5.7 Hz], 7.12—7.92 (30 H, aromatic H); ^{31}P-{^{1}H} n.m.r. (CDCl$_3$): δ 28.8 (d, 1 P, not assigned, ^{2}J(PP) 8], 45.7 [d, 1 P, ^{2}J(PP) 8 Hz].

[Pd{Ph$_2$PCHC(O)Ph}(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]PF$_6$ (**18**). A suspension of complex (**15**) (0.160 g, 0.18 mmol) was reacted with Ph$_2$PCH$_2$CH$_2$PPh$_2$ (0.143 g, 0.36 mmol) in CH$_2$Cl$_2$ (15

Table 3. Positional parameters and their estimated standard deviations for *trans*-$[NiCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.000	0.000	0.000	C(9)	−0.282 5(5)	−0.044 0(5)	0.119 1(3)
Cl	0.136 8(1)	0.125 9(1)	0.058 87(8)	C(10)	−0.298 9(5)	−0.163 4(5)	0.122 1(4)
P	−0.115 4(1)	0.014 1(1)	0.119 74(8)	C(11)	−0.426 0(6)	−0.211 6(6)	0.116 1(4)
O(1)	−0.206 0(4)	0.213 1(3)	0.014 9(2)	C(12)	−0.535 4(6)	−0.142 4(7)	0.108 1(4)
C(1)	−0.128 2(5)	0.163 7(4)	0.158 3(3)	C(13)	−0.521 8(6)	−0.025 6(7)	0.106 4(4)
C(2)	−0.155 8(5)	0.249 0(4)	0.082 6(3)	C(14)	−0.394 9(6)	0.027 2(6)	0.112 1(4)
C(3)	−0.120 9(5)	0.373 2(4)	0.094 6(3)	C(15)	−0.029 9(5)	−0.059 3(4)	0.211 1(3)
C(4)	−0.175 0(6)	0.451 0(5)	0.032 4(4)	C(16)	0.087 8(5)	−0.117 7(5)	0.199 5(4)
C(5)	−0.141 0(6)	0.568 7(5)	0.038 7(4)	C(17)	0.150 2(6)	−0.176 9(6)	0.269 8(5)
C(6)	−0.052 5(7)	0.605 4(5)	0.105 4(5)	C(18)	0.094 8(6)	−0.178 4(6)	0.348 9(4)
C(7)	−0.001 7(7)	0.528 7(5)	0.166 0(4)	C(19)	−0.020 0(7)	−0.120 1(6)	0.361 1(4)
C(8)	−0.037 3(6)	0.413 6(4)	0.161 9(3)	C(20)	−0.082 4(5)	−0.061 8(5)	0.291 9(4)

Table 4. Positional parameters and their estimated standard deviations for *trans*-$[NiI_2\{Ph_2PCH_2C(O)Ph\}_2]$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.000	0.000	0.000	C(9)	0.141 1(6)	−0.217 6(6)	0.132 5(3)
I	0.189 07(4)	0.099 15(6)	−0.067 33(2)	C(10)	0.159 6(7)	−0.194 0(7)	0.204 1(3)
P	0.179 7(2)	−0.093 4(2)	0.068 84(8)	C(11)	0.130 7(8)	−0.290 4(8)	0.250 3(4)
O(1)	0.132 8(5)	−0.268 1(5)	−0.053 8(3)	C(12)	0.086 9(8)	−0.412 9(8)	0.226 8(5)
C(1)	0.320 0(6)	−0.175 3(7)	0.024 8(3)	C(13)	0.068 2(7)	−0.436 4(7)	0.157 4(4)
C(2)	0.260 4(7)	−0.266 4(7)	−0.033 1(3)	C(14)	0.092 4(7)	−0.340 3(7)	0.110 1(4)
C(3)	0.363 4(6)	−0.352 6(6)	−0.063 2(3)	C(15)	0.280 5(6)	0.027 9(6)	0.122 7(3)
C(4)	0.309 1(8)	−0.449 9(8)	−0.109 5(4)	C(16)	0.204 2(8)	0.131 7(7)	0.147 5(4)
C(5)	0.398 4(9)	−0.533 8(8)	−0.139 1(4)	C(17)	0.275(1)	0.222 0(7)	0.191 5(4)
C(6)	0.547 0(8)	−0.522 1(8)	−0.123 9(4)	C(18)	0.421 1(9)	0.212 4(8)	0.209 6(4)
C(7)	0.604 1(7)	−0.429 6(7)	−0.077 8(4)	C(19)	0.497 3(8)	0.114 8(8)	0.185 8(4)
C(8)	0.513 6(7)	−0.346 1(7)	−0.047 4(3)	C(20)	0.428 6(7)	0.018 5(8)	0.141 9(4)

cm^3). After 5 min, $TlPF_6$ (0.140 g, 0.40 mmol) was added and the mixture was stirred for 1 h. The solution was filtered through Celite and pentane was added, affording yellow crystals of (**18**) (yield 0.325 g, 95%), m.p. 218 °C [Found: C, 57.90; H, 4.30. Calc. for $C_{46}H_{40}F_6OP_4Pd$ (M = 953.12): C, 57.95; H, 4.25%]; i.r. (KBr): ν(C⩦O) + ν(C⩦C) 1 511s cm^{-1}; ^1H n.m.r. ($CDCl_3$): δ 2.56 (d of complex m, PCH_2), 2.82 (d of complex m, PCH_2), 4.84 [d of virtual t, 1 H, PCH, ^{2+4}J(PH) 4.8, $^4J(P_{trans\text{-}O}H)$ 4.8 Hz], 7.16—7.96 (35 H, aromatic H); ^{31}P-{^1H} n.m.r. ($CDCl_3$): ABM spin system (where M is the P atom *trans* with respect to the O atom) with δ_A 38.1, δ_B 53.7, δ_M 56.1 [$^2J(P_AP_B)$ 362, $^2J(P_AP_M)$ 14, $^2J(P_BP_M)$ 28 Hz, signals A and B not assigned].

$[NiCl_2\{[Ph_2PCHC(Ph)O]_2PCl\}]$ (**19**). A solution of PCl_3 (0.055 g, 0.40 mmol) in toluene (5 cm^3) was dropwise added to a solution of complex (**12**) (0.230 g, 0.35 mmol) in toluene (25 cm^3). After stirring for a few minutes, a green precipitate appeared. The suspension was further stirred for 2 h. The solvent was removed *in vacuo* and the green residue was dissolved in a CH_2Cl_2–toluene mixture, affording an orange solution. Addition of pentane and cooling at −15 °C gave orange crystals of (**19**) (yield 0.265 g, 85%), m.p. >230 °C (Found: C, 63.25; H, 4.50. Calc. for $C_{40}H_{32}Cl_3NiO_2P_3{\cdot}C_6H_5Me$ (M = 894.83): C, 63.10; H, 4.50%]; i.r. (KBr): 1 597s, 1 567s cm^{-1}; ^1H n.m.r. ([$^2H_8$]toluene): δ 6.01 [d of virtual t, 2 H, PCH, $J(P_{Cl}H)$ 3.0, ^{2+4}J 6.0 Hz], 7.20—8.31 (30 H, aromatic H); ^{31}P-{^1H} n.m.r. (CH_2Cl_2–[$^2H_8$]toluene): δ −3.7 [d, 2 P, PPh_2, J(PP) 132], 83.9 [t, 1 P, PCl, J(PP) 132 Hz]; u.v. (CH_2Cl_2): 385 (ε 1 516), 308 (sh), 270 (sh), 258 (29 552), 219 (35 552) nm.

trans-$[NiCl_2\{[Ph_2PCHC(Ph)O]_2PPh\}]$ (**20**). A solution of $PPhCl_2$ (0.180 g, 1.15 mmol) in CH_2Cl_2 (10 cm^3) was added to a stirred solution of complex (**12**) (0.730 g, 1.10 mmol). After stirring for 0.25 h, the solution was concentrated. Addition of pentane afforded green crystals of (**20**) (yield 0.768 g, 83%), m.p. >260 °C [Found: C, 65.45; H, 4.30. Calc. for $C_{46}H_{37}Cl_2NiO_2P_3$ (M = 844.35): C, 65.45; H, 4.40%]; i.r. (KBr): 1 600s, 1 571s cm^{-1}; ^1H n.m.r. ($CDCl_3$): δ 5.86 [d of virtual t, 2 H, PCH, ^{2+4}J(PH) 5, ^4J(PH) 2.5 Hz], 6.65—8.07 (35 H, aromatic H); ^{31}P-{^1H} n.m.r. ($CDCl_3$): δ 2.2 [d, 2 P, PCH, J(PP) 87 Hz], 117.0 [t, 1 P, PO, J(PP) 87 Hz]; u.v. (CH_2Cl_2): 403 (ε 3 882), 310 (sh), 263 (28 623), 235 (sh), 216 (55 098) nm.

$[NiCl\{[Ph_2PCHC(Ph)O]_2PPh\}]PF_6$ (**21**). $TlPF_6$ (0.50 g, 0.14 mmol) and complex (**20**) (0.120 g, 0.14 mmol) were reacted in CH_2Cl_2 (10 cm^3). After stirring for 0.25 h, the suspension was filtered. Addition of hexane afforded orange crystals of (**21**) (yield 0.126 g, 93%), m.p. >250 °C [Found: C, 57.95; H, 4.00. Calc. for $C_{46}H_{37}ClF_6NiO_2P_4$ (M = 953.9): C, 57.95; H, 3.90%]; i.r. (KBr) 1 594s, 1 569s cm^{-1}; ^1H n.m.r. ($CDCl_3$): δ 6.02 [d of virtual t, 2 H, PCH, ^{2+4}J(PH) 6.6, ^4J(PH) 1.6 Hz], 6.99—7.82 (35 H, aromatic H); ^{31}P-{^1H} n.m.r. ($CDCl_3$): δ 1.6 [d, 2 P, PCH, J(PP) 96 Hz], 163.3 [t, 1 P, PO, J(PP) 96 Hz]; u.v. (CH_2Cl_2): 405 (ε 4 303), 277 (38 168), 232 (sh), 218 (58 779) nm.

Crystal Structure Determination of (**1**).—*Crystal data.* $C_{40}H_{34}Cl_2NiO_2P_2$, M = 738.28. Crystals were grown as red prisms from a toluene–pentane solution of (**12**) in the presence of HCl. Monoclinic, a = 10.079(3), b = 11.510(3), c = 15.411(3) Å, β = 93.42(2)°, U = 1 784 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 1.5405 Å), space group $P2_1/n$, Z = 2, D_c = 1.374 g cm^{-3}, F(000) = 764. Air-stable crystals cut out from a cluster of crystals with dimensions 0.20 × 0.24 × 0.28 mm, μ(Cu-K_α) = 33.10 cm^{-1}.

Data collection and processing. Philips PW 1100/16 diffractometer, θ/2θ flying step scan mode with $\Delta\theta$ = (1.00 + 0.143 tan θ)°, scan speed = 0.024° s^{-1}, graphite-monochromated Cu-K_α radiation; 2 600 reflections measured (4 < θ < 57°, ±*hkl*), 1 953 independent reflections having $I > 3\sigma(I)$. No intensity decay was observed during the data collection period. Intensity data were corrected for Lorentz, polarisation and absorption factors, the last computed by the empirical method of Walker and Stuart.[17]

Structure analysis and refinement. The structure was solved using heavy-atom and difference Fourier methods and refined by full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms were not located but introduced by their computed co-ordinates (C–H = 0.95 Å) in structure factor calculations and were given isotropic thermal parameters of $B = 1 + B_{eqv.}(\text{C})$ Å^2. The final difference map showed no significant maximum. The weighting scheme for the refinement was derived from $\sigma^2(F^2) = \sigma_{count}{}^2 + (0.08\ I)^2$ and gave a satisfactory agreement analysis. Final $R = 0.050$ and $R' = 0.060$. Scattering factors with corrections for the effects of anomalous dispersion were from ref. 18. Calculations were carried out on a PDP 11/60 computer using the Enraf-Nonius SDP/PDP package.[19] The final atomic co-ordinates are listed in Table 3.

Crystal Structure Determination of (**3**).—*Crystal data.* $C_{40}H_{34}I_2NiO_2P_2$, $M = 921.18$. Crystals were grown as dark red prisms from a CH_2Cl_2–pentane solution. Monoclinic, $a = 9.283(1)$, $b = 10.261(1)$, $c = 19.318(1)$ Å, $\beta = 96.20(1)°$, $U = 1\,829$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,73$ Å), space group $P2_1/c$, $Z = 2$, $D_c = 1.67$ g cm^{-3}, $F(000) = 908$. Air-stable crystals of dimensions 0.20 × 0.17 × 0.07 mm, $\mu(\text{Mo-}K_\alpha) = 23.21$ cm^{-1}.

Data collection and processing. Nonius CAD4 diffractometer, $\theta/2\theta$ mode with scan width = $(1 + 0.35 \tan\theta)^0$, counter aperture $D = (2 + 0.5 \tan\theta)$ mm, variable scan speed, graphite-monochromated Mo-K_α radiation; 3 188 reflections measured ($1 < \theta < 25°$, $hk \pm l$), 1 731 independent reflections with $I > 3\sigma(I)$. No intensity decay was observed during the data collection period. Intensity data were corrected for Lorentz and polarisation factors. Absorption corrections were omitted in view of the low linear absorption coefficient.

Structure analysis and refinement. The structure was solved using the MULTAN[20] program and refined as for (**1**) with isotropic thermal parameters of 6.0 Å^2 for the hydrogen atoms. A weighting scheme $w = [\frac{1}{4}|\sigma(I)^2/I + (0.06\ I)^2|]^{-1}$ gave a satisfactory analysis, and refinement converged at $R = 0.032$ and $R' = 0.041$. The final difference map showed no significant residual peaks. Scattering factors, corrections were as for (**1**). The final atomic co-ordinates are listed in Table 4.

Acknowledgements

We thank Mrs. A. Degremont for experimental assistance and Dr. M. L. Luke for discussion. The Groupement Scientifique CO_2(CNRS-SNPE) is acknowledged for financial support and for a grant to D. N.

References

1 W. Keim, A. Behr, B. Gruber, B. Hoffmann, F. H. Kowaldt, U. Kürschner, B. Limbäcker, and F. P. Sistig, *Organometallics*, 1986, **5**, 2356.
2 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**, 5115.
3 (*a*) S-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt, and D. Nobel, *J. Chem. Soc., Chem. Commun.*, 1987, 488; (*b*) P. Braunstein, D. Matt, D. Nobel, and J. Fischer, *ibid.*, p. 1530.
4 Part 10, S-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt, and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.
5 G. R. van Hecke and W. D. Horrocks, *Inorg. Chem.*, 1966, **5**, 1968.
6 P. Braunstein, D. Matt, F. Mathey, and D. Thavard, *J. Chem. Res.*, 1978, (*S*) 232; (*M*) 3041.
7 A. W. Verstuyft, D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, 1976, **15**, 1128.
8 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
9 H. Quichen, X. Minzhi, Q. Yanlong, X. Weihua, S. Meicheng, and T. Youqi, *J. Organomet. Chem.*, 1985, **287**, 419.
10 A. J. Carty, S. E. Jacobson, R. T. Simpson, and N. J. Taylor, *J. Am. Chem. Soc.*, 1975, **97**, 7254.
11 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 299.
12 M. Peuckert and W. Keim, *Organometallics*, 1983, **2**, 594.
13 P. Rigo, B. Corain, and A. Turco, *Inorg. Chem.*, 1968, **8**, 1623; J. W. Dawson, T. J. McLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, *J. Am. Chem. Soc.*, 1974, **14**, 4428; C. R. C. Coussmaker, M. Hely Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 1961, 2705.
14 M. D. Hobday and T. D. Smith, *J. Chem. Soc. A*, 1970, 1085.
15 F. R. Hartley, 'The Chemistry of Platinum and Palladium,' J. Wiley and Sons, New York, 1973.
16 F. Balegroune, P. Braunstein, D. Grandjean, D. Matt, and D. Nobel, *Organometallics*, submitted for publication.
17 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
18 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, Tables 2.2b and 2.3.1.
19 B. A. Frenz, 'The Enraf-Nonius CAD4-SDP,' in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G. C. Bassi, University Press, Delft, The Netherlands, 1978, pp. 64—71.
20 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.

Received 24th March 1987; *Paper* 7/538