Nickel(II) and Palladium(II) Complexes of Diphenylphosphinoacetone and its Enolate†

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Complexes of diphenylphosphinoacetone (HL = Ph_2PCH_2COMe), $[NiCl_2(HL)_2]$ **1**, $[PdCl_2(HL)_2]$ **2** and its enolate $[NiL_2]$ **3** and $[PdL_2]$ **4**, have been synthesized and characterized by ^{31}P, ^1H NMR and IR spectroscopy. Single-crystal X-ray diffraction studies of **1**–**3** reveal square-planar geometry at the central atom. There is a *trans* arrangement in **1** and **2** and a *cis* arrangement for **3**. A ^1H NMR spin-saturation transfer experiment indicates that the complex **2** exists as a *cis–trans* equilibrium mixture in $CDCl_3$ solution. Complex **4** has a structure analogous to that of **3**, as revealed by ^1H NMR spectroscopy. Steric reasons for the geometrical preferences are discussed.

The synthesis of transition-metal complexes containing heterofunctionalized phosphine ligands is a subject of increasing interest, particularly with respect to their application in homogeneous catalysis. β-Ketophosphines co-ordinate to transition metals as mono- or bi-dentate neutral ligands or they form, mainly under basic conditions, chelating β-phosphinoenolates.[1-5] Complexes containing such phosphinoenolate fragments have been successfully used for the oligomerization[6] and polymerization[7] of ethylene. Our previous attempt[8] to obtain diphenylphosphinoacetone according to Brunner *et al.*[9] resulted in the formation of a phosphorane-type compound instead. Here we report the synthesis of some complexes of this ligand (HL), obtained by the method of Lutsenko and co-workers,[10] and its corresponding enolate (L), together with their structural study in the solid state and in solution.

Results and Discussion

Interaction of diphenylphosphinoacetone (HL) with a solution of $NiCl_2{\cdot}6H_2O$ or a suspension of $PdCl_2$ (in this case with subsequent refluxing) in ethanol yields the red complex $[NiCl_2(HL)_2]$ **1** and yellow $[PdCl_2(HL)_2]$ **2**. The planar dsp^2 configuration of **1** and **2** in the solid state follows from their colours, the *trans* arrangement from the presence of a single strong band at 394 (**1**) and 353 cm^{-1} (**2**) in their IR spectra due to the M–Cl vibration and typical for the *trans* Cl–M–Cl moiety.

The *trans* square-planar configuration in these complexes is also established by X-ray crystal structure determinations of **1** and **2**. Both complexes crystallize in the same space group *Pbca* and have similar unit-cell parameters; they are actually isomorphous. The metal atoms occupy a centre of symmetry forming centrosymmetric molecules. The co-ordination square of the central atoms is formed by two phosphorus and two chlorine atoms, disposed in a *trans* arrangement. The molecular structures and the atomic numbering schemes are depicted in Figs. 1 and 2. Important bond lengths and angles are listed in Table 1.

Table 1 Selected interatomic distances (Å) and angles (°) for $[NiCl_2(HL)_2]$ **1**, $[PdCl_2(HL)_2]$ **2** and $[NiL_2]$ **3**

	1	**2**	**3**
M–P	2.224(1)	2.312(2)	2.185(1)
M–O	3.277(4)	3.324(7)	1.893(3)
M–Cl	2.165(1)	2.301(2)	
P–C(1)	1.833(4)	1.832(8)	1.756(4)
P–C(4)	1.811(4)	1.820(8)	1.817(5)
P–C(10)	1.823(4)	1.834(8)	1.818(5)
C(1)–C(2)	1.503(5)	1.52(1)	1.357(7)
C(2)–C(3)	1.498(6)	1.48(1)	1.500(7)
O–C(2)	1.202(5)	1.20(1)	1.314(5)
Cl–M–P	87.60(4)	92.60(8)	
Cl–M–P′	92.40(4)	87.40(8)	
O–M–P	63.01(6)	61.9(1)	85.6(1)
C(1)–C(2)–O	122.5(4)	122.0(8)	122.7(4)
O–C(2)–C(3)	122.4(4)	122.7(9)	115.1(4)

The phosphorus and the oxygen atoms in the β-ketophosphine ligand are in an eclipsed conformation [torsion angle P–C(1)–C(2)–O −14.9(5) (**1**) and −16(1)° (**2**)]. Thus the carbonyl oxygen atoms approach the metal atoms by 3.277(4) (**1**) and 3.324(7) Å (**2**) from below and above the plane forming a pseudo-octahedral geometry. There is, of course, no real bonding at such long distances, but the conformation might be due to dipolar interactions. This conformation is also prone to give a chelate as soon as the oxygen becomes more nucleophilic (see the enolate structure below). On each phosphorus atom one phenyl group has a conformation perpendicular to the co-ordination plane.

The nickel complex **1** is not soluble in benzene and changes slowly when it is dissolved in alcohols, chloroform or dichloromethane. It was therefore not possible to perform an NMR study in solution. This behaviour is explained in terms of an equilibrium between the diamagnetic square-planar form **1** and a paramagnetic tetrahedral one, the latter dissociating with loss of the phosphine.[4,11]

A different situation was observed for the palladium complex **2** in $CDCl_3$. In an ^{31}P and ^1H NMR study the presence of two isomers in approximately 1:1 ratio was detected. These are the isomeric *cis* and *trans* forms of **2**. According to literature data,[12]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

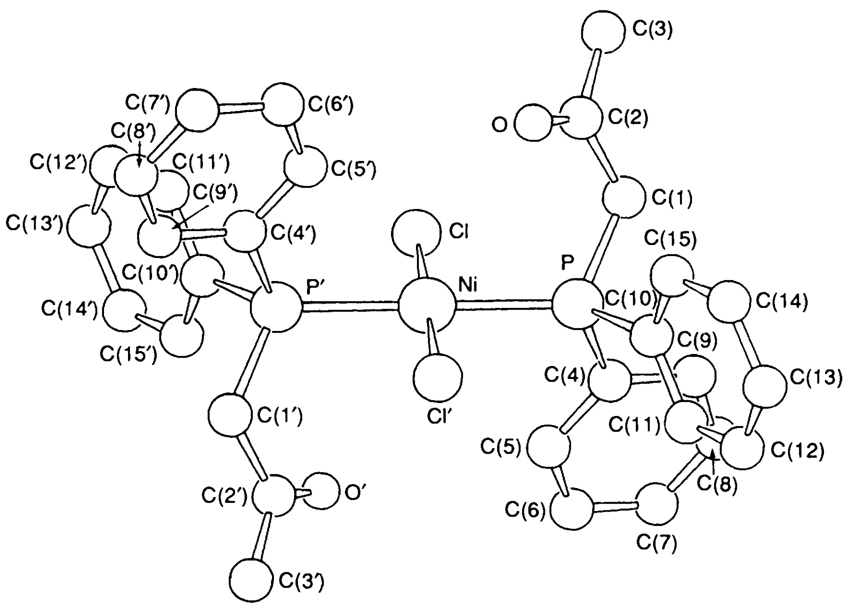

Fig. 1 Molecular structure of complex **1** with atomic numbering scheme

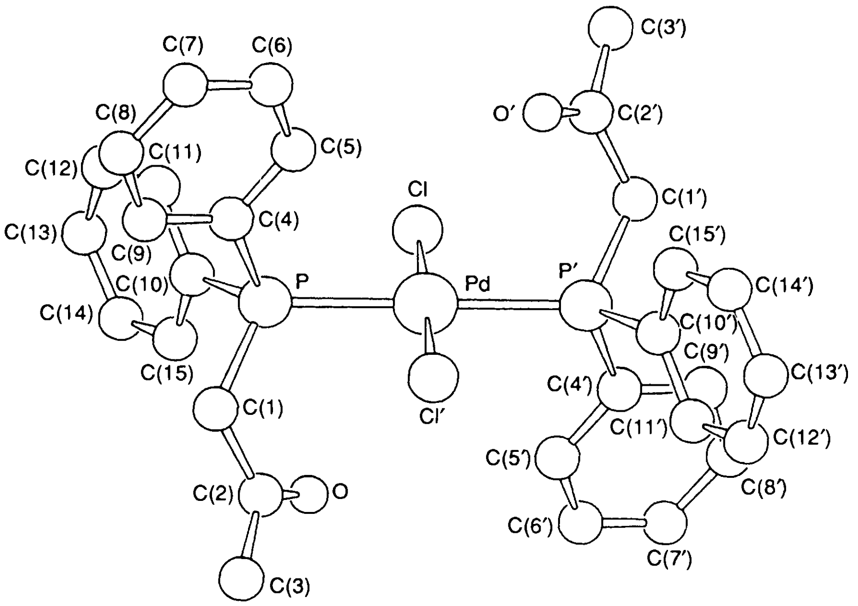

Fig. 2 Molecular structure of complex **2** with atomic numbering scheme

complexes of the type [PdX_2(phosphine)$_2$] are known to form *cis–trans* equilibrium mixtures in solution, while only one of the isomers can be isolated in the crystalline state. We confirmed this proposal by ^1H NMR spin-saturation transfer experiments. There are four signals in the non-phenyl region of the spectrum of the mixture: a singlet at δ 2.19 (CH_3) and a doublet at δ 3.84 (CH_2) for the *cis* isomer; a doublet at δ 2.36 (CH_3) and a (virtual) triplet at δ 3.79 (CH_2) for the *trans* isomer. The signals at δ 2.19 and 2.36 for the *cis* and *trans* form were subsequently irradiated. In both cases a decrease in the intensity of the non-irradiated methyl signals was observed, as a result of the exchange process between the two isomers. Parallel to this effect the signals of the methylene groups increased in intensity, probably due to the nuclear Overhauser effect. A similar behaviour in solution was recently reported by Braunstein and co-workers[3,4] for the related complex [$PdCl_2(Ph_2PCH_2COPh)_2$], although this information cannot be extended to the solid state. Our crystals of **1** and **2** are very uniform and show, as mentioned, only one isomer in the infrared spectrum.

Treatment of complexes **1** and **2** with a base (NaOMe in refluxing methanol) afforded the corresponding *cis* chelat complexes [NiL_2] **3** and [PdL_2] **4** [equation (1)]. Th

$$\textit{trans}\text{-}[MCl_2(Ph_2PCH_2COMe)_2] \xrightarrow[-2HCl]{NaOMe\ MeOH}$$

1 M = Ni
2 M = Pd

$$\textit{cis}\text{-}[\overline{M(Ph_2PCHCOMe})_2] \quad (1)$$

3 M = Ni
4 M = Pd

formation of the *cis* bis(enolate) [$\overline{Ni(Ph_2PCH{=}COPh})_2$] fron the corresponding acyclic dichloro compound was recentl described.[4] Complexes of the type [$\overline{M(Ph_2PCHCOR})_2$ (R = Ph; M = Ni,[4,13] Pd or Pt;[4] R = CF_3, M = Pd[14]) prepare independently all have *cis* geometry in contrast to the earlie reported[1] *trans*-[$\overline{M(Bu^t_2PCH{=}COR})_2$] (M = Ni, Pd, or P R = Ph or Bu^t). The *trans* geometry of the latter compounc was supposed to be due to the steric effect of the bulky Bı

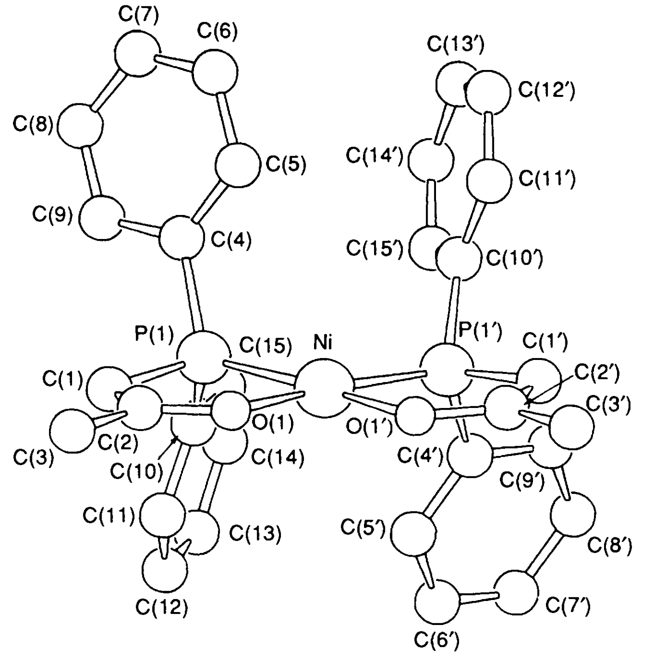

Fig. 3 Molecular structure of complex **3** with atomic numbering scheme

substituents.[4] Similarly to **1**, the nickel chelate **3** decomposes in alcohols, CH_2Cl_2 and $CHCl_3$, however its better solubility in benzene allowed NMR investigations. The signals of the PCH protons appear as doublets at δ 3.78 [J(PH) = 1.4 Hz] for **3** and at δ 3.78 [J(PH) = 3.32 Hz] for **4**. This is typical for complexes with rather small ^{2}J(PP) coupling constants, thus with a *cis* geometry,[3,4] whereas virtual triplets are reported for protons in H_2CP–M–PCH_2 groups with a *trans* arrangement of the phosphorus ligands.[1,15] The thus obtained bis(enolates) **3** and **4** in contrast to their acyclic precursors **1** and **2** show a relatively good thermal stability, so that molecular ion peaks at *m/z* 540 and 588, respectively, could be registered in their mass spectra.

The structure of the nickel complex **3** could also be established by a single-crystal X-ray diffraction study. Good-quality crystals were obtained from a benzene–dichloromethane solution. The molecular structure is shown in Fig. 3 together with the atomic numbering scheme. Selected bond distances and angles are in Table 1. Two phosphorus and two oxygen atoms in *cis* positions form the square-planar surroundings of the metal centre. The Ni atom itself lies on the two-fold axis (space group *C*2/*c*). The Ni–O and Ni–P distances [1.893(3) and 2.185(1) Å, respectively] are comparable to those found in *cis*-[$Ni(Ph_2PCHCOPh)_2$].[13] The conformation of the phenyl groups is such as to minimize their interaction on one phosphorus as well as between the two neighbouring groups. The intrinsic chelate angle P–Ni–O is quite close [85.6(1)°] to the ideal angle, and so is the angle O–Ni–O′ [86.1(1)°]. The angle P–Ni–P′ is the largest one [102.79(6)°]. Any larger group than phenyl should result in a distortion of the planar chelate or the square-planar geometry of the metal or eventually in a *trans* complex. The five-membered chelate ring is practically planar with no significant deviations [torsion angles P–Ni–O–C(2) 5.2(3)° and O–Ni–P–C(1) −6.6(1)°]. A comparison of the Ni–P bond lengths in **1** and **3**, 2.224(1) and 2.185(1) Å, respectively, indicates the expected differences in the relative *trans* effects of the ligands. The comparison of **1** and **3** shows a transformation of the carbonyl ligand (HL) with a CO double bond [1.202(5) Å] into an enolate system (L) with a C(1)–C(2) bond [1.357(7) Å] and a C(2)–O bond [1.314(5) Å] of intermediate length between double and single bonds.

Conclusion

In the solid state only *trans*-dichloro complexes of mono-coordinated β-ketophosphines seem to exist for nickel and palladium. The energy difference between such *cis* and *trans* complexes cannot be very high, since for **2** and a related complex described by Braunstein and co-workers[3,4] a *cis–trans* equilibrium is set up in solution. As can be seen from the structure of **3** a *cis* arrangement is only possible with a special conformation of the neighbouring phenyl groups. Although a *cis* complex [$MX_2(PR_3)_2$] should be more stable than the *trans* isomer, the steric interactions of the phosphorus substituents seem to be responsible for the geometry adopted by **1** and **2**. Different from the *cis* compounds **3** and **4**, in which the CH=CMeO part does not interfere with other ligands, this group has to be accommodated in the co-ordination sphere in addition to the two chloro ligands. Larger groups than phenyl do indeed give *trans*-bis(enolate) complexes of the nickel triad.[1]

With an extra methyl group on C(1) in the ligand $Ph_2PCHMeCMe{=}NPr^i$ we could isolate a nickel complex [$Ni(Ph_2PCMe{=}CMeO)_2$] from the reaction with aqueous nickel chloride corresponding to **3** in composition, but with the *trans* stereochemistry.[16] Obviously a slight change in the conformation of the phenyl groups in **3**, induced by the extra methyl group, is sufficient to favour the *trans* over the *cis* geometry. When the steric bulk is still larger, *e.g.* with the phosphinoimine ligand mentioned above or the ligands $Bu^t_2PCH_2CH{=}NC_6H_{11}$ and $Bu^t_2PCH_2CH{=}NBu^t$ only paramagnetic tetrahedral nickel complexes or chloro-bridged dimers are accessible under the same conditions.[17]

Experimental

All experiments including the synthesis of phosphines were carried out under an atmosphere of dry argon in Schlenk-type flasks. The ligand Ph_2PCH_2COMe was prepared according to the literature.[10] Infrared spectra were recorded on Perkin-Elmer 983 and 325 spectrometers in CsI for complexes **1** and **2** and in KBr for **3** and **4**, ^{1}H and ^{31}P NMR spectra on Bruker WP 80 SYFT and AM 360 instruments at 80 and 360 MHz for protons and at 32.4 MHz for phosphorus, and mass spectra on a CH7 FINNIGAN MAT with an electron-impact source (70 eV, *ca.* 1.12 × 10^{-17} J; 250 °C). Melting points were determined on a Kofler hot-stage microscope and are uncorrected.

Preparations.—*trans*-[$NiCl_2(Ph_2PCH_2COMe)_2$] **1**. The compound Ph_2PCH_2COMe (6.36 g, 26 mmol) was added to a solution of $NiCl_2 \cdot 6H_2O$ (3.12 g, 13 mmol) in ethanol (20 cm^3). The mixture was stirred for 10 min, then the red precipitate of complex **1** was filtered off, washed with cold EtOH (3 × 15 cm^3) and dried *in vacuo* (yield 4.15 g, 51.5%), m.p. 169–172 °C [from tetrahydrofuran (thf)] (Found: C, 58.25; H, 4.85; Cl, 11.5. Calc. for $C_{30}H_{30}Cl_2NiO_2P_2$: C, 58.65; H, 4.90; Cl, 11.55%); IR (CsI) ν(C=O) 1704, ν(Ni–Cl) 394 cm^{-1}.

trans-[$PdCl_2(Ph_2PCH_2COMe)_2$] **2**. The compound Ph_2PCH_2COMe (0.95 g, 3.9 mmol) was added dropwise to a stirred suspension of $PdCl_2$ (0.35 g, 1.9 mmol) in EtOH (25 cm^3). The mixture was refluxed for 3 h, decanted and the thus formed yellow precipitate recrystallized from thf (yield 0.62 g, 47.7%), m.p. 184–186 °C (Found: C, 54.20; H, 4.55; Cl, 10.65. Calc. for $C_{30}H_{30}Cl_2O_2P_2Pd$: C, 54.45; H, 4.55; Cl, 10.70%). IR (CsI): (C=O) 1708, ν(Pd–Cl) 353 cm^{-1}. NMR ($CDCl_3$): ^{1}H (360 MHz), δ 2.19 (s, CH_3, *cis* isomer), 2.36 [d, ^{4}J(PH) 1.8, CH_3, *trans* isomer], 3.79 [virtual t, ^{2+4}J(PH) 4.1, CH_2, *trans* isomer], 3.84 [d, ^{2}J(PH) 10.8 Hz, CH_2, *cis* isomer], and 7.11–7.75 (m, aromatic H); ^{31}P-{^{1}H}, δ 12.11 (*trans* isomer) and 22.35 (*cis* isomer).

cis-[$Ni(Ph_2PCHCOMe)_2$] **3**. Treatment of complex **1** (0.2 g, 0.32 mmol) with an excess of NaOMe in absolute MeOH (0.02 g, 0.87 mmol Na in 5 cm^3 MeOH) and refluxing the so-formed suspension for 0.5 h afforded **3** as orange plates after cooling to

Table 2 Positional parameters and their standard deviations for *trans*-$[\mathrm{NiCl_2(Ph_2PCH_2COMe)_2}]$ **1**

Atom	X/a	Y/b	Z/c
Ni	0.500 0(0)	0.000 0(0)	0.500 00(0)
Cl	0.362 7(1)	0.052 2(1)	0.443 02(7)
P	0.411 5(1)	−0.147 9(1)	0.536 96(5)
O	0.474 1(2)	−0.205 5(3)	0.385 6(1)
C(1)	0.333 4(3)	−0.214 6(4)	0.467 1(2)
C(2)	0.383 4(3)	−0.221 0(3)	0.394 4(2)
C(3)	0.312 3(4)	−0.250 0(5)	0.333 8(2)
C(4)	0.317 0(3)	−0.106 7(3)	0.603 5(2)
C(5)	0.233 3(3)	−0.173 2(4)	0.621 7(2)
C(6)	0.166 1(4)	−0.140 3(5)	0.675 1(3)
C(7)	0.180 0(4)	−0.041 6(5)	0.710 3(3)
C(8)	0.261 1(4)	0.025 4(5)	0.692 4(3)
C(9)	0.328 7(4)	−0.006 6(4)	0.639 0(3)
C(10)	0.479 2(3)	−0.263 5(3)	0.579 3(2)
C(11)	0.529 4(4)	−0.342 3(4)	0.537 7(3)
C(12)	0.581 7(4)	−0.430 5(4)	0.570 5(4)
C(13)	0.582 9(5)	−0.438 6(5)	0.643 9(4)
C(14)	0.533 8(4)	−0.358 6(5)	0.686 1(3)
C(15)	0.484 7(4)	−0.271 8(4)	0.653 7(3)

Table 3 Positional parameters and their standard deviations for *trans*-$[\mathrm{PdCl_2(Ph_2PCH_2COMe)_2}]$ **2**

Atom	X/a	Y/b	Z/c
Pd	0.500 0(0)	0.000 0(0)	0.500 00(0)
Cl	0.357 6(1)	0.053 4(2)	0.437 1(1)
P	0.591 1(1)	0.153 4(1)	0.462 4(1)
O	0.528 8(5)	0.209 1(6)	0.614 8(4)
C(1)	0.667 6(6)	0.218 8(7)	0.533 0(4)
C(2)	0.618 1(7)	0.223 4(6)	0.606 7(5)
C(3)	0.687 9(8)	0.245 2(8)	0.667 2(5)
C(4)	0.684 4(6)	0.113 3(6)	0.395 0(4)
C(5)	0.671 8(7)	0.014 0(7)	0.358 7(5)
C(6)	0.740 1(8)	−0.018 5(8)	0.307 3(5)
C(7)	0.819 8(7)	0.046 7(9)	0.289 4(5)
C(8)	0.834 7(7)	0.146 5(9)	0.324 9(5)
C(9)	0.766 5(6)	0.179 1(7)	0.377 5(5)
C(10)	0.522 1(5)	0.269 1(6)	0.421 0(5)
C(11)	0.517 8(7)	0.278 6(8)	0.347 1(5)
C(12)	0.464 9(8)	0.366(1)	0.316 3(6)
C(13)	0.415 6(8)	0.442 6(9)	0.358 8(8)
C(14)	0.417 4(8)	0.430 7(8)	0.432 3(8)
C(15)	0.469 2(6)	0.344 1(7)	0.463 1(6)

Table 4 Positional parameters and their standard deviations for *cis*-$[\overline{\mathrm{Ni(Ph_2PCHCO}}\mathrm{Me)_2}]$ **3**

Atom	X/a	Y/b	Z/c
Ni	0.5000(0)	0.6316(1)	0.2500(0)
P(1)	0.4738(1)	0.4879(1)	0.3386(1)
O(1)	0.4820(2)	0.7773(3)	0.3174(1)
C(1)	0.4681(3)	0.6102(5)	0.4094(2)
C(2)	0.4696(3)	0.7451(5)	0.3852(2)
C(3)	0.4603(4)	0.8687(5)	0.4347(3)
C(4)	0.3723(3)	0.3887(5)	0.3354(2)
C(5)	0.3096(3)	0.4073(5)	0.2789(3)
C(6)	0.2296(3)	0.3366(6)	0.2811(3)
C(7)	0.2124(4)	0.2541(6)	0.3379(3)
C(8)	0.2739(4)	0.2343(7)	0.3943(3)
C(9)	0.3540(4)	0.3025(6)	0.3935(3)
C(10)	0.5564(3)	0.3571(5)	0.3639(2)
C(11)	0.6323(3)	0.3998(6)	0.4030(3)
C(12)	0.7005(4)	0.3015(9)	0.4153(3)
C(13)	0.6918(5)	0.1669(9)	0.3899(4)
C(14)	0.6167(5)	0.1239(7)	0.3532(3)
C(15)	0.5486(4)	0.2177(5)	0.3405(3)

room temperature (yield 0.16 g, 89.9%), m.p. 234 °C (from MeOH) (Found: C, 65.40; H, 5.30%; M^+ 540. Calc. for $\mathrm{C_{30}H_{28}NiO_2P_2}$: C, 66.60; H, 5.20%; M^+ 540). IR (KBr): ν(C–C) + ν(C–O) 1520 cm^{-1}. NMR: ^{1}H ($\mathrm{C_6D_6}$, 80 MHz), δ 2.12 (s, 6 H, $\mathrm{CH_3}$), 3.78 [d, 4 H, ^2J(PH) 1.4 Hz, $\mathrm{CH_2}$] and 6.64–7.50 (m, 20 H, aromatic H); ^{31}P-{^{1}H} (thf–$\mathrm{C_6D_6}$ 2:1), δ 26.00.

cis-$[\overline{\mathrm{Pd(Ph_2PCHCO}}\mathrm{Me)_2}]$ **4**. The complex was prepared similarly to **3** from **2** (0.2 g, 0.3 mmol) as yellow prisms (yield 0.12 g, 67.8%), m.p. 242–243 °C (from thf) (Found: C, 61.65; H, 4.75%; M^+ 588. Calc. for $\mathrm{C_{30}H_{28}O_2P_2Pd}$: C, 61.20; H, 4.80%; M^+ 588). IR (KBr): ν(C–C) + ν(C–O) 1509 cm^{-1}. NMR ($\mathrm{CDCl_3}$): ^{1}H, δ 2.08 (s, 6 H, $\mathrm{CH_3}$), 3.78 [d, 4 H, ^2J(PH) 3.32 Hz, CH], and 6.93–7.37 (m, 20 H, aromatic H); ^{31}P-{^{1}H} $\mathrm{CDCl_3}$), δ 37.47.

Crystal Structure Determinations.—Complex **1**. $\mathrm{C_{30}H_{30}Cl_2NiO_2P_2}$, M = 614.11, red prisms from thf, orthorhombic, space group *Pbca*, a = 12.974(4), b = 12.016(2), c = 18.613(5) Å, U = 2902(1) Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centred reflections, λ = 1.540 51 Å), Z = 4, D_c = 1.406 g cm^{-3}, $F(000)$ = 1272. Air-stable crystals [with approximate dimensions 0.25 × 0.40 × 0.35 mm, μ(Cu-Kα) = 39.6 cm^{-1}] were measured on a Nonius CAD4 diffractometer; θ–2θ scan mode, variable scan speed, graphite monochromator, Cu-Kα radiation; 2926 reflections measured in the range 4.5 < 2θ < 153° (h 0–15, k 0–14, l −21 to 0), 1688 unique reflections with $I > 3\sigma(I)$. No intensity variation was observed during data collection. Intensity data were corrected for Lorentz and polarization factors, but not for absorption or extinction.

The structure was solved by heavy-atom and Fourier difference methods (SHELXS 86[18]) followed by several cycles of full-matrix least-squares refinement employing the SHELX 76[19] program system with scattering factors from the sources given therein. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found and refined isotropically except for the methyl group, where they were placed in calculated positions. The weighting scheme was $1/[\sigma^2(F_o) + 0.0003F_o^2]$. The last cycle of refinement included 218 variable parameters and gave R = 0.042 and R' = 0.048. No significant residual peaks were found in the final difference map. Calculations were carried out on a MicroVAX II computer. Fractional atomic coordinates are listed in Table 2.

Complex **2**. $\mathrm{C_{30}H_{30}Cl_2O_2P_2Pd}$, M = 661.84, yellow prisms from thf, orthorhombic, space group *Pbca*, a = 13.163(3), b = 12.053(2), c = 18.590(4) Å, U = 2949(1) Å^3 (from 17 automatically centred reflections, λ = 0.710 73 Å), Z = 4, D_c = 1.490 g cm^{-3}, $F(000)$ = 1344. An air-stable crystal [0.25 × 0.30 × 0.15 mm, μ(Mo-Kα) = 9.4 cm^{-1}] was measured on a Syntex P2$_1$ diffractometer; θ–2θ scan mode, variable scan speed, graphite-monochromated Mo-Kα radiation; 3067 reflections measured in the range of 4.5 < 2θ < 50° (h 0–15, k 0–22, l 0–14), 1175 unique reflections with $I > 3\sigma(I)$; no intensity decay was observed during the data collection period. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

The structure was solved and refined as for complex **1** with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions. The weighting scheme was $1/[\sigma^2(F_o) + 0.0005F_o^2]$. Final R = 0.038 and R' = 0.043 for 170 variable parameters. The final difference map showed no significant residual peaks. Fractional atomic coordinates are listed in Table 3.

Complex **3**. $\mathrm{C_{30}H_{28}NiO_2P_2}$, M = 541.21, orange plates from a $\mathrm{CH_2Cl_2}$–benzene solution, monoclinic, space group $C2/c$, a = 15.340(3), b = 9.494(2), c = 18.493(4) Å, β = 93.17(3)°, U = 2689(1) Å^3 (from 18 automatically centred reflections, λ = 1.540 51 Å), Z = 4, D_c = 1.337 g cm^{-3}, $F(000)$ = 1128.

Air-stable crystal [0.25 × 0.40 × 0.08 mm, μ(Cu-Kα) 23.6 cm^{-1}] measured on an Enraf-Nonius CAD4 diffractometer. Measurement conditions were as for complex **1**. 4997 Reflections measured (2θ range 4.5–153°, h −7 to 10, k −10 to 9, l −23 to 23), 2221 symmetry-independent reflections, 1838 with $I > 3\sigma(I)$. No intensity decay.

The structure was solved and refined as for complex **2**. The weighting scheme was $1/[\sigma^2(F_o) + 0.0003F_o^2]$. Final $R = 0.066$, $R' = 0.078$ for 160 variable parameters. No significant residual peaks in the final difference map were observed. Fractional atomic coordinates are listed in Table 4.

Bond lengths and angles were obtained using the program PLATON.[20] The molecular structures were drawn with the program SCHAKAL.[21]

Additional material available for all three structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 299.
2 H. D. Empsall, S. Johnson and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 302.
3 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.
4 P. Braunstein, D. Matt, D. Nobel, F. Balegroune, S.-E. Bouaoud, D. Grandjean and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1988, 353.
5 B. Guilbert, B. Demerseman, P. H. Dixneuf and C. Mealli, *J. Chem. Soc., Chem. Commun.*, 1989, 1035.
6 W. Keim, *Angew. Chem.*, 1990, **102**, 251; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235; M. Peuckert and W. Keim, *J. Mol. Catal.*, 1984, **22**, 289; W. Keim, *Chem.-Ing.-Tech.*, 1984, **56**, 850.
7 K. A. Ostoja Starzewski and J. Witte, *Angew. Chem.*, 1987, **99**, 76; W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 466.
8 O. Angelova, E. M. G. Kirilov, M. Kirilov, G. Petrov, J. Kaneti and J. Macicek, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1405.
9 H. Brunner, M. E. Dylla, G. A. M. Hecht and W. Pieronczyk, *Z. Naturforsch., Teil B*, 1982, **37**, 404.
10 Z. S. Novikova, M. V. Proskurnina, L. I. Petrovskaja, I. V. Bogdanova, N. P. Galitskova and I. F. Lutsenko, *Zh. Obshch. Khim.*, 1967, **37**, 2080.
11 L. Sacconi, F. Mani and A. Bencini, in *Comprehensive Co-ordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 5, pp. 108–110.
12 A. T. Hutton and C. P. Morely, in ref. 11, pp. 1158–1159.
13 H. Qichen, X. Minzhi, Q. Yanlong, X. Weihua, S. Meicheng and T. Youqi, *J. Organomet. Chem.*, 1985, **287**, 419; U. Klabunde, R. Mulhaupt, T. Herskovitz, A. H. Janowicz, J. Calabrese and S. D. Ittel, *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25**, 1989.
14 A. J. Carty, S. E. Jacobson, R. T. Simpson and N. J. Taylor, *J. Am. Chem. Soc.*, 1975, **97**, 7254.
15 H. tom Dieck and G. Hahn, *Z. Anorg. Allg. Chem.*, 1989, **577**, 74.
16 E. Georgiev, G. Hahn, H. tom Dieck, G. Fendesak, G. Petrov and M. Kirilov, unpublished work.
17 E. Zhelyaskova, G. Hahn, G. Fendesak and H. tom Dieck, unpublished work; E. Zhelyaskova, Diploma thesis, University of Hamburg, 1990.
18 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Solution, University of Göttingen, 1986.
19 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.
20 A. L. Spek, PLATON, *Computional Crystallography*, Clarendon Press, Oxford, 1982.
21 E. Keller, SCHAKAL, *Chem. Unserer Zeit.*, 1980, **14**, 56.

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