Phosphorus Double Functionalisation by Template Condensations; Formation of P–C and P–O Bonds from Metallocycles. Synthesis and Crystal Structure of *cis*-[$\overline{\text{PdCl}_2\{\text{Ph}_2\text{P}}$CHC(Ph)OP(Ph)(*o*-$C_6H_4CH_2NMe_2H$)}]Cl

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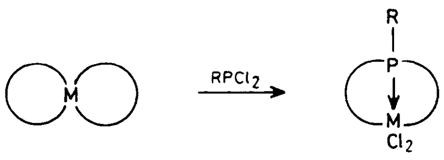
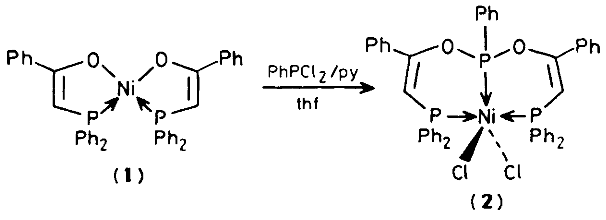
The air-stable bis-chelate complexes *cis*-[$\overline{\text{Ni}\{\text{Ph}_2\text{PCHC(O}}$)Ph}$_2$] (**1**) and [(L)$\overline{\text{Pd}\{\text{Ph}_2\text{PCHC(O}}$)Ph}] [(**3**), (LH) = dimethylbenzylamine; (**5**), (LH) = 8-methylquinoline] react smoothly with 1 equiv. of $PhPCl_2$ to afford coupling products [(**2**), and (**4**) and (**6**), respectively], involving the O atom of the enolate ligand and the Pd-bound C atom of the cyclometallated ligand.

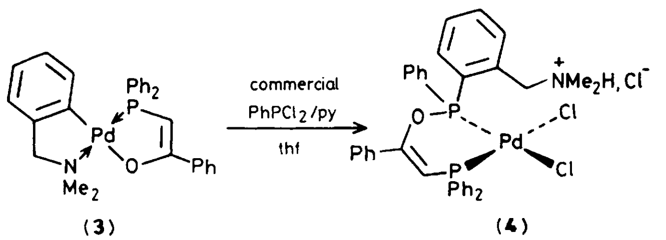
Template condensation reactions have been used rarely for the synthesis of trivalent phosphorus compounds.[1] However, the synthetic strategy depicted in Scheme 1, involving double coupling between phosphorus and a transition-metal bound atom, has considerable potential for the controlled construction of polyfunctional ligands. With this in mind, and as part of our studies on the ambident reactivity of transition-metal-co-



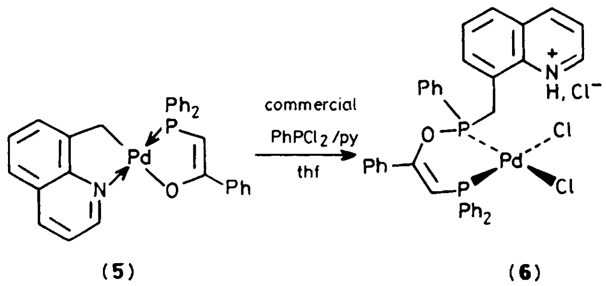
Scheme 1



Scheme 2



Scheme 3



Scheme 4

ordinated phosphino-enolates,[2] we treated *cis*-[$\overline{\text{Ni}\{\text{Ph}_2\text{PCH-C(O)Ph}\}_2}$] (**1**)† with 1 equiv. of $PhPCl_2$ in tetrahydrofuran (thf) (Scheme 2). The complex (**2**) was produced by double nucleophilic substitution of the P–Cl bonds by the enolate oxygen atoms; its spectroscopic properties† are consistent with a trigonal bipyramidal environment about the Ni atom.

In order to investigate the possibility of generalizing this reaction to systems containing two *different* metallocycles, thereby generating trivalent phosphorus compounds with three different substituents, the bicylic compound [$\overline{(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{Pd}\{\text{Ph}_2\text{PCHC(O)Ph}\}}$] (**3**)[3] was treated with 1 equiv. of $PhPCl_2$ (thf; 25 °C). Since we found that the resulting complex could be better isolated and purified in the form of the hydrochloride (**4**),† we used commercial $PhPCl_2$, which contains traces of HCl. However, in order to prevent enolate protonolysis,[4] the reaction of Scheme 3 was performed in the presence of pyridine (py), acting as an HCl trap. In the last step of the reaction, the acidic proton of pyH^+Cl^- is then transferred to the NMe_2 group.

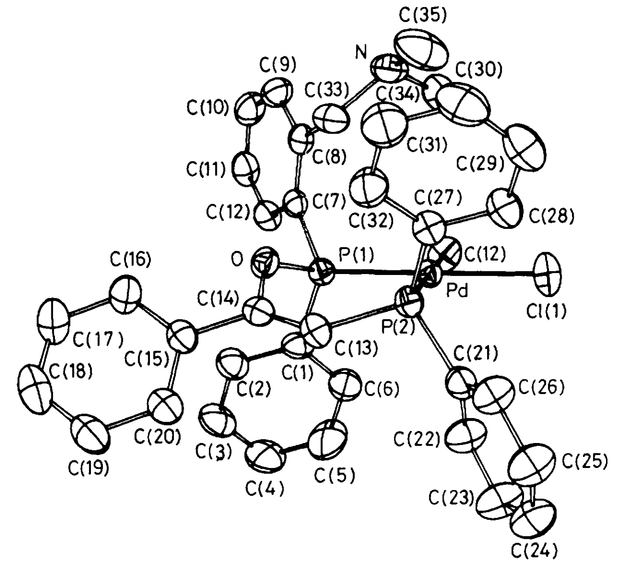


Figure 1. View of the structure of the cation of (**4**) (the H atom bonded to N is not shown). Selected distances (Å) and angles (°): Pd–Cl(1) 2.330(1), Pd–Cl(2) 2.352(1), Pd–P(1) 2.202(1), Pd–P(2) 2.244(1), P(1)–C(1) 1.803(3), P(1)–C(7) 1.803(3), P(1)–O 1.634(2), O–C(14) 1.399(4), C(14)–C(13) 1.329(5), C(13)–P(2) 1.796(4); Cl(1)–Pd–Cl(2) 92.00(4), Cl(1)–Pd–P(1) 178.17(4), P(1)–Pd–P(2) 92.06(4), P(1)–O–C(14) 121.7(2), P(2)–C(13)–C(14) 127.0(3).

This phosphorus double functionalisation was confirmed by the *X*-ray structure determination‡ of (**4**) (Figure 1). The chelating $\overline{\text{P(1) P(2)}}$ arm of the new $\overline{\text{P P N}}$ ligand is reminiscent of that found in *cis*-[$\overline{\text{PdCl}_2\{\text{Ph}_2\text{PCHC(Ph)OPPh}_2\}}$][3] or in [$\overline{\text{W(CO)}_4\{\text{Ph}_2\text{PCHC(Ph)OPPh}_2\}}$];[5] the $\overline{\text{P(1) N}}$ arm is unprecedented.

Notwithstanding the numerous (insertion) reactions involving the metal–carbon bond of cyclometallated compounds,[6] isolation of metal complexes resulting from carbon–phosphorus bond formation had not been achieved prior to this work, although they have been suggested as key intermediates in the synthesis of some important functional phosphines.[7]

This novel P–C coupling reaction involving a cyclometallated ligand has been extended to the case of an aliphatic carbon atom, as shown in Scheme 4 which involves the metallated 8-methylquinoline ligand. Spectroscopic and analytical data unambiguously support the structure depicted for the product (**6**).†

The potential of these new reactions, involving air-stable organometallic complexes, for the synthesis of complexes of functional phosphines, will be further evaluated.

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† *Procedure*. All reactions and operations, including the distillation of the solvents, were carried out under N_2. Compound (**1**) was prepared quantitatively by treating [$NiCl_2\{Ph_2PCH_2C(O)Ph\}_2$] with NaOEt in EtOH (*cf.* the analogous Pd complex[3]).

Compound (**2**). This green complex was isolated in 83% yield; i.r. (KBr) 1600s and 1571s cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 5.86 [d of virtual t, 2H, PCH, ^{2+4}J(PH) 5, ^4J(PH) 2.5 Hz] and 6.65—8.07 (35H, aromatic H); $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$) δ 2.2 [d, 2P, PCH, J(PP) 87 Hz] and 117.0 [t, 1P, PO, J(PP) 87 Hz] p.p.m.; u.v. (CH_2Cl_2; ε in $mol^{-1}\ dm^3\ cm^{-1}$) 403 (ε 3882), 310sh, 263 (28 623), 235sh, and 216 nm (55 098).

Compound (**4**). The complex slowly precipitated from the reaction mixture; 70% isolated yield; i.r. (KBr) 1597s, 1567m, and 1466s cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 2.50 (d, 3H, Me, ^3J 3.9 Hz), 2.78 (d, 3H, Me, ^3J 4.3 Hz), δ_A 4.70 and δ_B 5.22 [ABMX spin system, with M = N*H*, X = P(1), 2H, NCH_2, ^2J(AB) 14, ^3J(AM) 2.3, ^3J(BM) 2.9, ^4J(AX) *ca.* 0, ^4J(BX) 8.5 Hz], 5.90 [dd, 1H, P(2)CH, J(PH) 1.3 and 6.6 Hz], 6.94—8.65 (24H, aromatic H), and 12.41 (br s, 1H, NH); $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$) δ 2.0 (s, Ph_2*P*C), and 126.2 (s, Ph*P*O) p.p.m.

Compound (**6**). This complex was prepared in 75% yield by the reaction of [$\overline{(\text{C}_{10}\text{H}_8\text{N})\text{Pd}\{\text{Ph}_2\text{PCHC(O)Ph}\}}$] (**5**)[3] with 1 equiv. of commercial $PhPCl_2$, under the same conditions as for (**4**); i.r. (KBr) 1601s, 1570m, 1495m, and 1475w cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ_A 5.18 and δ_B 5.37 [ABX spin system with X = P, 2H, PCH_2,^2J(AB) 13.8, ^2J(AX) 4.7, ^2J(BX) 14 Hz], 5.51 [dd, 1H, PCH, J(PH) 1.1 and 7.3 Hz], and 7.18—8.78 (26 H, aromatic H); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2) δ 4.2 (s, *P*CH) and 135.2 (s, *P*O); $^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2) δ 34.53 [d, PCH_2, J(PC) 31.6 Hz], 91.30 [PCH, J(PC) 64.5 Hz], and 163.71 (s, CO) p.p.m.

‡ *Crystal data for* (**4**)·CH_2Cl_2: $C_{35}H_{34}Cl_3NOP_2Pd\cdot CH_2Cl_2$, M = 844.31, monoclinic, space group $P2_1/n$, a = 16.192(4), b = 15.191(4), c = 14.960(4) Å, β = 91.56(2)°, U = 3678.4 Å^3, Z = 4, D_c = 1.524 g cm^{-3}, F(000) = 1712, graphite-monochromated *X*-radiation, λ = 0.71069 Å, μ(Mo-K_α) = 9.793 cm^{-1}. Nonius CAD-4 diffractometer, $2 < \theta < 22°$, 4952 independent reflections, 3717 observed with $F_o^2 \geqslant 3\sigma(F_o^2)$. The structure was solved by Patterson techniques and refined by full-matrix least-squares methods to a final R = 0.027, R_w = 0.048. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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