Synthesis of a New Bifunctional Hemilabile Ligand by Insertion of PhNCO into a Co-ordinated β-Phosphinoketonate. Crystal Structure of $[(o\text{-}C_6H_4CH_2NMe_2)Pd(Ph_2PC[C(O)NHPh][C(Ph)O])]$

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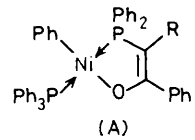
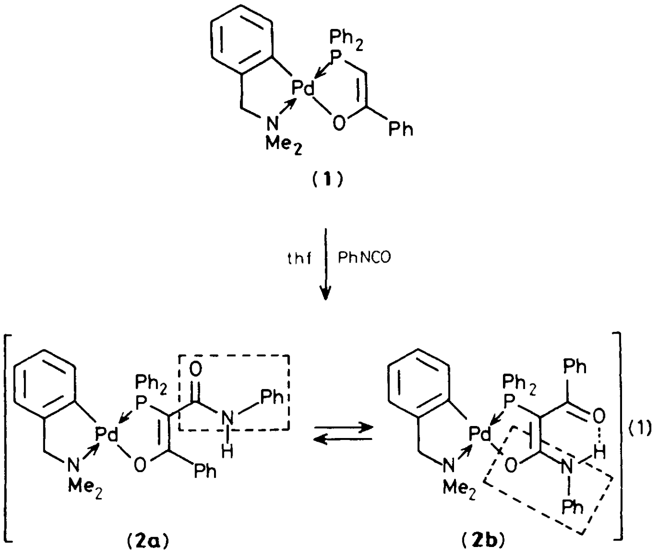
The air-stable complex $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCHC(O)Ph\}]$ (**1**) is an ambident reactive species which readily reacts with PhNCO affording the two isomers (**2a**) (title complex) and (**2b**) which formally result from insertion of isocyanate into the C–H bond of the phosphinoketonate; the resulting bifunctional phosphine ligand displays hemilabile character.

β-Phosphinoketonates are an important class of bidentate ligands. Complexes of type (A), containing such ligands are currently used as industrial catalysts for the oligomerisation of ethylene at relatively low temperatures and pressures.[1] Since small changes in the structure of tertiary phosphines often induce unexpected properties in their complexes,[2] it was of interest to find new related ligands which could be directly derived from co-ordinated phosphinoketonates. For our study, the ketonate of choice was $[Ph_2PCHC(O)Ph]^-$ and its reactivity was investigated when co-ordinated to a Pd^{II} centre bearing an ancillary three-electron donor cyclometallated ligand.

The complex $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCHC(O)Ph\}]$ (**1**) was prepared in quantitative yield by treating



(A)



[(o-$C_6H_4CH_2NMe_2$)]PdCl{$Ph_2PCH_2C(O)Ph$}][3] with NaH (1 equiv.) in tetrahydrofuran (thf). Complex (**1**) readily reacts with phenylisocyanate to afford a mixture of the C-alkylated isomeric products (**2a**) and (**2b**), equation (1).† They formally result from the nucleophilic addition of the PC–H bond of the phosphinoketonate across the C=O bond of PhNCO (Michael-type reaction). No O–C bond formation was observed under the reaction conditions.

The structure of (**2a**), shown in Figure 1, was determined by a single crystal *X*-ray analysis.‡ The palladium centre is in a nearly planar environment and is complexed by two chelates whose bite angles are respectively 83.7(1)° [P(1)–Pd–O(1)] and 82.7(2)° [C(1)–Pd–N(1)]. The keto-oxygen atom remains bonded to palladium whereas the amide function does not interact with the metal. The newly formed C(10)–C(18) bond has a length of 1.474(7) Å, indicative of electron delocalization within the ligand system.

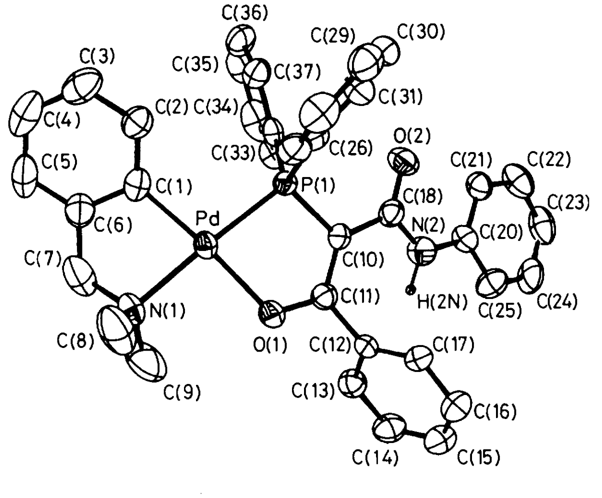
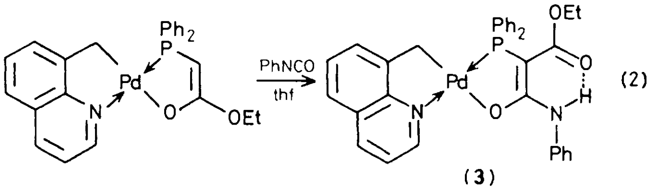
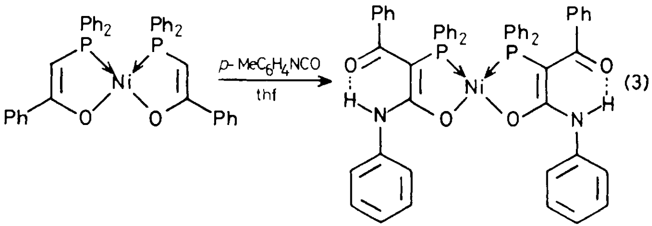


Figure 1. View of the structure of (**2a**). Selected distances (Å) and angles (°): Pd–P(1) 2.234(1), P(1)–C(10) 1.796(5), C(10)–C(11) 1.388(7), C(10)–C(18) 1.474(7), C(18)–N(2) 1.384(6), C(18)–O(2) 1.231(7), C(11)–O(1) 1.280(6), Pd–O(1) 2.096(3), Pd–C(1) 1.989(5), Pd–N(1) 2.139(4); P(1)–C(10)–C(11) 114.5(4), O(2)–C(18)–N(2) 120.3(4), C(10)–C(11)–O(1) 123.1(4), C(11)–O(1)–Pd 117.4(4).



(3)



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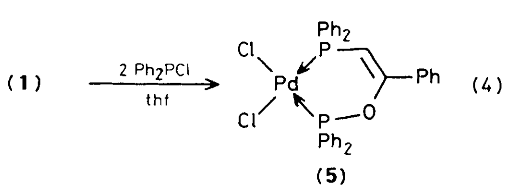

(5)

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† *Procedure:* All reactions and operations, including the distillation of the solvents were carried out under N_2. To a stirred solution of (**1**) (0.110 g, 0.20 mmol) in tetrahydrofuran (thf) (50 ml) phenylisocyanate (0.5 ml) was added. After stirring for 3 h, the solution was filtered. Addition of pentane afforded a white powder which was washed with Et_2O. Recrystallisation from CH_2Cl_2–pentane gave white crystals (0.117 g, 87%). One of these crystals was used for an *X*-ray analysis and was shown to have structure (**2a**). Isomer (**2b**) could not be identified in the solid although in solution, isomers (**2a**) and (**2b**) are always simultaneously present. I.r. (KBr): 3399 cm^{-1} [m, ν(NH) of (**2a**)], i.r. (CH_2Cl_2): 1631 (w), 1600 (w), 1591 (w), 1516 cm^{-1} (s); ^1H n.m.r. ($CDCl_3$): δ 2.86 [d, 6H, NMe_2 of (**2a**), ^4J(PH) 2.2 Hz], 2.92 [d, 6H, NMe_2 of (**2b**), ^4J(PH) 2.2 Hz], 3.90 (d, 2H, NCH_2 of (**2a**), ^4J(PH) 1.2 Hz], 4.02 [d, 2H, NCH_2 of (**2b**), ^4J(PH) 1.3 Hz], 6.27—8.14 (aromatic H), 6.50 [s, 1H, NH of (**2a**), exchanges with D_2O], 13.25 [br.s, 1H, NH of (**2b**), exchanges with D_2O]; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 29.0 (s) and 42.9 p.p.m. (s).

Compound (**3**): i.r. (KBr) 1484 (s), 1561 (s), 1597 (s), 1637 (s) cm^{-1}; ^1H n.m.r. (C_6D_6) δ 0.87 (t, 3H, CH_2CH_3, ^3J 7.0 Hz), 3.29 (br.s, 2H, CH_2Pd), 4.08 (q, 2H, OCH_2, ^3J 7.0 Hz), 7.05—9.08 (21H, aromatic H), 12.4 (s, 1H, NH); $^{31}P\{^1H\}$ n.m.r. (C_6D_6–thf): δ 25.4 p.p.m. (s).

Compound (**4**): i.r. (KBr): 1454 (m), 1463 (m), 1533 (s), 1558 (sh), 1596 cm^{-1} (m); ^1H n.m.r. ($CDCl_3$): δ 2.38 (s, 6H, Me), 6.15—7.56 (38H, aromatic H), 12.60 (br.s, 2H, NH); $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 23.0 p.p.m. (s).

Compound (**5**): i.r. (KBr): ν(C=C) 1600 cm^{-1} (s), ^1H n.m.r. (CD_2Cl_2): δ 5.97 [dd, PCH, J(PH) 2.0 Hz]; $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 4.2 [d, Ph_2PC, J(PP) 6 Hz], 129.5 p.p.m. [d, Ph_2PO, J(PP) 6 Hz].

‡ *Crystal data* for (**2a**): $C_{36}H_{33}N_2O_2PPd$, M = 663.05, monoclinic, space group $P2_1/c$, a = 14.898(9), b = 10.583(2), c = 19.118(9) Å, β = 90.43(2)°, U = 3014 Å^3, Z = 4, D_c = 1.46 g cm^{-3}, $F(000)$ = 1360, graphite monochromated *X*-radiation, λ = 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ = 6.93 cm^{-1}. Nonius CAD-4 diffractometer $1 < \theta < 25°$, 5456 independent reflections, 2929 observed with $F_o^2 \geqslant 3\sigma(F_o^2)$. The structure was solved by heavy atom methods and refined by least squares to a final R = 0.033, R_w = 0.041. 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.

The new functional ligand resulting from the PhNCO insertion reaction can be viewed as a ambident phosphino diketonate, whose possible rotation about the P–C bond accounts for the observation of isomers (**2a**) and (**2b**). The structure of isomer (**2b**) was deduced (i) from the observation of a broad signal at δ_H 13.25 in the ^{1}H n.m.r. spectrum, characteristic for the N–H · · · O proton of this isomer, and (ii) by comparison with the structure of (**3**),† obtained as the only isomer in the reaction of equation (2), and for which the N–H · · · O proton appears at δ_H 12.4.

Dissolution in CD_2Cl_2 at −10 °C of the solid containing crystals of (**2a**) afforded a solution containing isomers (**2a**) (major) and (**2b**) (minor) which are present at equilibrium (25 °C) in a *ca.* 1 : 1 ratio. The equilibration is slow on the n.m.r. time scale. Furthermore, we could determine that at room temperature, the isocyanate insertion is not reversible, in contrast to related CO_2 insertion reactions.[4] Therefore, this isomerization does not proceed by deinsertion of PhNCO but results from the hemilabile character of the $\widehat{P\,O}$ chelates. There is currently a strong interest in such ligands because they can stabilize, in the solid state, highly reactive co-ordinatively unsaturated species.

Reaction (1) is somewhat analogous to the recently reported insertion reactions of PhNCO or CO_2 into olefinic C–H bonds, leading to acrylamides (Ni)[5] or acrylic acid (Mo),[6] respectively. This reaction has a general potential, as shown for example by equation (3) where a double isocyanate insertion occurs, affording (**4**)† in *ca.* 70% yield.

Whereas in reaction (1) the C atom of the enolate is the reactive centre, nucleophilic attack of the oxygen of (**1**) occurs with PPh_2Cl, affording (**5**) quantitatively, equation (4). It has recently been shown that the co-ordinated phosphine–phosphinite ligand thus formed may also be generated by thermal treatment of $[PdCl_2\{Ph_2PCH_2C(O)Ph\}_2]$,[3] or photochemically from $Ph_2PCH(COPh)PPh_2$ in the co-ordination sphere of tungsten.[7]

Reactions (1)—(4) illustrate the ambident reactivity of the co-ordinated $[Ph_2PCHC(O)Ph]^-$ ligand and its potential for the synthesis of new functional ligands.

We thank the C.N.R.S. and S.N.P.E. for financial support and for a grant to D. N. and Johnson Matthey Technology Centre for a generous loan of $PdCl_2$.

Received, 3rd November 1986; Com. 1571

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