Contribution from the Laboratoire de Chimie de Coordination, Associé au CNRS (UA 416),
Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cédex, France,
and Laboratoire de Cristallochimie, Associé au CNRS (UA 254), Université de Rennes I,
Avenue du Général Leclerc, F-35042 Rennes Cédex, France

Complexes with Functional Phosphines. 12.[1] Carbon–Carbon Coupling Reactions by Isocyanate Insertion into Nickel-, Palladium-, and Platinum-Coordinated β-Phosphino Enolates. Molecular Structures of $[(C_{10}H_8N)Pd(Ph_2PC\{C(O)OEt\}\{{=}C(O)NHPh\})]$ and *cis*-$[Ni(Ph_2PC\{C(O)Ph\}\{{=}C(O)NH(p\text{-}MeC_6H_4)\})_2]\cdot CH_2Cl_2$

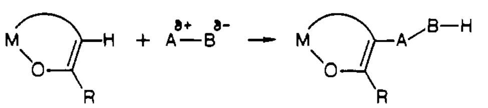
Salah-Eddine Bouaoud,† Pierre Braunstein,*,‡ Daniel Grandjean,† Dominique Matt,*,‡
and Dominique Nobel‡

Received October 14, 1987

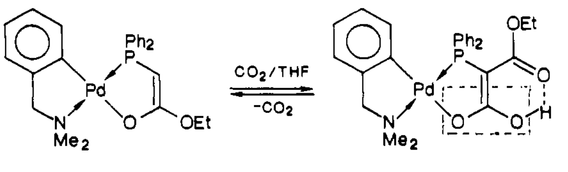
Phenyl isocyanate was reacted with $[(C\ N)Pd\{R_2PCH{=}C(O)OEt\}]$ (**1**, $C\ N$ = o-$C_6H_4CH_2NMe_2$, R = Ph; **2**, $C\ N$ = $C_{10}H_8N$, R = Ph; **3**, $C\ N$ = o-$C_6H_4CH_2NMe_2$, R = c-C_6H_{11}) to afford the complexes $[(C\ N)Pd(R_2PC\{C(O)OEt\}\{{=}C(O)NHPh\})]$ (**4**–**6**), respectively, resulting from isocyanate insertion into the C–H bond of the enolate. Complex **5** has been characterized by a complete single-crystal X-ray diffraction study: triclinic, space group $P\bar{1}$ with $Z = 2$, $a = 9.276$ (2) Å, $b = 12.290$ (7) Å, $c = 14.336$ (8) Å, $\alpha = 70.38$ (3)°, $\beta = 86.70$ (2)°, $\gamma = 69.18$ (2)°, $V = 1435.6$ Å^3, and ρ(calcd) = 1.478 g cm^{-3}. The structure has been refined for the 2676 reflections with $I > 3\sigma(I)$ to $R = 0.037$ and $R_w = 0.045$. In this molecule the polyfunctional phosphine is P,O(amide)-bonded to the metal center, and the NH proton is in strong interaction with the conjugated ester group. With the exception of the P-bonded aryl groups, this molecule displays a high degree of planarity. When phenyl isocyanate was reacted with the related ketonates $[(C\ N)Pd\{Ph_2PCH{=}C(O)Ph\}]$ (**7**, $C\ N$ = o-$C_6H_4CH_2NMe_2$; **8**, $C\ N$ = $C_{10}H_8N$), two C–C coupling products were formed, namely $[(C\ N)Pd(Ph_2PC\{{=}C(O)Ph\}\{C(O)NHPh\})]$ (**9a** and **10a**, respectively) and $[(C\ N)Pd(Ph_2PC\{C(O)Ph\}\{{=}C(O)NHPh\})]$ (**9b** and **10b**, respectively). These are present in a ca. 1:1 ratio and were shown to be in equilibrium. An exchange mechanism between the **a** and **b** forms is proposed. A comparison is made between the carbon–carbon coupling reactions involving complexes **1**–**3**, **7**, and **8** and the heterocumulenes ArNCO and CO_2. The ArNCO coupling reaction also occurred when the β-phosphino ketonate was coordinated to other metals. With *cis*-$[Ni\{Ph_2PCH{=}C(O)Ph\}_2]$ (**11**), the complexes *cis*-$[Ni(Ph_2PC\{C(O)Ph\}\{{=}C(O)NH(Ar)\})_2]$ (**12**, Ar = Ph; **13**, Ar = p-MeC_6H_4) were formed as a result of isocyanate insertion into each PC–H bond. The molecular structure of **13**·CH_2Cl_2 has been determined by X-ray diffraction: triclinic, space group $P\bar{1}$ with $Z = 2$, $a = 14.363$ (4) Å, $b = 14.602$ (12) Å, $c = 14.324$ (4) Å, $\alpha = 112.23$ (4)°, $\beta = 109.56$ (2)°, $\gamma = 99.19$ (4)°, $V = 2475.4$ Å^3, and ρ(calcd) = 1.364 g cm^{-3}. The structure has been refined for the 3325 reflections with $I > 4.5\sigma(I)$ to $R = 0.042$ and $R_w = 0.053$. The coordination around the Ni atom is approximately square planar, with Ni–P and Ni–O bond lengths of respectively 2.170 (3) Å (average) and 1.877 (4) Å (average). Whereas each of the N-bonded aryl groups is conjugated with the planar diketonate system, the phenyl groups attached to the keto groups are almost perpendicular to the metal coordination plane in order to minimize repulsions with the neighboring PPh_2 groups. The reaction of phenyl isocyanate with *cis*-$[Pt\{Ph_2PCH{=}C(O)Ph\}_2]$ gave the monoinsertion product $[Pt\{Ph_2PCH{=}C(O)Ph\}(Ph_2PC\{C(O)Ph\}\{{=}C(OH)NPh\})]$ (**15**), in which a third bonding mode (P,N) of this class of functional phosphines was found. All complexes were characterized by elemental analyses and IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

Chelating enolates possessing a hydrogen atom in the position β to the coordinated oxygen atom are known to undergo reactions with electrophiles at the methine position:[2]



Such reactions have initially been shown to occur on coordinated β-diketonates or β-keto imine derivatives but have been applied only minimally to systems containing a trivalent phosphorus atom as one end of the chelate. In our laboratory, we have found that this reaction type could be extended to β-phosphino enolates.[3] Thus, reaction of CO_2 with complex **1** instantaneously led to the coupling product of eq 1, which resulted from the formal insertion of CO_2 into the olefinic C–H bond. This turned out to be a reaction of considerable interest for CO_2 chemistry, in particular, because of involving CO_2 activation via reversible C–C bond formation.[4] These Michael-type reactions also provide a means of chemically modifying a functional phosphine ligand.[5] Chelates with P,O donor atoms constitute a very important class of ligands for homogeneous catalysis. Indeed complexes containing a dissymmetric ligand often possess properties drastically different from those observed for similar complexes containing symmetrical ligands. Furthermore, in a number of P,O chelate complexes, easy and reversible metal–oxygen dissociation occurs, providing a



(1)

---

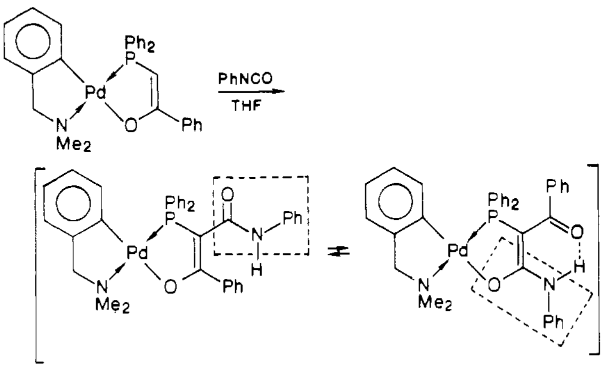
† Université de Rennes.
‡ Université Louis Pasteur.

(1) Part 11: Braunstein, P.; Matt, D.; Nobel, D.; Balegroune, F.; Bouaoud, S.-E.; Grandjean, D.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1988**, 353.
(2) See for example: (a) Collman, J. P. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 132. (b) Nelson, J. H.; Howells, P. N.; Landen, G. L.; DeLullo, G. C.; Henry, R. A. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. 3, 921.
(3) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.
(4) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.*, in press.
(5) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *J. Chem. Soc., Chem. Commun.* **1987**, 488.
(6) Behr, A.; Freundenberg, U.; Keim, W. *J. Mol. Catal.* **1986**, *35*, 9.
(7) Agbossou, S.; Bonnet, M. C.; Tkatchenko, I. *Nouv. J. Chim.* **1985**, *5*, 311.

0020-1669/88/1327-2279$01.50/0

readily accessible coordination site for an incoming substrate, a key prerequisite for homogeneous catalysis.[8,9]

The reaction of eq 1 was found to depend strongly on the nature of the phosphino enolate used. Thus, with complexes containing the ketonate $[Ph_2PCH{=}C(O)Ph]^-$, no reaction occurred with CO_2 under ambient conditions.[12] However, the more reactive heterocumulenes Ar—N=C=O (Ar = aromatic ring) were found to insert into the olefinic C-H bond of the latter ligand,[5] in a manner reminiscent of that of eq 1, in agreement with the general view that isocyanates are CO_2-like molecules (eq 2). From their unsymmetrical nature, one might furthermore anticipate the observation of isomeric structures, i.e., the formation of M-O or M-N bonds, not available with CO_2 itself. Stoichiometric insertion reactions of carbon dioxide and isocyanates occurring via C-C coupling[10] are of high current interest since they are relevant to the catalytic functionalization of unsaturated hydrocarbons.[4,11] In this paper, we will describe novel aspects of the coupling reaction of coordinated β-phosphino enolates with aryl isocyanates and describe the coordination properties of the resulting multifunctional ligands for which hemilabile behavior may be observed and for which tuning of three different coordination modes can be accomplished. A preliminary report on aspects of this work has appeared.[5]



(2)

Experimental Section

All reactions were performed in Schlenk-type flasks under purified nitrogen by using previously detailed procedures.[12] The solvents and organic isocyanates were distilled under nitrogen and dried prior to use. *Caution*! Isocyanates are both toxic and lacrymatory. Infrared spectra were recorded in the region 4000–400-cm^{-1} on a Perkin-Elmer 398 spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 200.1 and 81.1 MHz, respectively, on a FT Bruker WP-200 SY instrument. ^1H and ^{31}P chemical shifts are given relative to external Me_4Si and H_3PO_4, respectively. A positive sign denotes a shift downfield from that of the reference.

Syntheses. The complexes $[(C\ N)Pd\{Ph_2PCH{=}C(O)R\}]$[3,12] (where CH N = *N,N*-dimethylbenzylamine ($C_6H_5CH_2NMe_2$) and 8-methylquinoline ($C_{10}H_9N$); R = Ph, OEt) and *cis*-$[M\{Ph_2PCH{=}C(O)Ph\}]$[1] (with M = Ni (**11**), Pt (**14**)) were obtained as reported previously. By analogy with the synthesis of **1**, the complex $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Cy_2PCH{=}C(O)OEt\}]$ (**3**) was prepared in nearly quantitative yield by treating $[(o\text{-}C_6H_4CH_2NMe_2)PdCl\{Cy_2PCH_2C(O)OEt\}]$ with NaH in THF for 15 h (IR (KBr): 1525 (ν(C—O) + ν(C=C)) vs cm^{-1}. ^1H NMR (C_6D_6): δ 0.89–2.33 (22 H, cyclohexyl H), 1.32 (t, 3 H, CH_3CH_2, ^3J = 7.0 Hz), 2.43 (d, 6 H, NMe_2, $^4J(PH)$ = 2.0 Hz), 3.12 (d, 1 H, PCH, $^2J(PH)$ = 2.1 Hz), 3.48 (d, 2 H, NCH_2, $^4J(PH)$ = 0.9 Hz), 4.20 (q, 2 H, OCH_2, ^3J = 7.0 Hz), 6.95–7.55 (4 H, aromatic H)).

$[(o\text{-}C_6H_4CH_2NMe_2)Pd(Ph_2PC\{C(O)OEt\}\{{=}C(O)NHPh\})]$ (4). Phenyl isocyanate (1 mL, ca. 9 mmol) was added dropwise at room temperature to a stirred solution of $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH{=}C(O)OEt\}]$ (**1**) (0.128 g, 0.25 mmol) in THF (10 mL). After being stirred for 1 h, the solution was filtered, and hexane was added to the filtrate to precipitate a white powder, which was washed several times with Et_2O. Recrystallization from THF/hexane afforded white, air-stable crystals of **1** (0.130 g, 82%) (mp 190 °C dec). Anal. Calcd for $C_{32}H_{33}N_2O_3PPd$ (M_r = 631.00): C, 60.91; H, 5.27; N, 4.55. Found: C, 60.69; H, 5.20; N, 4.38. IR (KBr): 1485 s, 1560 s, 1587 s, 1625 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.72 (t, 3 H, CH_3, ^3J = 7.1 Hz), 2.83 (d, 6 H, NMe_2, $^4J(PH)$ = 2.2 Hz), 3.82 (q, 2 H, OCH_2, ^3J = 7.1 Hz), 3.88 (d, 2 H, NCH_2, $^4J(PH)$ = 1.7 Hz), 6.61–7.88 (19 H, aromatic H), 11.23 (s, 1 H, NH). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 31.0 (s).

$[(C_{10}H_8N)Pd(Ph_2PC\{C(O)OEt\}\{{=}C(O)NHPh\})]$ (5). This complex was prepared by using a procedure similar to that for **4**, starting from 0.130 g (0.25 mmol) of $[(C_{10}H_8N)Pd\{Ph_2PCH{=}C(O)OEt\}]$ (**2**). The product was recrystallized from THF/hexane, affording white, air-stable crystals suitable for X-ray analysis (0.135 g, 84 %) (mp 200 °C dec). Anal. Calcd for $C_{33}H_{29}N_2O_3PPd$ (M_r = 639.00): C, 62.03; H, 4.57; N, 4.38. Found: C, 62.3; H, 4.42; N, 4.40. IR (KBr): 1484 s, 1561 s, 1597 s, 1637 s cm^{-1}. ^1H NMR (C_6D_6): δ 0.87 (t, 3 H, CH_2CH_3, ^3J = 7.1 Hz), 3.29 (br s, 2 H, CH_2Pd), 4.08 (q, 2 H, OCH_2, ^3J = 7.1 Hz), 7.05–9.08 (21 H, aromatic H), 12.4 (s, 1 H, NH). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 25.4 (s).

$[(o\text{-}C_6H_4CH_2NMe_2)Pd(Cy_2PC\{C(O)OEt\}\{{=}C(O)NHPh\})]$ (6). This complex was prepared by using a procedure similar to that for **4**, starting from 0.131 g (0.25 mmol) of **3**. This highly soluble complex was obtained as a pale yellow solid foam (100% spectroscopic yield), difficult to purify. It was only characterized spectroscopically. IR (KBr): 1480 s, 1497 s, 1557 s, 1590 vs, 1612 ms, 1620 ms cm^{-1}. ^1H NMR ($CDCl_3$): δ ca. 1.1–2.5 (22 H, cyclohexyl H), 1.31 (t, 3 H, CH_3CH_2, ^3J = 7.1 Hz), 2.71 (d, 6 H, NMe_2, $^4J(PH)$ = 2.2 Hz), 3.88 (d, 2 H, NCH_2, $^4J(PH)$ < 1 Hz), 4.16 (q, 2 H, OCH_2, ^3J = 7.1 Hz), 6.90–7.50 (9 H, aromatic H), 11.32 (s, 1 H, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.4 (s).

$[(o\text{-}C_6H_4CH_2NMe_2)Pd(Ph_2PC\{{=}C(O)Ph\}\{C(O)NHPh\})]$ (9a) and $[(o\text{-}C_6H_4CH_2NMe_2)Pd(Ph_2PC\{C(O)Ph\}\{{=}C(O)NHPh\})]$ (9b). To a stirred solution of $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH{=}C(O)Ph\}]$ (**7**) (0.110 g, 0.20 mmol) in THF (50 mL) was added dropwise PhNCO (0.5 mL, ca. 4.5 mmol). After being stirred for 3 h, the solution was filtered. Addition of pentane afforded a white, air-stable powder, which was washed with Et_2O. Recrystallization from CH_2Cl_2/pentane gave white crystals (0.117 g, 87%). One of these crystals was shown to have structure **9a** (X-ray analysis). Anal. Calcd for $C_{36}H_{33}N_2O_2PPd$ (M_r = 663.06): C, 65.21; H, 5.02; N, 4.22. Found: C, 64.92; H, 4.91; N, 3.94. Isomer **9b** could not be unambiguously identified in the solid thus obtained, although in solution **9a** and **9b** were always simultaneously present in a ca. 1:1 ratio at room temperature. Dissolution of the crystals at −30 °C afforded a mixture of **9a** (major product) and **9b** (minor product). IR (KBr): 3399 (ν(NH) of **9a**) m cm^{-1}. IR (CH_2Cl_2): 1516 ms, 1591 w, 1600 w, 1631 w cm^{-1}. ^1H NMR (CD_2Cl_2, at room temperature): δ 2.86 (d, 6 H, NMe_2 of **9b**, $^4J(PH)$ = 2.2 Hz), 2.92 (d, 6 H, NMe_2 of **9a**, $^4J(PH)$ = 2.2 Hz), 3.90 (d, 2 H, NCH_2 of **9b**, $^4J(PH)$ = 1.2 Hz), 4.02 (d, 2 H, NCH_2 of **9a**, $^4J(PH)$ = 1.3 Hz), 6.27–8.14 (48 H, aromatic H), 6.50 (s, 1 H, NH of **9a**, exchanges with D_2O), 13.25 (br s, 1 H, NH of **9b**, exchanges with D_2O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.0 (s), 42.9 (s) (signals not assigned).

Reaction of $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH{=}C(O)Ph\}]$ with *p*-MeC_6H_4NCO. The reaction of 0.010 g of **7** in 1 mL of CD_2Cl_2 and ca. 0.005 g of *p*-MeC_6H_4NCO was followed by ^1H NMR spectroscopy. After ca. 1.5 h, more than 70% of **1** was converted. As for **9**, the reaction product was shown to be present in the form of two isomers (**9a**:**9b** ≈ 1:1). ^1H NMR (CD_2Cl_2, room temperature): δ 2.22 (s, Me (isocyanate)), 2.38 (s, Me (isocyanate)), 2.84 (d, NMe_2, $^4J(PH)$ < 1 Hz), 2.91 (d, NMe_2, $^4J(PH)$ < 1 Hz), 3.87 (s, NCH_2), 4.04 (s, NCH_2), 6.54 (s, NH of isomer **a**), 6.28–8.15 (aromatic H), 13.17 (br s, NH of isomer **b**).

$[(C_{10}H_8N)Pd(Ph_2PC\{{=}C(O)Ph\}\{C(O)NHPh\})]$ (10a) and $[(C_{10}H_8N)Pd(Ph_2PC\{C(O)Ph\}\{{=}C(O)NHPh\})]$ (10b). To a stirred so-

---

[8] Braunstein, P.; Matt, D.; Nobel, D.; Bouaoud, S.-E.; Carluer, B.; Grandjean, D.; Lemoine, P. *J. Chem. Soc., Dalton Trans.* **1986**, 415 and references cited therein.

[9] (a) Bressan, M.; Morandini, F.; Morvillo, A.; Rigo, P. *J. Organomet. Chem.* **1985**, *280*, 139. (b) Lindner, E.; Schober, U.; Stängle, M. *Ibid.* **1987**, *331*, C13. (c) Lindner, E.; Meyer, S. *Ibid.* **1988**, *339*, 193.

[10] (a) Alvarez, R.; Carmona, E.; Cole-Hamilton, D. J.; Galindo, A.; Guttiérrez-Puebla, E.; Monge, A.; Podeva, M. I.; Ruiz, C. *J. Am. Chem. Soc.* **1985**, *107*, 5529. (b) Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 771. (c) Hoberg, H.; Hernandez, E. *J. Chem. Soc., Chem. Commun.* **1986**, 544. (d) Hoberg, H.; Hernandez, E. *J. Organomet. Chem.* **1987**, *328*, 403.

[11] Hoberg, H.; Sümmermann, K.; Milchereit, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 325.

[12] Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

lution of $[(C_{10}H_8N)Pd\{Ph_2PCH{=}C(O)Ph\}]$ (**8**) (0.100 g, 0.18 mmol) in THF (50 mL) was added PhNCO (0.5 mL, ca. 4.5 mmol). After being stirred for 3 h, the solution was filtered. Addition of pentane to the filtrate precipitated a white, air-stable powder, which was recrystallized from CH_2Cl_2/pentane, affording white crystals of **10** (0.109 g, 90%). Anal. Calcd for $C_{37}H_{29}N_2O_2PPd$ (M_r = 671.05): C, 66.23; H, 4.36; N, 4.17. Found: C, 66.37; H, 4.44; N, 4.06. IR (KBr): 1488 s, 1500 s, 1513 s, 1589 ms, 1598 m, 1635 s, 3420 (ν(NH) of **10a**) m cm^{-1}. When crystals of **10** were dissolved at 0 °C, both isomers **10a** (major) and **10b** (minor) were detected (Figure S-1). When equilibrium was attained at room temperature, **10a** and **10b** were found to be present in a ca. 1:1 ratio. ^1H NMR (C_6D_6): δ 3.10 (d, 2 H, CH_2Pd of **10b**, ^3J(PH) < 1 Hz), 3.37 (d, 2 H, CH_2Pd of **10a**, ^3J(PH) < 1 Hz), 6.50 (s, 1 H, NH of **10a**, exchanges with D_2O), 6.56–9.17 (52 H, aromatic H), 14.51 (s, 1 H, NH of **10b**, exchanges with D_2O). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 23.6 (s), 37.8 (s) (signals not assigned).

Reaction of $[(C_{10}H_8N)Pd\{Ph_2PCH{=}C(O)Ph\}]$ with p-MeC_6H_4NCO. This reaction was followed by ^1H NMR spectroscopy (CD_2Cl_2), with 0.010 g of **8** and ca. 0.005 g of p-MeC_6H_4NCO. After ca. 1.5 h the conversion was between 50 and 60% completed and, as for **10**, the reaction product was present in the form of two isomers, in a ca. 1:1 ratio. ^1H NMR (CD_2Cl_2, room temperature): δ 2.22 (s, Me (isocyanate)), 2.33 (s, Me (isocyanate)), 2.85 (d, NCH_2, ^3J(PH) = 1.2 Hz), 3.09 (d, NCH_2, ^3J(PH) = 1.2 Hz), 6.46 (s, NH of isomer **a**, exchanges with D_2O), 6.56–8.43 (aromatic H), 13.30 (s, NH of isomer **b**).

***cis*-$[Ni(Ph_2PC\{C(O)Ph\}\{=C(O)NHPh\})_2]$ (12).** PhNCO (0.5 mL, ca. 4.5 mmol) and *cis*-$[Ni\{Ph_2PCH{=}C(O)Ph\}_2]$ (**11**) (0.150 g, 0.23 mmol) were reacted in CH_2Cl_2 (15 mL). After being stirred for 1 h, the solution was filtered and pentane was added to it, affording orange, air-stable crystals of **12** (0.180 g, 87%; mp 226 °C). Anal. Calcd for $C_{54}H_{42}N_2NiO_4P_2$ (M_r = 903.58): C, 71.78; H, 4.69; N, 3.10. Found: C, 69.93; H, 4.50; N, 3.03. IR (KBr): 1472 s, 1500 sh, 1540 vs, 1560 sh, 1598 s cm^{-1}. ^1H NMR (toluene-d_8): δ 6.59–8.27 (40 H, aromatic H), 13.80 (s, 2 H NH). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/toluene-d_8): δ 22.8 (s).

***cis*-$[Ni(Ph_2PC\{C(O)Ph\}\{=C(O)NH(p\text{-}MeC_6H_4)\})_2]$ (13).** This complex was prepared by using a procedure similar to that of **12**, starting from 0.212 g (0.32 mmol) of *cis*-$[Ni\{Ph_2PCH{=}C(O)Ph\}_2]$ (**11**) and 0.5 mL (ca. 4 mmol) of p-MeC_6H_4NCO. The product was recrystallized from CH_2Cl_2/pentane, yielding orange, air-stable crystals suitable for X-ray analysis (0.226 g, 76%; mp 202 °C). Anal. Calcd for $C_{56}H_{46}N_2NiO_4P_2 \cdot CH_2Cl_2$ (M_r = 1016.57): C, 67.35; H, 4.76; N, 2.76. Found: C, 68.30, H, 4.80; N, 2.90. IR (KBr): 1454 m, 1463 m, 1533 s, 1558 sh, 1596 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.38 (s, 6 H, Me), 6.15–7.56 (38 H, aromatic H), 12.60 (br s, 2 H, NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.0 (s).

***cis*-$[Pt\{Ph_2PCH{=}C(O)Ph\}(Ph_2PC\{C(O)Ph\}\{=C(OH)NPh\})]$ (15).** To a stirred solution of *cis*-$[Pt\{Ph_2PCH{=}C(O)Ph\}_2]$ (0.400 g, 0.50 mmol) in THF (20 mL) was added PhNCO (1 mL, ca. 9 mmol). The solution was stirred for 1 week. It was filtered and concentrated under reduced pressure to ca. 5 mL, and Et_2O was added to precipitate a white powder that was washed with Et_2O (2 × 10 mL) and then dried in vacuo. Recrystallization from CH_2Cl_2/pentane afforded white crystals of **15** (0.275 g, 60%; mp 215 °C dec). Anal. Calcd for $C_{47}H_{37}NO_3P_2Pt$ (M_r = 920.85): C, 61.30; H, 4.05; N, 1.52. Found: C, 61.45; H, 4.22; N, 1.49. IR (KBr): 1482 s, 1510 s br cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.75 (dd with ^{195}Pt satellites, 1 H, PCH, J(PH) = 1.3 Hz and 6.2 Hz, ^3J(HPt) = 30.0 Hz), 6.41–8.03 (35 H, aromatic H), 18.83 (d, 1 H, NH, ^4J(PH) = 1.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.1 (d with ^{195}Pt satellites, ^2J(PP) ≈ 13 Hz, J(PPt) = 3327 Hz), 18.0 (d with ^{195}Pt satellites, ^2J(PP) ≈ 13 Hz, J(PPt) = 3262 Hz).

Table I. Crystal Data and Data Collection Parameters for **5** and **13**·CH_2Cl_2

formula	$C_{33}H_{29}N_2O_3PPd$	$C_{56}H_{46}N_2NiO_4P_2 \cdot CH_2Cl_2$
fw	639.00	1016.57
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.276 (2)	14.363 (4)
b, Å	12.290 (7)	14.602 (12)
c, Å	14.336 (8)	14.324 (4)
α, deg	70.38 (3)	112.23 (4)
β, deg	86.70 (2)	109.56 (2)
γ, deg	69.18 (2)	99.19 (4)
V, Å^3	1435.6	2475.4
Z	2	2
ρ(calcd), g cm^{-3}	1.478	1.364
cryst dimens, mm	0.20 × 0.14 × 0.06	0.30 × 0.15 × 0.10
F(000)	652	1056
systematic absences	none	none
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonias CAD-4
radiation (graphite monochromator)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
linear abs coeff, cm^{-1}	7.268	6.125
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range, deg	$1 + 0.35 \tan \theta$	$1 + 0.35 \tan \theta$
θ limits, deg	1–25	1–25
octants collcd	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$
no. of data collcd	5255	8489
no. of unique data used	2676 ($F_o^2 > 3\sigma(F_o^2)$)	3325 ($F_o^2 > 4.5\sigma(F_o^2)$)
no. of variables	362	614
decay, %	<2	<2
$R = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0.037	0.042
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.045	0.053
GOF = $[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_{observns} - N_{params})]^{1/2}$	0.905	1.529
largest shift/esd, final cycle	0.02	1.98
largest peak, e/Å^3	0.55	0.66

X-ray Structural Determinations. $[(C_{10}H_8N)Pd(Ph_2PC\{C(O)OEt\}\{=C(O)NHPh\})]$ (5). Crystals of **5** have a prismatic habit and were obtained by slow diffusion of hexane into a THF solution of **5**. Cell constants and other pertinent data are presented in Table I. All data collections were obtained at room temperature, 23 ± 2 °C. Precise lattice parameters were determined by standard Enraf-Nonius least-squares methods using 25 carefully selected reflections. Intensity data were collected on an automatic four-circle diffractometer. No intensity decay was observed during the data collection period. For all subsequent computations the Enraf-Nonius SDP package was used.[13] Intensities were corrected for Lorentz-polarization factors. Absorption corrections were omitted in view of the low linear absorption coefficient. The crystal structure was solved by using the MULTAN program[14] and refined by full-matrix least squares with anisotropic thermal parameters for all nonhydrogen atoms. The function minimized was $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where the weight is $4I/\sigma^2(I) + (0.06I)^2$. Hydrogen atoms were introduced by their computed coordinates (C–H = 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of B = 5.0 Å^2. The final difference map showed no significant residual peaks. The neutral-atom scattering factors used for all atoms and anomalous scattering factors for all non-hydrogen atoms were obtained from standard sources.[15] Atomic coordinates with estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table II. Refinement results are given in Table I. Hydrogen atom coordinates (Table S-I), anisotropic thermal parameters for all non-hydrogen atoms (Table S-II), a listing of the observed and calculated structure factor amplitudes used in the refinement (Table S-III), and a complete list of bond distances and angles (Table S-IV) are available as supplementary material.[16]

***cis*-$[Ni(Ph_2PC\{C(O)Ph\}\{=C(O)NH(p\text{-}MeC_6H_4)\})_2] \cdot CH_2Cl_2$ (13·CH_2Cl_2).** Orange crystals of **13**·CH_2Cl_2 were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of **13**. All pertinent crystallographic data for this compound are given in Table I. The structure determination was performed as for **5**, the only difference being that the hydrogen atoms were assigned isotropic thermal parameters of B = 8.0 Å^2. Atomic coordinates with estimated standard deviations are given in Table III. Refinement results are given in Table I. Hydrogen atom coordinates (Table S-V), anisotropic thermal parameters for the nonhydrogen atoms (Table S-VI), a listing of the observed and calculated structure factor amplitudes used in the refinement (Table S-VII), and a complete list of bond distances and angles (Table S-VIII) are available as supplementary material.

Results and Discussion

PhNCO Coupling with Pd-Coordinated Phosphino Enolate

---

(13) Frenz, B. A. In *Computing in Crystallography*; Schenk, H.; Olthof-Hazekamp, R.; van Koningsveld, H.; Bassi, G. C., Eds.; University Press: Delft, The Netherlands, 1978; p 64–71.

(14) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368–376.

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 99.

(16) See paragraph at end of paper regarding supplementary material.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for **5**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Pd	0.17509 (5)	0.22530 (4)	0.11812 (3)	2.842 (9)
P	0.1363 (2)	0.0541 (1)	0.20931 (9)	2.79 (3)
O1	0.2518 (4)	0.2233 (3)	0.2546 (3)	2.59 (9)
O2	0.1346 (4)	−0.1368 (3)	0.3968 (3)	3.9 (1)
O3	0.2191 (5)	−0.0697 (4)	0.5022 (3)	5.0 (1)
N1	0.2102 (5)	0.3849 (4)	0.0310 (3)	3.6 (1)
N2	0.2954 (6)	0.1288 (4)	0.4216 (3)	4.1 (1)
C1	0.1011 (7)	0.2285 (5)	−0.0134 (4)	4.1 (2)
C2	0.1075 (6)	0.3429 (5)	−0.0931 (4)	3.7 (2)
C3	0.0614 (8)	0.3751 (7)	−0.1894 (5)	5.8 (2)
C4	0.070 (1)	0.4846 (8)	−0.2604 (6)	8.0 (3)
C5	0.1265 (9)	0.5589 (7)	−0.2343 (6)	7.1 (3)
C6	0.1758 (7)	0.5300 (6)	−0.1360 (5)	4.9 (2)
C7	0.1644 (6)	0.4212 (5)	−0.0660 (4)	3.4 (1)
C8	0.2693 (7)	0.4523 (5)	0.0598 (5)	4.7 (2)
C9	0.2856 (8)	0.5601 (6)	−0.0064 (6)	5.8 (2)
C10	0.2392 (8)	0.5978 (6)	−0.1022 (6)	5.7 (2)
C11	−0.0623 (6)	0.0633 (4)	0.2054 (4)	2.8 (1)
C12	−0.1252 (6)	0.0544 (5)	0.1239 (4)	3.8 (1)
C13	−0.2815 (7)	0.0779 (6)	0.1139 (5)	5.0 (2)
C14	−0.3766 (7)	0.1087 (6)	0.1865 (5)	4.8 (2)
C15	−0.3144 (7)	0.1155 (5)	0.2681 (4)	4.0 (2)
C16	−0.1579 (6)	0.0934 (5)	0.2776 (4)	3.2 (1)
C17	0.2517 (6)	−0.0845 (5)	0.1815 (4)	3.0 (1)
C18	0.2074 (7)	−0.1842 (5)	0.1991 (5)	4.3 (2)
C19	0.3041 (9)	−0.2906 (6)	0.1841 (5)	5.9 (2)
C20	0.4493 (8)	−0.2975 (6)	0.1518 (5)	6.0 (2)
C21	0.4934 (7)	−0.1979 (7)	0.1320 (5)	6.1 (2)
C22	0.3954 (7)	−0.0908 (6)	0.1459 (4)	4.5 (2)
C23	0.1936 (6)	0.0417 (5)	0.3285 (4)	3.1 (1)
C24	0.1854 (7)	−0.0566 (5)	0.4166 (4)	3.8 (1)
C25	0.1104 (8)	−0.2315 (6)	0.4807 (5)	5.5 (2)
C26	0.052 (1)	−0.3066 (7)	0.4420 (6)	7.5 (2)
C27	0.2483 (6)	0.1348 (5)	0.3318 (4)	3.2 (1)
C28	0.3426 (6)	0.2104 (5)	0.4496 (4)	3.8 (1)
C29	0.3846 (8)	0.1764 (6)	0.5483 (5)	5.3 (2)
C30	0.4298 (9)	0.2520 (7)	0.5841 (5)	7.4 (2)
C31	0.435 (1)	0.3595 (7)	0.5214 (6)	8.0 (2)
C32	0.398 (1)	0.3927 (6)	0.4227 (6)	8.0 (2)
C33	0.3528 (9)	0.3182 (6)	0.3867 (5)	5.8 (2)

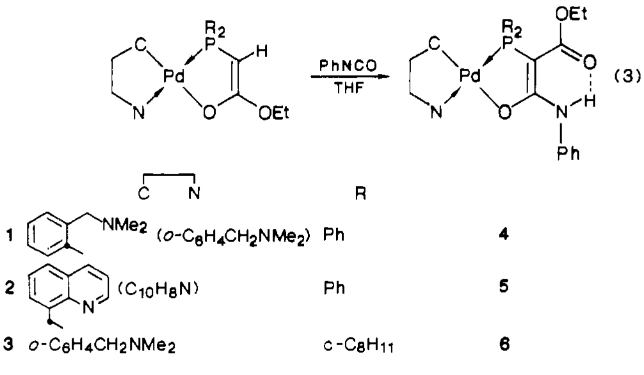
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters: $B = (4/3)[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for **13**·CH_2Cl_2

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ni	0.25785 (5)	0.17631 (5)	0.24335 (5)	2.09 (1)
P1	0.2690 (1)	0.0227 (1)	0.2161 (1)	2.12 (3)
P2	0.3058 (1)	0.2011 (1)	0.1239 (1)	2.15 (3)
O1	0.2232 (3)	0.1788 (3)	0.3593 (3)	3.08 (9)
O2	0.2331 (3)	0.3049 (2)	0.2767 (3)	2.69 (9)
O3	0.1536 (3)	−0.0959 (3)	0.3832 (3)	4.5 (1)
O4	0.2944 (4)	0.4687 (3)	0.1103 (3)	7.1 (1)
N1	0.1772 (3)	0.1034 (3)	0.4565 (3)	3.0 (1)
N2	0.2217 (4)	0.4450 (3)	0.2476 (3)	3.4 (1)
C1	0.2083 (4)	0.0987 (4)	0.3758 (4)	2.2 (1)
C2	0.2176 (4)	0.0041 (4)	0.3078 (4)	2.4 (1)
C3	0.1878 (4)	−0.0898 (4)	0.3147 (4)	2.7 (1)
C4	0.1817 (4)	−0.1904 (4)	0.2310 (4)	2.8 (1)
C5	0.0851 (5)	−0.2603 (4)	0.1464 (5)	3.7 (2)
C6	0.0749 (6)	−0.3557 (5)	0.0676 (5)	4.6 (2)
C7	0.1618 (6)	−0.3847 (4)	0.0725 (5)	4.8 (2)
C8	0.2593 (5)	−0.3176 (4)	0.1563 (5)	4.7 (2)
C9	0.2687 (5)	−0.2208 (4)	0.2340 (5)	3.7 (2)
C10	0.1664 (4)	0.1894 (4)	0.5344 (4)	2.9 (1)
C11	0.1050 (5)	0.1672 (5)	0.5849 (5)	4.1 (2)
C12	0.0947 (5)	0.2473 (5)	0.6662 (5)	4.8 (2)
C13	0.1425 (5)	0.3497 (5)	0.7004 (5)	4.4 (2)
C14	0.1347 (6)	0.4369 (7)	0.7926 (7)	7.5 (3)
C15	0.2027 (5)	0.3706 (5)	0.6485 (5)	4.2 (2)
C16	0.2145 (5)	0.2930 (4)	0.5653 (4)	3.6 (2)
C17	0.4011 (4)	0.0190 (4)	0.2610 (4)	2.5 (1)
C18	0.4522 (4)	−0.0004 (4)	0.1903 (5)	3.3 (2)
C19	0.5550 (5)	0.0053 (5)	0.2308 (5)	4.7 (2)
C20	0.6102 (5)	0.0293 (6)	0.3381 (6)	5.4 (2)
C21	0.5628 (5)	0.0494 (6)	0.4107 (6)	5.6 (2)
C22	0.4598 (5)	0.0454 (5)	0.3717 (5)	4.1 (2)
C23	0.1902 (4)	−0.0815 (4)	0.0748 (4)	2.5 (1)
C24	0.0925 (4)	−0.0776 (4)	0.0182 (5)	3.1 (2)
C25	0.0265 (6)	−0.1568 (5)	−0.0875 (6)	5.1 (2)
C26	0.0550 (6)	−0.2390 (5)	−0.1375 (5)	5.0 (2)
C27	0.1518 (5)	−0.2434 (4)	−0.0823 (5)	3.9 (2)
C28	0.2199 (4)	−0.1652 (4)	0.0246 (4)	2.9 (2)
C29	0.2460 (4)	0.3574 (4)	0.2249 (4)	2.5 (1)
C30	0.2858 (4)	0.3223 (4)	0.1437 (4)	2.4 (1)
C31	0.3139 (5)	0.3847 (4)	0.0945 (5)	3.7 (2)
C32	0.3718 (5)	0.3561 (4)	0.0249 (5)	3.8 (2)
C33	0.4785 (6)	0.4065 (6)	0.0716 (6)	6.4 (3)
C34	0.5322 (6)	0.3865 (7)	0.0071 (7)	8.4 (3)
C35	0.4777 (6)	0.3163 (7)	−0.1063 (6)	8.5 (3)
C36	0.3751 (6)	0.2694 (7)	−0.1503 (6)	7.3 (3)
C37	0.3213 (5)	0.2883 (5)	−0.0873 (5)	5.2 (2)
C38	0.1872 (4)	0.4993 (4)	0.3268 (4)	2.9 (1)
C39	0.1656 (5)	0.4665 (4)	0.3984 (5)	3.4 (2)
C40	0.1304 (4)	0.5281 (4)	0.4719 (5)	3.5 (2)
C41	0.1174 (4)	0.6206 (4)	0.4761 (5)	3.2 (2)
C42	0.0798 (5)	0.6843 (5)	0.5547 (5)	4.7 (2)
C43	0.1415 (5)	0.6513 (4)	0.4048 (5)	4.2 (2)
C44	0.1740 (5)	0.5926 (4)	0.3315 (5)	4.3 (2)
C45	0.4414 (4)	0.2154 (4)	0.1594 (4)	2.5 (1)
C46	0.5078 (5)	0.2603 (5)	0.2719 (5)	4.0 (2)
C47	0.6127 (5)	0.2817 (6)	0.3065 (6)	5.6 (2)
C48	0.6546 (5)	0.2598 (6)	0.2330 (6)	5.8 (2)
C49	0.5914 (5)	0.2144 (5)	0.1210 (6)	5.0 (2)
C50	0.4849 (4)	0.1932 (5)	0.0837 (5)	3.6 (2)
C51	0.2277 (4)	0.1069 (4)	−0.0222 (4)	2.1 (1)
C52	0.1348 (4)	0.1182 (4)	−0.0798 (5)	3.1 (2)
C53	0.0722 (5)	0.0470 (5)	−0.1896 (5)	4.3 (2)
C54	0.1003 (5)	−0.0352 (5)	−0.2447 (5)	4.7 (2)
C55	0.1921 (5)	−0.0469 (5)	−0.1872 (5)	3.9 (2)
C56	0.2555 (4)	0.0227 (4)	−0.0759 (4)	2.9 (1)
Cl1	0.5321 (5)	0.5583 (4)	0.4198 (5)	25.9 (3)
Cl2	0.5267 (4)	0.7397 (5)	0.3856 (5)	23.3 (3)
C57	0.472 (1)	0.678 (1)	0.4328 (9)	16.4 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters: $B = (4/3)[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

Ligands. When an excess of phenyl isocyanate was reacted with the bis chelate complexes [(C N)Pd{R_2PCH=C(O)OEt}] (**1**–**3**) (R = Ph or c-C_6H_{11}; CH N = *N*,*N*-dimethylbenzylamine, $C_6H_5CH_2NMe_2$, or 8-methylquinoline, $C_{10}H_9N$), complexes **4**–**6** were formed, respectively, in a nearly quantitative yield (eq 3).



These complexes formally result from the nucleophilic attack of the carbon atom α to the phosphorus of the phosphino enolate ligand on the carbon atom of PhNCO, followed by a 1,3 hydrogen shift. Whether decoordination of the oxygen atom of the enolate precedes or follows the C–C bond-forming step of this Michael-type addition reaction cannot yet be established. In the course of this reaction the cyclometalated ligand remains unchanged. The new phosphine ligand thus formed contains two functionalities: an ester group and an amido group. Although phosphine–amides have previously been reported,[17–20] this reaction

Table IV. Selected IR and NMR Data

complex	no.	IR,[a] cm^{-1}	^1H NMR,[b] δ: NH (or OH)	^1H NMR,[b] δ: other	$^{31}P\{^1H\}$ NMR,[c] δ
[(*o*-$C_6H_4CH_2NMe_2$)Pd(Ph_2PC{C(O)OEt}{=C(O)NHPh})]	**4**	1485, 1560 1587, 1625	11.23	2.83 (NMe_2, $^4J(PH) = 2.2$) 3.88 (NCH_2, $^4J(PH) = 1.7$)	31.0
[($C_{10}H_8N$)Pd(Ph_2PC{C(O)OEt}{=C(O)NHPh})]	**5**	1484, 1561 1597, 1637	12.4	3.29 (CH_2Pd)	25.4
[(*o*-$C_6H_4CH_2NMe_2$)Pd(Cy_2PC{C(O)OEt}{=C(O)NHPh})]	**6**	1480, 1497 1557, 1590 1612, 1620	11.32	2.71 (NMe_2, $^4J(PH) = 2.2$) 3.88 (NCH_2, $^4J(PH) < 1$)	47.4
[(*o*-$C_6H_4CH_2NMe_2$)Pd(Ph_2PC{C(O)Ph}{C(O)NHPh})]	**9a**	3399 (ν(NH))	6.50	2.92 (NMe_2, $^4J(PH) = 2.2$) 4.02 (NCH_2, $^4J(PH) = 1.3$)	29.0, 42.9
	9b		13.25	2.86 (NMe_2, $^4J(PH) = 2.2$) 3.90 (NCH_2, $^2J(PH) = 1.2$)	
[($C_{10}H_8N$)Pd(Ph_2PC{C(O)Ph}{C(O)NHPh})]	**10a**	3420 (ν(NH))	6.50	3.37 (CH_2Pd, $^3J(PH) < 1$)	23.6, 37.8
	10b		14.51	3.10 (CH_2Pd, $^3J(PH) < 1$)	
cis-[Ni(Ph_2PC{C(O)Ph}{=C(O)NHPh}$)_2$]	**12**	1472, 1500 1540, 1560 1598	13.80		22.8
cis-[Ni(Ph_2PC{C(O)Ph}{=C(O)NH(*p*-MeC_6H_4)}$)_2$]	**13**	1454, 1463 1533, 1558 1596	12.60	2.38 (Me)	23.0
cis-[Pt{Ph_2PCH=C(O)Ph}(Ph_2PC{C(O)Ph}{=C(OH)NPh})]	**15**	1482, 1510	18.83 ($^4J(PH) = 1.0$)	4.75 (PCH, $J(PH) = 1.3, 6.2$)	−1.1 ($J(PPt) = 3327$, $^2J(PP) \approx 13$) 18.0 ($J(PPt) = 3262$)

[a] Recorded as KBr disk. [b] Spectra recorded in $CDCl_3$ except for those of **5** and **10** in C_6D_6, that of **9** in CD_2Cl_2, and that of **12** in toluene-d_8; *J* values in Hz. [c] Spectra recorded in $CDCl_3$, except those of **4**, **5**, and **10** in C_6D_6/THF and that of **12** in toluene-d_8.

Table V. Selected Bond Lengths (Å) and Angles (deg) for **5**

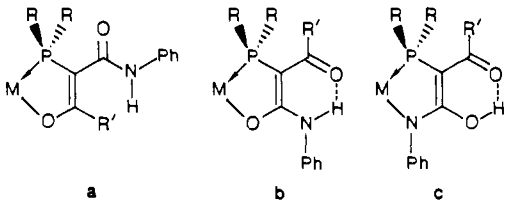
Pd–P	2.214 (2)	C(23)–C(24)	1.446 (7)
Pd–O(1)	2.110 (4)	C(23)–C(27)	1.421 (9)
Pd–N(1)	2.067 (5)	C(24)–O(2)	1.345 (9)
Pd–C(1)	2.027 (7)	C(24)–O(3)	1.226 (7)
P–C(11)	1.809 (6)	C(27)–N(2)	1.354 (8)
P–C(17)	1.822 (5)	C(27)–O(1)	1.273 (6)
P–C(23)	1.760 (6)		
Pd–P–C(23)	100.6 (2)	O(3)–C(24)–O(2)	121.0 (5)
P–C(23)–C(27)	115.3 (3)	Pd–C(1)–C(2)	108.4 (5)
C(23)–C(27)–O(1)	122.7 (5)	C(1)–C(2)–C(7)	118.3 (5)
C(27)–O(1)–Pd	116.9 (4)	C(2)–C(7)–N(1)	116.1 (5)
O(1)–Pd–P	84.5 (1)	C(7)–N(1)–Pd	113.8 (5)
C(27)–N(2)–C(28)	131.0 (4)	N(1)–Pd–C(1)	83.3 (2)
C(23)–C(24)–O(3)	126.0 (7)		

Table VI. Selected Bond Lengths (Å) and Angles (deg) for **13**·CH_2Cl_2

Ni–P(1)	2.170 (2)	O(1)–C(1)	1.278 (7)
Ni–P(2)	2.170 (3)	O(2)–C(29)	1.284 (8)
Ni–O(1)	1.876 (4)	C(1)–C(2)	1.416 (7)
Ni–O(2)	1.878 (4)	C(29)–C(30)	1.425 (9)
P(1)–C(2)	1.789 (7)	C(2)–C(3)	1.419 (9)
P(1)–C(17)	1.806 (6)	C(30)–C(31)	1.43 (1)
P(1)–C(23)	1.811 (4)	C(3)–O(3)	1.261 (9)
P(2)–C(30)	1.770 (6)	C(31)–O(4)	1.256 (8)
P(2)–C(45)	1.795 (6)	C(1)–N(1)	1.354 (8)
P(2)–C(51)	1.813 (4)	C(29)–N(2)	1.330 (7)
Ni–P(2)–C(30)	99.9 (2)	O(1)–Ni–O(2)	85.4 (2)
P(2)–C(30)–C(29)	111.3 (5)	P(1)–Ni–P(2)	102.4 (1)
C(30)–C(29)–O(2)	120.6 (6)	C(30)–C(31)–O(4)	122.2 (7)
C(29)–O(2)–Ni	122.0 (4)	C(29)–N(2)–C(38)	131.4 (6)
O(2)–Ni–P(2)	86.2 (1)		

constitutes, to our knowledge, the first synthesis of such a ligand via a C–C coupling reaction. For instance, phosphine–amides have been described as resulting from insertion reactions of isocyanates into P–H bonds[18] or from reactions of phosphine–acids[19] or phosphine–amines,[20] respectively, with secondary amines or acyl chlorides.

As shown by ^{31}P NMR spectroscopy, only one isomer was formed in the reaction of eq 3. The ^1H NMR spectra of complexes **4**–**6** revealed the presence of a signal in the range 11.2–12.4 ppm (see Table IV) that was assigned to the amide proton after a D_2O–NH exchange experiment. This value reflects hydrogen bonding with the oxygen atom of the neighboring ester group, thus forming a stable six-membered ring. In their IR spectra, three medium to strong bands appear in the region 1550–1625 cm^{-1} (see Experimental Section), which are due to the conjugated ligand system. The absence of a typical ν(N–H) vibration band rules out a coordination of type **a** but does not however unambiguously exclude a ligand arrangement involving nitrogen coordination (type **c**). In order to elucidate these points, an X-ray analysis was performed on complex **5**. Its molecular structure is depicted in



---

[17] See for example: (a) Issleib, K. *Phosphorus Sulfur* **1976**, *2*, 219. (b) DuBois, D.; Myers, W. H.; Meek, D. M. *J. Chem. Soc., Dalton Trans.* **1975**, 1011. (c) Empsall, H. D.; Hyde, E. M.; Pawson, D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1292.

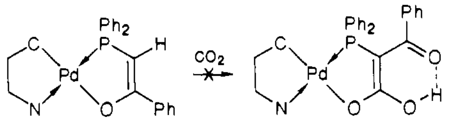
[18] See for example: (a) Buckler, S. A. *J. Org. Chem.* **1959**, *24*, 1460. (b) Thewissen, D. H. M. W.; Ambrosius, H. P. M. M.; van Gaal, H. L. M.; Steggerda, J. J. *J. Organomet. Chem.* **1980**, *192*, 101. (c) Belg. Appl. 654 329 to Shell Intern Research Maatschappij.; *Chem. Abstr.* **1966**, *65*, 8960h. (d) Thewissen, D. H. M. W.; Ambrosius, H. P. M. M. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*(11), 344.

[19] Hedden, D.; Roundhill, D. M. *Inorg. Chem.* **1985**, *24*, 4152.

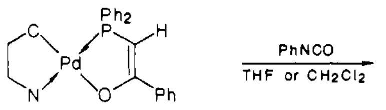
[20] (a) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5014. (b) Park, S.; Hedden, D.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* **1985**, *5*, 1305.

Figure 1. Selected bond distances and angles are given in Table V. The structural determination establishes that the functional phosphine has a **b**-type coordination with respect to the metal. The planarity of the six-membered ring constituted by N(2), C(27), C(23), C(24), O(3), and H(2N) (maximum deviation 0.06 Å) is in agreement with the expected hydrogen bond between the amide proton and the carbonyl oxygen of the ester group. The plane of this ring makes an angle of 2.4° with the palladium coordination plane. The bond lengths C(27)–N(2), C(27)–C(23), and C(24)–O(3) of respectively 1.354 (8), 1.421 (9), and 1.226 (7) Å have values between those of single and double bonds, indicating a high degree of electron delocalization within this cycle. It is noteworthy that there is also electron delocalization within the P,O chelate, as shown by the relatively short P–C(23) (1.760 (6) Å) and C(27)–O(1) (1.273 (6) Å) bond distances. The plane of the phenyl ring attached to the nitrogen atom N(2) makes an angles of 5.0° with the palladium coordination plane, which itself makes an angle of 3.0° with the plane of the metalated-8-methylquinoline ligand. With the exception of the PPh_2 group, this molecule displays a remarkable planarity. The distances and angles within the C,N ligand are unexceptional and comparable to those found in other palladium complexes.[21]

In order to study the possible influence of the nucleophilicity of the carbon atom α to phosphorus upon the course of the reaction of eq 3, we studied the reaction of phenyl isocyanate with the Pd(II) complexes **7** and **8** containing the phosphino ketonate $[Ph_2PCH{=}C(O)Ph]^-$. Indeed in this ligand, less electron density is expected on the $C_{\alpha\text{-}P}$ atom, since $-C(O)Ph$ is a stronger electron-withdrawing group than $-C(O)OEt$. This is in keeping with the fact that the previously reported C–C coupling reaction between CO_2 and the $C_{\alpha\text{-}P}$ atom of complexes **1–3** *does not* occur with **7** or **8** (eq 4). However, the latter complexes reacted with PhNCO, which is analogous to and more reactive than CO_2, to afford the isomers **9a,b** and **10a,b**, respectively (eq 5). The reaction rate did not depend significantly on the solvent used, THF or CH_2Cl_2.

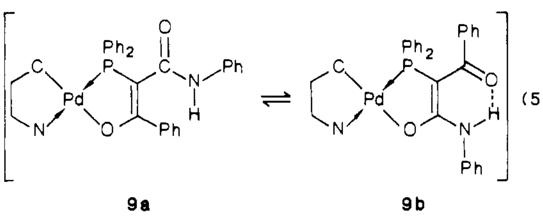


(4)



7, C N = o-$C_6H_4CH_2NMe_2$

8, C N = $C_{10}H_8N$



(5)

9a **9b**
10a **10b**

Furthermore, it is interesting to note that under similar conditions (THF, room temperature) the lithium salt of $[Ph_2PCHC(O)Ph]^-$ did not react with phenyl isocyanate; $^{31}P\{^1H\}$ NMR analysis of the reaction mixture after hydrolysis showed the presence of $Ph_2PCH_2C(O)Ph$ as the only P-containing product. When the reaction of eq 5 was monitored at −20 °C by ^1H NMR spectroscopy, the signals of both isomers appeared simultaneously, preventing the identification of the primary product. In contrast to the reaction of eq 3, where only the **b**-type coordination is observed, each of the two oxygen atoms of the resulting ligand is now capable of metal bonding. The structure of **9a** was determined by a single-crystal X-ray analysis, the results of which have been described elsewhere.[10] The amide proton of this isomer is characterized by a strong ν(N–H) absorption band at 3399 cm^{-1} in its IR (KBr) spectrum and by a signal, at 6.50 ppm in its ^1H NMR spectrum, that disappears slowly upon addition of D_2O. The structure of isomer **9b** was deduced from a broad ^1H NMR signal at δ 13.25, a chemical shift close to that found for complexes **4–6**. When the solid containing crystals of **9a** was dissolved in $CDCl_3$ at −30 °C, **9a** was detected as the major isomer (similar observations were made for **10a**; see Figure S-1 in the supplementary material). Equilibration occurred (**9a**:**9b** ratio ca. 1:1) when room temperature was reached. However, spin-transfer experiments showed that this isomerization is slow on the NMR time scale. Furthermore, within the range −20 to +100 °C, the position of the equilibrium is temperature independent, suggesting a small entropy difference between the two isomers. When a toluene-d_8 solution was heated for 72 h at 90 °C, small quantities of complex **7** were formed, being present beside equimolar amounts of **9a** and **9b**. Attempts to perform a complete thermal PhNCO-deinsertion reaction only led to decomposition of the reaction mixture. In view of the very similar reactivity of **7** and **8** vis-à-vis isocyanate insertion, cross-experiments were conducted in order to determine whether the room-temperature equilibrium shown in eq 5 could proceed via isocyanate deinsertion/reinsertion. It was found that **10a,b** cannot be produced by reacting **9a,b** with **8**. Neither does **7** act as a PhNCO trap when reacted with **10a,b** (eq 6 and 7). As checked by ^1H NMR spectroscopy, addition

$$\mathbf{9a,b} + \mathbf{8} \not\longrightarrow \mathbf{10a,b} + \mathbf{7} \qquad (6)$$

$$\mathbf{10a,b} + \mathbf{7} \not\longrightarrow \mathbf{9a,b} + \mathbf{8} \qquad (7)$$

of an excess of p-MeC_6H_4NCO to **9** or **10** also left the corresponding equilibria unchanged, without isocyanate exchange occurring, although the p-MeC_6H_4NCO analogues of **9** and **10** could be independently prepared from **7** or **8** by using the procedure leading to **9** or **10**, respectively (see Experimental Section) (eq 8). These experiments definitely establish that the exchange

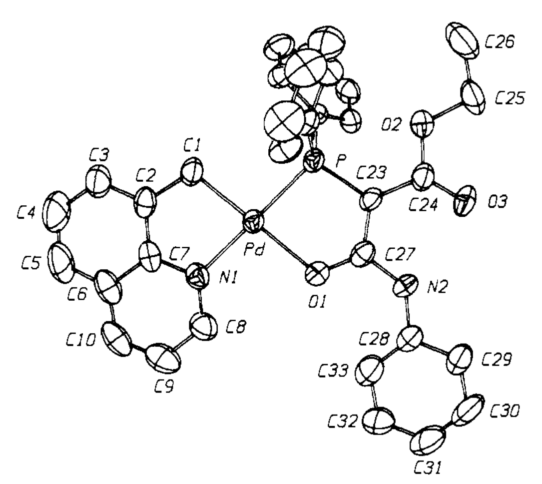
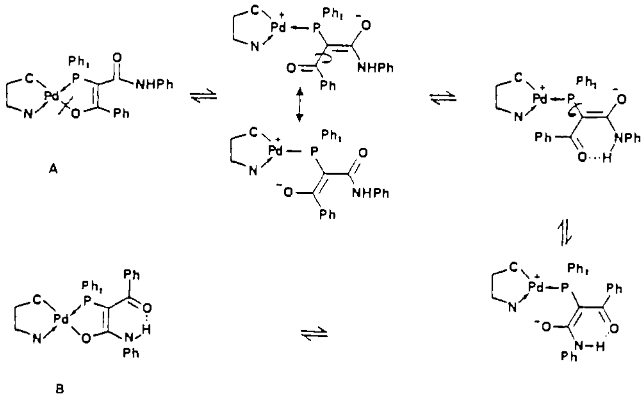


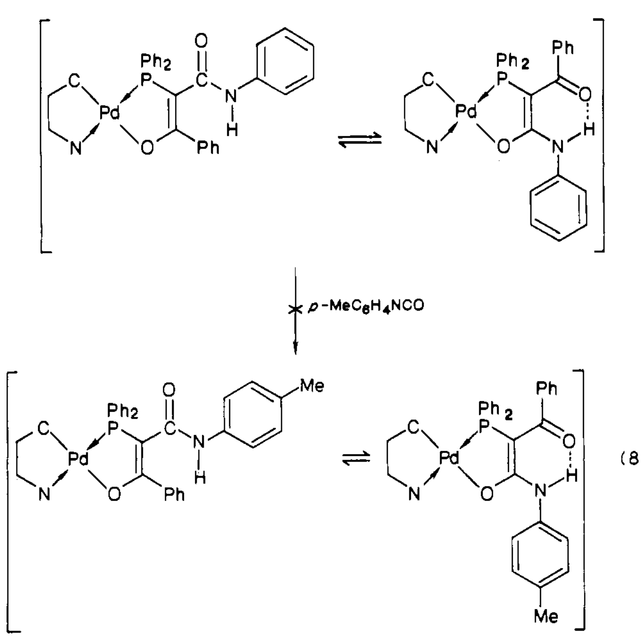
Figure 1. ORTEP drawing of **5**. The hydrogen atom bonded to N(2) is not represented.

Scheme I



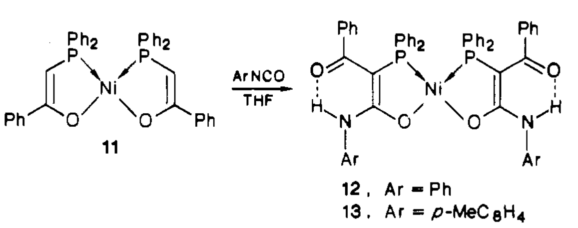
---

(21) Braunstein, P.; Fischer, J.; Matt, D.; Pfeffer, M. *J. Am. Chem. Soc.* **1984**, *106*, 410.



$\overline{\text{C} \quad \text{N}}$ = o-$C_6H_4CH_2NMe_2$ or $C_{10}H_8N$

between **9a** and **9b** (or **10a** and **10b**) *does not proceed* via PhNCO deinsertion. Therefore, we suggest that the mechanism involves Pd–O bond dissociation followed by the rearrangement shown in Scheme I. This rearrangement implies (i) an easy rotation about the P–C bond and (ii) a rotation about the C(P)–C(Ph) bond. The facile Pd–O bond dissociation is likely to be promoted by the high trans influence of the Pd-bound carbon atom, as observed in the easily reversible reactions of **1**–**3** with CO_2. The formation of a planar ring contaning a N–H···O system certainly is a driving force for the transformation of **9a** into **9b** (or **10a** into **10b**). On the other hand, in the **b** isomers, some repulsive interactions between the PPh_2 group and the ketoaryl could account for the reverse transformation (**b** form → **a** form). Although this repulsion does not appear to be always crucial for the stability of the ligand in a **b**-type bonding fashion (see below), we note that for complexes **4**–**6**, in which there is practically no PPh_2/OEt steric interaction, the preferred isomer **b** does not isomerize.



(9)

11

12, Ar = Ph
13, Ar = p-MeC_6H_4

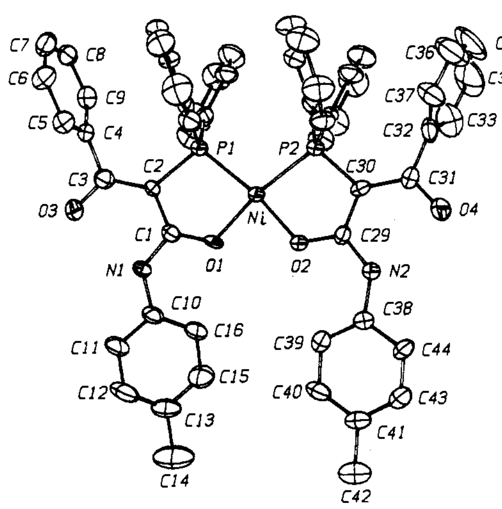
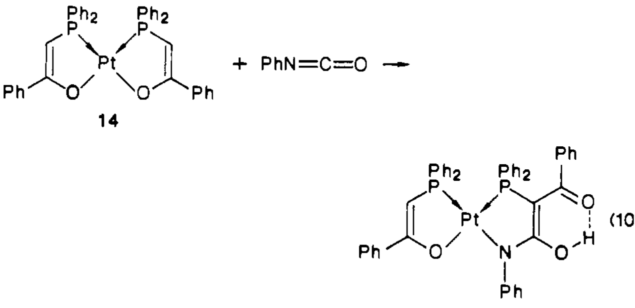


Figure 2. ORTEP drawing of **13**·CH_2Cl_2. The dichloromethane molecule is not shown. The hydrogen atoms bonded to N(1) and N(2) are not represented.



14

15

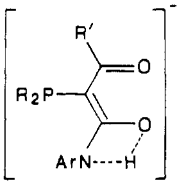
PhNCO Coupling with Ni- or Pt-Bonded [$Ph_2PCH{=}C(O)Ph$]$^-$. Isocyanate insertion into the β-phosphino ketonate [$Ph_2PCH{=}C(O)Ph$]$^-$ also occurred when this ligand was coordinated to a nickel atom. Thus, reaction of PhNCO or p-MeC_6H_4NCO with **11** led to complexes **12** and **13**, respectively, in more than 70% yield (eq 9). Complexes **12** and **13** were characterized by NH···O signals at 13.8 and 12.6 ppm, respectively, in their ^1H NMR spectrum. Other characteristic NMR and IR data are given in the Experimental Section or in Table IV. In order to determine the molecular geometry of these complexes, an X-ray diffraction study was performed on **13**. An ORTEP drawing of this molecule is shown in Figure 2. The nickel atom is in a nearly planar environment, the maximum deviation with respect to the mean coordination plane being 0.139 (1) Å. The phosphorus atoms occupy cis positions, and the value of the P(1)–Ni–P(2) angle of 102.4 (1)° reflects some repulsion between the PPh_2 groups, which also results in their phenyl rings, situated on the same side of the metal coordination plane, being almost parallel to each other (ca. 7 and 12°). As found in complex **5**, each ring containing a NH proton is quasi-planar (maximum deviation 0.035 Å) and forms an angle of ca. 5° with the nitrogen-bound tolyl group. Note however that the conjugation within the six-membered rings does not extend to the phenyl groups bonded to the keto functions, as can be deduced from the value of the angle between these planes (near 80°). The spatial arrangement of the C_6H_5 group is likely to minimize the steric interaction with the phosphino group. The metal–oxygen bonds in **13** are notably shorter than that in complex **5** (average 1.877 (4) Å in **13** vs 2.110 (4) Å in **5**), reflecting i.a. the smaller ionic radius of Ni(II) vs Pd(II). This Ni–O bond distance is similar to that found in **11**.[22] All other distances within the metallocycles appear to be normal. It is noteworthy that the multifunctional phosphines in **12** and **13** only display a coordination mode of type **b**. The question whether or not both isocyanates insert in a simultaneous or in a stepwise fashion cannot be answered at the moment. When the reactions of eq 9 were monitored by ^{31}P and ^1H NMR, we detected the formation of several intermediates that slowly disappeared with simultaneous formation of the final product. One of these species was identified as free $Ph_2PCH_2C(O)Ph$ (by ^{31}P and ^1H NMR). The latter could result from protonation of unreacted **11** with the proton made more acidic through isocyanate insertion (CH → NH), the resulting species then dissociating the $Ph_2PCH_2C(O)Ph$ ligand. Other intermediates, containing two nonequivalent cis phosphorus atoms (AB spin systems, with $^2J \approx 75$ Hz) were observed but not identified although they could correspond to mono and bis insertion products (with respective isomers). When the reaction with PhNCO was carried out with the related Pt complex **14**, only mono insertion was observed (eq 10), affording complex **15** in which the diketonate ligand is P,N-bonded (see below), i.e., in a type **c** fashion. This reaction occurred much more slowly than that with **11**, with only 60% yield after 1 week of reaction time. The IR (KBr) spectrum of **15** shows a strong band at 1510 cm^{-1} owing to ν(C⋯O) + ν(C⋯C) of the remaining β-phosphino ketonate ligand. The $^{31}P\{^1H\}$ NMR spectrum displays two signals at re-

---

[22] Huang, Q.; Xu, M.; Quian, Y.; Xu, W.; Shao, M.; Tang, Y. *J. Organomet. Chem.* **1985**, *287*, 419.

spectively −1.1 and 18.0 ppm, with a ^2J(PP) coupling constant of ca. 13 Hz, which unambiguously establishes the cis nature of this complex. The rather similar J(PtP) values of 3327 and 3262 Hz are consistent with phosphorus atoms in trans position with respect to OR^- or NR_2^-.[12,19] The presence in the ^1H NMR spectrum of a doublet of doublets with Pt satellites at 4.75 ppm for the PCH proton is also in agreement with phosphorus atoms occupying cis positions. The trans arrangements P→Pt–O and P→Pt–N observed in **14** and **15** are consistent with an antisymbiotic effect between the hard enolate or amido and the soft phosphine ligands.[23] This was also the case for the trans arrangements P→Ni–O found in complexes **11**–**13**, although Ni(II) is not a soft Lewis acid. The OH proton is characterized by a signal at 18.8 ppm. This high chemical shift value is in agreement with the results reported by Forsên et al.[24] about symmetrically bonded protons of the type O–H--O and excludes a coordination of type **b** for which the chemical shift of the NH proton is expected in the range 11–14 ppm. The occurrence of a single insertion into complex **14** could be related to the formation of a strong Pt–N bond and a consequently diminished nucleophilicity of the remaining $Ph_2PCH{=}C(O)Ph^-$ ligand.

In conclusion, transition-metal-coordinated β-phosphino enolates of the type $[R_2PCH{=}C(O)R']^-$ undergo a facile C–C coupling reaction with aryl isocyanates to afford complexes with multifunctional ligands of the general formula



Whereas, when R′ = OEt, Pd(II) complexes had been shown precisely to react readily and reversibly with CO_2, no reaction occurs under similar conditions when R′ = Ph, the carbon atom α to the phosphorus having insufficient electron density to undergo C–C coupling with the CO_2 molecule. This discrimination is no longer observed with the more reactive heterocumulenes Ar—N=C=O. According to the nature of R′, and to that of the complexed metal, three possible bonding modes were shown to occur in which the new ligand formed acts as either a P,O(keto or ester), a P,O(amide), or a P,N chelate. In some cases (complex **9** or **10**), the resulting ligand behaves as a hemilabile P,O ligand. In all the isocyanate coupling reactions presented here, metal–oxygen (keto) bond dissociation occurs, but at which stage of the reaction this is accomplished, i.e., before or after C–C bond formation, still remains an open question. A possible development of this work would be to perform catalytically this stoichiometric carbon–carbon coupling reaction. We are presently investigating further reactions of electrophiles with β-phosphino enolates in order to generate new polyfunctional phosphines.

Acknowledgment. This research was supported by GS-CO_2 (CNRS-SNPE). We are grateful to Prof. J. Fischer for the drawing of the ORTEP plots, to F. Balegroune for assistance with the structure determination of **5**, to Prof. J. H. Nelson for interesting discussions, and to Dr. M. A. Luke for a critical proofreading of the manuscript.

Registry No. **1**, 79110-94-4; **2**, 79110-93-3; **3**, 105813-68-1; **4**, 114157-57-2; **5**, 114157-58-3; **6**, 114157-59-4; **7**, 111287-12-8; **8**, 103836-23-3; **9a**, 111263-71-9; **9b**, 111263-72-0; **10a**, 114157-61-8; **10b**, 111263-69-5; **11**, 97954-27-3; **12**, 114157-62-9; **13**·CH_2Cl_2, 114157-63-0; **14**, 113693-77-9; **15**, 114157-56-1; $[(o\text{-}C_6H_4NMe_2)Pd(Ph_2PC\{C(O)NH(p\text{-}C_6H_4Me)\}\{C(O)Ph\})]$, 114157-64-1; $[(o\text{-}C_6H_4NMe_2)Pd(Ph_2PC\{C(O)Ph\}\{C(O)NH(p\text{-}C_6H_4Me)\}]$, 114157-65-2; $[(C_{10}H_8N)Pd(Ph_2PC\{C(O)NH(p\text{-}C_6H_4Me)\}\{C(O)Ph\})]$, 114183-81-2; $[(C_{10}H_8N)Pd(Ph_2PC\{C(O)Ph\}\{C(O)NH(p\text{-}C_6H_4Me)\})]$, 114157-66-3; $[(o\text{-}C_6H_4NMe_2)PdCl\{Cy_2PCH_2C(O)OEt\}]$, 105813-69-2; PhNCO, 103-71-9; $p\text{-}MeC_6H_4NCO$, 622-58-2.

Supplementary Material Available: For **5** and **13**·CH_2Cl_2, respectively, tables of hydrogen atom coordinates (Tables S-I and S-V) and anisotropic thermal parameters (Tables S-II and S-VI) and complete lists of bond distances and angles (Tables S-IV and S-VIII) and for **10a** the ^1H NMR spectrum at 0 °C (Figure S-1) (21 pages); observed and calculated structure factors (Tables S-III and S-VII) (30 pages). Ordering information is given on any current masthead page.

---

(23) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

(24) Altman, L. J.; Laungani, D.; Gunnarson, G.; Wennerström, H.; Forsên, S. *J. Am. Chem. Soc.* **1978**, *100*, 8264.