a ferrous complex in aqueous solution. Thus, the peak shift between 670 and 634 nm for FeTsPc complexes is not always a valid indication of the valence state of the metal. It may instead be more directly an indication of the substituents that occupy the axial binding sites of the iron.

The XANES data in this report tend to verify Kunzl's law, which states that the energy shift of the absorption edge will vary linearly with the valence of the absorbing species. Figure 2 shows the positive shift of absorption edge structure with oxidation state for the 0, +2, +2.5, and +3 states of Fe.

The coincidence of absorption edges for ferric ion in either Fe_2O_3 or FeTsPc showed that edge position is a strong function of oxidation state and is not perturbed by other factors. Both Kunzl's law and the valence/edge position correlation are demonstrated by Wong et al.[12] in a detailed study of vanadium compounds. All the features of the absorption edge and pre-edge (threshold, 1s→3d pre-edge peak, absorption edge, and 1s→4p peak) are found to vary linearly with oxidation state, although the rate of change varies between these components. Also in that study, spectra of vanadyl phthalocyanine and vanadyl tetraphenylporphyrin were taken for comparison to many other inorganic vanadium complexes. The main edges of VOPc and VOTPP, where V is nominally in the +4 state, lie between those of V_4O_7 and V_2O_4.

The fact that Wong observed that the N_4 chelates of vanadyl ion showed a slightly smaller chemical shift than V_2O_4 (13.4 vs. 14.0 eV) demonstrates the effect of coordination number and electronegativity of the bonding ligands on total energy shift. The concept of coordination charge, where the formal valence of a metal is reduced by a factor corresponding to the degree of covalency of the bonding ligands, has been employed to explain such differences in absorption edge shifting.[12,52] In our case, these effects were found to be small enough that we could compare the chemical shifts of iron in phthalocyanine to those of the oxide standards directly.

In summary $Fe^{III}TsPc$ has been found to complex OH⁻ and CO and is believed to produce a reduced state of the metal and a ligand radical of the macrocycle. Further research into the chemistry of this complex and the electronic structural changes that accompany it was under way.

Registry No. [Fe^{III}TsPc]Cl, 103817-69-2; Fe^{III}TsPc(OH)(CO), 103834-82-8; CO, 630-08-0.

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Complexes of Functional Phosphines. 10.[1] Palladium Complexes with the Ligands Ph2PCH2COPh, (Ph2PCHCOPh)⁻, and Ph2PCHC(Ph)OPPh2. Crystal and Molecular Structure of cis-[PdCl2{Ph2PCHC(Ph)OPPh2}]

Salah-Eddine Bouaoud,[2b] Pierre Braunstein,*[2a] Daniel Grandjean,[2b] Dominique Matt,[2a] and Dominique Nobel[2a]

(Diphenylphosphino)acetophenone, Ph2PCH2COPh (L), was synthesized by reacting Ph2PCl with PhCOCH2Li in THF. In the complexes [PdCl2L2] (1), [(η^3-C4H7)PdClL] (2), [(o-C6H4CH2NMe2)PdClL] (3), [(C10H8N)PdClL] (4), and [(C14H13N2)-PdClL] (5), L behaves as a monodentate ligand (through phosphorus), and in [(o-C6H4CH2NMe2)Pd{Ph2PCH2C(O)Ph}]-[CF3SO3] (6), [(C10H8N)Pd{Ph2PCH2C(O)Ph}][CF3SO3] (7), and [(C14H13N2)Pd{Ph2PCH2C(O)Ph}][CF3SO3] (8), L behaves as a chelating ligand (through phosphorus and the keto group). Treatment of 3–5 with NaH in THF led to the corresponding enolato-phosphine complexes 9–11, in which the P,O-chelate ligand behaves as a three-electron donor. Reaction of Li2PdCl4 with 2 equiv of L in the presence of NEt3 afforded cis-[Pd{Ph2PCHC(O)Ph}2] (12). Thermolysis of 1 in toluene resulted in the quantitative formation of cis-[PdCl2{Ph2PCHC(Ph)OPPh2}] (13). The molecular structure of 13 has been determined by X-ray diffraction: monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 10.602$ (6) Å, $b = 19.503$ (4) Å, $c = 14.631$ (9) Å, $\beta = 97.27(3)°$, and d(calcd) = 1.476 g/cm³. The structure was solved by using 2780 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ and refined to conventional $R = 0.038$, $R_w = 0.049$. The coordination around Pd is square planar, with Cl(1)–Pd–Cl(2) and P(1)–Pd–P(2) angles of 91.77 (6) and 92.88 (6)°, respectively. The puckering of the six-membered ring is accompanied by a large P(1)–O(1)–C(14) angle of 131.1 (4)°. All complexes were characterized by elemental analyses and IR, ¹H NMR, and ³¹P{¹H} NMR spectroscopy.

Introduction

Since the discovery of the ethylene polymerization catalyst A by Keim et al.,[3] the search for active complexes of functional phosphines has become a subject of increasing interest.[4] During the last few years, many functional phosphines have been shown to confer unusual physicochemical properties to their complexes, and/or allow them to partake in reactions of catalytic relevance. Thus phosphinoanisoles of type B may stabilize a polar transition state in oxidative-addition reactions,[5] the pinacolone derivative C is a dinucleating ligand that can maintain two different metals in close proximity,[6] and in the rhodium complex D, the hemilabile P,S-ligand generates a highly reactive, coordinatively unsaturated species in solution.[7]

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A

B

C

D
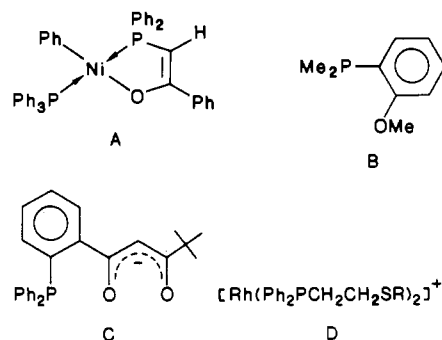
We now report a new and convenient synthesis of the β-keto phosphine Ph_2PCH_2COPh (L), together with some complexes derived from it. We also describe the synthesis and X-ray structure determination of *cis*-$[PdCl_2\{Ph_2PCHC(Ph)OPPh_2\}]$ (**13**), obtained by thermal transformation of $[PdCl_2L_2]$.

Experimental Section

All reactions were performed in Schlenk-type flasks under argon. Details of the experimental procedure used throughout this work, including reagents and analytical measurements, have been described in previous papers from our laboratory.[1,8] The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 200 and 81 MHz, respectively, on a FT Bruker WP-200 SY instrument. Mass spectra were measured on a Thomson THN 208 or a Kratos mass spectrometer (EI).

Syntheses. Ligand. Ph_2PCH_2COPh (L). To a solution of dry diisopropylamine (4.83 g, 47.7 mmol) in THF (50 mL) was added dropwise at -78 °C a 1.55 M hexane solution of n-C_4H_9Li (30.7 mL, 47.7 mmol). After the mixture was stirred for 0.5 h, a solution of dry acetophenone (5.73 g, 47.7 mmol) in THF (20 mL) was added dropwise. The mixture was stirred for 2 h at -78 °C and then transfered via a cannula into a Schlenk flask containing PPh_2Cl (10.52 g, 47.7 mmol) in THF (50 mL). After the mixture was stirred for 12 h at room temperature, the solvent was removed in vacuo. The residue was treated with toluene, and the resulting suspension was filtered in order to remove LiCl. The filtrate was then evaporated to dryness, and the yellow-white residue was purified by column chromatography (Kieselgel 60), using ethyl acetate (5%)–cyclohexane as eluant. The ligand was isolated as a white solid (11.60 g, 38.2 mmol, 80%) (mp 71 °C). Anal. Calcd for $C_{20}H_{17}OP$ (M_r = 304.33): C, 78.93; H, 5.63. Found: C, 78.79; H, 5.60. IR (KBr): 1572 mw, 1589 m, 1670 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 3.80 (s, 2 H, CH$_2$, ^2J(PH) $\sim$ 0 Hz), 7.2–8.1 (15 H, aromatic H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ −17.1 (s). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 40.54 (d, CH$_2$, ^1J(PC) = 21.5 Hz), 196.94 (d, C=O, ^2J(PC) = 8.1 Hz). MS: m/e 304 (M$^+$, 20%), 303 (M$^+$ − 1, 100%).

Complexes. $[PdCl_2(SEt_2)_2]$,[9] $[(\eta^3$-$C_4H_7)Pd(\mu$-Cl)]$_2$,[10] and the cyclometalated complexes $[(\widehat{C N})Pd(\mu$-Cl)]$_2$ (where $\widehat{C H N}$ = dimethylbenzylamine ($C_6H_5CH_2NMe_2$),[11] 8-methylquinoline ($C_{10}H_9N$),[12] and acetophenone N-phenylhydrazone ($C_{14}H_{14}N_2$)[13] were obtained by literature methods.

$[PdCl_2(Ph_2PCH_2COPh)_2]$ (1). A solution of Ph_2PCH_2COPh (0.953 g, 3.14 mmol) in THF (15 mL) was added to a solution of $PdCl_2(SEt_2)_2$ (0.560 g, 1.57 mmol) in THF (5 mL). The solution turned light yellow, and after 0.2 h a pale yellow precipitate appeared. The latter was filtered and washed with pentane (0.850 g, 71%). Recrystallization from CH$_2$Cl$_2$ (or CHCl$_3$) afforded, as shown by ^1H and $^{31}P\{^1H\}$ NMR, a mixture of *cis*- and *trans*-PdCl$_2$(Ph$_2$PCH$_2$COPh)$_2$. Anal. Calcd for $C_{40}H_{34}Cl_2O_2$-P_2Pd (M_r = 785.96): C, 61.13; H, 4.36. Found: C, 61.00; H, 4.31. ^1H NMR (CDCl$_3$): δ 4.37 (virtual t, CH$_2$, ^{2+4}J(PH) = 7.9 Hz, trans isomer), 4.42 (d, CH$_2$, ^2J(PH) = 11.2 Hz, cis isomer), 7.12–7.95 (aromatic H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 13.4 (s, trans isomer), 22.6 (s, cis isomer).

$[(\eta^3$-$C_4H_7)PdCl(Ph_2PCH_2COPh)]$ (2). (Diphenylphosphino)acetophenone (0.240 g, 0.79 mmol) and $[(\eta^3$-$C_4H_7)Pd(\mu$-Cl)]$_2$ (0.156 g, 0.40 mmol) were reacted in CH$_2$Cl$_2$ (10 mL). After the mixture was stirred

for 1 h, pentane was added. After the resulting mixture was cooled to -15 °C, white crystals of **2** precipitated (0.330 g, 83%) (mp $\sim$65 °C). Anal. Calcd for $C_{24}H_{24}ClOPPd$ (M_r = 501.28): C, 57.51; H, 4.83. Found: C, 57.30; H, 4.93. IR (KBr): 1575 m, 1595 m, 1665 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 1.88 (s, 3 H, Me), 2.62 (s br, 1 H, H^d), 3.08 (s br, 1 H, H^c), 3.42 (d, 1 H, H^a, J(PH^a) = 10.6 Hz), 4.37 (d, 2 H, PCH$_2$, ^2J(PH) = 9.2 Hz), 4.44 (d, 1 H, H^b, J(PH^b) = 8 Hz), 7.28–7.89 (15 H, aromatic H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 18.0 (s).

$[(o$-$\widehat{C_6H_4CH_2NMe_2})PdCl(Ph_2PCH_2COPh)]$ (3). (Diphenylphosphino)acetophenone (0.304 g, 1.0 mmol) and $[(o$-$\widehat{C_6H_4CH_2NMe_2})Pd(\mu$-Cl)]$_2$ (0.276 g, 0.50 mmol) were reacted in CH$_2$Cl$_2$ (10 mL). After the mixture was stirred for 0.25 h, the resulting solution was filtered. Addition of pentane to the filtrate afforded pale yellow, air-stable crystals of **3** (0.550 g, 95%) (mp 147 °C). Anal. Calcd for $C_{29}H_{29}ClNOPPd$ (M_r = 580.38): C, 60.02; H, 5.04. Found: C, 59.74; H, 4.90. IR (KBr): 1576 ms, 1589 m, 1670 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 2.79 (d, 6 H, NMe$_2$, ^4J(PH) = 2.7 Hz), 4.01 (d, 2 H, NCH$_2$, ^4J(PH) = 2.2 Hz), 4.53 (d, 2 H, PCH$_2$, ^2J(PH) = 10.9 Hz), 6.28–7.92 (19 H, aromatic H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 29.5 (s).

$[(\widehat{C_{10}H_8N})PdCl(Ph_2PCH_2COPh)]$ (4). (Diphenylphosphino)acetophenone (0.304 g, 1.0 mmol) and $[(\widehat{C_{10}H_8N})Pd(\mu$-Cl)]$_2$ (0.284 g, 0.50 mmol) were reacted in CH$_2$Cl$_2$ (20 mL). After the mixture was stirred for 1 h, the resulting solution was filtered; addition of pentane resulted in deposition of pale yellow, air-stable, crystals. Recrystallization from CH$_2$Cl$_2$/pentane afforded pure **4** (0.535 g, 91%) (mp 196 °C). Anal. Calcd for $C_{30}H_{25}ClNOPPd$ (M_r = 588.36): C, 61.24; H, 4.28. Found: C, 61.12; H, 4.12. IR (KBr): 1575 m, 1590 m, 1670 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 2.87 (d, 2 H, CH$_2$Pd, ^3J(PH) = 4.1 Hz), 4.63 (d, 2 H, PCH$_2$, ^2J(PH) = 10.1 Hz), 7.25–10.20 (21 H, aromatic H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 28.5 (s).

$[(\widehat{C_{14}H_{13}N_2})PdCl(Ph_2PCH_2COPh)]$ (5). (Diphenylphosphino)acetophenone (0.304 g, 1.0 mmol) and $[(\widehat{C_{14}H_{13}N_2})Pd(\mu$-Cl)]$_2$ (0.351 g, 0.50 mmol) were reacted in CH$_2$Cl$_2$ (10 mL). After the mixture was stirred for 0.2 h, the resulting solution was filtered. Addition of pentane to the filtrate afforded orange, air-stable, crystals of **5** (0.590 g, 90%) (mp 183 °C). Anal. Calcd for $C_{34}H_{30}ClN_2OPPd$ (M_r = 655.45): C, 62.30; H, 4.61; N, 4.27. Found: C, 60.84;[14] H, 4.55; N, 4.08. IR (KBr): 1570 m, 1590 s, 1621 w, 1670 s, 3206 (ν(N–H)) m cm^{-1}. ^1H NMR (CDCl$_3$): δ 2.31 (s, 3 H, CH$_3$), 4.51 (d, 2 H, PCH$_2$, ^2J(PH) = 10.3 Hz), 6.42–7.99 (24 H, aromatic H), 8.82 (d, 1 H, NH, ^4J(PH) = 2.6 Hz). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 27.4 (s).

$[(o$-$\widehat{C_6H_4CH_2NMe_2})Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$ (6). A solution of **3** (0.580 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL) was added to a stirred suspension of AgCF$_3$SO$_3$ (0.257 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL). After being stirred for 1 h, the reaction mixture was filtered through Celite. Addition of pentane to the filtrate afforded pale yellow, air-stable, crystals of **6** (0.604 g, 87%) (mp 170 °C dec). Anal. Calcd for C_{30}-$H_{29}F_3O_4PPdS$ (M_r = 694.02): C, 51.92; H, 4.21. Found: C, 51.97; H, 4.07. IR (KBr): 1570 s, 1591 s, 1604 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 3.06 (d, 6 H, NMe$_2$, ^4J(PH) = 2.6 Hz), 4.13 (d, 2 H, NCH$_2$, ^4J(PH) = 2.1 Hz), 4.86 (d, 2 H, PCH$_2$, ^2J(PH) = 11.5 Hz), 6.47–8.18 (19 H, aromatic H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 34.8 (s).

$[(\widehat{C_{10}H_8N})Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$ (7). A solution of **4** (0.588 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL) was added to a stirred suspension of AgCF$_3$SO$_3$ (0.257 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL). After being stirred for 1 h, the reaction mixture was filtered through Celite. Addition of pentane to the filtrate afforded pale yellow, air-stable, crystals of **7** (0.581 g, 82%) (mp 173 °C dec). Anal. Calcd for $C_{31}H_{25}F_3NO_4PPdS$ (M_r = 701.98): C, 53.04; H, 3.59. Found: C, 50.29; H, 3.50. IR (KBr): 1570 s, 1592 s, 1607 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 3.26 (d, 2 H, CH$_2$Pd, ^3J(PH) = 3.8 Hz), 4.71 (d, 2 H, PCH$_2$, ^2J(PH) = 11.0 Hz), 7.25–9.13 (21 H, aromatic H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 29.8 (s).

$[(\widehat{C_{14}H_{13}N_2})Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$ (8). A solution of **5** (0.655 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL) was added to a stirred suspension of AgCF$_3$SO$_3$ (0.257 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL). After being stirred for 1 h, the reaction mixture was filtered through Celite. Addition of pentane to the filtrate afforded pale yellow, air-stable, crystals of **8** (0.614 g, 80%) (mp 165 °C dec). Anal. Calcd for $C_{35}H_{30}F_3N_2O_4PPdS$ (M_r = 769.07): C, 54.66; H, 3.93; N, 3.64. Found: C, 54.42; H, 3.81; N, 3.40. IR (KBr): 1563 s, 1568 sh, 1588 s, 1596 s, 3240 (ν(NH)) m cm^{-1}. ^1H NMR (CDCl$_3$): δ 2.61 (s, 3 H, CH$_3$), 4.44 (d, 2 H, CH$_2$, ^2J(PH) = 11.5 Hz), 6.60–7.90 (25 H, aromatic H), 7.45 (s, 1 H, NH).

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(14) Experimental C analysis results lower than required by theory have frequently been found in other palladium complexes containing this cyclometalated ligand.[8]

$^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 34.8 (s).

[(o-C$_6$H$_4$CH$_2$NMe$_2$)Pd{Ph$_2$PCHC(O)Ph}] (9). A solution of 3 (0.200 g, 0.34 mmol) in THF (10 mL) was added to a stirred suspension of NaH (0.017 g, 0.7 mmol) in THF (10 mL). After being stirred for 9 h, the reaction mixture was filtered. Addition of pentane resulted in deposition of a yellow powder, which was recrystallized from THF/pentane, affording pale yellow, air-stable, crystals of 9 (0.175 g, 93%) (mp 156 °C dec). Anal. Calcd for C$_{29}$H$_{28}$NOPPd (M_r = 543.92): C, 64.04; H, 5.19. Found: C, 63.94; H, 5.45. IR (KBr): 1477 s, 1505 s, 1575 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.93 (d, 6 H, NMe$_2$, ^4J(PH) = 2.3 Hz), 3.99 (d, 2 H, NCH$_2$, ^4J(PH) = 1.8 Hz), 4.92 (d, 1 H, PCH, ^2J(PH) = 2.4 Hz), 6.65–7.93 (19 H, aromatic H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 32.1 (s).

[(C$_{10}$H$_8$N)Pd{Ph$_2$PCHC(O)Ph}] (10). A solution of 4 (0.588 g, 1.0 mmol) in THF (10 mL) was added to a stirred suspension of NaH (0.030 g, 1.25 mmol) in THF (20 mL). After being stirred for 5 h at room temperature, the suspension was filtered. The solution was concentrated and pentane was added, affording pale yellow, air-stable, crystals of 10, which were recrystallized from THF/pentane (0.387 g, 70%) (mp 175 °C subl). Anal. Calcd for C$_{30}$H$_{24}$NOPPd (M_r = 551.90): C, 65.29; H, 4.38. Found: C, 65.41; H, 4.62. IR (KBr) 1474 s, 1499 s, 1580 w cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.26 (d, 2 H, CH$_2$, ^3J(PH) = 2.6 Hz), 4.97 (d, 1 H, PCH, ^2J(PH) = 1.8 Hz), 7.34–9.35 (21 H, aromatic H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 28.2 (s).

[(C$_{14}$H$_{13}$N$_2$)Pd{Ph$_2$PCHC(O)Ph}] (11). A solution of 5 (0.655 g, 1.0 mmol) in THF (10 mL) was added to a stirred suspension of NaH (0.024 g, 1.0 mmol) in THF (10 mL). After 10 min, a change in color to red was observed. After being stirred for 4 h, the reaction mixture was filtered. Addition of pentane resulted in deposition of an orange powder. Recrystallization from THF/pentane afforded orange, air-stable, crystals of 11 (0.433 g, 70%) (mp 165 °C dec). Anal. Calcd for C$_{34}$H$_{29}$N$_2$OPPd (M_r = 618.99): C, 65.97; H, 4.72; N, 4.53. Found: C, 63.06;[14] H, 4.57; N, 4.08. IR (KBr): 1481 s, 1494 ms, 1511 s, 1571 m, 1597 m, 3250 (ν(NH)) m cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 1.84 (s, 3 H, CH$_3$), 5.09 (d, 1 H, PCH, ^2J(PH) = 2.1 Hz), 6.82–7.99 (aromatic H and NH). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 29.8 (s).

***cis*-[Pd{Ph$_2$PCHC(O)Ph}$_2$] (12).** A solution of Ph$_2$PCH$_2$COPh (0.215 g, 0.71 mmol) and NEt$_3$ (0.100 g, 0.99 mmol) in MeOH (10 mL) was added to a solution of Li$_2$PdCl$_4$ (0.092 g, 0.35 mmol) in MeOH (5 mL). The mixture turned yellow and 12 precipitated (0.050 g). The latter was filtered off, and the filtrate was slowly concentrated in vacuo with formation of yellow, air-stable, crystals of 12. These were collected, washed with cold ether and dried in vacuo (total yield 0.199 g, 80%) (mp 215 °C dec). Anal. Calcd for C$_{40}$H$_{32}$O$_2$P$_2$Pd (M_r = 713.04): C, 67.38; H, 4.52. Found: C, 66.31; H, 4.47. IR (KBr): 1484 s, 1513 s, 1583 w cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 4.75 (d, 2 H, PCH, ^2J(PH) = 2.1 Hz), 6.74–8.39 (36 H, aromatic H). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 37.7 (s).

***cis*-[PdCl$_2${Ph$_2$PCHC(Ph)OPPh$_2$}] (13).** A suspension of 1 (0.786 g, 1.0 mmol) in toluene (20 mL) was refluxed for 4 h. Then the solvent was removed in vacuo and the white residue washed with pentane. Recrystallization from CH$_2$Cl$_2$/pentane afforded air-stable, white crystals of 13 (0.619 g, 93%) (mp >230 °C slow dec). Anal. Calcd for C$_{32}$H$_{26}$Cl$_2$OP$_2$Pd (M_r = 665.81): C, 57.73; H, 3.94. Found: C, 57.76; H, 3.91. IR (KBr): 1570 s, 1600 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.97 (dd, 2 H, PCH, ^2J(PH) = 2.0 Hz, ^4J(PH) = 6.0 Hz), 7.32–7.87 (30 H, aromatic H). ^{31}P{^{1}H} NMR (CDCl$_3$/CH$_2$Cl$_2$): δ 4.2 (d, PCH, J(PP) = 6.0 Hz), 129.5 (d, PO, J(PP) = 6.0 Hz). MS: m/e 666 (M$^+$ + 1, 35%), 631 (M$^+$ + 1 – Cl, 100%).

X-ray Data Collection and Structural Determination for 13. Well-formed white needles were grown by slow diffusion of pentane into a CH$_2$Cl$_2$ solution of 13. 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 obtained 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.[15] 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[16] and refined by full-matrix least-squares with aniso-

Table I. Crystal Data and Data Collection for 13

formula	C$_{32}$H$_{26}$Cl$_2$OP$_2$Pd
M_r	665.83
cryst syst	monoclinic
a, Å	10.602 (6)
b, Å	19.503 (4)
c, Å	14.631 (9)
β, deg	97.27 (3)
V, Å^3	3001
Z	4
cryst dimens, mm	0.35 × 0.15 × 0.10
$F(000)$	1344
ρ_{calcd}, g/cm^3	1.476
space group	$P2_1/c$
systematic absences	($h0l$), $l = 2n$; ($0k0$), $k = 2n$
diffractometer	Nonius CAD-4
radiation	λ(Mo Kα) = 0.710 69 Å
linear abs coeff, cm^{-1}	9.173
transmission factors: max, min	0.86, 0.86
scan type	$\omega/2\theta$
scan range, deg	(1 + 0.35 tan θ)
θ limits, deg	1–25
octants collcd	$\pm h, +k, +l$
no. of data collcd	5242
no. of unique data used	2780 ($F_o^2 \geq 3\sigma(F_o^2)$)
no. of variables	344
$R_{int} = \sum(F_o^2 - \langle F_o^2 \rangle)/\sum F_o^2$	0.058
$R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$	0.038
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum\|F_o\|^2]^{1/2}$	0.049
$GOF = [\sum w(\|F_o\| - \|F_c\|)^2/(N_{observns} - N_{params})]^{1/2}$	1.208
std error in an observn of unit weight, e	1.208
largest shift/esd, final cycle	0.14
largest peak, e/Å^3	0.66

tropic thermal parameters for all non-hydrogen atoms. The function minimized was $\sum w(\|F_o\| - \|F_c\|)^2$, where the weight w is $^1/_4[\sigma(I)^2/I + (0.06I)^2]^{-1}$. Hydrogen atoms were introduced by their computed coordinates 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.[17] 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), and a listing of the observed and calculated structure factor amplitudes used in the refinement (Table S-III) are available as supplementary material.[18]

Results and Discussion

The β-keto phosphine Ph$_2$PCH$_2$COPh (L) was conveniently prepared by reacting PhCOCH$_2$Li with Ph$_2$PCl in THF(eq 1).
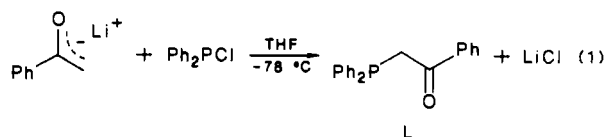
After purification by column chromatography, L was obtained as a pure white solid in ca. 80% yield. Characterizing data are given in the Experimental Section and in Table III.

To the best of our knowledge, this represents the first one-step synthesis of a keto-phosphine ligand from a trivalent phosphorus precursor.[19] The related t-Bu$_2$PCH$_2$COR (R = Ph, t-Bu) ligands have been obtained by deprotonation of the corresponding

(15) Frenz, B. A. In *The Enraf-Nonius CAD4-SDP in Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; University Press: Delft, The Netherlands, 1978; pp 64–71.

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

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

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

(19) Erastov, O. A.; Nikonov, G. N. *Russ. Chem. Rev. (Engl. Transl.)* **1984**, *53*, 309–382.

Table II. Positional Parameters and Their Estimated Standard Deviations for cis-[PdCl₂{Ph₂PCHC(Ph)OPPh₂}] **(13)**

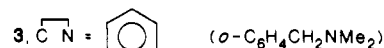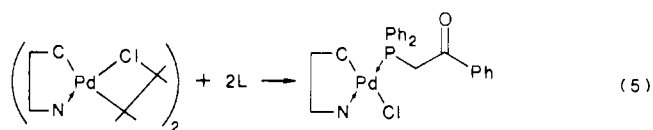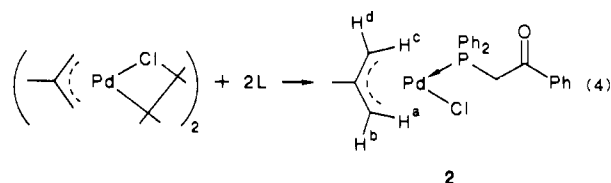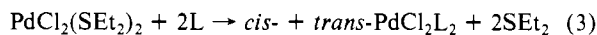| atom	x	y	z	$B,^a$ Å^2
Pd	0.44815 (4)	0.19461 (2)	0.21723 (3)	3.202 (8)
Cl(1)	0.2252 (1)	0.1894 (1)	0.2023 (1)	4.81 (4)
Cl(2)	0.4645 (2)	0.07469 (8)	0.2163 (1)	4.87 (4)
P(1)	0.6582 (1)	0.19442 (9)	0.2392 (1)	3.47 (3)
P(2)	0.4379 (2)	0.30851 (8)	0.2125 (1)	3.49 (3)
O(1)	0.7327 (4)	0.2691 (2)	0.2648 (4)	5.5 (1)
C(1)	0.7323 (6)	0.1635 (4)	0.1432 (4)	3.9 (1)
C(2)	0.8640 (6)	0.1609 (5)	0.1493 (5)	5.6 (2)
C(3)	0.9202 (7)	0.1379 (5)	0.0760 (5)	6.4 (2)
C(4)	0.8466 (7)	0.1158 (5)	−0.0037 (5)	6.1 (2)
C(5)	0.7173 (7)	0.1188 (4)	−0.0102 (4)	5.8 (2)
C(6)	0.6591 (6)	0.1429 (4)	0.0626 (4)	4.4 (2)
C(7)	0.7233 (6)	0.1474 (3)	0.3406 (4)	3.9 (1)
C(8)	0.7548 (7)	0.0800 (4)	0.3363 (5)	5.3 (2)
C(9)	0.7983 (9)	0.0440 (4)	0.4162 (6)	7.2 (2)
C(10)	0.8106 (8)	0.0772 (5)	0.5000 (5)	7.4 (2)
C(11)	0.7803 (8)	0.1438 (5)	0.5044 (5)	6.9 (2)
C(12)	0.7344 (7)	0.1798 (4)	0.4257 (5)	5.6 (2)
C(13)	0.5799 (5)	0.3521 (3)	0.2131 (4)	3.3 (1)
C(14)	0.6994 (6)	0.3338 (3)	0.2409 (4)	3.4 (1)
C(15)	0.8042 (5)	0.3838 (3)	0.2527 (4)	2.9 (1)
C(16)	0.7807 (7)	0.4525 (3)	0.2593 (5)	4.6 (2)
C(17)	0.8839 (9)	0.4978 (4)	0.2742 (6)	7.1 (2)
C(18)	1.0066 (8)	0.4717 (5)	0.2830 (6)	8.7 (2)
C(19)	1.0267 (7)	0.4046 (5)	0.2766 (6)	8.2 (2)
C(20)	0.9291 (6)	0.3619 (4)	0.2602 (5)	5.5 (2)
C(21)	0.3746 (6)	0.3459 (3)	0.3109 (4)	3.5 (1)
C(22)	0.3351 (7)	0.3040 (4)	0.3782 (4)	5.0 (2)
C(23)	0.2977 (8)	0.3336 (4)	0.4565 (5)	5.9 (2)
C(24)	0.2994 (8)	0.4025 (4)	0.4684 (5)	6.2 (2)
C(25)	0.3398 (8)	0.4441 (4)	0.4012 (5)	5.8 (2)
C(26)	0.3778 (7)	0.4162 (4)	0.3222 (5)	4.8 (2)
C(27)	0.3484 (7)	0.3404 (4)	0.1063 (4)	4.7 (2)
C(28)	0.4097 (8)	0.3622 (4)	0.0349 (5)	6.5 (2)
C(29)	0.340 (1)	0.3828 (5)	−0.0484 (5)	8.5 (3)
C(30)	0.214 (1)	0.3811 (5)	−0.0571 (6)	9.3 (3)
C(31)	0.1509 (8)	0.3595 (4)	0.0115 (6)	7.6 (2)
C(32)	0.2169 (7)	0.3394 (4)	0.0953 (5)	5.7 (2)

^{a} B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(11) + b^2\beta(22) + c^2\beta(33) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

phosphonium salts (ca. 60% yield).[20] The reaction of eq 1 has been extended to the synthesis of the ester phosphines Ph₂PCH₂CO₂Et and PhP(CH₂COOEt)₂ (eq 2).[21]

$$EtO-C(=O)-CH_2-Li^+ + Ph_nPCl_{3-n} \xrightarrow[-78\ °C]{THF}$$

$$Ph_nP(CH_2COOEt)_{3-n} + (3-n)LiCl \quad (2)$$

$$n = 2, 1$$
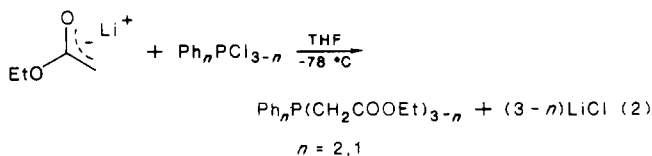
When $n = 2$, the spectroscopic yield (^{31}P{^{1}H} NMR) is quantitative.[21] It is noteworthy that these reactions lead to P–C rather than P–O bond formation.

Keto-Phosphine Complexes. As ligands, β-keto phosphines may coordinate in a unidentate fashion through the P atom (type I) or as P,O-chelates (type II). To our knowledge, only one complex containing the Ph₂PCH₂COPh ligand has been reported: [W-(CO)₄(Ph₂POH)(Ph₂PCH₂COPh)], obtained in 20% yield upon photohydrolysis of [W(CO)₄{Ph₂PCHC(Ph)OPPh₂}].[22] The complexes of type I, **1–5** (eq 3–5), were prepared by reacting L with the appropriate palladium(II) complex.

$$PdCl_2(SEt_2)_2 + 2L \rightarrow \text{cis-} + \text{trans-}PdCl_2L_2 + 2SEt_2 \quad (3)$$

2

3. C̄N̄ = (o-C₆H₄CH₂NMe₂)

4. C̄N̄ = (C₁₀H₈N)

5. C̄N̄ = (C₁₄H₁₃N₂)
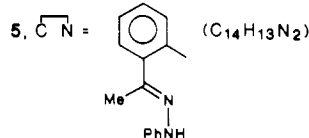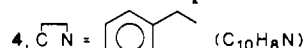
The IR spectra of these complexes show a strong absorption band between 1665 and 1680 cm⁻¹, typical for an uncoordinated ketone function (see Table III).

During the reaction of eq 3, a pale yellow precipitate was formed, which could be dissolved in CH₂Cl₂ or CHCl₃. The ^{31}P{^{1}H} NMR spectrum of these solutions showed two resonances in a ca. 4:5 ratio at 22.6 and 13.4 ppm, assigned[23] respectively to the cis and trans isomers of PdCl₂L₂. The ^{31}P{^{1}H} NMR spectrum of the supernate indicated the presence of trans-**1** as the main isomer. Despite numerous attempts, these two isomers could not be fully separated from each other. The ^{31}P{^{1}H} NMR data for **2–5** are unexceptional (Table III). In the ¹H NMR spectra (Table III) of cis-**1** and **2–5**, the PCH₂ protons appear as doublets owing to coupling with the phosphorus atom, whereas in trans-**1** they appear as a virtual triplet, characteristic of a trans-P–Pd–P arrangement. The assignment of the alkyl protons of **2** follows that for related complexes.[24]

Complexes **3–5** were reacted with 1 equiv of AgCF₃SO₃ to give quantitatively the cationic complexes **6–8** (eq 6). In their IR spectra, the ν(C=O) stretching frequency falls markedly from

3. C̄N̄ = o-C₆H₄CH₂NMe₂   **6**
4. C̄N̄ = C₁₀H₈N   **7**
5. C̄N̄ = C₁₄H₁₃N₂   **8**

(6)
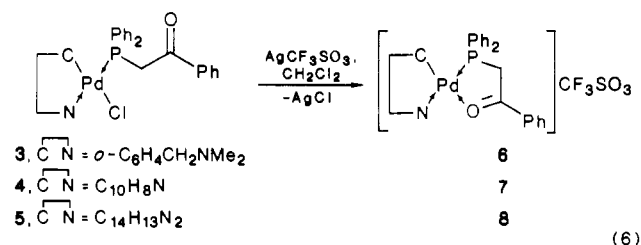
1670 cm⁻¹ in free L to ca. 1570 cm⁻¹, indicating a coordination of the keto group. In all complexes, the phosphorus atom remains coordinated to the metal, as deduced, inter alia, from the chemical shift values (see Table III) or the existence of a typical ^4J(PH) or ^3J(PH) value for the CH₂NPd protons of **6** or the CH₂Pd protons of **7**, respectively. The N–H proton of the hydrazone ligand in **5** appears at 8.82 ppm in the ¹H NMR spectrum, whereas in the corresponding cation **8**, its signal, identified by D₂O exchange, shifts to 7.45 ppm. The relatively low ν(NH) frequencies in **5** and **8** could be due to intramolecular hydrogen bonding with

(20) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 299–301.
(21) Braunstein, P.; Matt, D., unpublished results.
(22) Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 863–867.

(23) Grim, S. O.; Keiter, R. L. *Inorg. Chim. Acta* **1970**, *4*, 56–60.
(24) Sakakibara, M.; Takahashi, Y.; Sakai, S.; Ishii, Y. *J. Organomet. Chem.* **1971**, *27*, 139–147.

Table III. Selected IR and NMR Data for Complexes 1-13

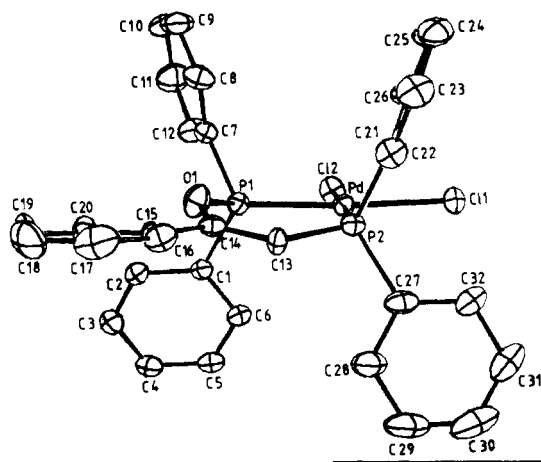| complex	no.	IR,[a] cm⁻¹	¹H NMR,[c] δ		³¹P{¹H} NMR,[d] δ
			phosphorus ligand	other	
Ph_2PCH_2COPh	L	1670 ($\nu(CO)$)	3.80 (CH_2, $^2J(PH) = 0$ Hz)		-17.1
$[PdCl_2(Ph_2PCH_2COPh)_2]$	1	1677, 1671 ($\nu(CO)$)[b]	4.37 (CH_2, $^{2+4}J(PH) =$ 7.9 Hz, trans isomer)		13.4 (trans)
			4.42 (CH_2, $^2J(PH) =$ 11.2 Hz, cis isomer)		22.6 (cis)
$[(\eta^3\text{-}C_4H_7)PdCl(Ph_2PCH_2COPh)]$	2	1665 ($\nu(CO)$)	4.37 (CH_2, $^2J(PH) =$ 9.2 Hz)	1.88 (Me), 2.62 (H^d), 3.08 (H^c), 3.42 (H^a), 4.44 (H^b)	18.0
$[(o\text{-}C_6H_4CH_2NMe_2PdCl(Ph_2PCH_2COPh)]$	3	1670 ($\nu(CO)$)	4.53 (CH_2, $^2J(PH) =$ 10.9 Hz)	2.79 (NMe_2, $^4J(PH) =$ 2.7 Hz), 4.01 (NCH_2, $^4J(PH) = 2.2$ Hz)	29.5
$[(C_{10}H_8N)PdCl(Ph_2PCH_2COPh)]$	4	1677 ($\nu(CO)$)	4.63 (CH_2, $^2J(PH) =$ 10.1 Hz)	2.87 (CH_2Pd, $^3J(PH) =$ 4.1 Hz)	28.4
$[(C_{14}H_{13}N_2)PdCl(Ph_2PCH_2COPh)]$	5	1670 ($\nu(CO)$), 3206 ($\nu(NH)$)	4.51 (CH_2, $^2J(PH) =$ 10.3 Hz)	2.31 (Me), 8.82 (NH, $^4J(PH) = 2.6$ Hz)	27.4
$[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$	6	1567 ($\nu(CO)$)	4.86 (CH_2, $^2J(PH) =$ 11.5 Hz)	3.06 (NMe_2, $^4J(PH) =$ 2.6 Hz), 4.13 (NCH_2, $^4J(PH) = 2.1$ Hz)	34.8
$[(C_{10}H_8N)Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$	7	1570 ($\nu(CO)$)	4.71 (CH_2, $^2J(PH) =$ 11.0 Hz)	3.26 (CH_2Pd, $^3J(PH) =$ 3.8 Hz)	29.8
$[(C_{14}H_{13}N_2)Pd\{Ph_2PCH_2C(O)Ph\}][CF_3SO_3]$	8	1563 ($\nu(CO)$), 3240 ($\nu(NH)$)	4.44 (CH_2, $^2J(PH) =$ 11.5 Hz)	2.61 (Me), 7.45 (NH)	34.8
$[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCHC(O)Ph\}]$	9	1477, 1505	4.92 (CH, $^2J(PH) =$ 2.4 Hz)	2.93 (NMe_2, $^4J(PH) =$ 2.3 Hz) 3.99 (NCH_2, $^4J(PH) =$ 1.8 Hz)	32.1
$[(C_{10}H_8N)Pd\{Ph_2PCHC(O)Ph\}]$	10	1474 ($\nu(C\text{—}O) + \nu(C\text{=}C)$), 1499	4.97 (CH, $^2J(PH) =$ 1.8 Hz)	3.26 (CH_2Pd, $^3J(PH) =$ 2.6 Hz)	28.3
$[(C_{14}H_{13}N_2)Pd\{Ph_2PCHC(O)Ph\}]$	11	1511 ($\nu C\text{—}O) + \nu(C\text{=}C)$), 3250 ($\nu(NH)$)	5.09 (CH, $^2J(PH) =$ 2.1 Hz)	1.84 (Me)	29.8
$cis\text{-}[Pd\{Ph_2PCHC(O)Ph\}_2]$	12	1484, 1513 ($\nu(C\text{—}O) + \nu(C\text{=}C)$)	4.75 (CH, $^2J(PH) =$ 2.1 Hz)		37.7
$cis\text{-}[PdCl_2\{Ph_2PCHC(Ph)OPPh_2\}]$	13	1600 ($\nu(C\text{=}C)$)	5.97 (CH, $J(PH) =$ 2.0, 6.0 Hz)		4.2, 129.5 ($J(PP) =$ 6.0 Hz)

[a] Recorded as KBr disk. [b] Observed $\nu(CO)$ in mixtures of *cis*- and *trans*-1. [c] Spectra recorded in CDCl₃, except for those of **10** (CD₂Cl₂) and **12** (C₆D₆). [d] Spectra recorded in CDCl₃, except for that of **12** (CH₂Cl₂/C₆D₆).

the neighboring chlorine or oxygen atom, respectively.

Enolato-Phosphine Complexes. Complexes 3-5 were reacted with 1 equiv of NaH, affording the air-stable enolato complexes 9-11, respectively (eq 7).

(7)

3, $\overline{\text{C N}}$ = o-$C_6H_4CH_2NMe_2$ 9
4, $\overline{\text{C N}}$ = $C_{10}H_8N$ 10
5, $\overline{\text{C N}}$ = $C_{14}H_{13}N_2$ 11

The typical $\nu(C\text{=}O)$ absorption of the precursors 3-5 is replaced in these complexes by strong absorptions in the range 1477-1511 cm⁻¹, attributable to the mixed $\nu(C\text{—}O) + \nu(C\text{=}C)$ of the enolate system. The deprotonation reaction of eq 7 occurs with retention of the *trans*-N-Pd-P arrangement (¹H NMR evidence, Table III). The PCH proton appears in the ¹H NMR spectrum of 9-11 as a doublet at ca. 5.0 ppm ($^2J(PH) \sim 2$ Hz) (Table III). Comparison with the chemical shift value of ca. 3.2 ppm found for this proton in the corresponding $[(\overline{\text{C N}})\text{Pd-}\{Ph_2PCHC(O)OEt\}]$ complexes[8] indicates that this proton has more olefinic character in 9-11; i.e., the contribution of resonance form I is stronger than that of resonance form II.

I   II

The opposite is true when Y = OEt. This is consistent with the observation that 9-11 do not react with CO_2 (eq 8) under ambient conditions, whereas the complexes with Y = OEt react with CO_2 via nucleophilic attack of the carbon atom α to the phosphorus atom.[8]

(8)

The quantitative synthesis of the bis(enolato) complex 12 was achieved by reacting Li_2PdCl_4 with 2 equiv of L in the presence of NEt_3 (eq 9). This complex can also be obtained in high yield

(9)

12

by treating a THF solution of 1 with NaH, or a CH_2Cl_2 solution of $Pd(acac)_2$ with 2 equiv of Ph_2PCH_2COPh. Infrared and NMR data for 12 are given in Table III. The ¹H NMR spectrum displays a doublet at 4.75 ppm with $^2J(PH) = 2.1$ Hz, in keeping with the phosphorus atoms occupying cis positions. With the bulky *tert*-butyl substituents on phosphorus, only the *trans*-Pd[*t*-Bu₂PCHC(O)Ph]₂ complexes were isolated.[20] It is interesting to note that the nickel analogue of 12 has been recently prepared by the reaction of Ni(cod)₂ with the phosphorus ylide Ph₃PCHCOPh in the presence of Ph₃As.[25] In the presence of

Figure 1. Molecular structure of cis-[PdCl$_2${Ph$_2$PCHC(Ph)OPPh$_2$}] (13).

Ph$_3$P, the same reaction led to the monophosphino enolato complex Ni(Ph)[Ph$_2$PCHC(O)Ph](PPh$_3$) (A).[3a]

Thermolysis of 1 and Molecular Structure of 13. When a toluene solution of complex 1 was refluxed for 4 h, the new complex cis-[PdCl$_2${Ph$_2$PCHC(Ph)OPPh$_2$}] 13 was formed quantitatively (eq 10).

(10)
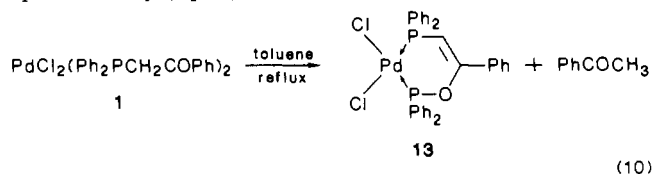
The infrared spectrum of 13 shows a strong band at 1600 cm^{-1}, assigned to the vibration of the newly formed carbon–carbon double bond, whereas the ν(CO) band of the precursor has disappeared. The ^{31}P{^{1}H} NMR spectrum of 13 shows two doublets at 4.2 and 129.5 ppm (with J(PP) = 6.0 Hz), which are at typical values for coordinated phosphine and phosphinite groups, respectively. The PCH proton appears as a doublet of doublets owing to coupling with both phosphorus atoms. The small coupling constant of 2.0 Hz is tentatively assigned to ^2J(PH), by analogy with the values encountered for similar coupling in, e.g., complexes 9–12 (Table III). The structure of 13 was confirmed by an X-ray diffraction study.

The molecular structure of 13 is represented in Figure 1 together with the atomic numbering scheme. Selected bond distances and angles are given in Table IV. The palladium is in an approximately square-planar environment, with the chlorine atoms, as expected, occupying cis positions owing to the size of the chelating ligand. The Pd–Cl(1) and Pd–Cl(2) bond distances [2.349 (2) and 2.345 (2) Å, respectively] are comparable to those found in cis-[PdCl$_2${Ph$_2$P(CH$_2$)$_3$PPh$_2$}] [2.351 (1) and 2.358 (2) Å].[26] The Pd–P(1) distance [2.210 (2) Å] is noticeably shorter than Pd–P(2) [2.225 (2) Å], reflecting the increased s character of the former bond due to the presence of the electronegative oxygen.[27] A partial view of the molecule showing the distortion of the six-membered ring is depicted in Figure 2. Schematically, one can consider the atoms O(1) and C(13) to be situated one on either side of the mean plane constituted by the other atoms of the ring. The angular strain is most evident around O(1), the P(1)–O(1)–C(14) angle of 131.1 (4)° being about 10° greater than the values found for the angles P–O–C in other 6-membered rings such as [Re(CO)$_4${Ph$_2$POCH$_2$C(CH$_3$)$_2$CH$_2$}] [121.2 (6)°][28] or

(25) Qichen, H.; Minzhi, X.; Yanlong, Q.; Weihua, X.; Meicheng, S.; Youqi, T. *J. Organomet. Chem.* **1985**, *287*, 419–426.
(26) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432–2438.
(27) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.
(28) Lindner, E.; von Au, G. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1104–1110.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in Complex 13

|			
Pd–Cl(1)	2.349 (2)	P(1)–C(7)	1.806 (6)
Pd–Cl(2)	2.345 (2)	P(2)–C(13)	1.727 (5)
Pd–P(1)	2.210 (2)	P(2)–C(21)	1.816 (6)
Pd–P(2)	2.225 (2)	P(2)–C(27)	1.824 (6)
P(1)–O(1)	1.676 (5)	O(1)–C(14)	1.344 (7)
P(1)–C(1)	1.799 (6)	C(13)–C(14)	1.331 (7)
Cl(1)–Pd–Cl(2)	91.77 (6)	O(1)–P(1)–C(7)	97.9 (3)
Cl(1)–Pd–P(1)	176.07 (6)	Pd–P(2)–C(13)	116.9 (2)
Cl(1)–Pd–P(2)	89.75 (6)	Pd–P(2)–C(21)	113.4 (2)
Cl(2)–Pd–P(1)	85.72 (6)	Pd–P(2)–C(27)	112.6 (2)
Cl(2)–Pd–P(2)	177.30 (6)	C(13)–P(2)–C(21)	102.0 (3)
P(1)–Pd–P(2)	92.88 (6)	C(13)–P(2)–C(27)	101.3 (3)
Pd–P(1)–O(1)	117.9 (2)	P(1)–O(1)–C(14)	131.1 (4)
Pd–P(1)–C(1)	114.8 (2)	O(1)–C(14)–C(13)	122.6 (6)
Pd–P(1)–C(7)	113.2 (2)	C(14)–C(13)–P(2)	131.8 (5)
O(1)–P(1)–C(1)	103.1 (3)	O(1)–C(14)–C(15)	115.1 (5)
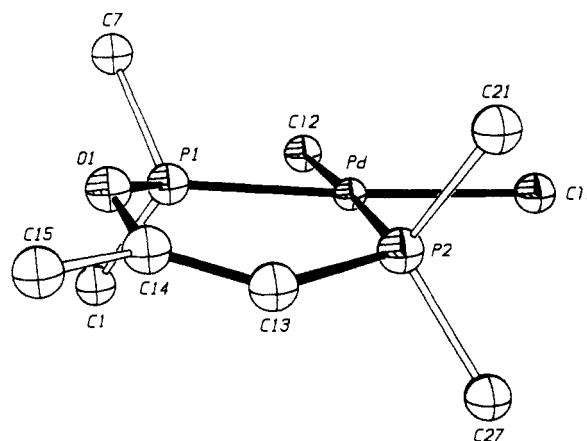
Figure 2. Partial view of 13 showing the puckering of the six-membered metallacycle.

[W(CO)$_4${Ph$_2$PCHC(Ph)OPPh$_2$}] [123.3 (4)°].[22] Whereas the latter complex was formed upon irradiation of [W(CO)$_4$-{Ph$_2$PCH(COPh)PPh$_2$}],[22] the mechanism for the synthesis of 13 involves intramolecular coupling between two cis-Ph$_2$PCH$_2$COPh ligands in 1, followed by elimination of acetophenone (eq 10) (^{1}H NMR evidence and characteristic smell). The thermally induced P–C bond cleavage in Ph$_2$P–CH$_2$COPh would liberate the base (CH$_2$COPh)$^-$, which could then rapidly deprotonate the activated methylene group of the second Ph$_2$PCH$_2$COPh coordinated ligand. A radical mechanism is less likely, in view of the failure to obtain 13 upon UV irradiation of 1.

It is noteworthy that 1 does not react with PhNH$_2$ in dry toluene at room temperature. Nor at higher temperature (reflux) is imine formation observed, only 13 being formed in this case.

Supplementary Material Available: Tables of calculated hydrogen atom coordinates (Table S-I), thermal parameters (Table S-II), bond distances and angles (Table S-IV), and selected least-squares planes (Table S-V) (6 pages); a table of calculated and observed structure factors (Table S-III) (17 pages). Ordering information is given on any current masthead page.