Synthesis and Chemistry of New Complexes of Palladium(0) and Platinum(0) with Chelating Phosphine Amide Ligands. X-ray Structure of *cis*-Bis(*o*-(diphenylphosphino)-*N*-benzoylanilino)palladium(II)

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The compound *o*-$Ph_2PC_6H_4NHC(O)Me$ has been prepared by the reaction between *o*-$Ph_2PC_6H_4NH_2$ and acetyl chloride. The compound has been used to synthesize Pd(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$, $PdCl_2$(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$, and Pd(*o*-$Ph_2PC_6H_4NC(O)Me)_2$ along with their Pt analogues. The zerovalent complexes have one monodentate and one bidentate *o*-$Ph_2PC_6H_4NHC(O)Me$ ligand. At elevated temperatures the free and complexed N ligands interchange. In chloroform solvent Pt(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ reacts with H_2 to give *trans*-PtHCl(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ along with $dbaH_2$. The corresponding reaction with D_2 gives the platinum deuteride complex. The reaction between $Pd_2(dba)_3$dba and *o*-$Ph_2PC_6H_4NHC(O)Ph$ gives the divalent complex Pd(*o*-$Ph_2PC_6H_4NC(O)Ph)_2$. This compound crystallizes in a monoclinic unit cell ($P2_1/c$) with a = 18.496 (7) Å, b = 16.806 (4) Å, c = 16.490 (5) Å, β = 104.83 (2)°, and Z = 4. The P,N chelate complex has a cis stereochemistry.

The intramolecular acceleration of organic reactions is a well-known effect. Similar features are both expected and found in inorganic and organometallic chemistry, and these reactions can be used to "activate" strong bonds toward reactivity at transition-metal centers. Numerous examples exist for the intramolecular insertion of a complexed metal into a C–H bond,[2] but little published work exists on the use of an analogous strategy to insert a metal center into an N–H bond. In view of our recent finding that some phosphine amide compounds would undergo intramolecular (or "chelate-assisted") oxidative addition of the N–H bond to rhodium(I) and iridium(I),[3] we theorized that an amide N–H bond of a chelated phosphine amide ligand should add to a zerovalent palladium or platinum center.[4]

Useful and readily available precursor complexes are the zerovalent compounds with coordinated dibenzylideneacetone $(PhCH{=}CH)_2CO$ (dba) ligands bonded through the olefinic bonds. For palladium the compound is $Pd_2(dba)_3$dba, and for platinum the analogous product is $Pt(dba)_2$.[5] The stoichiometry of the palladium complex has been verified by structural characterization, where one dba molecule in the crystal was found to be uncomplexed. In their reactions with excess of monodentate phosphine ligands L, the former compound gives PdL_3 (or PdL_4) and the latter compound gives $Pt(dba)L_2$. We have therefore used these Pd(0) and Pt(0) compounds with the phosphine amide ligands *o*-$Ph_2PC_6H_4NHC(O)Me$ and *o*-$Ph_2PC_6H_4NHC(O)Ph$, in order to synthesize amide complexes and to investigate whether the electron-rich metal center will insert into the N–H bond.

Experimental Section

Materials. *o*-(Diphenylphosphino)aniline,[6] $Pd_2(dba)_3$dba,[5] and $Pt(dba)_2$[5] were prepared according to the literature methods. All solvents were dried and distilled under nitrogen before use. Toluene, dichloromethane, diethyl ether, and *n*-hexane used for preparations of compounds 1, 4, and 8 were deaerated by pumping while alternatively freezing and melting. THF was distilled from Na/benzophenone under nitrogen before use.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 383 spectrometer. NMR spectra were recorded on a Bruker AC-200 FT NMR spectrometer (^1H, 200.13 MHz; ^{31}P, 81.015 MHz; ^{13}C, 50.323 MHz) or on a JEOL FX60 (^{31}P, 24.15 MHz) or on a Varian EM390 (^1H, 90 MHz). Variable-temperature NMR experiments for compound 1 were performed on a Bruker AC-200. Temperature calibrations were carried out by using ethylene glycol and methanol for high- and low-temperature regions, respectively. Conductance measurements were obtained with an Industrial Instruments RC-16B2 conductivity bridge in nitromethane solution under nitrogen at 25 °C. Microanalyses were carried out by Galbraith Laboratories, Inc. When solvent molecules are included in the formulation, the relative amounts are determined by integration of the ^1H NMR spectra of the complexes. All samples were vacuum dried for 24–48 h at ambient temperature.

***o*-(Diphenylphosphino)-*N*-acetylaniline (*o*-$Ph_2PC_6H_4NHC(O)Me$).** *o*-(Diphenylphosphino)aniline (2.46 g, 8.9 mmol) and dry pyridine (2.12 g, 26.7 mmol) were dissolved in THF (10 mL) contained in a 50-mL Schlenk flask fitted with a rubber septum and connected to a nitrogen source. Acetyl chloride (0.70 g, 8.9 mmol) was rapidly added to the stirred solution via syringe through the septum. Pyridine hydrochloride precipitated immediately. The suspension was stirred for 30 min. The white precipitate was removed by vacuum filtration and washed with dry THF (10 mL, in portions). Removal of solvent

(1) (a) Tulane University. (b) University of Delaware.

(2) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327–352. Omae, I. *Coord. Chem. Rev.* **1982**, *42*, 31–54, 245–257. Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183–194. Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73–86. Kolomnikov, I. S.; Kukolev, V. P.; Vol'pin, M. E. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 399–413. Prokof'ev, A. K.; Bregadze, V. I.; Okhlobystin, O. Yu. *Russ. Chem. Rev. (Engl. Transl.)* **1970**, *39*, 196–212. Kraihanzel, C. S. *J. Organomet. Chem.* **1974**, *73*, 137–185. Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; pp 213–222. Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York, 1974. Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Montery, CA, 1985. Shaw, B. L. *J. Organomet. Chem.* **1980**, *250*, 307–318.

(3) Hedden, D.; Roundhill, D. M. *Inorg. Chem.*, in press.

(4) Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254–258.

(5) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065–1066. Pierpont, C. G.; Mazza, M. C. *Inorg. Chem.* **1974**, *13*, 1891–1895. Udai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–266. Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1978**, *17*, 134–137. Cherwinski, W. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1405–1409. Keasey, A.; Mann, B. E.; Yates, A.; Maitlis, P. M. *J. Organomet. Chem.* **1978**, *152*, 117–123.

(6) Cooper, M. K.; Downes, J. M. *Inorg. Chem.* **1978**, *17*, 880–884.

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gave a viscous, white oil. Excess pyridine was removed by washing the oil with water (6 × 20 mL). The oil was dissolved in dichloromethane (15 mL), and the solution was then dried over anhydrous magnesium sulfate. The solution was filtered, and the volume was reduced to ca. 3 mL. *n*-Hexane (50 mL) was added to the solution, and the whole was then kept overnight at −10 °C. The white precipitate which formed in the solution was filtered and washed with *n*-hexane (3 × 10 mL). A small amount of phosphine oxide[7] formed during the course of reaction, and this was removed by column chromatography on silica gel (60–200 mesh, 1 cm × 20 cm column) with dichloromethane eluant. The volume of resulting colorless solution was reduced to ca. 3 mL. *n*-Hexane (50 mL) was added to the white viscous solution which was then stored overnight at −10 °C. The analytically pure compound was isolated by filtration and dried in vacuo: yield 2.1 g (74%); mp 109–111 °C. Anal. Calcd for $C_{20}H_{18}NOP$: C, 75.2; H, 5.68; N, 4.39. Found: C, 75.3; H, 5.71; N, 4.21. All samples were vacuum dried for 24–48 h at ambient temperature.

Pd(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$·0.5CH_2Cl_2 (1). $Pd_2(dba)_3$dba (400 mg, 0.32 mmol) and *o*-$Ph_2PC_6H_4NHC(O)Me$ (818 mg, 2.56 mmol) were placed in a 50-mL Schlenk vessel fitted with a filter stick assembly and a magnetic stir bar. The system was deoxygenated by conventional techniques. Dry deaerated toluene (30 mL) was added to the reaction flask through a stainless-steel needle, and the suspension was stirred for 30 min. The orange precipitate which formed during the course of the reaction was filtered through the filter stick. The compound was dissolved in dry deaerated dichloromethane (10 mL). Filtering under nitrogen removed metallic palladium, and diethyl ether (30 mL) was added to the orange filtrate. An orange compound precipitated, and this material was isolated by filtration. After being washed with diethyl ether (2 × 20 mL), the complex was dried in vacuo; yield 420 mg (64%). Anal. Calcd for $C_{57.5}H_{51}N_2O_2P_2ClPd$: C, 67.6; H, 5.03; N, 2.74. Found: C, 66.6; H, 5.20; N, 2.96. Λ_M (0.51 × 10^{-3} mol in CH_3NO_2) = 1.06 Ω^{-1} cm^2 mol^{-1}. The complex contains small amounts of complex **3** as impurity.

$PdCl_2$(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$·CH_2Cl_2 (2). Na_2PdCl_4 (102 mg, 0.35 mmol) was dissolved in acetonitrile (15 mL), and the brown-red solution was filtered. A solution of *o*-$Ph_2PC_6H_4NHC(O)CH_3$ (220 mg, 0.69 mmol) in acetonitrile (20 mL) was rapidly added to the stirred $PdCl_4^{2-}$ solution. A yellow precipitate was formed immediately. After being stirred for 20 min, the precipitate was isolated from the solution by filtration. The yellow compound was washed successively with acetonitrile, water, and diethyl ether. The compound was recrystallized from dichloromethane and diethyl ether and dried in vacuo; yield 280 mg (89%). Anal. Calcd for $C_{41}H_{38}N_2O_2P_2Cl_4Pd$: C, 54.7; H, 4.25; N, 3.11. Found: C, 54.3; H, 4.31; N, 3.03.

Pd(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$·0.5CH_2Cl_2·0.25Et_2O (3). Complex **2** (100 mg, 0.11 mmol) was dissolved in dry, oxygen-free dichloromethane (10 mL). Triethylamine (0.11 g, 1.1 mmol) was added to the solution. The reaction mixture was stirred for 30 min under nitrogen. Addition of diethyl ether (50 mL) gave a yellow precipitate. The yellow compound was isolated by filtration, recrystallized from dichloromethane and diethyl ether, and dried in vacuo; yield 78 mg (90%). Anal. Calcd for $C_{41.5}H_{37.5}ClN_2O_{2.25}P_2Pd$: C, 62.2; H, 4.71; N, 3.49. Found: C, 62.5; H, 4.77; N, 3.49.

Pt(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$·0.5CH_2Cl_2 (4). $Pt(dba)_2$ (199 mg, 0.3 mmol) and *o*-$Ph_2PC_6H_4NHC(O)Me$ (383 mg, 1.2 mmol) were used to prepare this compound. The experimental method used for the preparation of this compound was analogous to that used in the synthesis of **1**, except that in this case the reaction flask was immersed in a water bath at 60 °C. The green precipitate which formed during the course of reaction was filtered, recrystallized from dichloromethane and diethyl ether, and then dried in vacuo; yield 203 mg (61%). Anal. Calcd for $C_{57.5}H_{51}ClN_2O_2P_2Pt$: C, 62.2; H, 4.63; N, 2.52. Found: C, 61.7; H, 4.78; N, 2.64. Λ_M (0.49 × 10^{-3} mol in CH_3NO_2) = 0.68 Ω^{-1} cm^2 mol^{-1}.

***cis*-Pd(*o*-$Ph_2PC_6H_4NC(O)Ph)_2$·0.5Et_2O (5).** $Pd_2(dba)_3$dba (200 mg, 0.16 mmol) and *o*-$Ph_2PC_6H_4NHC(O)Ph$ (488 mg, 1.28 mmol) were placed in a 50-mL Schlenk vessel equipped with a magnetic stir bar and fitted with a gas dispersion tube/stainless steel tube filtration assembly. The vessel was deoxygenated. Dry, oxygen-free toluene (15 mL) was transferred to the vessel, and the resulting purple suspension was rapidly stirred. After 30 min an orange solution had formed. This solution was filtered under nitrogen into a second Schlenk vessel, and the solvent was removed by evaporation under vacuum to give an orange solid. Chromatography of an acetone solution of the orange solid in air (60–200 mesh silica gel, 5 cm × 20 cm column) using a hexane/isopropyl alcohol mixture as eluant gave dba (160 mg, theoretical yield 168 mg) and *cis*-$Pd(o\text{-}Ph_2PC_6H_4NC(O)Ph)_2$ (240 mg). Recrystallization of the palladium complex from methanol and diethyl ether gave yellow needle-like crystals. Filtration, followed by washing with diethyl ether (10 mL), gave the pure complex as the ether solvate. Vacuum drying of the complex gave a fine yellow powder; yield 230 mg (80%). Anal. Calcd for $C_{52}H_{45}N_2O_{2.5}P_2Pd$: C, 68.9; H, 5.00; N, 3.09; Pd, 11.7; mol wt, 870. Found: C, 68.3; H, 4.80; N, 3.06; Pd, 11.8; mol wt (osmometer in toluene), 904.

***trans*-$PtCl_2$(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ (6).** K_2PtCl_4 (400 mg, 0.96 mmol) was dissolved in an acetonitrile/water mixture (13 mL/4 mL). A solution of *o*-$Ph_2PC_6H_4NHC(O)Me$ (616 mg, 1.93 mmol) in acetonitrile was added to the stirred $PtCl_4^{2-}$ solution. After a few minutes a pale yellow precipitate was formed. After 30 min, the complex was filtered and then successively washed with acetonitrile, water, and ethanol. The pale yellow compound was recrystallized from a mixture of dichloromethane and *n*-hexane and then dried in vacuo; yield 782 mg (90%). Anal. Calcd for $C_{40}H_{36}N_2O_2P_2Cl_2Pt$: C, 53.1; H, 4.01; N, 3.10. Found: C, 53.1, 52.7; H, 4.12; N, 3.51, 2.98. ^1H NMR spectroscopy shows the presence of 15% CH_2Cl_2 and 15% Et_2O, which when included in the calculated values improves the agreement.

***cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)Me)_2$ (7).** Complex **6** (200 mg, 0.19 mmol) was suspended in acetonitrile (10 mL). Triethylamine (0.19 g, 1.9 mmol) was then added to the solution. The reaction mixture was refluxed for 4 h under nitrogen. A white precipitate formed during the course of reaction. The product was filtered and washed with acetonitrile and diethyl ether. The white compound was recrystallized from dichloromethane and *n*-hexane and then dried in vacuo; yield 111 mg (70%). Anal. Calcd for $C_{40}H_{34}N_2O_2P_2Pt$: C, 57.8; H, 4.12; N, 3.37. Found: C, 57.6; H, 4.51; N, 3.42.

Pt(dba)(*o*-$Ph_2PC_6H_4NHC(O)Ph)_2$ (8). This complex was prepared in an analogous manner to complex **1** using $Pt(dba)_2$ (199 mg, 0.3 mmol) and *o*-$Ph_2PC_6H_4NHC(O)Ph$ (458 mg, 1.2 mmol). No precipitate was observed in the solution during the reaction, but the color of the solution changed from deep purple to green during the course of the reaction. After 1 h, *n*-hexane was added to the green solution. The compound was isolated by filtration and recrystallized from a mixture of dichloromethane and *n*-hexane to give complex **8** (~80–90% yield) mixed with $Pt(o\text{-}Ph_2PC_6H_4NC(O)Ph)_2$.[8]

Reaction of 1 with O_2. Complex **1** (10 mg) was dissolved in a CH_2Cl_2/acetone-d_6 mixture in a 10-mm NMR tube. Oxygen gas was bubbled through the solution for 10 min. Changes in the ^1H and $^{31}P\{^1H\}$ NMR spectra showed that **3** and a small amount of *o*-$Ph_2P(O)C_6H_4NHC(O)Me$ were formed in the solution.

Reaction of 1 with O_2 in the Presence of Excess *o*-$Ph_2PC_6H_4NHC(O)Me$. Complex **1** (10 mg) and *o*-$Ph_2PC_6H_4NHC(O)Me$ (20 mg) were dissolved in a CH_2Cl_2/acetone-d_6 in a 10-mm NMR tube. Oxygen gas was bubbled through the solution for 10 min. Complex **3**, a significant amount of *o*-$Ph_2P(O)C_6H_4NHC(O)Me$, and unreacted *o*-$Ph_2PC_6H_4NHC(O)Me$ were observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of 3 with HCl. Complex **3** (200 mg, 0.25 mmol) was dissolved in dichloromethane (40 mL). Hydrogen chloride gas was bubbled through the solution for 30 min. A yellow compound was precipitated by the addition of *n*-hexane (50 mL). The compound was isolated by filtration and recrystallized from a mixture of dichloromethane and *n*-hexane. After the compound was washed with *n*-hexane (2 × 20 mL), the product was dried

(7) The compound *o*-$Ph_2P(O)C_6H_4NHC(O)Me$ can also be prepared from *o*-$Ph_2PC_6H_4NHC(O)Me$ and hydrogen peroxide (20% solution) in toluene solvent at 80 °C. The compound can be identified by IR (ν(P=O) 1160 cm^{-1}) and ^{31}P (δ 36.5) NMR spectroscopy.

(8) Hedden, D.; Roundhill, D. M. *Inorg. Chem.* **1985**, *24*, 4152–4158.

Table I. Crystal, Data Collection, and Data Refinement Parameters

(a) Crystal Parameters

formula	$PdC_{50}H_{40}N_2O_2P_2 \cdot C_4H_{10}O$	β, deg	104.83 (2)
fw	943.2	V, Å^3	4954 (2)
cryst system	monoclinic	Z	4
space group	$P2_1/c$	μ(Mo Kα) cm^{-1}	4.62
a, Å	18.496 (7)	ρ(calcd), g cm^{-3}	1.264
b, Å	16.806 (4)	color	yellow
c, Å	16.490 (5)	size, mm	0.22 × 0.30 × 0.39

(b) Data Collection

diffractometer	Nicolet R3	scan speed, deg min^{-1}	var 5–20
radiation	Mo Kα (λ = 0.71073 Å)	reflns collected	6910
monochromator	graphite	unique reflns	6440
T, °C	22	unique rflns, $F_o > 3\sigma(F_o)$	3431
std rflns	3 std/97 rflns		
scan tech	$\theta/2\theta$	R(int)	0.044
scan range, deg	$4 < 2\theta < 45$		

(c) Refinement

R_F, %	7.27	Δ/σ (last)	0.036
R_{wF}	6.76	highest peak, e Å^{-3}	1.20 (1.12 Å from Pd)
GOF	1.493		

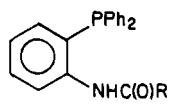


Figure 1. Structure of *o*-(diphenylphosphino)-*N*-acetylaniline (R = Me) and *o*-(diphenylphosphino)-*N*-benzoylaniline (R = Ph).

in vacuo; yield 203 mg (89%). The obtained compound was identical with complex **2** by IR, ^{1}H NMR, and ^{31}P{^{1}H} NMR spectral measurements.

Reaction of 3 with $CDCl_3$ in the Presence of H_2. Complex **3** (10 mg) was dissolved in $CDCl_3$ in a 10-mm NMR tube. The solution in the NMR tube was then stored under a hydrogen atmosphere (ca. 1 atm) for 24 h. The ^{31}P{^{1}H} NMR spectrum showed that complex **2** was formed in the solution. This compound was isolated and shown to be identical with complex **2** by IR spectroscopy.

Crystallographic Structure Determination

A yellow crystal of **5**, obtained by recrystallization from diethyl ether, was mounted in a capillary tube with a drop of mother liquor. Preliminary photographic characterization showed $2/m$ Laue symmetry, and systematic absences uniquely defined the space group as $P2_1/c$. Extensive decay (60%) in the intensity of the standard reflections occurred during data collection, due either to solvent loss or to radiation decay (or to a combination of both); the data were corrected for the decay. No correction for absorption was required. Crystallographic data are given in Table I.

The structure was solved by standard heavy-atom methods, and all remaining non-hydrogen atoms were located from a series of difference Fourier syntheses. A poorly resolved molecule of diethyl ether ("S" suffix in atom list) was located, and fragments of another molecule of diethyl ether or of a different small molecule, well removed from either the palladium complex or the whole diethyl ether molecule, were also found (CX, CY, CZ). These solvent molecules and fragments were refined isotropically, while the remaining non-hydrogen atoms were anisotropically refined. The phenyl rings (series 30–80) were constrained as rigid hexagons (C–C = 1.395 Å). Hydrogen atoms were incorporated as idealized, updated contributions, C–H = 0.95 Å, U = 1.2U attached C atom. No attempt to fix hydrogen atoms to N(1) or N(2) was made due to orientational uncertainty. All software is contained in the SHELXTL library (Nicolet Corp., Madison, WI).

Atomic coordinates are provided in Table II, and selected bond distances and angles in Table III. Additional crystallographic data are available as supplementary material.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	x	y	z	U
Pd	2835 (1)	9906 (1)	2221 (1)	31 (1)[a]
P(1)	2542 (2)	8786 (2)	1479 (2)	37 (1)[a]
P(2)	2967 (2)	9532 (2)	3547 (2)	40 (1)[a]
N(1)	2500 (5)	10311 (5)	959 (5)	36 (4)[a]
N(2)	3133 (5)	11014 (5)	2789 (6)	40 (4)[a]
O(1)	1901 (4)	11240 (5)	−17 (5)	61 (4)[a]
O(2)	3654 (6)	12267 (5)	2792 (7)	96 (6)[a]
C(1)	2068 (6)	10937 (7)	702 (8)	45 (5)[a]
C(2)	3543 (7)	11582 (7)	2544 (8)	56 (6)[a]
C(10)	2886 (6)	9066 (7)	589 (7)	43 (5)[a]
C(11)	2786 (5)	9865 (7)	395 (7)	40 (4)[a]
C(12)	2971 (6)	10154 (8)	−328 (7)	55 (5)[a]
C(13)	3307 (8)	9615 (8)	−767 (8)	70 (6)[a]
C(14)	3428 (7)	8841 (8)	−547 (8)	62 (6)[a]
C(15)	3217 (6)	8550 (8)	131 (8)	51 (5)[a]
C(20)	2792 (7)	10456 (7)	3978 (8)	53 (6)[a]
C(21)	2900 (6)	11151 (7)	3535 (8)	46 (5)[a]
C(22)	2730 (7)	11893 (8)	3818 (8)	53 (6)[a]
C(23)	2529 (9)	11942 (10)	4567 (10)	77 (8)[a]
C(24)	2465 (9)	11300 (10)	5031 (11)	86 (8)[a]
C(25)	2625 (8)	10542 (8)	4775 (8)	68 (6)[a]
C(30)	1645 (4)	11264 (5)	1307 (5)	51 (6)[a]
C(31)	1282 (4)	10763 (5)	1750 (5)	46 (5)[a]
C(32)	885 (4)	11086 (5)	2286 (5)	71 (4)[a]
C(33)	851 (4)	11909 (5)	2379 (5)	93 (9)[a]
C(34)	1215 (4)	12409 (5)	1936 (5)	113 (10)[a]
C(35)	1612 (4)	12087 (5)	1400 (5)	78 (7)[a]
C(40)	3914 (4)	11333 (5)	1853 (5)	50 (6)[a]
C(41)	3874 (4)	11868 (5)	1196 (5)	65 (7)[a]
C(42)	4240 (4)	11698 (5)	574 (5)	80 (8)[a]
C(43)	4644 (4)	10993 (5)	608 (5)	80 (8)[a]
C(44)	4684 (4)	10458 (5)	1264 (5)	74 (7)[a]
C(45)	4319 (4)	10627 (5)	1887 (5)	55 (6)[a]
C(50)	2931 (4)	7822 (4)	1809 (5)	40 (5)[a]
C(51)	2536 (4)	7120 (4)	1552 (5)	62 (6)[a]
C(52)	2880 (4)	6385 (4)	1774 (5)	87 (9)[a]
C(53)	3620 (4)	6352 (4)	2254 (5)	82 (8)[a]
C(54)	4015 (4)	7053 (4)	2510 (5)	73 (7)[a]
C(55)	3671 (4)	7788 (4)	2288 (5)	58 (6)[a]
C(60)	3837 (3)	9132 (5)	4208 (5)	40 (5)[a]
C(61)	4490 (3)	9208 (5)	3939 (5)	57 (6)[a]
C(62)	5172 (3)	8958 (5)	4456 (5)	74 (7)[a]
C(63)	5202 (3)	8631 (5)	5241 (5)	75 (7)[a]
C(64)	4549 (3)	8555 (5)	5510 (5)	80 (8)[a]
C(65)	3866 (3)	8805 (5)	4993 (5)	57 (6)[a]
C(70)	1529 (3)	8660 (5)	1087 (5)	44 (5)[a]
C(71)	1158 (3)	8914 (5)	283 (5)	56 (6)[a]
C(72)	379 (3)	8880 (5)	21 (5)	85 (8)[a]
C(73)	−28 (3)	8592 (5)	563 (5)	79 (8)[a]
C(74)	343 (3)	8338 (5)	1367 (5)	74 (7)[a]
C(75)	1122 (3)	8372 (5)	1629 (5)	62 (6)[a]
C(80)	2233 (4)	8878 (5)	3692 (5)	45 (5)[a]
C(81)	2349 (4)	8058 (5)	3762 (5)	50 (5)[a]
C(82)	1766 (4)	7554 (5)	3825 (5)	80 (7)[a]
C(83)	1067 (4)	7871 (5)	3818 (5)	94 (8)[a]
C(84)	952 (4)	8691 (5)	3748 (5)	103 (9)[a]
C(85)	1535 (4)	9194 (5)	3685 (5)	62 (6)[a]
O(1s)	600 (15)	5444 (14)	1718 (16)	296 (11)
C(1s)	1090 (26)	5152 (28)	2751 (32)	322 (21)
C(2s)	1326 (22)	4300 (26)	3164 (24)	287 (18)
C(3s)	311 (19)	6031 (21)	885 (23)	248 (15)
C(4s)	354 (19)	1103 (19)	4694 (20)	241 (14)
CX	4656 (15)	3487 (16)	2975 (17)	195 (11)
CY	2835 (17)	3940 (18)	2374 (19)	236 (14)
CZ	3960 (20)	3965 (21)	2435 (22)	274 (16)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

The two ligands used in this study are *o*-(diphenylphosphino)-*N*-acetylaniline and *o*-(diphenylphosphino)-*N*-benzoylaniline (Figure 1). The latter compound has been described previously,[8] but the former compound is

Table III. Selected Bond Distances (Å) and Angles (deg) for $PdC_{50}H_{40}N_2O_2P_2$

(a) Bond Distances			
Pd-P(1)	2.235 (3)	N(1)-C(1)	1.32 (1)
Pd-P(2)	2.227 (3)	N(2)-C(2)	1.34 (1)
Pd-N(1)	2.126 (9)	C(1)-O(1)	1.26 (1)
Pd-N(2)	2.094 (9)	C(2)-O(2)	1.22 (1)
(b) Bond Angles (deg)			
P(1)-Pd-P(2)	104.5 (1)	Pd-P(1)-C(10)	98.0 (4)
P(1)-Pd-N(1)	76.4 (2)	Pd-P(2)-C(20)	99.2 (4)
P(1)-Pd-N(2)	173.3 (3)	Pd-N(1)-C(1)	124.6 (8)
P(2)-Pd-N(1)	169.3 (3)	Pd-N(1)-C(11)	114.5 (6)
P(2)-Pd-N(2)	82.1 (3)	Pd-N(2)-C(2)	127.0 (9)
N(1)-Pd-N(2)	97.5 (3)	Pd-N(2)-C(21)	115.3 (7)
C(1)-N(1)-C(11)	121 (1)	N(1)-C(1)-O(1)	127 (1)
C(2)-N(2)-C(21)	118 (1)	N(2)-C(2)-O(2)	129 (1)
O(2)-C(1)-C(30)	115.5 (9)	O(2)-C(2)-C(40)	116 (1)

Table IV. IR Spectral Data in Nujol (cm^{-1})

compd	ν_{NH}[a]	ν_{CO}[b]	δ_{NH}[c]
o-$Ph_2PC_6H_4NHC(O)Me$	3375	1688	1500
1	3241	1702,[d] 1698, 1695[d]	
2	3318	1698	1487
3	...	1602	...
4	3240	1701,[d] 1696, 1692[d]	
5	...	1600	...
6	3304	1701	1499
7		1605	
8	3394	1676,[d] 1673, 1667[d]	

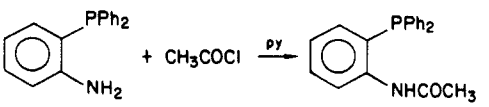
[a] Weak. [b] Strong. [c] Medium. [d] Shoulder.

Table V. ^1H NMR Spectral Data[a]

compd	chem shifts[b] NH	HC=CH	CH_3	solv
o-$Ph_2PC_6H_4NHC(O)Me$	7.8 (br, 1 H)	...	1.9 (3 H)	$CDCl_3$
1[d]	9.15 (1 H)	5.31 (m, 1 H) 4.43 (m, 1 H)	1.67 (3 H) 1.07 (3 H)	CD_2Cl_2[f]
2[c]	8.40 (2 H)	...	1.58 (6 H)	$CDCl_3$
3[d]	...	...	2.31 (6 H)	$CDCl_3$
4[d]	9.03 (1 H)	3.64 (m, 1 H)[e] 3.12 (m, 1 H)	1.63 (3 H) 1.04 (3 H)	CD_2Cl_2[f]
5	...	...	...	
6[c]	8.48 (2 H)	...	1.57 (6 H)	$CDCl_3$
7[c]	...	...	2.34 (6 H)	$CDCl_3$
8[d]	9.05 (1 H)	4.18 (m, 1 H)[e] 3.82 (m, 1 H)	...	CD_2Cl_2[f]

[a] Recorded at 25 °C. All phenyl protons were observed at 5.8–8.5 ppm. Spectral lines are singlets unless otherwise noted; br = broad, m = multiplet. [b] ppm, relative to Me_4Si. [c] Recorded on a Varian EM-390 at 90 MHz. [d] Recorded on a Bruker AC200 at 200.13 MHz. [e] ^{195}Pt satellites were observed. [f] Recorded under a nitrogen atmosphere.

unknown. The compound has been prepared by the acetylation of *o*-(diphenylphosphino)aniline (eq 1). The IR



(1)

and NMR spectra data are collected in Tables IV–VII, and these data correspond closely with those obtained for the previously prepared meta isomer.[9] We anticipate that changing the substituent group on the carbonyl functionality between methyl and phenyl will induce minimal electronic variation at the N–H group (ν(NH) = 3375 cm^{-1} (R = Me), ν(NH) = 3350 cm^{-1} (R = Ph)), but we expect that there will be a significant stereochemical difference between the methyl and phenyl analogues, especially for complexes having bis-cis ligands.

(9) Schiemenz, G. P.; Röhlk, K., *Phosphorus* **1971**, *1*, 187–190.

Table VI. $^{31}P\{^1H\}$ NMR Spectral Data[a]

compd	chem shifts[b]		solv
o-$Ph_2PC_6H_4$-NHC(O)Me	−19.9		$CDCl_3$
1[d]	P_A, 16.9;[e] P_B, 15.2[e]		CH_2Cl_2/acetone-d_6[i]
2[c]	20.4		$CDCl_3$
3[c]	42.5		$CDCl_3$
4[d]	P_A, 19.7;[f] P_B, 17.9[g]	J_{Pt-P_A} = 4143 J_{Pt-P_B} = 3520 $J_{P_A-P_B}$ = 37	CH_2Cl_2/acetone-d_6[i]
5	39.7		CH_2Cl_2/acetone-d_6
6[c]	17.6	J_{Pt-P} = 2474	$CDCl_3$
7[c]	21.1	J_{Pt-P} = 3206	CH_2Cl_2/acetone-d_6
8[d]	P_A, 19.5;[h] P_B, 18.7[h]	J_{Pt-P} = 3562 J_{Pt-P_A} = 4123 $J_{P_A-P_B}$ = 33	CH_2Cl_2/acetone-d_6[i]

[a] Recorded at 25 °C unless otherwise noted. [b] ppm, relative to 85% H_3PO_4. J in hertz (Hz). Spectral lines are singlets unless otherwise noted. [c] Recorded on a JEOL FX60 at 24.15 MHz. [d] Recorded on a Bruker AC200 at 81.015 MHz. [e] Two equal broad peaks ($\Delta\nu_{1/2}$ = 19 Hz) are observed at 25 °C. The chemical shift difference between the two peaks decreases as the temperature is increased in chlorobenzene/toluene-d_8. Finally only one peak is observed at 75 °C. The process is reversible. [f] Five paired peaks are observed with different intensities. The differences between each paired lines were the same as that between two peaks observed in P_B splitting. The chemical shift is calculated for the paired peaks with the highest intensity. [g] Two broad peaks ($\Delta\nu_{1/2}$ = 9 Hz) are observed. The integration ratio between P_A and P_B groups is unity. [h] Chemical shifts are calculated for the AB spin system ($\Delta\nu_{1/2}$ = 3 Hz). [i] Recorded under a nitrogen atmosphere.

Table VII. $^{13}C\{^1H\}$ NMR Spectral Data[a]

compd	chemical shifts[b]	solv
o-$Ph_2PC_6H_4NHC(O)Me$	24.2 (CH_3), 168.14 (CO)	$CDCl_3$
1	23.43, 22.52 (CH_3), 190.70 (CO, dba), 169.08, 167.76 (CO), 77.65, 77.23, 72.73 (C=C)	CD_2Cl_2[c]
2	23.41 (CH_3), 168.40 (CO)	$CDCl_3$
3	27.43 (CH_3), 175.04 (CO)	$CDCl_3$
4	23.17, 22.07 (CH_3); 198.37 (CO, dba), 168.65, 167.72 (CO), 64.02, 63.42, 62.25, 61.63, 60.67 (C=C)	$CDCl_3$[c]
6	23.37 (CH_3), 168.38 (CO)	$CDCl_3$
7	27.00 (CH_3), 174.95 (CO)	$CDCl_3$

[a] Recorded on a Bruker AC200 (50.323 MHz) at 25 °C. [b] ppm, relative to $SiMe_4$. [c] Under a nitrogen atmosphere.

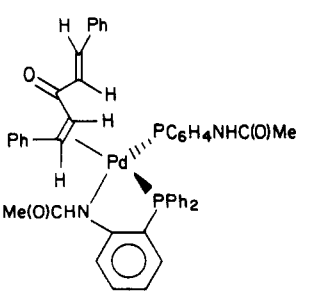


Figure 2. Structure of Pd(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$.

Treating $Pd_2(dba)_3$dba with *o*-$Ph_2PC_6H_4NHC(O)Me$ in toluene solvent under a nitrogen atmosphere gives Pd(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ (1) in 64% yield (eq 2).

$$^1/_2Pd_2(dba)_3dba + 2o\text{-}Ph_2PC_6H_4NHC(O)Me \rightarrow Pd(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2 + dba \quad (2)$$

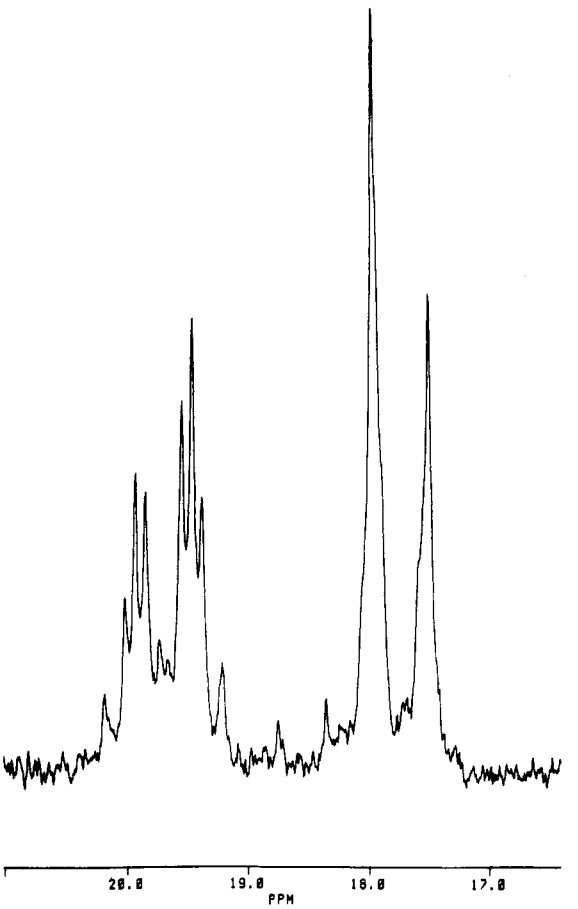


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of Pt(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ (**4**) in CH_2Cl_2/acetone-d_6 solvent under N_2 at ambient temperature.

The spectral data are consistent with an 18-electron structure where the dba is coordinated monodentate via an olefinic bond, and the *o*-(diphenylphosphino)-*N*-acetylanilide ligands are different, one being complexed bidentate via P and N and the other being a monodentate P-bonded ligand to palladium(0) (Figure 2).

The chosen ligands are designed to favor N- over O-coordination by ring size preference; N-chelation leads to the formation of the favored five-membered ring complex, whereas O-chelation gives a seven-membered ring. Throughout this paper we justify N-coordination by spectral data comparison with the structurally characterized complex **5**, by the observed shifts in ν(NH), and by the lack of shift in ν(CO) in the zerovalent complexes from the position in the uncomplexed ligands. For the data in Tables V, VI, and VII we assigned the peaks at δ 1.67 (3 H) and 1.07 (3 H) to the free and complexed amide, respectively, the peaks at δ 5.31 (1 H) and 4.43 (1 H) to the inequivalent vinyl hydrogens of the coordinated alkene of dba, the peaks at δ 16.9 (1 P) and 15.2 (1 P) to the bidentate and monodentate phosphorus, respectively, and the peaks at δ 23.43 (1 C) and 22.52 (1 C) to the two methyl carbons. By comparison the methyl carbon in *o*-$Ph_2PC_6H_4NHC(O)Me$ is found at δ 24.2. The phosphorus resonances are broad at ambient temperature ($\Delta\nu_{1/2}$ = 19 Hz), but on heating the solution to 75 °C the resonances reversibly coalesce to a single line. Monodentate–bidentate pairwise exchange at the amide ligands is therefore being observed at ambient temperature in CD_2Cl_2 solvent. The analogous platinum complex **4** also shows broad ($\Delta\nu_{1/2}$ = 9 Hz) resonances in the $^{31}P\{^1H\}$ NMR spectrum. This $^{31}P\{^1H\}$ NMR spectrum of **4** shows unexpected multiplicity in the resonance centered at δ 19.7 (P_A) (Figure 3). The resonance is a composite of five doublet splittings, each separated by 37 Hz which corresponds with $^2J_{P_AP_B}$ observed in the resonance line from P_B. These pairwise sets of lines have different intensities. The only reasonable explanation appears to be that we are observing a group of rotomers which are in slow equilibrium on the NMR time scale. Such a group could be formed from different orientations between the dba and the *o*-$Ph_2PC_6H_4NHC(O)Me$ ligands. The resonance centered at δ 19.7 (P_A) corresponds with the bidentate ligand; thus the restricted chelate phosphorus shows chemical shift changes which are sensitive to environment. This proposal is speculative, but it is further supported by the observation that increasing the temperature of the solution from ambient to 70 °C causes the multiplicity to collapse to a single broad line. The $^{13}C\{^1H\}$ NMR spectrum shows resonances for the two inequivalent methyl groups at δ 23.2 and 22.1, along with ^{13}CO resonances at δ 168.7 and 167.7 and a third ^{13}CO resonance at δ 198.4 due to the carbonyl group of the coordinated dba ligand. The resonances due to the coordinated olefin are found as a multiplet in the range δ 58–68.

The complex Pd(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ (**1**) shows the expected chemistry of a zerovalent palladium compound. In chloroform solvent under a hydrogen atmosphere, halogen atom abstraction is observed leading to the formation of $PdCl_2$(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ (**2**), along with Pd(*o*-$Ph_2PC_6H_4NC(O)Me)_2$ (**3**) (eq 3). Complex **2** can also be synthesized from $PdCl_4^{2-}$ and *o*-$Ph_2PC_6H_4NHC(O)Me$ (eq 4). Complex **1** is stable in di-

$$\text{Pd(dba)(}o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Me)}_2 \xrightarrow[-\text{dba}]{\text{H}_2/\text{CHCl}_3} \underset{\mathbf{2}}{\text{PdCl}_2(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Me)}_2} + \underset{\mathbf{3}}{\text{Pd}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NC(O)Me)}_2} \quad (3)$$

$$\text{PdCl}_4^{2-} + 2o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Me} \rightarrow \underset{\mathbf{2}}{\text{PdCl}_2(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Me)}_2} + 2\text{Cl}^- \quad (4)$$

chloromethane solution under a nitrogen atmosphere, but upon addition of oxygen to the reaction mixture the compound quickly converts to Pd(*o*-$Ph_2PC_6H_4NC(O)Me)_2$ (**3**) (eq 5). We assume the other product to be hydrogen

$$\begin{array}{l} \text{Pd(dba)(}o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Me)}_2 + \text{O}_2 \\ \qquad\qquad \xrightarrow{\text{CH}_2\text{Cl}_2} \underset{\mathbf{3}}{\text{Pd}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NC(O)Me)}_2} + \text{H}_2\text{O}_2 \quad (5) \\ \text{PdCl}_2(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Me)}_2 + 2\text{Et}_3\text{N} \\ \qquad\qquad + 2\text{Et}_3\text{N}\cdot\text{HCl} \end{array}$$

peroxide. Alternately this complex **3** can be prepared by the base-induced elimination of hydrogen chloride from $PdCl_2$(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$. This latter reaction is reversible since complex **2** can be readily formed from **3** by the addition of HCl. A solution of Pd(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ in chloroform solvent in an NMR tube gives Pd(*o*-$Ph_2PC_6H_4NC(O)CH_3)_2$. Apparently the reaction involves the dissociation of the complexed alkene of dba, followed by the oxidative hydrogen loss from the unobserved intermediate Pd(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ to give the product complex (eq 6). It is apparent, therefore,

$$\text{Pd(dba)(}o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Me)}_2 \xrightarrow{\text{CDCl}_3} \underset{\mathbf{3}}{\text{Pd}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NC(O)Me)}_2} + \text{dba} + \text{H}_2 \quad (6)$$

that the formation of two products in eq 3 results from a competition between halogen atom abstraction and oxidative elimination of hydrogen. We presume that halogen abstraction occurs with an intermediate hydride complex

or with the transient complex Pd(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$.

Reactions with Hydrogen. The interaction of these complexes with hydrogen gas reveals some interesting chemical transformations. The complex Pd(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ in chloroform solvent obviously behaves differently under a nitrogen or a hydrogen atmosphere. Under a nitrogen atmosphere the sole product is **3**, but under hydrogen gas a mixture of both complex **3** and the dichloro complex **2** is formed, the latter being the predominant product. The reaction under nitrogen is an oxidative dehydrogenation reaction (eq 6). By contrast, the formation of the dichloro complex **2** under a H_2 atmosphere (eq 3) implies that palladium hydride intermediates may be initially formed and that these compounds undergo atom transfer halogenation reactions with chloroform. The formation of a mixture of complexes **2** and **3** in eq 3 can be readily explained by the observation that complex **3** itself is converted slowly into **2** by addition of hydrogen to a chloroform solution of the complex (eq 7). This reaction provides an interesting example of a

$$\underset{\mathbf{3}}{Pd(o\text{-}Ph_2PC_6H_4NC(O)Me)_2} + H_2 \xrightarrow{CHCl_3} \underset{\mathbf{2}}{PdCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2} \quad (7)$$

transfer hydrogenation with the added hydrogens being transferred from palladium to the amido nitrogen. Of course, direct addition of hydrogen to amido nitrogens without the intermediacy of palladium hydrides is conceptually feasible, but we believe that such a pathway is unlikely. The requirement of chloroform as a chlorine atom donor is shown by the observation that complex **1** undergoes no change after 24 h under hydrogen in a $CH_2Cl_2/(CD_3)_2CO$ solvent mixture.

In an attempt to verify that the source of the NH hydrogen atoms was the added hydrogen gas, we have carried out the reaction in (7) under an atmosphere of deuterium rather than hydrogen. We find that the substitution of hydrogen by deuterium gives the *same* products with an NH bond, but at a much slower rate. The observation of protonated (rather than deuterated) N–H bonds likely results from H/D exchange subsequent to product formation. The formation of product complex under D_2 requires several days of reaction time, thereby making it difficult to completely exclude all water. A further complication is the probability that we are observing an accelerated H/D exchange with solvent via an agostic N–D interaction. Such a pathway has been found for similar palladium(II) and platinum(II) complexes with closely analogous hybrid phosphine amide ligands.

The complex Pt(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ (**4**) is significantly more solution stable than is the palladium analogue **1**. Nevertheless, under an oxygen atmosphere, solutions of the complex will convert to Pt(*o*-$Ph_2PC_6H_4NC(O)Me)_2$ (**7**), along with small quantities of the phosphine oxide *o*-$Ph_2P(O)C_6H_4NHC(O)Me$ (eq 8). If

$$Pt(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2 + O_2 \rightarrow Pt(o\text{-}Ph_2PC_6H_4NC(O)Me)_2 + dba + H_2O_2 \quad (8)$$

excess ligand *o*-$Ph_2PC_6H_4NHC(O)Me$ is present in the solution, the platinum(0) complex will, as expected, catalyze the oxidation of the phosphine to phosphine oxide. The reaction of the zerovalent platinum complex **4** with hydrogen provides a better insight into the reaction chemistry than does the analogous palladium system **1**, when complex **4** in $CDCl_3$ solvent is treated with hydrogen the products are *trans*-PtHCl(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ and partially hydrogenated dba (PhCH=CHCOCH$_2$CH$_2$Ph; $\delta(CH_2)$ 2.72 (t), 2.90 (t, $^3J(HH)$ = 7 Hz)) (eq 9). The hydride complex can be isolated from the

$$Pt(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2 + H_2 \xrightarrow{CDCl_3} trans\text{-}PtHCl(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2 + PhCH{=}CHCOCH_2CH_2Ph \quad (9)$$

solution by addition of *n*-hexane and recrystallized from benzene and *n*-hexane. The hydride complex shows IR bands (Nujol mull) at 3264 (ν(NH)), 2274 (ν(PtH)), and 1696 cm^{-1} (ν(CO)). The NMR spectral data are as follows: $\delta(^1H)$ −15.7 (t, ^1J(PtH) = 1242 Hz, ^2J(PH) = 13 Hz), 9.09 (s, N*H*), 1.49 (s, CH_3); $\delta(^{31}P\{^1H\})$ 24.4 (^1J(PtP) = 2814 Hz). When CW irradiation is applied in the phenyl region, we observe the hydride coupled ^{31}P spectrum as a doublet (^2J(PH) = 13 Hz). This result confirms the monohydride structure. Treating an acetone solution of this complex with sodium iodide for 1 h gives *trans*-PtHI(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ (eq 10), which is characterized by

$$trans\text{-}PtHCl(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2 + I^- \rightarrow trans\text{-}PtHI(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2 + Cl^- \quad (10)$$

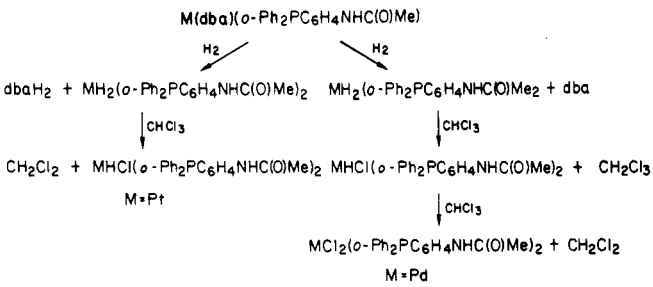
IR bands at 3221 (ν(NH)), 2237 (ν(PtH)), 1700 cm^{-1} (ν(CO)) and by NMR resonances at $\delta(^1H)$ −10.5 (t, ^1J(PtH) = 1288 Hz, ^2J(PH) = 11 Hz) and $\delta(^{31}P\{^1H\})$ 21.2 (^1J(PtP) = 2680 Hz). These shifts (IR and NMR) correspond closely with those found between iodides and chlorides in hydride complexes *trans*-$PtHXL_2$ (X = Cl, I; L = tertiary phosphine).[10]

The reaction between complex **4** and deuterium gas gives the corresponding deuteride *trans*-PtDCl(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$, along with PhCH=CHCOCHDCHDPh. The complex is characterized by ν(PtD) at 1624 cm^{-1} and the deuterated dba by δ(CHD) at 2.72 (d) and 2.90 (d) with $^3J_{HH}$ = 7 Hz. In addition to the platinum deuteride complex we also find minor products in the reaction mixture which have deuterium bound to nitrogen (ν(ND) = 2397 cm^{-1} (br)). This result confirms that our earlier postulate of facile H/D exchange on nitrogen is likely. For the palladium complex **1** we observe no reaction with hydrogen in $CH_2Cl_2/(CD_3)_2CO$ solvent, but with the platinum complex **4** we detect the formation of small amounts of *trans*-PtHCl(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ in the majority of unreacted material. A key to understanding these reactivity differences is the finding that for the palladium complex **1** the reactions with hydrogen liberate *free* dba, but the analogous reactions of the platinum complex **4** gives partially *hydrogenated* dba. In each case we anticipate hydride formation from hydrogen, but the lower reactivity of palladium may result from a competitive complexation between H_2 and free dba. For platinum the hydrogenation of the dba results in the irreversible loss of $dbaH_2$. We conclude that the reaction pathways with hydrogen follow those outlined in Scheme I. These reactions are interesting because it has been well documented that the triphenylphosphine complexes of palladium(0) and platinum(0), $M(PPh_3)_3$ (M = Pd, Pt), do *not* react with hydrogen. The addition of hydrogen to platinum(0) has previously been observed only with complexes having alkylphosphine ligands.

Under the conditions of these reactions, complex **4** reacts with hydrogen to give a stoichiometric amount of $dbaH_2$. It is unclear from our data presented so far whether the complex Pt(dba)(*o*-$Ph_2PC_6H_4NHC(O)Me)_2$ or *trans*-

(10) Roundhill, D. M. *Adv. Organomet. Chem.* **1975**, *13*, 273–361.

Scheme I



$PtHCl(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2$ is the active species for dba hydrogenation. As a check on this question, we find that the latter hydride complex is inactive as a hydrogenation catalyst for dba but that the Pt(0) complex catalytically gives $dbaH_2$, along with a small quantity of olefin polymerization product. Catalyzed deuteration of dba to give $dbaD_2$ occurs, but at a significantly slower rate.

For the phenyl-substituted ligand $o\text{-}Ph_2PC_6H_4NHC(O)Ph$ we can isolate the analogous platinum complex $Pt(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2$, but the palladium analogue is much less stable and readily converts to *cis*-$Pd(o\text{-}Ph_2PC_6H_4NC(O)Ph)_2$ (**5**) in the presence of traces of oxygen (eq 11). The structure of this complex has been confirmed by X-ray crystallography.

$$^1/_2Pd_2(dba)_3\cdot dba + 2o\text{-}Ph_2PC_6H_4NHC(O)Ph \xrightarrow{O_2} \underset{\mathbf{5}}{cis\text{-}Pd(o\text{-}Ph_2PC_6H_4NC(O)Ph)_2} + 2dba + H_2O_2 \quad (11)$$

Molecular Structure of $Pd(o\text{-}Ph_2PC_6H_4NC(O)Ph)_2$ (5). The X-ray structure of this complex confirms that the compound is an amido palladium(II) structure having a cis geometry. The oxidation state is verified by the finding of a planar geometry about palladium. The bite angle of the P,N chelate moiety is less than 90° (P(1)–Pd–N(1) = 76.4 (2)° and P(2)–Pd–N(2) = 82.1 (3)°). The Pd–N distances (Pd–N(1) = 2.126 (9) Å and Pd–N(2) = 2.094 (9) Å) are normal, and the C=O distances (C(1)–O(1) = 1.26 (1) Å and C(2)–O(2) = 1.22 (1) Å) are short as expected. The C–N distances (N(1)–C(1) = 1.32 (1) Å and N(2)–C(2) = 1.34 (1) Å) are significantly longer than the carbonyls. An Ortep representation of the molecule is given in Figure 4.

Reaction Pathways. It is apparent that the reaction between $Pd_2(dba)_3dba$ is not leading to the complete substitution of the dba ligand as we had anticipated. Furthermore we find that the products $M(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2$ (M = Pd, Pt) do not undergo substitution of the final dba molecule even when additional $o\text{-}Ph_2PC_6H_4NHC(O)Me$ is added. It is difficult to be convinced that electronic differences between triphenylphosphine and these P,N chelate ligands will cause the alkene group in dba to be more tightly bound to these chelate complexes. A more reasonable answer lies in the fact that chelation of one amide arm in $Pd(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2$ causes the product to be a coordinately saturated 18-electron compound. If the final substitution step is primarily associative, it is unfavorable for a 20-electron intermediate to be formed with a third bonded phosphine. A dissociative pathway via amide loss to give a 16-electron intermediate is a feasible route, but since there is an uncoordinated amide group on the other phosphine ligand, this functionality can effectively compete with an incoming phosphine ligand because it is an intramolecular association to give a chelate complex.

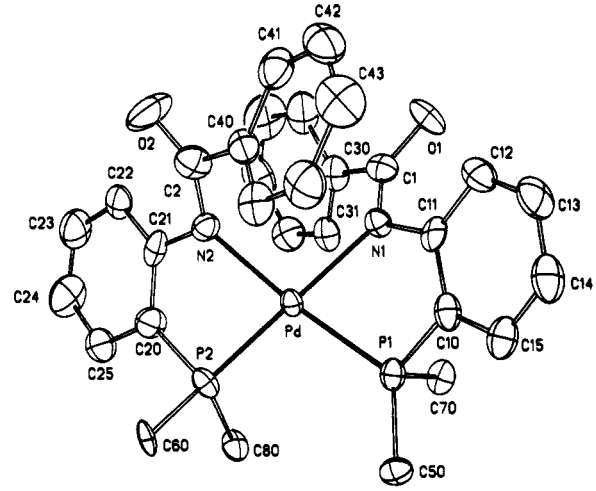


Figure 4. Molecular structure and atom labeling scheme for $PdC_{50}H_{40}N_2O_2P_2$ shown with 40% thermal ellipsoids. The 50–80 series phenyl rings bonded to P(1) and P(2) are shown as the ipso atoms only.

As a check we find that $Pd_2(dba)_3dba$ does react with excess triphenylphosphine in dichloromethane solvent to give $Pd(PPh_3)_3$ with complete substitution of the dba ligands. In toluene solution, however, incomplete substitution occurs leading to the precipitation of $Pd(dba)(PPh_3)_2$ (eq 12). The finding of partial substitution is due

$$^1/_2Pd_2(dba)_3\cdot dba + 2PPh_3 \rightarrow Pd(dba)(PPh_3)_2 + dba \quad (12)$$

to precipitation of the intermediate, since addition of dichloromethane to this reaction mixture causes solubilization and conversion to $Pd(PPh_3)_3$ (eq 13).

$$Pd(dba)(PPh_3)_2 + PPh_3 \rightarrow Pd(PPh_3)_3 + dba \quad (13)$$

We have not been able to yet induce the complexes $M(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2$ (M = Pd, Pt) to undergo N–H addition to give a metal hydride. We do not observe hydrides as intermediates in the oxygen-induced conversion to $M(o\text{-}Ph_2PC_6H_4NC(O)Me)_2$ or in the atom transfer chlorination to $MCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Me)_2$. Indeed, in the former reaction we find no evidence for partial hydrogenation of dba indicating the intermediacy of any hydride complexes. We can only conclude that our failure to observe intramolecular N–H addition, as with phosphine substitution, is a consequence of its failure to occur at a coordinately saturated center.

Although we have been unable to isolate pure palladium(0) complexes with $o\text{-}Ph_2PC_6H_4NHC(O)Ph$, we can readily prepare $Pt(dba)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2$ from $Pt(dba)_2$.

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Registry No. 1, 102133-30-2; 2, 102133-31-3; 3, 102133-32-4; 4, 102133-33-5; 5, 99642-35-0; $5\cdot 0.5Et_2O$, 102209-58-5; 6, 102153-38-8; 7, 102133-34-6; 8, 102133-35-7; $o\text{-}Ph_2PC_6H_4NHC(O)Me$, 102133-36-8; $Pd_2(dba)_3$, 51364-51-3; Na_2PdCl_4, 13820-53-6; $Pt(dba)_2$, 35915-79-8; K_2PtCl_4, 10025-99-7; $o\text{-}Ph_2(O)C_6H_4NHC(O)Me$, 102133-37-9; o-(diphenylphosphino)aniline, 65423-44-1; acetyl chloride, 75-36-5.

Supplementary Material Available: Tables of observed and calculated structure factors, bond lengths, bond angles, ansiotropic temperature factors, and hydrogen coordinates and temperature factors (26 pages). Ordering information is given on any current masthead page.