mation in either a carborane or a metallacarborane cluster.

A plausible, but clearly unproven, reaction sequence which is consistent with both the above cage rearrangements and with the formation of an $[\eta^3\text{-}C_4(CH_3)_4H]Ni$ group is outlined in eq 1–5.

$$\mathrm{Ni + CH_3C_6H_5 \rightarrow Ni(CH_3C_6H_5)_x} \tag{1}$$

$$\mathrm{Ni(CH_3C_6H_5)_x + C_2B_7H_{11} \rightarrow \eta^1\text{-}C_2B_7H_{10}Ni^{II}(H)(CH_3C_6H_5)} \tag{2}$$

$$\mathrm{\eta^1\text{-}C_2B_7H_{10}Ni^{II}(H)(CH_3C_6H_5) + 3MeC{\equiv}CMe \rightarrow \eta^1\text{-}C_2B_7H_{10}Ni^{II}(H)(\eta^2\text{-}C_2Me_2)_3} \tag{3}$$

$$\mathrm{\eta^1\text{-}C_2B_7H_{10}Ni^{II}(H)(\eta^2\text{-}C_2Me_2)_3 \rightarrow Me_2C_4B_7H_{10}Ni^{II}(H)(\eta^2\text{-}C_2Me_2)_2} \tag{4}$$

$$\mathrm{Me_2C_4B_7H_{10}Ni^{II}(H)(\eta^2\text{-}C_2Me_2)_2 \rightarrow Me_3C_3B_7H_7Ni^{II}(\eta^3\text{-}C_4Me_4H)} \tag{5}$$

Thus, the initially formed toluene-solvated nickel atoms[49] (eq 1) could react via an oxidative-addition process to yield an 18e nickel hydride complex such as in eq 2. The toluene could be displaced by three 2-butyne molecules (eq 3), and then one of the alkynes could become incorporated into the cage as shown in eq 4. Cage rearrangement, as discussed above, coupled with dimerization and hydrogen transfer to the remaining two coordinated 2-butyne ligands would yield the final product (eq 5).

Again it must be emphasized that the above sequence is entirely speculative, but it is clear from the results described herein that the very highly reactive metal atoms, or the organometallic intermediates which are produced in these reactions, cannot only be used to produce traditional types of metallaboron complexes but also can cause dramatic and unprecedented rearrangements to yield new types of hybrid organometallic/metallaboron clusters.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for the support of this research. We also thank Dr. George Furst and Dr. Pat Carroll for their assistance in performing NMR and X-ray crystallographic studies.

Registry No. I, 99531-65-4; II, 99496-28-3; III, 99496-29-4; IV, 99496-30-7; V, 99496-31-8; VI, 99510-58-4; VII, 99496-32-9; 2,6-$C_2B_7H_{11}$, 42319-46-0; 2-[η-C_5H_5)Co-6,9-$C_2B_7H_9$, 41348-07-6; 8-(η-C_5H_5)Co-6,7-$C_2B_7H_{11}$, 52760-69-7; 4,7-(η-C_5H_5)$_2$Co$_2$-2,3-$C_2B_7H_9$, 76046-88-3; 2,3,5-(η-C_5H_5)$_3$Co$_3$-1,7-$C_2B_7H_9$, 50803-51-5; 2-(η-C_5H_5)Co-1,6-$C_2B_7H_9$, 41348-11-2; Co, 7440-48-4; Fe, 7439-89-6; Ni, 7440-02-0; C_5H_6, 542-92-7; $CH_3C_6H_5$, 108-88-3; $(CH_3)_3C_6H_3$, 108-67-8; 2-butyne, 503-17-3.

Supplementary Material Available: Tables of general temperature factors, molecular planes, calculated hydrogen positions, and observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Reaction Chemistry of Some New Hybrid Phosphine Amide Complexes of Platinum(II) and Palladium(II). Isolation and X-ray Structure Determination of an Ortho-Metalated Platinum(II) Complex Derived from a Chelated Phosphine Amide Complex of Platinum(II)

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Refluxing the complex *trans*-$PtCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2$ in DMF/Et_3N gives the cyclometalated complex *cis*-$Pt(o\text{-}Ph_2PC_6H_4NC(O)C_6H_4)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)$. The complex crystallizes in a triclinic $P\bar{1}$ space group with $a = 12.038$ (3) Å, $b = 12.576$ (5) Å, $c = 16.220$ (6) Å, $\alpha = 105.80$ (3)°, $\beta = 104.84$ (3)°, and $\gamma = 95.73$ (3)°. The structure shows respective values of 2.063 (7) and 2.065 (8) Å for Pt–N(1) and Pt–C(3). The monodentate P-bonded PNH(CPhO) ligand shows a close "agostic" interaction of the type N–H···Pt. The hydrogen atom has been located at a distance of 2.318 (22) Å from Pt. The analogous palladium complex has been synthesized. The transfer of the ortho carbon hydrogen to the amido nitrogen has been confirmed by deuteration studies using $o\text{-}Ph_2PC_6H_4NHC(O)C_6D_5$. The "agostic" hydrogen atom undergoes H/D exchange with benzene, acetonitrile, or chloroform. These cyclometalated complexes add HCl to give *cis*-$MCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2$ (M = Pd, Pt). With CF_3CO_2H the reaction is reversible, and N-alkylation occurs with Me_2SO_4 to give $[Pd(o\text{-}Ph_2PC_6H_4N(Me)C(O)C_6H_4)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)]SO_4Me$. These amido complexes are stable to water and acetic acid.

Recently we have synthesized two new amido phosphine compounds having an amido substituent bonded to the ortho position of a phenyl phosphine moiety. In particular these compounds are $o\text{-}Ph_2PC_6H_4NHC(O)Ph$ and $o\text{-}Ph_2PC_6H_4C(O)NHPh$. These ligands are shown in Figure 1. These compounds have been chosen for the synthesis of complexes in which the (M–P–N) chelate ring have the preferred five- and six-membered ring sizes. Following a preliminary communication,[2] the first paper in this series

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[1] (a) Tulane University. (b) University of delaware.

[2] Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. R. *J. Am. Chem. Soc.* **1984**, *106*, 5014–5016.

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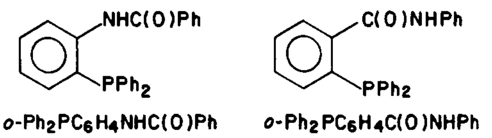

Figure 1. Structures of *o*-$Ph_2PC_6H_4NHC(O)Ph$ and *o*-$Ph_2PC_6H_4C(O)NHPh$.

described the ligand synthesis and characterization, along with the preparation of a series of amide complexes of the type MCl_2L_2 (L = *o*-$Ph_2PC_6H_4NHC(O)Ph$, *o*-$Ph_2PC_6H_4C(O)NHPh$) and amido complexes ML_2 (L = *o*-$Ph_2PC_6H_4NC(O)Ph$, *o*-$Ph_2PC_6H_4C(O)NPh$).[3] In the complexes MCl_2L_2 the ligands L are bonded solely via phosphorus. Interconversion between these amide and amido complexes has been effected by the addition of strong base or the strong acid HCl.

These amido phosphine compounds have been prepared with a number of desired goals targeted. One such goal is to investigate the facility with which a hydrogen can be transferred from nitrogen either to an external base by deprotonation or to a metal by an intramolecular oxidative addition process. A second aim of this paper is an evaluation of the chemical reactivity of an amido ligand complexed to platinum(II) and palladium(II). Although amido complexes of the early transition elements are common, only relatively few complexes are known where such a ligand is coordinated to a platimum group metal,[4] and therefore their reaction chemistry is largely unexplored. This paper focuses on the proton-transfer reactions which can be observed between the free amides and the complexed amido ligands in these complexes and also on probing the chemical reactivity of an amido ligand coordinated to a platinum group element.

Finally we will present data which suggests that we have isolated a complex which provides the first example of a compound having an "agostic" interaction between a transition-metal center and a hydrogen atom bonded to a nitrogen atom of an amido functionality. The synthesis and reaction chemistry of these platinum and palladium complexes comprises a major portion of this article.

These new hybrid phosphine amide ligands *o*-$Ph_2PC_6H_4NHC(O)Ph$ and *o*-$Ph_2PC_6H_4C(O)NHPh$ coordinate to platinum(II) and palladium(II) in either a monodentate or a bidentate mode. In the former case coordination is via the phosphorus atom, while in the latter case both the phosphorus and secondary nitrogen atoms are coordinated. The various bonding modes and stereochemistries can be determined by a combination of $^{31}P\{^1H\}$ NMR, ^1H NMR, and IR spectroscopy. Coordination of a phosphine ligand to Pt(II) or Pd(II) usually results in a downfield shift of between 10 and 50 ppm in the ^{31}P NMR chemical shift. Structural characterization by IR spectroscopy uses changes in the frequencies of the amide I, II, and III bands to identify the mode of amide coordination. Complexation via oxygen will shift the amide I band to lower frequency, whereas coordination via amide nitrogen will increase the amide I frequency. Thirdly coordination via a nitrogen atom of the iminol tautomer will result in ν(CN) being found in the 1600–1650 cm^{-1} range and ν(CO) in the 1300–1400 cm^{-1} range. Coordination via an N-deprotonated amide causes a simplification of the IR spectrum since the ν(NH) and amide II bands disappear. Coordination of a secondary amide via nitrogen results in a downfield shift of the NH resonance in the ^1H NMR spectrum.[3]

Experimental Section

Many of the experimental details relevant to the synthesis and characterization of these new complexes have been described in the first paper in this series.[3] The details here are either additional or are specific to individual complexes. Far-infrared spectra were recorded on a Hitachi Perkin-Elmer FIS3 spectrophotometer. The 360-MHz ^1H NMR spectra of *cis*-$Pt(o\text{-}Ph_2PC_6H_4NC(O)C_6H_4)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)$ (**1**) was measured as a solution in $CDCl_3$ on a NTC-360 spectrometer at the Colorado State University Regional NMR Center. Conductivity measurements were carried out in a conductivity cell connected to an Industrial Instruments RC-16B2 conductivity bridge. All measurements were made at 25 ± 0.5 °C. The cell constant of 0.417 cm^{-1} was determined from the conductance of a 0.100 m aqueous KCl solution. Acetonitrile for synthetic uses and conductivity measurements was dried by refluxing over CaH_2 under a nitrogen atmosphere, and dichloromethane for conductivity measurements was dried by refluxing over P_2O_5 under nitrogen. Fresh samples of each were distilled immediately prior to use. The synthesis of the ligands and the following complexes have been described in our previous article:[3] *trans*-$PtCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2$ (**9**), $PdCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2$ (**10**), *trans*-$Pt(o\text{-}Ph_2PC_6H_4C(O)NPh)_2$ (**11**), *cis*-$Pd(o\text{-}Ph_2PC_6H_4C(O)NPh)_2$ (**12**), *cis*-$Pd(o\text{-}Ph_2PC_6H_4C(O)NPh)_2$ (**13**), *cis*-$Pt(o\text{-}Ph_2PC_6H_4NC(O)Ph)_2$ (**14**). Spectral simulations were made by using the LAOCOON III program.

***cis*-$Pt(o\text{-}Ph_2PC_6H_4NC(O)C_6H_4)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)\cdot C_6H_5CH_3$ (1).** Complex **9** (400 mg, 0.39 mmol) was suspended in a mixed DMF/Et_3N (19 mL/1 mL) solvent. The yellow suspension was stirred under reflux for 1 h and then allowed to cool. Addition of water (30 mL) precipitated a white solid. This complex was isolated by vacuum filtration and the solid washed successively with water (3 × 10 mL) and ethanol (3 × 5 mL). The solid was purified by recrystallization. Cooling a saturated boiling toluene solution to −10 °C gave the product as transparent cubic crystals, which were filtered and dried in vacuo. Filtrate concentration gave an additional 50 mg of the compound for a total yield of 347 mg (85%); mp >300 °C. Anal. Calcd for $C_{57}H_{46}N_2O_2P_2Pt$: C, 65.3; H, 4.42; N, 2.67; P, 5.91; Cl, 0.00. Found: C, 65.4; H, 4.38; N, 2.66; P, 6.02; Cl, <0.05. The analogous procedure in refluxing acetonitrile solvent can also be used to prepare the complex. The reaction times required were longer but the complex precipitated during the course of the reaction.

***cis*-$Pt(o\text{-}Ph_2PC_6H_4NC(O)Ph)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)Cl$ (2).** This complex has been identified as an intermediate in the synthesis of **1**. If **1** was prepared by refluxing **9** as a suspension in MeCN/Et_3N (19 mL/1 mL) solvent, a white precipitate was formed after 60–90 min. This precipitate was a mixture of **1** and **2**. Separation of **1** and **2** was achieved by preparative scale TLC. Elution with CH_2Cl_2 separated the two complexes, **2** being the least mobile band.

$Pd(o\text{-}Ph_2PC_6H_4NC(O)C_6H_4)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)$ (3). Complex **10** (266 mg, 0.28 mmol) and DABCO (250 mg, 2.2 mmol) were suspended in acetonitrile (20 mL). The suspension was stirred for 3 h, during which time the mixture remained heterogeneous as the yellow color discharged. The white precipitate was filtered, washed with acetone (4 × 50 mL), and dried in vacuo. Yield 240 mg (97%); mp 290–292 °C (yellows above 90 °C). Anal. Calcd for $C_{50}H_{38}N_2O_2P_2Pd$: C, 69.3; H, 4.41; P, 7.15. Found: C, 68.6; H, 4.66; P, 6.88. Recrystallization from chloroform by addition of diethyl ether gave the complex containing $^2/_3$ mol of chloroform in the lattice. Anal. Calcd for $C_{50.6}H_{38.6}Cl_2N_2O_2Pd$: C, 64.3; H, 4.11; N, 2.87. Found: C, 64.4; H, 4.34; N, 2.94.

Benzoyl-d_5 Chloride. Benzoic-d_5 acid (1.0 g, 8.2 mmol) and thionyl chloride (8.2 g, 68.0 mmol) were placed in a 25-mL one-neck round-bottom flask fitted with a calcium sulfate drying tube. The mixture was stirred for 5 days. Distillation at ambient pressure gave $SOCl_2$ (80 °C) followed by product (190 °C): yield 0.92 g (80%) of clear liquid.

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***o*-(Diphenylphosphino)-*N*-benzoylaniline (*o*-$Ph_2PC_6H_4NHC(O)C_6D_5$).** Using the method developed for *o*-$Ph_2PC_6H_4NHC(O)Ph$ using *o*-$Ph_2PC_6H_4NH_2$ (1.1 g, 0.4 mmol) and benzoyl-d_5 chloride (0.58 g, 0.4 mmol) gave crude product. The compound was purified by recrystallization from CH_2Cl_2/hexane: yield 0.75 g (50%); mp 104–105 °C.

***trans*-$Pt(OCOCF_3)_2$(*o*-$Ph_2PC_6H_4C(O)NHPh)_2$ (4).** Complex **11** (200 mg, 0.21 mmol) was dissolved in dichloromethane (5 mL). Excess trifluoroacetic acid (0.5 mL) was added dropwise to the solution, causing it to change from a yellow-green to a pale yellow color. The solution was allowed to stand for 10 min, and then a hexane/diethyl ether (10:1) mixture was added dropwise to precipitate a pale yellow solid. The product was collected by vacuum filtration, washed with hexane (5 mL), and dried in vacuo; yield 195 mg (78%). Anal. Calcd for $C_{54}H_{40}F_6N_2O_2P_2Pt$: C, 54.8; H, 3.40; P, 5.23; F, 9.62. Found: C, 54.7; H, 3.61; P, 5.38; F, 9.33.

***cis*-[Pt(*o*-$Ph_2PC_6H_4C(O)NPh$)(*o*-$Ph_2PC_6H_4C(O)NHPh$)(CF_3CO_2H)]CF_3CO_2 (5).** A solution of **12** (100 mg, 0.11 mmol) in dichloromethane (5 mL) was treated with excess trifluoroacetic acid. After 10 min the pale yellow solution was filtered and the solvent removed to yield an oil. Stirring the oil for 12 h with diethyl ether caused it to solidify. The off-white powder was filtered, washed with diethyl ether, and dried in vacuo: yield 112 mg (90%); mp 144–146 °C (with decomp). Anal. Calcd for $C_{54}H_{40}F_6N_2O_6P_2Pt$: C, 54.8; H, 3.40; F, 9.63. Found: C, 54.0; H, 3.68; F, 9.47.

$Pd(OCOCF_3)_2$(*o*-$Ph_2PC_6H_4NHC(O)Ph)_2$ (6). The complex Pd(*o*-$Ph_2PC_6H_4NC(O)Ph)_2 \cdot 0.5(C_2H_5)_2O$ (90 mg, 0.1 mmol) in acetone (10 mL) was treated with excess trifluoroacetic acid (0.2 mL). After 1 h the solution was filtered and then reduced in volume to ca. 2 mL. Dropwise addition of a mixture of hexane and diethyl ether (10:1 ratio; 20 mL) precipitated a yellow powder which was filtered, washed with hexane (10 mL), and dried in vacuo: yield 106 mg (93%); mp 184–186 °C. Anal. Calcd for $C_{54}H_{40}F_6N_2O_6P_2Pd$: C, 59.1; H, 3.67; F, 10.2. Found: C, 58.7; H, 3.81; F, 10.4.

$Pd(OCOCF_3)_2$(*o*-$Ph_2PC_6H_4C(O)NHPh)_2 \cdot 2CF_3CO_2H$ (7). Complex **13** (100 mg, 0.11 mmol) in dichloromethane (5 mL) was treated with excess trifluoroacetic acid. The yellow solution immediately darkened. After 10 min the solution was filtered and then reduced in volume to ca. 2 mL. Addition of hexane (10 mL) precipitated a yellow oil which solidified upon standing (12 h). The bright yellow microcrystals were collected by filtration, washed with hexane (10 mL), and dried in vacuo; yield 125 mg (86%). Anal. Calcd for $C_{58}H_{40}F_{12}N_2O_2P_2Pd$: C, 52.6; H, 3.05; F, 17.2. Found: C, 52.1; H, 3.30; F, 17.6.

[Pd(*o*-$Ph_2PC_6H_4N(Me)C(O)C_6H_4$)(*o*-$Ph_2PC_6H_4NHC(O)Ph$)]$SO_4Me$ (8). A solution of compound **2** (210 mg, 0.24 mmol) in chloroform (20 mL) was treated with dimethyl sulfate (61 mg, 0.48 mmol). After 2 h the dark yellow solution was reduced in volume to ca. 4 mL. Addition of diethyl ether (20 mL) gave an oily yellow solid which solidified after 12 h at -10 °C. The complex was filtered and dried in vacuo: yield 190 mg (79%); mp 187–189 °C (with decomp.). Anal. Calcd for $C_{52}H_{46}N_2O_2P_2PdS$: C, 62.8; H, 4.66. Found: C, 62.6; H, 4.27.

X-ray Structural Determination. Crystals of complex **1** were obtained by recrystallization from $CHCl_3$ and mounted on a fine glass fiber. Preliminary photographic characterization showed the specimen to belong to the triclinic crystal system. The space group $P\bar{1}$ was assumed and later proven correct by the chemically reasonable and well-behaved solution and refinement of the structure. Table I provides crystal, data collection, and refinement parameters.

The location of the Pt atom was obtained from a sharpened Patterson projection and was used to locate the remaining non-hydrogen atoms by difference Fourier syntheses. A severely disordered, substoichiometric molecule of $CHCl_3$ (site occupancy ~20%) was located and refined. In the final cycles of refinement (blocked cascade), the non-hydrogen atoms except for the carbon atoms of the five terminal phenyl groups were refined with anisotropic temperature factors. Additionally, the same five phenyl groups were treated as rigid hexagons, d(C–C) = 1.395 Å. With the exception of H(2) which was located and refined, all hydrogen atom contributions were calculated in idealized locations (d(C–H) = 0.96 Å; $U = 1.2U$ attached). Computer programs used in the data collection, data reduction, and refinement are contained in the P3 and SHELXTL (3.0) program libraries distributed by the Nicolet Corp., Madison, WI.

Table I. Crystal, Data Collection, and Refinement Parameters for *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)C_6H_4$)(*o*-$Ph_2PC_6H_4NHC(O)Ph$)

formula	$PtC_{45}H_{39}N_2O_2P_2$
cryst system, space group	triclinic, $P\bar{1}$
a, b, c, Å	12.038 (3), 12.576 (5), 16.220 (6)
α, β, γ, deg	105.80 (3), 104.84 (3), 95.75 (3)
V, Å^3	2245.6 (13)
Z	2
cryst size, mm	0.21 × 0.26 × 0.41
μ, cm^{-1}	32.9 (Mo Kα)
min, max, transm	0.566, 0.484
diffractometer	Nicolet R3
temperature, °C	23
correctns to data	Lp, absorption (ψ scan), decay
scan speed, deg min^{-1}	var 3.5–10
scan technique	$\theta/2\theta$
std reflns	3/197 (4% decay)
scan range, deg	$4 < 2\theta < 45$
data collected	$\pm h, \pm k, +l$
unique reflns	5632 (5858 collected)
unique reflns, $F_0 > 3\sigma(F_o)$	5115
R (av redun data)	0.0126
R_F, R_{wF}, GOF[a]	0.0375, 0.0402, 1.626
g[b]	0.008
slope, normal prob plot	1.244
highest peak, final diff map, e Å^{-3}	1.03 (in $CHCl_3$)

[a] $R_F = \sum|\Delta|/\sum|F_o|$, $R_{wF} = \sum(|\Delta|w^{1/2})/\sum(|F_o|w^{1/2})$, and GOF = $[w(\Delta^2/(N_{obsd} - N_{par})]^{1/2}$, $\Delta = |F_o| - |F_o|$. [b] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

In the final difference map the seven highest peaks in the range 0.81–1.03 e Å^{-3} were all associated with the disordered solvent molecule. These were followed by a diffuse and chemically meaningless background (<0.5 e Å^{-3}). Fractional atomic coordinates are provided in Table II. Additional supplementary material has been deposited with our preliminary communication.[2]

Results and Discussion

In the first paper of this series we have outlined in detail the spectroscopic methods used to characterize the products.[3] We briefly summarize the salient features again here in order to guide the reader through the chemistry reported in this paper. Coordination of a phosphine ligand to Pt(II) and Pd(II) result in a downfield shift of between 10 and 50 ppm in the ^{31}P NMR chemical shift, and for the Pt(II) complexes we can use $^1J(PtP)$ values to deduce stereochemistry. For the chelated phosphine amido complexes we also need to include ring shifts before we can interpret ^{31}P chemical shift values.

Complexes **9** and **10** can be readily prepared by the addition of 2 equiv of *o*-$Ph_2PC_6H_4NHC(O)Ph$ to MCl_4^{2-} (M = Pt, Pd) (eq 1).[3] Complex **9** does not react with

$$MCl_4^{2-} + 2\textit{o}\text{-}Ph_2PC_6H_4NHC(O)Ph \rightarrow MCl_2(\textit{o}\text{-}Ph_2PC_6H_4NHC(O)Ph)_2 + 2Cl^- \quad (1)$$

9, M = Pt
10, M = Pd

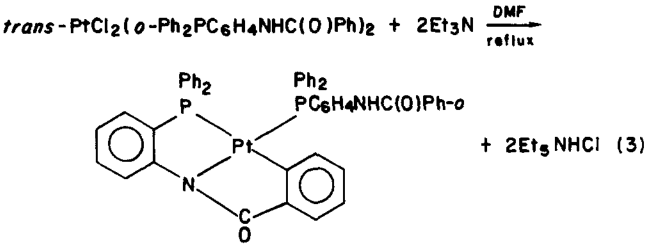
triethylamine or DABCO at ambient temperature, either as a suspension in DMF or acetonitrile or as a solution in chloroform. When, however, the suspension of **9** in triethylamine/acetonitrile is refluxed for 60–90 min, a yellow solution is formed, and *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)Ph)_2$ (**14**) can be isolated (eq 2). At these lower reflux temperatures this cis amido complex is the final product.

Intramolecular Ortho Metalation of a Benzoyl Group. When a suspension of **9** and triethylamine in

$$\underset{\mathbf{9}}{trans\text{-}PtCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2} + 2Et_3N \rightarrow$$

$$\underset{\mathbf{14}}{cis\text{-}\overline{Pt(o\text{-}Ph_2PC_6H_4N}C(O)Ph)_2} + 2Et_3NHCl \quad (2)$$

DMF is refluxed, a clear solution is obtained. Addition of water precipitates complex 1 as a white powder (eq 3).



Complex 1 is slightly soluble in chloroform but insoluble in other organic solvents. The infrared spectrum (Nujol) shows absorptions characteristic of both a o-$Ph_2PC_6H_4NHC(O)Ph$ ligand (ν(NH) 3200, 3150 cm^{-1}; amide I, 1675 cm^{-1}, amide II, 1515 cm^{-1}, amide III, 1290 cm^{-1}) and a o-$Ph_2PC_6H_4NC(O)Ph$ ligand (amide I, 1620 cm^{-1}, amide III, 1320 cm^{-1}). The presence of a o-$Ph_2PC_6H_4NHC(O)Ph$ group is further supported by the observation of a resonance at δ 11.0 characteristic of a NH group.

The $^{31}P\{^1H\}$ NMR spectrum supports a structure with mutually cis phosphorus atoms coordinated to platinum(II) where the o-$Ph_2PC_6H_4NC(O)Ph$ ligand is bidentate and the o-$Ph_2PC_6H_4NHC(O)Ph$ is monodentate. The downfield resonance at δ 26.2 (P_A) is characteristic of a phosphine ligand in a five-membered ring[5] and is therefore assigned to o-$Ph_2PC_6H_4NC(O)Ph$. The upfield resonance at δ 2.4 (P_B) is due to the phosphorus of monodentate o-$Ph_2PC_6H_4NC(O)Ph$. The spectrum has been simulated for an AB pair flanked by satellites due to coupling with ^{195}Pt ($I = {}^1/_2$, 33.7% abundance). A value of 14 Hz for $^2J(PP)$ is found, which necessitates mutually cis phosphorus atoms. The magnitude of $^1J(PtP_B)$ at 3334 Hz is an expected value for a phosphine trans to an amido ligand which is low in the trans influence series.[4] The 1905-Hz coupling constant $^1J(PtP_A)$ is characteristic of a phosphine *trans* to a σ-alkyl or σ-aryl ligand bonded to platinum(II). The aryl ligand in the fourth coordination position about platinum is an ortho-metalated carbon of the benzoyl group. The low solubility of the complex in organic solvents precludes measurement of a $^{13}C\{^1H\}$ NMR spectrum, and the metalated structure has been confirmed by X-ray crystallography on a single crystal.

The coordination geometry about platinum is distorted planar with angles P(1)–Pt–P(2) = 100.6 (1)°, P(1)–Pt–N(1) = 83.7 (2)°, N(1)–Pt–C(3) = 81.2 (3)°, and P(2)–Pt–C(3) = 94.5 (3)° (Figure 2). The distances Pt–P(1) of 2.298 (2) Å and Pt–P(2) of 2.259 (2) Å are normal, the increased Pt–P(1) length being indicative of the higher trans influence of a σ-aryl ligand as compared to an amido ligand. The Pt–N(1) distance is 2.063 (7) Å which falls within the range of 2.02 (1)–2.09 (2) Å found for the small number of such complexes which have been structurally characterized.[6] Selected bond distances and angles are collected in Table III. The most interesting feature of the structure is the location of the amide group of the monodentate o-$Ph_2PC_6H_4NHC(O)Ph$ ligand. It is apparent from Figure 2 that this amido group lies close to the platinum center below the coordination plane. The hydrogen bonded to the amide nitrogen has been located on difference maps at a distance of 2.318 (22) Å from platinum (Figure 3). This Pt–H(2) distance is close to that which would be expected for a weak bonding interaction. Recently the term "agostic" has been used to discuss the various manifestations of covalent interactions between carbon–hydrogen groups and transition-metal centers in

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

atom	x	y	z	U_{iso}, Å^2
Pt	1661.9 (2)	1851.5 (2)	2500.2 (2)	33 (0)^a
P(1)	914 (2)	77 (2)	2459 (1)	35 (0)^a
P(2)	3504 (2)	1659 (2)	2491 (1)	35 (0)^a
N(1)	4 (5)	2145 (5)	2495 (4)	29 (3)^a
N(2)	3535 (6)	2886 (6)	4480 (4)	53 (3)^a
H(2)	2937 (17)	2697 (14)	4048 (13)	93 (8)
O(1)	−1131 (7)	3512 (7)	2476 (6)	96 (4)^a
O(2)	4155 (7)	2988 (7)	5938 (5)	86 (4)^a
C(1)	−185 (8)	3179 (8)	2499 (6)	57 (4)
C(2)	863 (8)	3936 (7)	2527 (6)	54 (4)^a
C(3)	1899 (7)	3521 (6)	2553 (5)	42 (3)^a
C(4)	2860 (9)	4247 (7)	2565 (6)	58 (4)^a
C(5)	2797 (10)	5323 (8)	2572 (7)	78 (5)^a
C(6)	1768 (11)	5710 (8)	2519 (8)	89 (5)^a
C(7)	824 (10)	5024 (8)	2511 (7)	74 (5)^a
C(8)	3357 (8)	2965 (7)	5286 (5)	55 (4)^a
C(11)	−560 (6)	242 (7)	2475 (5)	42 (3)^a
C(12)	−1343 (7)	−622 (8)	2509 (6)	51 (4)^a
C(13)	−2422 (7)	−442 (9)	2582 (6)	65 (4)^a
C(14)	−2726 (8)	572 (9)	2613 (6)	66 (5)^a
C(15)	−1976 (7)	1443 (8)	2579 (6)	55 (4)^a
C(16)	−855 (7)	1283 (7)	2509 (5)	43 (3)^a
C(21)	2226 (5)	−1174 (4)	3417 (3)	45 (2)
C(22)	2668 (5)	−1482 (4)	4184 (3)	53 (2)
C(23)	2373 (5)	−1003 (4)	4963 (3)	61 (2)
C(24)	1636 (5)	−215 (4)	4976 (3)	61 (2)
C(25)	1193 (5)	94 (4)	4210 (3)	51 (2)
C(26)	1488 (5)	−385 (4)	3430 (3)	37 (2)
C(31)	825 (5)	−838 (4)	695 (4)	56 (2)
C(32)	628 (5)	−1700 (4)	−100 (4)	80 (3)
C(33)	328 (5)	2816 (4)	−144 (4)	93 (4)
C(34)	227 (5)	−3070 (4)	622 (4)	78 (3)
C(35)	424 (5)	−2208 (4)	1424 (4)	56 (2)
C(36)	724 (5)	−1092 (4)	1460 (4)	41 (2)
C(41)	4624 (5)	266 (4)	3401 (3)	46 (2)
C(42)	4984 (5)	−740 (4)	3457 (3)	55 (2)
C(43)	4690 (5)	−1674 (4)	2690 (3)	61 (2)
C(44)	4036 (5)	−1602 (4)	1869 (3)	55 (2)
C(45)	3675 (5)	−597 (4)	1813 (3)	45 (2)
C(46)	3969 (5)	337 (4)	2580 (3)	38 (2)
C(51)	4691 (4)	1379 (5)	1176 (4)	56 (2)
C(52)	4811 (4)	1395 (5)	347 (4)	67 (3)
C(53)	3957 (4)	1735 (5)	−237 (4)	76 (3)
C(54)	2983 (4)	2059 (5)	8 (4)	74 (3)
C(55)	2863 (4)	2043 (5)	838 (4)	54 (2)
C(56)	3717 (4)	1703 (5)	1422 (4)	41 (2)
C(61)	1357 (5)	3385 (5)	4726 (4)	57 (2)
C(62)	240 (5)	3462 (5)	4808 (4)	71 (3)
C(63)	−75 (5)	3192 (5)	5507 (4)	88 (3)
C(64)	727 (5)	2845 (5)	6122 (4)	92 (4)
C(65)	1843 (5)	2768 (5)	6040 (4)	80 (3)
C(66)	2159 (5)	3038 (5)	5341 (4)	49 (2)
C(71)	4675 (7)	2704 (6)	3408 (5)	41 (2)
C(72)	5701 (8)	3051 (7)	3240 (6)	56 (2)
C(73)	6658 (9)	3737 (8)	3948 (7)	70 (3)
C(74)	6602 (9)	4058 (9)	4780 (7)	70 (3)
C(75)	5577 (8)	3776 (8)	4973 (7)	59 (2)
C(76)	4597 (7)	3099 (7)	4285 (5)	45 (2)
C(99)^b	7086 (32)	4826 (30)	1398 (25)	56 (9)
Cl(2)^b	5907 (17)	4908 (17)	1816 (15)	151 (12)^a
Cl(3)^b	6946 (23)	4035 (22)	469 (16)	225 (15)^a
Cl(4)^b	7311 (36)	6209 (29)	1620 (17)	126 (16)^a
Cl(5)^b	7713 (22)	6093 (25)	1392 (16)	101 (12)^a

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

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[6] Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* 1982, *1*, 918–930. Zipprich, M.; Pritzkow, H.; Jarder, J. *Angew. Chem. Int. Ed. Engl.* 1976, *15*, 225–226.

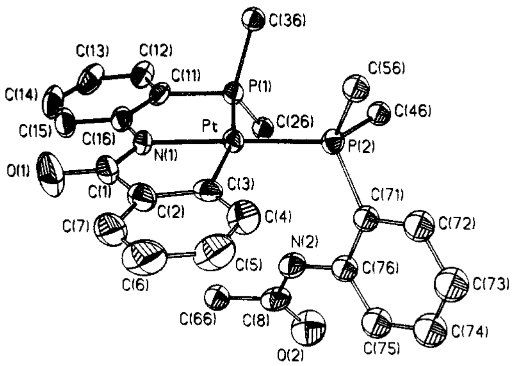


Figure 2. ORTEP diagram for *cis*-$\mathrm{Pt}(o\text{-}\mathrm{Ph_2PC_6H_4NC(O)C_6H_4})(o\text{-}\mathrm{Ph_2PC_6H_4NHC(O)Ph})$ (1). Terminal phenyl groups shown as pivotal atom only.

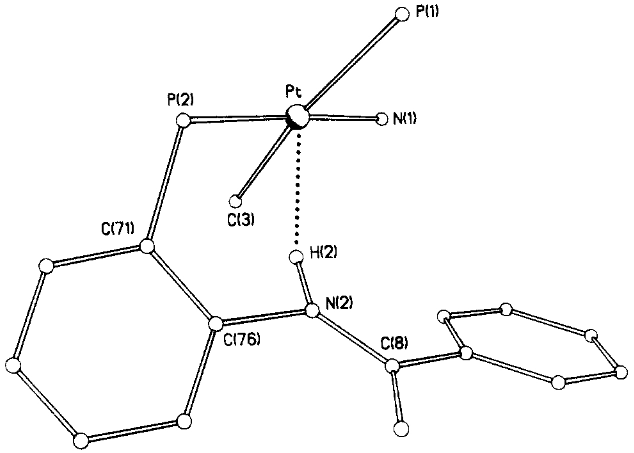


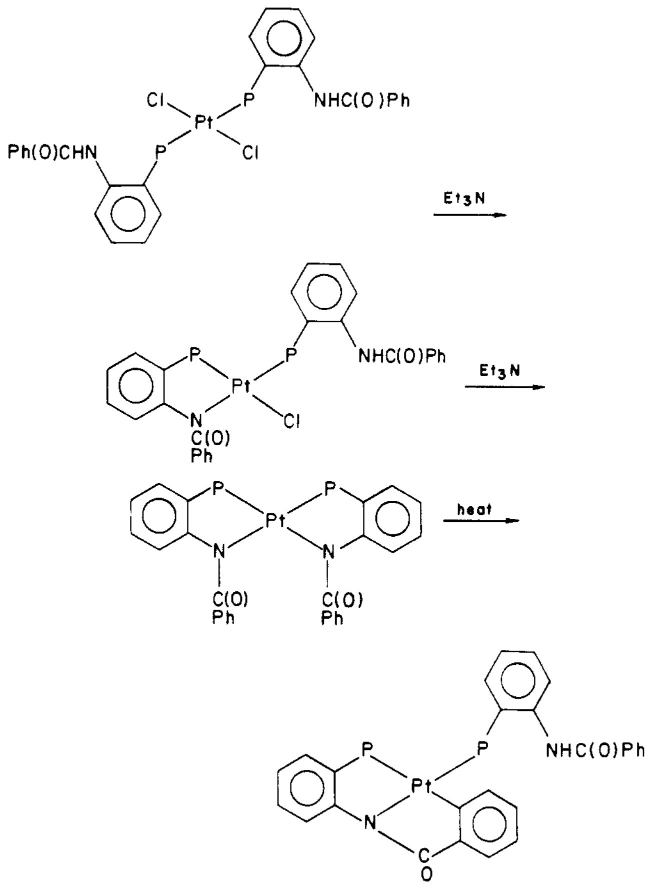
Figure 3. ORTEP diagram for *cis*-$\mathrm{Pt}(o\text{-}\mathrm{Ph_2PC_6H_4NC(O)C_6H_4})(o\text{-}\mathrm{Ph_2PC_6H_4NHC(O)Ph})$ (1) showing the location of the "agostic" N–H···Pt bond.

Table III. Selected Bond Distances of Angles for *cis*-$\mathrm{Pt}(o\text{-}\mathrm{Ph_2PC_6H_4NC(O)C_6H_4})(o\text{-}\mathrm{Ph_2PC_6H_4NHC(O)Ph})$

	(a) Bond Distances (Å)		
Pt-P(1)	2.298 (2)	N(1)-C(1)	1.342 (12)
Pt-P(2)	2.259 (2)	C1-O(1)	1.247 (13)
Pt-N(1)	2.063 (7)	C(1)-C(2)	1.485 (14)
Pt-C(3)	2.065 (8)	C(2)-C(3)	1.396 (14)
Pt-H(2)	2.318 (22)	P(2)-C(71)	1.848 (6)
P(1)-C(11)	1.814 (8)	C(71)-C(76)	1.405 (12)
C(11)-C(16)	1.382 (13)	C(76)-N(2)	1.411 (12)
C(16)-N(1)	1.431 (11)	N(2)-C(8)	1.357 (12)
H(2)-N(2)	1.04 (3)	C(8)-O(2)	1.225 (11)
	(b) Bond Angles (deg)		
P(1)-Pt-P(2)	100.6 (1)	N(1)-C(1)-O(1)	125.6 (9)
P(1)-Pt-N(1)	83.7 (2)	N(1)-C(1)-C(2)	113.4 (8)
P(1)-Pt-C(3)	164.8 (3)	C(1)-C(2)-C(3)	118.6 (8)
P(2)-Pt-N(1)	175.6 (2)	Pt-C(3)-C(2)	110.9 (6)
P(2)-Pt-C(3)	94.5 (3)	Pt-P(2)-C(71)	115.4 (3)
N1)-Pt-C(3)	81.2 (3)	C(46)-P(2)-C(56)	102.1 (3)
Pt-P(1)-C(11)	100.4 (3)	P(2)-C(11)-C(76)	122.4 (6)
C(26)-P(1)-C(36)	107.9 (3)	C(71)-C(76)-N(2)	121.4 (6)
P(1)-C(11)-C(16)	117.5 (6)	C(76)-N(2)-C(8)	128.8 (7)
C(11)-C(16)-N(1)	118.2 (8)	N(2)-C(8)-O(2)	121.5 (9)
C(16)-N(1)-C(1)	123.8 (7)	N(2)-C(8)-C(66)	116.8 (7)

organometallic compounds,[7] and we propose that complex 1 shows an "agostic" interaction of the type N–H···Pt. This interaction is also identifiable in the solid-state infrared spectrum (Nujol mull) of 1 which shows the ν(NH) band at 3200 and 3150 $\mathrm{cm^{-1}}$. This position represents a shift of 150–200 $\mathrm{cm^{-1}}$ to low frequency over the value of ν(NH) found in the free ligand (3350 $\mathrm{cm^{-1}}$) or in the monodentate P-bonded complex 9 (3340 $\mathrm{cm^{-1}}$).[3]

Scheme I. Conversion of *trans*-$\mathrm{PtCl_2}(o\text{-}\mathrm{Ph_2PC_6H_4NHC(O)Ph})_2$ into *cis*-$\mathrm{Pt}(o\text{-}\mathrm{Ph_2PC_6H_4NC(O)C_6H_4})(o\text{-}\mathrm{Ph_2PC_6H_4NHC(O)Ph})$ (1)



1

We have no conclusive proof that this "agostic" N–H···Pt interaction is present in chloroform solutions of the complex, although circumstantial evidence suggests that the solution structure is analogous. The ^{1}H NMR spectrum of complex 1 shows a resonance at δ 11.0 for NH, which represents a downfield shift of 2.3 ppm from that found in free $o\text{-}\mathrm{Ph_2PC_6H_4NHC(O)Ph}$ and of 2.0 ppm from δ(NH) in 9.[3] No coupling ^1J(PtH) is observed in the 360-MHz ^{1}H NMR spectrum of 1 at ambient temperature or at −50 °C. If there is any s character in the Pt–H bond we would expect to observe ^1J(PtH) coupling, unless, of course, the peaks are unobserved because of chemical shift anisotropy broadening.

Intramolecular Hydrogen Transfer. The cyclometalated complex 1 was initially discovered while attempting to prepare $\mathrm{Pt}(o\text{-}\mathrm{Ph_2PC_6H_4NC(O)Ph})_2$. A plausible explanation for the formation of 1 from 9 is shown in Scheme I. The first step involves deprotonation of the free amide group followed by intramolecular amido substitution of a chloride ligand to give complex 2. The substitution occurs with isomerization, which is unexpected since substitutions at platinum(II) typically occur with retention of stereochemistry. It is apparent that the intermediate 2 then undergoes a second analagous halide substitution reaction to give *cis*-$\mathrm{Pt}(o\text{-}\mathrm{Ph_2PC_6H_4NC(O)Ph})_2$

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[7] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408. Eisenstein, O.; Jean, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1177–1186. Brookhart, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161–4166. Ashworth, T. V.; Liles, D. C.; Singleton, E. *Organometallics* **1984**, *3*, 1851–1855. Rothwell, I. P. *Polyhedron* **1985**, *4*, 177–200.

(**14**). This second replacement occurs with stereochemical retention at platinum(II). The formation of the C-metalated complex **1** results from a subsequent thermal reaction of complex **14** induced by the high reaction temperatures produced in refluxing DMF.

The formation of **1** can be prevented by using lower reaction temperatures. Refluxing **9** with triethylamine as a suspension in acetonitrile solvent gives a mixture of **2** and **14** (^{31}P δ 9.5 (^1J(PtP) = 3241 Hz)) (eq 4).[3] The

$$\underset{\textbf{9}}{trans\text{-PtCl}_2(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)Ph})_2} \xrightarrow[\text{CH}_3\text{CN}]{\text{Et}_3\text{N}}$$

$$\underset{\textbf{2}}{cis\text{-Pt}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NC(O)Ph})(o\text{-Ph}_2\text{C}_6\text{H}_4\text{NHC(O)Ph})\text{Cl}}$$

$$+ \underset{\textbf{14}}{cis\text{-Pt}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NC(O)Ph})_2} \quad (4)$$

percentage of complex **2** in the reaction mixture does not exceed 5%, and it is identified as *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)Ph$)(*o*-$Ph_2PC_6H_4NHC(O)Ph$)Cl by ^{31}P{^{1}H} NMR spectroscopy. Spectral simulation shows the observed spectrum to be an AB pair flanked by ^{195}Pt satellites. A value of 14 Hz for ^2J(PP) verifies a cis stereochemistry for the phosphines,[3] and the respective shift values of δ 23.7 (^1J(PtP) = 3750 Hz and −4.9 (^1J(PtP) = 3073 Hz) confirm that one phosphorus is contained in a five-membered chelate ring, and the other one is P-bonded monodentate to platinum(II). The magnitudes of ^1J(PtP) indicate that each phosphine ligand is trans to a ligand of low trans influence (chloro and amido). At ambient temperatures the complexes **14** and **2** are indefinitely stable both in solution and the solid state. Refluxing complex **14**, either alone or with **2**, in chloroform, acetonitrile, toluene, or hexane solvent, gives **1** as the sole product even in the absence of added base. No intermediates have been observed in this final step. In the preliminary communication we have suggested that the reaction may involve an intermediate platinum(IV) hydride complex PtH(*o*-$Ph_2PC_6H_4NC(O)C_6H_4$)(*o*-$Ph_2PC_6H_4NC(O)Ph$).[1] Such an intermediate is formed by oxidative addition of the C–H bond to platinum(II). Some support for this premise is found in the observation that ortho metalation is not observed under a high pressure of CO, where presumably the blocked fifth coordination position prevents the addition step at a coordinately unsaturated center.

Deuteration Experiments. The conversion of complex **14** into **1** via a platinum(IV) hydride intermediate involves intramolecular C–H addition to platinum(II) followed by N–H reductive elimination. Such a pathway transfers an ortho hydrogen on the benzoyl group of a complexed *o*-$Ph_2PC_6H_4NC(O)Ph$ group onto the coordinated nitrogen of the second *o*-$Ph_2PC_6H_4NC(O)Ph$ ligand to give monodentate P-bonded *o*-$Ph_2PC_6H_4NHC(O)Ph$. The ideal ligand to test this premise is *o*-$Ph_2PC_6H_4NHC(O)$-2,5-$C_6H_3D_2$, but in view of its synthetic inaccessibility in high yield, we have prepared *o*-$Ph_2PC_6H_4NHC(O)C_6D_5$ for the deuterium-transfer experiments. The complex *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)C_6D_5)_2$ has been prepared by initially synthesizing *trans*-$PtCl_2$(*o*-$Ph_2PC_6H_4NHC(O)C_6D_5)_2$ from the ligand and $PtCl_4^{2-}$ in acetonitrile solvent and then converting this intermediate to the product by a 5-day reaction with sodium *tert*-butoxide. Comparison of the ^{31}P{^{1}H} NMR and the IR spectra of the deuterated and nondeuterated compounds shows no changes except for an additional band due to ν(C–D) at 2290 cm^{-1} in *trans*-$PtCl_2$(*o*-$Ph_2PC_6H_4NHC(O)C_6D_5)_2$ and at 2275 cm^{-1} in *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)C_6D_5)_2$. Refluxing *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)C_6D_5)_2$ for 15 min in dry toluene gives a mixture of *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)C_6D_4$)(*o*-$Ph_2PC_6H_4NDC(O)C_6D_5$) (**1a**) and *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)C_6D_4$)(*o*-$Ph_2PC_6H_4NHC(O)C_6D_5$) (**1b**). Longer reaction times of approximately 1 h give only **1b**. Refluxing **1b** in C_6D_6 converts it into **1a** (eq 5). For

$$cis\text{-Pt}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NC(O)C}_6\text{D}_4)\text{-}$$

$$\underset{\textbf{1b}}{(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NHC(O)C}_6\text{D}_5)} \xrightarrow[\text{reflux}]{\text{C}_6\text{D}_6}$$

$$cis\text{-Pt}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NC(O)C}_6\text{D}_4)\text{-}$$

$$\underset{\textbf{1a}}{(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{NDC(O)C}_6\text{D}_5)} \quad (5)$$

complete **1b** we find ν(CD) at 2350 and 2310 cm^{-1} and ν(NH) at 3150 cm^{-1}. For compound **1a** we again find ν(CD) bands at 2350 and 2310 cm^{-1}, but now there are bands due to ν(ND) at 2260 and 2270 cm^{-1}. This experiment provides support for the premise that the cyclometalation reaction involves transfer of a hydrogen atom from the benzoyl phenyl ring to the complexed nitrogen of the second *o*-$Ph_2PC_6H_4NC(O)Ph$ ligand, followed by H/D exchange at nitrogen with the solvent. This mechanism results in one *o*-$Ph_2PC_6H_4NC(O)Ph$ group becoming an ortho-metalated tridentate ligand, and the other *o*-$Ph_2PC_6H_4NC(O)Ph$ moiety becoming a monodentate *o*-$Ph_2PC_6H_4NHC(O)Ph$ ligand. Although not fully proven, it is reasonable to assume that it is an ortho hydrogen which is transferred from the benzoyl group. No intermediates are observed, but our preferred pathway still involves oxidative addition of the C–H group followed by reductive elimination of the N–H moiety from a hydrido platinum(IV) intermediate. The observed scrambling of our H/D label from the solvent was completely unexpected. The exchange is subsequent to metalation since refluxing complex **1** in $CDCl_3$, C_6D_6, or CD_3CN solvent results in conversion of the N–H bond into N–D. This process can be reversed by refluxing N-deuterated product in toluene or CH_3CN solvent. Refluxing either the uncomplexed compound *o*-$Ph_2PC_6H_4NHC(O)Ph$ or complex **9** in CD_3CN for 24 h causes *no* H/D exchange. It appears therefore that the "agostic" N–H(D)···Pt interaction facilitates the H(D) atom to exchange with solvent, possibly by a weakening of the N–H(D) bond.

A second feature of this ortho-metalation reaction relates to the isotope effect for the conversion of **14** into the C-metalated complex **1**. The hydrogen transfer to give **1** can be effected rapidly by refluxing **14** in benzene, acetonitrile, or chloroform, but even when *cis*-Pt(*o*-$Ph_2PC_6H_4NC(O)C_6D_5)_2$ (deuterated **14**) is refluxed up to 12 h in these lower boiling point solvents, there is no detectable ortho-metalated product. This result implies that there is a substantial kinetic isotope effect for the ortho-metalation reaction. Kinetic isotope effects (k_H/k_D) for cyclometalation reactions are often in the region of 6,[8] but no values are known for reductive elimination of N–H(D) step. Our overall hydrogen transfer reaction may indeed show a very high deuterium isotope effect if it occurs by a series of steps, each having a high k_H/K_D ratio. The major

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[8] Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, C55–C57.

Table IV. ^{1}H and ^{31}P{^{1}H} NMR Data for the New Complexes

complex	$\delta(^{31}P)$; J/Hz	$\delta(^1H)$
cis-Pt(o-Ph$_2$PC$_6$H$_4$NC(O)C$_6$H$_4$)(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph) (**1**)	P$_A$, 26.2; P$_B$, 2.4; ^2J(PP) = 14; ^1J(PtP$_A$) = 1905; ^1J(PtP$_B$) = 3334	11.0 (NH)
cis-Pt(o-Ph$_2$PC$_6$H$_4$NC(O)Ph)(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph)Cl (**2**)	P$_A$, 23.7; P$_B$, −4.9; ^2J(PP) = 14; ^1J(PtP$_A$) = 3750; ^1J(PtP$_B$) = 3073	
cis-Pd(o-Ph$_2$PC$_6$H$_4$NC(O)C$_6$H$_4$)(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph) (**3**)	P$_A$, 23.1; P$_B$, 19.3; ^2J(PP) = 32	10.3 (NH)
trans-Pt(OCOCF$_3$)$_2$(o-Ph$_2$PC$_6$H$_4$C(O)NHPh)$_2$ (**4**)	7.2; ^1J(PtP) = 2760	11.8 (NH)
cis-[Pt(o-Ph$_2$PC$_6$H$_4$C(O)NPh)(o-Ph$_2$PC$_6$H$_4$C(O)NHPh)(CF$_3$CO$_2$H)]CF$_3$CO$_2$ (**5**)	P$_A$, 10.7; P$_B$, 2.1; ^2J(PP) = 11.6; ^1J(PtP$_A$) = 3120; ^1J(PtP$_B$) = 4150	9.4 (NH)
Pd(OCOCF$_3$)$_2$(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph)$_2$ (**6**)	30.5 (br)	
Pd(OCOCF$_3$)$_2$(o-Ph$_2$PC$_6$H$_4$C(O)NHPh)$_2$·2CF$_3$CO$_2$H (**7**)	37.8	11.8 br (OH + NH)
cis-[Pd(o-Ph$_2$PC$_6$H$_4$N(Me)C(O)C$_6$H$_4$)(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph)]MeSO$_4$ (**8**)	P$_A$, 31.5; P$_B$, 30.8 (−55 °C)	

problem to quantifying this ratio is our observed H/D exchange between the "agostic" N–H group and the solvent. This feature creates difficulty in accurately measuring the kinetic ratio obtained in the metalation reaction.

The analogous ortho-metalated palladium(II) complex *cis*Pd(o-Ph$_2$PC$_6$H$_4$NC(O)C$_6$H$_4$)(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph) (**3**) can be prepared by reacting a suspension of **10** in acetonitrile with excess DABCO (eq 6). The yield is

$$\underset{\mathbf{10}}{\mathrm{PdCl_2(}o\mathrm{\text{-}Ph_2PC_6H_4NHC(O)Ph)_2}} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{DABCO}} \underset{\mathbf{3}}{cis\text{-}\mathrm{Pd(}o\mathrm{\text{-}Ph_2PC_6H_4NC(O)C_6H_4)(}o\mathrm{\text{-}Ph_2C_6H_4NHC(O)Ph)}} \tag{6}$$

quantitative. When triethylamine is used as base, the mixture must be heated to reflux to obtain **3**. The colorless complex is slightly soluble in CHCl$_3$ and CH$_2$Cl$_2$ but insoluble in other organic solvents. Crystals can be grown from a saturated CHCl$_3$ solution to which diethyl ether has been added. Spectral simulation of the ^{31}P NMR spectrum gives an AB pattern with δ(P$_A$) 23.1, δ(P$_B$) 19.3, and ^2J(PP) = 32 Hz. The ring shift for the phosphorus in a chelate is very small. In this palladium complex **3** we measure Δ(P$_A$–P$_B$) to be only 3.8 ppm whereas the platinum analogue **2** shows a 23.8 ppm difference.

The infrared spectrum of **3** as a Nujol mull shows absorptions characteristic of o-Ph$_2$PC$_6$H$_4$NHC(O)Ph (ν(NH) 3240 cm^{-1}, amide I, 1675 cm^{-1}, amide II, 1510 cm^{-1}, amide III, 1295 cm^{-1}) and of o-Ph$_2$PC$_6$H$_4$NC(O)Ph (amide I, 1610 cm^{-1}, amide III, 1340 cm^{-1}). Interaction of the amide hydrogen with palladium is indicated by the 100 cm^{-1} low frequency of ν(NH) as compared to free ligand and also by the downfield shift of the NH proton resonance by 1.5 ppm from free ligand to δ 10.3. Again the complex undergoes H/D exchange at the "agostic" NH with deuterated solvents such as C$_6$D$_6$, CDCl$_3$, and CD$_3$CN. No H/D exchange is found at the NH position of **10**, even after prolonged reflux.

The ortho-metalated palladium complex is more readily formed than the platinum analogue. Neither Pd(o-Ph$_2$PC$_6$H$_4$NC(O)Ph)$_2$[9] nor Pd(o-Ph$_2$PC$_6$H$_4$NC(O)Ph)(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph)Cl can be formed from treating **10** with the base DABCO. The only observed product is the metalated complex **3**.

Chemical Reactivity of Chelated Amido Ligands to Brønsted Acids. Amido complexes of high-valent early-transition-metal ions are well-known. The compounds are stable thermodynamically, but chemically the complexes are moisture sensitive and react rapidly with water to give oxo and hydroxo complexes.[4] By contrast the amido complex **1** has been isolated by the addition of water to the reaction mixture, and the amido complexes **14**, **11**, **12**, and **13** are quite stable to hydrolysis. Nevertheless monomeric amido complexes have a nonbonded lone pair of electrons on the coordinated nitrogen, and we find that strong acids such as HCl will protonate these amido ligands at nitrogen.[3]

It is useful now for us to qualitatively investigate the reactivity of these monomeric amido complexes to Brønsted acids and electrophiles. In addition to using water and HCl as Brønsted acids, we have now added acetic and trifluoroacetic acids to these new amido complexes. These two acids span a wide range of strength, yet in each case the anionic ligand which may coordinate is a carboxylate group. All the amido complexes are resistant to attack by acetic acid. The amido complexes show no evidence of protonation by this reagent, and they can be recovered unchanged from the solutions. Trifluoroacetic acid, like HCl, is a sufficiently strong acid that protonation at nitrogen occurs, and the weakly coordinating amide ligand is replaced by a trifluoroacetate group. Reaction of excess trifluoroacetic acid with dichloromethane solutions of **11**, **12**, *cis*-Pd(o-Ph$_2$PC$_6$H$_4$NC(O)Ph)$_2$, and **13** gives respectively *trans*-Pt(OCOCF$_3$)$_2$(o-Ph$_2$PC$_6$H$_4$C(O)NHPh)$_2$, **4**, *cis*-[Pt(o-Ph$_2$PC$_6$H$_4$C(O)NPh)(o-Ph$_2$PC$_6$H$_4$C(O)NHPh)(CF$_3$CO$_2$H)]CF$_3$CO$_2$, **5**, Pd(OCOCF$_3$)$_2$(o-Ph$_2$PC$_6$H$_4$NHC(O)Ph)$_2$, **6**, and Pd(OCOCF$_3$)$_2$(o-Ph$_2$PC$_6$H$_4$C(O)NHPh)$_2$·2CF$_3$CO$_2$H, **7**. As with the analogous reaction with HCl,[3] this protonation reaction occurs with retention of stereochemistry. The pertinent ^{31}P{^{1}H}, ^{1}H NMR, and IR data which confirm the structures of the compounds and the stereochemistries of the platinum complexes are as follows. **4**: δ_P 7.2 (^{1}J(PtP) = 2760 Hz); δ_H 11.8; ν(NH) 3260 cm^{-1} (CH$_3$CN solvent), ν(OCOCF$_3$) 1790, 1745 cm^{-1}, amide I 1695 cm^{-1}. **5**: δ_{P_A} 10.7 (^1J(PtP$_A$) = 3120 Hz), δ_{P_B} 2.1 (^1J(PtP$_B$) = 4150 Hz, ^2J(P$_A$P$_B$) = 11.6 Hz), δ_H 9.4 (br); ν(NH) 3270 cm^{-1} (br), ν(OCOCF$_3$) 1790, 1745 cm^{-1} (o-Ph$_2$PC$_6$H$_4$NHC(O)Ph), 1610 cm^{-1} (o-Ph$_2$PC$_6$H$_4$NC(O)Ph), 1695 cm^{-1} for amide I (CH$_3$CN solvent). **6**: δ_P 30.5 (br); ν(OCOCF$_3$) 1775 cm^{-1} (br). **7**: δ_P

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[9] Prepared from Pd$_2$(dibenzylideneacetone)$_3$ and o-Ph$_2$PC$_6$H$_4$NHC(O)Ph.

37.8; δ_H = 11.8 (br) (OH + N*H*); ν(NH) and ν(OH) 3250, 3210, 3160 cm^{-1}, $\nu(OCOCF_3)$ 1775 cm^{-1}. The NMR data are collected in Table IV.

For these complexes the observation of $\nu(OCOCF_3)$ bands in the 1750–1800 cm^{-1} region is diagnostic of monodentate O-bonded trifluoroacetate ligands. Hydrogen bonding between the acidic amide protons and either the trifluoroacetate or amide oxygens is indicated by the low-field resonance of the NH proton at δ 11.8, a downfield shift of 3 ppm from *o*-$Ph_2PC_6H_4C(O)NHPh$. The ν(NH) band is too broad to be observed in Nujol, but it is found in the region of 3250 cm^{-1} in acetonitrile solvent. Similarly the broad absorption bands characteristic of uncoordinated amide and the trifluoroacetate groups are very broad in the solid-state infrared spectrum, but in acetonitrile solvent the bands sharpen. For complex **4** the amide I and ν(CO) bands of the trifluoroacetate ligand can be identified at the respective positions of 1695, 1745, and 1790 cm^{-1}. The complex is a weak electrolyte in acetonitrile solvent. At high concentrations of the complex (0.7 mM) the solution conductivity Λ_M is 50 Ω^{-1} cm^2 mol^{-1}, but at low concentrations (0.034 mM) the value of Λ_M is 117 Ω^{-1} cm^2 mol^{-1}. This latter value approaches that characteristic of a 1:1 electrolyte.[10] These data show that a trifluoroacetate ligand undergoes replacement by acetonitrile. This equilibrium is shown in eq 7. The ionic complex **5** has

$$\underset{\mathbf{4}}{trans\text{-}Pt(OCOCF_3)_2(o\text{-}Ph_2PC_6H_4C(O)NHPh)_2} + MeCN \rightarrow trans\text{-}[Pt(OCOCF_3)(o\text{-}Ph_2PC_6H_4C(O)NHPh)_2MeCN]\text{-}CF_3CO_2 \quad (7)$$

an equivalent conductivity of 130 Ω^{-1} cm^2 mol^{-1}, in acetonitrile solvent which is that expected for a 1:1 electroyte. Complex **7** is slightly conducting, but the small value of 10.6 Ω^{-1} cm^2 mol^{-1} is likely due to the presence of trifluoroacetic acid.

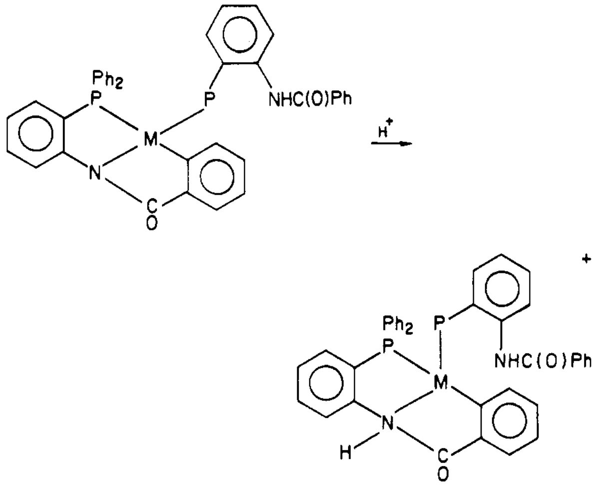
The ortho-metalated complexes **1** and **3** present an interesting case for probing reactivities to Brønsted acids and electrophilic methylating agents. Two sites of attack at coordinated ligands are present in each molecule. It is plausible that protonation or electrophilic attack can occur at the coordinated phenyl carbon,[11] or at the amido nitrogen, or at both.

The ortho-metalated complexes **1** and **3** undergo protonation with HCl. In each case both the metal–aryl and metal–amido bonds undergo protolysis, and the respective products are *cis*-$PtCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2$ and **10** (eq 8). With trifluoroacetic acid, protonation of **1** and **3** again

$$cis\text{-}M(o\text{-}Ph_2PC_6H_4NC(O)C_6H_4)\text{-}(o\text{-}Ph_2PC_6H_4NHC(O)Ph) + 2HCl \rightarrow cis\text{-}MCl_2(o\text{-}Ph_2PC_6H_4NHC(O)Ph)_2 \quad (8)$$

$$M = Pt, Pd$$

occurs, but now the reaction is reversible. In the presence of excess CF_3CO_2H both the Pt and Pd complexes give a single ^{31}P NMR resonance. For **1** this peak is at δ 9.8 ($^1J(PtP)$ = 3241 Hz), and for **3** the resonance is at δ 38.4 ($\nu_{1/2}$ = 50 Hz). Neither product is isolable since addition of hexane to the solutions causes reversion back to **1** and **3**, respectively. We suggest that protonation occurs at the amido ligand to give $[M(o\text{-}Ph_2PC_6H_4N(H)C(O)C_6H_4)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)]^+$ (eq 9). This complex has both



(9)

an internal and an external amide group, and coordination of each amide to M will cause the complex to be pentacoordinate and fluxional. Attempts to obtain satisfactory ^{31}P NMR spectra at low temperature were unsuccessful because of the solidification of trifluoroacetic acid. Alkylation of **3** also occurs at the amide nitrogen rather than at the coordinated aryl carbon atom. Complex **3** reacts with dimethyl sulfate in chloroform solvent to give $[Pd(o\text{-}Ph_2PC_6H_4N(Me)C(O)C_6H_4)(o\text{-}Ph_2PC_6H_4NHC(O)Ph)]\text{-}SO_4Me$ (**8**) (eq 10). This complex **8** now has a tertiary

$$Pd(o\text{-}Ph_2PC_6H_4NC(O)C_6H_4)\text{-}(o\text{-}Ph_2PC_6H_4NHC(O)Ph) + Me_2SO_4 \rightarrow Pd(o\text{-}Ph_2PC_6H_4N(Me)C(O)C_6H_4)\text{-}(o\text{-}Ph_2PC_6H_4NHC(O)Ph)]SO_4Me \quad (10)$$

amine coordinated to palladium(II), and since *N*-methyl heterolytic cleavage is much less facile than N–H deprotonation, this methylated product is stable in the solid state and can be isolated. The spectroscopic data are as follows: ν(NH) 3450 cm^{-1}, amide I 1610 cm^{-1}, ν(S=O) 1200 cm^{-1}. $^{31}P\{^1H\}$ shows δ 33.8 ($\nu_{1/2}$ = 10 Hz at 25 °C) which broadens on lowering the temperature. At −55 °C two peaks ($\nu_{1/2}$ = 5 Hz) are observed at δ 30.8 and 31.5. The exchange process can be explained again on the basis of a pentacoordinate intermediate.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates for **1** (37 pages). Ordering information is given on any current masthead page.

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