ond step is a CO insertion reaction into the metal–carbon bond of the thiametallacycle to yield complex 8 containing an acyl function. Both of these steps can be reversed by mild heating or by the application of UV–vis irradiation. We have observed a similar CO insertion into the complex $Os_3(CO)_{10}[(\mu\text{-}SCH_2CMe_2CH_2)_3]$.[4] However, in that example the keto function bridges the cluster in a μ-η^2 mode.

Alper et al. have produced γ-thiobutyrolactones catalytically via regiospecific carbonylations of thietane, 2-methylthietane, and 3-methoxythietane using cobalt and ruthenium carbonyls as catalyst precursors.[16] We believe that compounds 6 and 8 provide viable models for intermediates that might be involved in the catalytic reactions observed by Alper. Efforts to obtain further support for this are in progress.

In related studies we have shown that nucleophiles including Cl^- add directly to the bridging 3,3-DMT ligand in complex 2 to open the thietane ring through cleavage of a carbon–sulfur bond.[4,5] Herein, we have demonstrated that the addition of Cl^- to the thiametallacyclic complex 6 proceeds by addition to the metal atoms and not to the opened thietane ligand. Thus, the thiametallacyle in 6 is not as susceptible to nucleophilic addition as is the intact, bridging 3,3-DMT ligand in 2.

(16) Wang, M. D.; Calet, S.; Alper, H. *J. Org. Chem.* **1989**, *54*, 20.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Basic Energy Sciences of the U.S. Department of Energy for support of this research.

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters (15 pages). Ordering information is given on any current masthead page. Structure factor tables for the structural analyses of compounds 3, 4, and 9 were deposited previously.[3,4a]

OM9211733

Reactions of Amides with Zerovalent and Divalent Palladium and Platinum Complexes

David R. Schaad and Clark R. Landis*

Departments of Chemistry and Biochemistry, University of Colorado—Boulder, Boulder, Colorado 80309, and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received October 21, 1991

The reactions of amides ($RCONH_2$ and $CF_3SO_2NH_2$) with $L_2Pd(CH_3)_2$ and $L_2Pt(CH_3)_2$ and with transient L_2Pt^0 to yield new complexes containing palladium– and platinum–amido nitrogen bonds are reported. Photolysis of $Pt(C_2O_4)(PEt_3)_2$ (1) in the presence of amide generates products of the type *trans*-PtH(HNR)$(PEt_3)_2$ (R = SO_2CF_3 (**1a**), $COCF_3$ (**1b**)). Reaction of amides with *trans*-$PtH(CH_3)(PEt_3)_2$ (**2**), *cis*-$PdMe_2(PEt_3)_2$ (**3**), *cis*-$PtMe_2(PEt_3)_2$ (**4**), $PdMe_2$(dcpe) (**5**), $PdMe_2$(dmpe) (**6**), and $PtMe_2$(COD) (**7**) produces **1a,b**, *trans*-PdMe(HNR)$(PEt_3)_2$ (R = SO_2CF_3 (**3a**), $COCF_3$ (**3b**), $COCF_2H$ (**3c**), COPh (**3d**)), PtMe(HNR)$(PEt_3)_2$ (R = SO_2CF_3 (**4a**), $COCF_3$ (**4b**)), PdMe(HNR)(dcpe) (R = SO_2CF_3 (**5a**), $COCF_3$ (**5b**), COPh (**5c**)), PdMe$(HNSO_2CF_3)$(dmpe) (**6a**), and PtMe(HNR)(COD) (R = SO_2CF_3 (**7a**), $COCF_3$ (**7b**)), respectively. The stereochemistry and topologies of the new compounds are established by multinuclear NMR spectroscopy. The relevance of these reactions to hydroamination catalysis is discussed.

Introduction

The activation of N–H bonds[1] by transition-metal complexes[2] is an integral feature of recent developments in hydroamination catalysis.[3,4] Our research on the design of new hydroamination catalysts has focused on the reactions of amides at metal centers because (1) amides are synthetic equivalents of the simplest hydroamination reagent, ammonia, and (2) the relatively high acidity of amide vs ammonia N–H bonds may provide a lower energy pathway for metal-facilitated functionalization. We have previously reported that amides react with *cis*-$FeH_2(dmpe)_2$, $FeH(C_6H_4PPhCH_2CH_2PPh_2)$(dppe), and *cis*-RuH(naphthyl)$(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane) to generate *trans*-M(H)(RNH)$(diphosphine)_2$ complexes.[5] Herein we report the extension of these studies to zerovalent and divalent palladium and platinum compounds containing phosphine and olefin ligands.

Steps relevant to hydroamination catalysis include transition-metal-promoted N–H bond activation, insertion of an olefin into a M–C or M–N bond, and reductive elimination or protonolysis to form the hydroamination product and regenerate the catalyst. We report the re-

* To whom correspondence should be addressed at the University of Wisconsin.

(1) Herein we use the term N–H bond activation to indicate cleavage of an N–H bond induced by a metal center via homolytic cleavage, heterolytic cleavage, or oxidative addition.

(2) (a) Roundhill, D. M *Inorg. Chem.* **1970**, *9*, 254. (b) Nelson, J. H.; Schmidt, J. L.; Henry, R. A.; Moore, D. W.; Jonassen, H. B. *Inorg. Chem.* **1970**, *9*, 2678. (c) Sappa, E.; Milone, L. *J. Organomet. Chem.* **1973**, *61*, 383. (d) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3098. (e) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328. (f) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006. (g) Susa-Fink, G. *Z. Naturforsh., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 454. (h) Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56. (i) Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett* **1982**, 207. (j) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5014. (k) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472. (l) Lin, Y. C.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1984**, *272*, 207. (m) Park, S.; Hedden, D.; Roundhill, D. M. *Organometallics* **1986**, *5*, 2151. (n) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (o) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971. (p) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (q) Park, S.; Johnson, M. P.; Roundhill, D. M. *Organometallics* **1989**, *8*, 1700. (r) Ladipo, F. T.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 4172. (s) Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1146.

(3) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 6738.

0276-7333/92/2311-2024$03.00/0

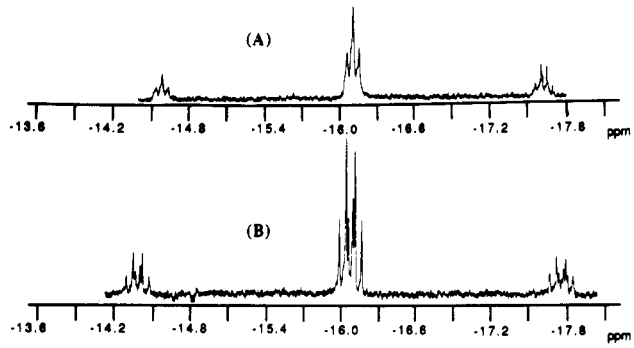


Figure 1. ^1H NMR hydride signals (300 MHz, acetonitrile-d_3; with ^{195}Pt satellites): (A) *trans*-$PtH(HNCOCF_3)(PEt_3)_2$; (B) *trans*-$PtH(H^{15}NCOCF_3)(PEt_3)_2$.

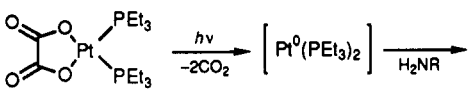
actions of amides to form complexes of the general formula *trans*-$MX(amido)Y_2$ (M = Pt, Pd; X = H, CH_3; Y = PEt_3, Y_2 = dcpe (1,2-bis(dicyclohexylphosphino)ethane), dmpe, COD (1,5-cyclooctadiene)) by two routes. One, formal N–H oxidative addition to a Pt(0) intermediate, is analogous to the oxidative addition of the N–H bond of aniline to an Ir(I) center in the hydroamination cycle reported by Casalnuovo et al.[3] The other, protonolysis of a M–C bond in divalent palladium and platinum compounds, has been proven to occur in the catalytic hydroamination pathway reported by Marks et al.[4]

Results

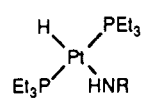
Formation of *trans*-$PtH(HNR)(PEt_3)_2$ (1a,b). Method 1. Trogler et al.[6] have reported that irradiation of $Pt(C_2O_4)(PEt_3)_2$ (1) with UV light in the presence of substrates XY (X = Me, MeO, Et_3Si; Y = Cl, H) yields complexes of the type $PtXY(PEt_3)_2$, formed by the loss of 2 equiv of CO_2 followed by oxidative addition of XY to a Pt(0) intermediate (eq 1). The oxalate complex has been shown to react photochemically with hydrogen[7] and disilenes[8] as well, to form Pt(II) complexes.

$$Pt(C_2O_4)(PEt_3)_2 \xrightarrow[-2CO_2]{h\nu} [Pt^0(PEt_3)_2] \xrightarrow{XY} Pt^{II}(PEt_3)_2XY \quad (1)$$

Small-scale photolysis of 1 in the presence of the acidic amides[9] triflamide and trifluoroacetamide produces *trans*-$PtH(HNR)(PEt_3)_2$ (R = SO_2CF_3 (**1a**), $COCF_3$ (**1b**)) complexes (eq 2), presumably via the highly reactive Pt(0) intermediate. The products are characterized readily by



1



(2)

R = SO_2CF_3 (1a), $COCF_3$ (1b)

multinuclear NMR spectroscopy. For both **1a** and **1b**, the ^1H NMR spectrum displays an upfield triplet (δ –19 (**1a**) and δ –16 (**1b**)) with ^{195}Pt satellites, thus establishing the presence of a platinum hydride. The $^{31}P\{^1H\}$ spectra of **1a,b** exhibit clean singlets, whereas $^{31}P\{^1H$ off-resonance$\}$ NMR experiments, in which all of the protons are decoupled except those at very high field (i.e. the metal hydrides), result in doublets. These results establish that one hydride is coupled to equivalent phosphine ligands. The $^{31}P–^{195}Pt$ satellite coupling constants (J_{P-Pt}) are approximately 2700 Hz, consistent with a trans geometry. Phosphorus–platinum coupling constants for trans platinum phosphines generally are less than 3000 Hz, whereas those for the cis analogues typically are greater than the trans couplings by a factor of 1.5.[10] When ^{15}N-labeled amide is used, the ^1H NMR spectrum shows that the hydride triplet is split into a doublet of triplets with ^{195}Pt satellites (Figure 1), thus confirming the connectivity of the amido functionality trans to the hydride. As in all cases when ^{15}N-labeled amide is employed, the broad amide N–H resonance is further split into a doublet by the labeled nitrogen. Additionally, when triflamide-d_2 is employed, neither hydride nor amide proton resonances are observed.

When the photolysis is carried out in the presence of excess amide, products tentatively identified as *trans*-$Pt(HNR)_2(PEt_3)_2$ (R = SO_2CF_3, $COCF_3$) form in addition to the hydride products, **1a,b**, in a ratio of ca. 1:(2–3) of bis- to mono(amide). The *trans*-$Pt(HNSO_2CF_3)_2(PEt_3)_2$ complex is characterized partially by the presence of a new amide N–H ^1H resonance at δ 3.3 that is integrated as two protons and by a new singlet $^{31}P\{^1H\}$ resonance at δ 19. No hydride resonances, other than those assignable to **1a,b**, are observed in the ^1H NMR spectrum. $^{31}P–^{195}Pt$ coupling constants of approximately 2700 Hz in the ^{31}P NMR spectrum indicate a trans geometry. Furthermore, no $^{31}P–^{15}N$ coupling is observed when ^{15}N-labeled amide is used; we commonly fail to observe $^{31}P–^{15}N$ coupling for cis-disposed phosphorus and nitrogen ligands. The $^{31}P\{^1H$ off-resonance$\}$ NMR spectrum exhibits a singlet; this is consistent with a complex that does not contain a hydride. Because the trans bis(amide) and trans hydrido amide products formed concurrently, it was difficult to isolate pure samples of **1a,b** on a larger photolytic scale.

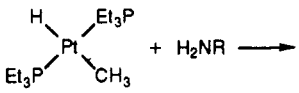
Palladium analogues of **1a,b** could not be isolated under the same photolytic conditions. Photolysis of $Pd(C_2O_4)(PEt_3)_2$ in the presence of triflamide appears to have produced *trans*-$Pd(HNSO_2CF_3)_2(PEt_3)_2$. The ^1H NMR spectrum exhibits no metal hydride resonances, and the amide N–H resonance is integrated as two protons. Additionally, the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ 26 for the equivalent triethylphosphine ligands, which do not show any further splitting when a $^{31}P\{^1H$ off-resonance$\}$ experiment is conducted or when ^{15}N-labeled triflamide is employed. Neither cis nor trans $^{31}P–^{15}N$ couplings were observed. Because trans $^{31}P–^{15}N$ couplings are usually large and cis $^{31}P–^{15}N$ couplings are commonly too small to be observed for these types of compounds (vide infra), the product is tentatively identified as *trans*-$Pd(H^{15}NSO_2CF_3)_2(PEt_3)_2$.

Irradiation of $Pd(C_2O_4)$(dcpe) in the presence of acidic amides showed no photoreductive elimination of the oxalate ligand when subjected to our experimental conditions. We note, however, that Trogler et al. have shown that $Pd(C_2O_4)$(dppe) is a photolytically reactive complex.[6b]

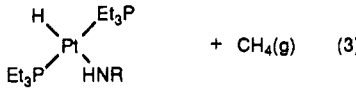
Formation of *trans*-$PtH(HNR)(PEt_3)_2$ (1a,b). Method 2. Because the isolation of pure products **1a,b** on a large scale proved troublesome, an alternate route was developed. Complexes **1a,b** could be isolated in high yields

(4) (a) Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. (b) Gagne, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716. (c) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275.
(5) Schaad, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 1628.
(6) (a) Paonessa, R. S.; Trogler, W. C. *Organometallics* **1982**, *1*, 768. (b) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647.
(7) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038.
(8) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517.
(9) (a) Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963. (b) Trepka, R. D.; Harrington, J. K.; Belisle, J. W. *J. Org. Chem.* **1974**, *39*, 1094.
(10) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

by heterolytic cleavage of the Pt–C bond in *trans*-PtH(CH$_3$)(PEt$_3$)$_2$ (**2**)[11] with acidic amides (eq 3). Dissolved methane gas is observed by ^{1}H NMR spectroscopy[12,13] when the reaction is carried out in a sealed tube with unlabeled amide.



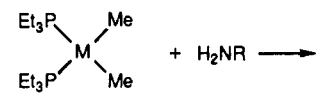
2



R = SO_2CF_3 (**1a**), $COCF_3$ (**1b**)

The isolated solids display NMR spectra that are identical with the spectra for complexes **1a,b** prepared by photolysis. When deuterated amides are employed, the hydride resonance is still observed and the methane produced is >95% CH_3D, indicating that amide acts as the exclusive hydrogen source for methane elimination. In contrast, we have reported previously that the reaction of triflamide-d_2 with *cis*-RuHNp(dmpe)$_2$[5] yields naphthalene without incorporation of deuterium. We have shown that this reaction does not proceed via a sequence of oxidative addition followed by reductive elimination.

Formation of Palladium and Platinum Alkyl Amido Complexes. A. Reaction of *cis*-PdMe$_2$(PEt$_3$)$_2$ (3) and *cis*-PtMe$_2$(PEt$_3$)$_2$ (4) with Amides. The reactions of **3**[14] and **4**[15] with amides (eq 4) produce compounds of the general formula *trans*-MCH$_3$(HNR)(PEt$_3$)$_2$ (M = Pd, R = SO_2CF_3 (**3a**), $COCF_3$ (**3b**), $COCF_2H$ (**3c**), COPh (**3d**); M = Pt, R = SO_2CF3 (**4a**), $COCF_3$ (**4b**)). Singlet ^{31}P{^{1}H} NMR resonances are displayed for **3a–d** and **4a,b** indicating the equivalence of the triethylphosphine ligands. Complexes **4a,b** show ^{31}P–^{195}Pt coupling constants in the ^{31}P{^{1}H} NMR spectra of approximately 2800 Hz, further indicative of a trans geometry. The attachment of the methyl group to the metal is revealed in the ^{1}H NMR spectrum: triplet methyl resonances (due to P–H coupling) are observed at $\delta \sim 0$ for the platinum and palladium complexes. For the platinum compounds **4a,b**, additional resonances in the form of ^{195}Pt satellites (J_{H-Pt}) with a coupling constant of ~75 Hz are observed for the methyl resonance. ^{1}H NMR spectroscopy shows dissolved methane gas in solution when the reaction is carried out in a sealed tube.



M = Pd (**3**), Pt (**4**)

R = SO_2CF_3 (**3a**, **4a**), $COCF_3$ (**3b**, **4b**) $COCF_2H$ (**3c**), COPh (**3d**)

When ^{15}N-labeled amide is employed in reactions with **3** and **4**, the broad amide proton resonance splits further into a doublet. In most cases the cis ^{31}P–^{15}N coupling is too small to be observed, although it is observed for the less acidic amide **3d** (~3 Hz). For the complexes where no cis ^{31}P–^{15}N coupling is observed, the connectivity of the amido group trans to the methyl ligand is further characterized by ^{13}C{^{1}H} NMR spectroscopy. For **3a**, the ^{13}C{^{1}H} resonance of the palladium methyl ligand shows large ^{13}C–^{15}N (10 Hz) and smaller ^{13}C–^{31}P (4 Hz) couplings.

For the reaction of triflamide with **4**, monitored using ^{31}P{^{1}H} NMR and ^{15}N-triflamide, an initial mixture of cis (~90%) and trans (~10%) products form at room temperature. The cis product displays two inequivalent ^{31}P resonances. A doublet of doublets with Pt satellites (J_{P-Pt} = 3970 Hz), indicative of a phosphorus ligand trans to the ^{15}N-amido functionality and cis to another inequivalent phosphorus ligand, is observed, in addition to a doublet (no cis ^{15}N–^{31}P coupling) for the other phosphorus ligand cis to the ^{15}N label. The trans product displays a singlet ^{31}P resonance (J_{P-Pt} = 2827 Hz) for the equivalent triethylphosphine ligands. Furthermore, two distinct amide proton doublets are observed in the ^{1}H NMR spectrum. As the mixture is heated, the ratio of trans to cis product increases. After 3 h at 60 °C, only the trans product is present and can be isolated as a pure solid. The reaction apparently proceeds by initial formation of the cis complex followed by slow isomerization to the trans product.

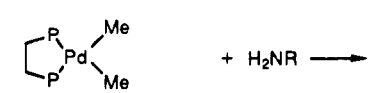
Qualitatively the reaction rates of **3** and **4** with amides depend on the acidity of the amide; the more acidic the amide, the faster the reaction. For example, triflamide reacts immediately at room temperature, whereas the other amides require increasing amounts of heating time as the amide acidity decreases.

When complexes **3** and **4** were reacted with excess amide, only mono(amide) products formed. Heating **3** or **4** with a 3-fold excess of amide for 18 h in benzene or acetonitrile at 60 °C showed no sign of bis(amide) formation.

Cleavage of the metal alkyl group of palladium and platinum complexes by protic reagents, e.g. HCl or ethanol, is well documented.[14,15] Reactions of acidic amides with **3** and **4** very likely proceed via direct protonolysis of the M–C bond by the amide, resulting in the evolution of methane. However, methane formation via N–H oxidative addition of the amide followed by reductive elimination cannot be ruled out.

B. Reaction of PdMe$_2$(dcpe) (5) and PdMe$_2$(dmpe) (6) with Amides. Because *trans*-Pt(amido)(CH$_3$)(PEt$_3$)$_2$ complexes formed from nonchelating cis phosphine starting materials, we explored the reactions of divalent palladium and platinum complexes (**5** and **6**) containing bis-chelating phosphines as a means of controlling stereochemistry. Reactions with amides could then produce complexes with a cis disposition of alkyl and amido ligands, thus enhancing the opportunity for C–N reductive eliminations to occur.

Complexes of the type PdMe(HNR)(dcpe) (R = SO_2CF_3 (**5a**), $COCF_3$ (**5b**), COPh (**5c**)) and PdMe(HNR)(dmpe) (R = SO_2CF_3 (**6a**)) are formed by reaction with amides (eq 5). The connectivity of the compounds is most easily determined by the ^{31}P{^{1}H} NMR spectra of products containing ^{15}N-labeled amides. With unlabeled amide the ^{31}P{^{1}H} NMR spectrum shows two distinct doublets for the the two inequivalent phosphorus atoms due to their mutual



P⌒P = dcpe (**5**), dmpe (**6**)

R = SO_2CF_3 (**5a**, **6a**), $COCF_3$ (**5b**), COPh (**5c**)

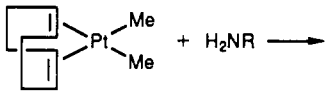
(11) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263.
(12) Dissolved methane gas in benzene-d_6 appears at δ 0.14.
(13) Bernheim, R. A.; Lavery, B. J. *J. Chem. Phys.* **1965**, *42*, 1464.
(14) Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008.
(15) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705.

coupling. The primary feature of the ^1H NMR spectrum is the palladium methyl ligand, which appears as a doublet of doublets at $\delta \sim 0.5$, being split by both the phosphorus trans and the phosphorus cis to it.

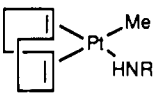
When ^{15}N-labeled amide is employed, further splitting due to the ^{15}N nucleus is observed. The $^{31}P\{^1H\}$ spectra display both cis (J_{P-N} ca. 3 Hz) and trans (J_{P-N} ca. 47 Hz) $^{31}P-^{15}N$ coupling, splitting each of the inequivalent doublets into doublets of doublets (Figure 2). The downfield ^{31}P resonance is assigned to the phosphorus atom trans to the ^{15}N-amido functionality, exhibiting a large doublet trans $^{31}P-^{15}N$ coupling that is further split into a doublet of doublets by the inequivalent cis phosphorus atom. The upfield ^{31}P resonance is assigned to the phosphorus that is cis to the ^{15}N-amido ligand, appearing as a doublet due to coupling with the inequivalent cis phosphorus atom that is further split by the smaller cis $^{31}P-^{15}N$ coupling.

No $Pd(HNR)_2(dcpe)$ products were observed when complexes **5** or **6** and excess amide were heated at 60 °C in acetonitrile for 18 h.

C. Reaction of $PtMe_2(COD)$ (7) with Amides. The reaction of acidic amides with **7**[16] produces $PtMe(HNR)(COD)$ (R = SO_2CF_3 (**7a**), $COCF_3$ (**7b**)) complexes (eq 6). These complexes contain a coordinated olefin and



7



+ CH_4(g) (6)

R = SO_2CF_3 (**7a**), $COCF_3$ (**7b**)

cis alkyl and amido ligands. This presents the opportunity not only for C–N reductive eliminations but also for stoichiometric hydroamination reactions.

The geometries of **7a,b** are deduced concisely by ^1H NMR spectra of complexes containing ^{15}N-labeled amide. For the reaction of unlabeled amide with **7**, two separate cyclooctadiene vinyl resonances are observed, compared to a single broad resonance in the starting material, indicating that the ligands on the platinum are no longer equivalent. A new platinum methyl resonance appears in the ^1H NMR spectrum at $\delta \sim 0.5$ with ^{195}Pt satellites (J_{Pt-H} = 68 Hz). Dissolved methane gas also is observed by ^1H NMR spectroscopy.

When ^{15}N-amide is employed in reactions with **7**, the platinum methyl resonance is split into a doublet (due to cis ^{15}N coupling) with ^{195}Pt satellites (Figure 3) and the amide proton resonance is split into a doublet. The high-field vinyl resonance has a ^{195}Pt satellite coupling constant (J_{Pt-H} = 71 Hz) about twice that of the low-field vinyl multiplet (J_{Pt-H} = 34 Hz). Additional splitting of the high-field cyclooctadiene vinyl mutliplet is observed when ^{15}N-labeled amide is used. This is consistent with the data presented by Clark and Manzer[16] in which the cyclooctadiene olefinic protons trans to an electron-withdrawing group exhibit a ^{195}Pt satellite coupling constant larger than those that are cis.

No $Pt(HNR)_2(COD)$ product formation was observed when **7** was heated at 60 °C in chloroform with a 3-fold excess of amide for 4 days.

Attempted Reactions of Palladium and Platinum Complexes with Olefins. Because the complexes pre-

(16) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

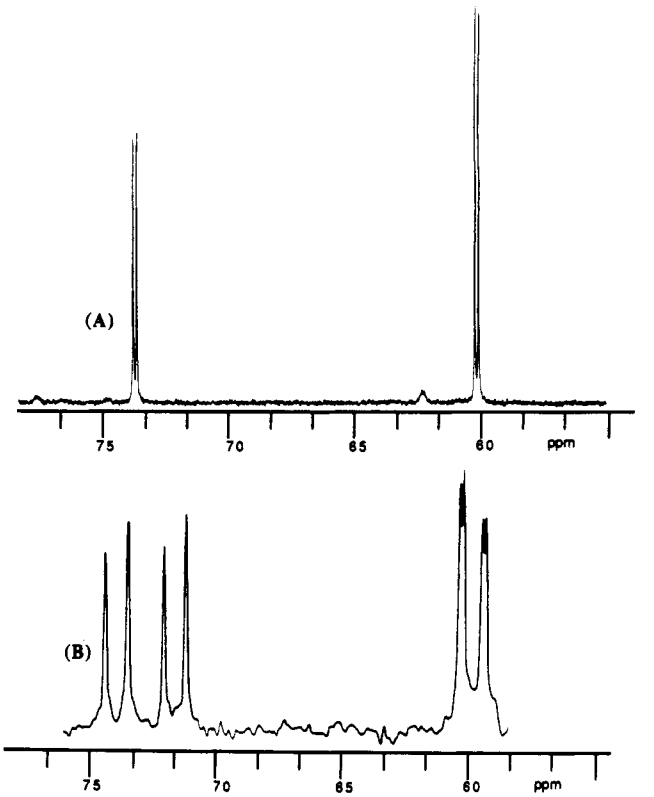


Figure 2. (A) 121.4-MHz $^{31}P\{^1H\}$ NMR spectrum of $PdMe(HNSO_2CF_3)(dcpe)$ in benzene-d_6. (B) 36.4-MHz $^{31}P\{^1H\}$ NMR spectrum of $PdMe(H^{15}NSO_2CF_3)(dcpe)$ in benzene-d_6.

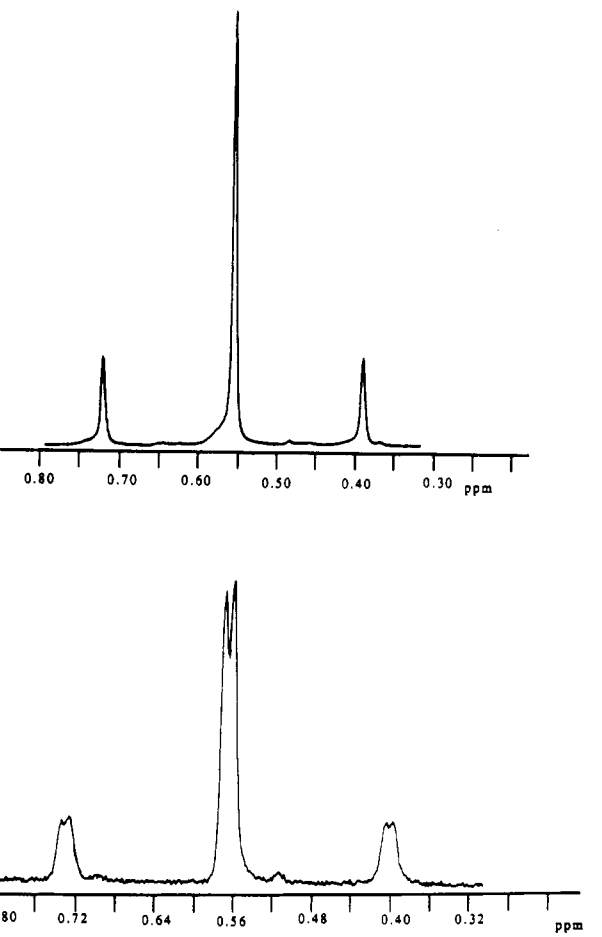


Figure 3. ^1H NMR Pt–CH_3 resonances (200 MHz, $CDCl_3$; with ^{195}Pt satellites): (A, top) $PtMe(HNSCO_2CF_3)(COD)$; (B, bottom) $PtMe(H^{15}NSO_2CF_3)(COD)$.

pared in this report contain potentially reactive M–N bonds their ability to undergo insertion and elimination reactions analogous to those proposed for catalytic hydroamination reactions was explored.

We have reacted activated olefins such as acrylonitrile, cinnamonitrile, and methyl acrylate with complexes containing M–H and M–N bonds (**1a,b**) as well as those that contain M–C and M–N bonds (**3a–7a**). Preliminary results indicate that no reaction occurs when the olefin and metal complex are heated together in solution at 60 °C for approximately 18 h. Furthermore, the compounds do not undergo any C–N reductive eliminations or any other decomposition when heated to temperatures as high as 70 °C for several days. Although complexes **7a,b** contain both olefin and cis alkyl and amido ligands, neither C–N reductive elimination nor olefin insertion reactions were observed even when the compounds were heated at 75 °C in $CDCl_3$ for 4 days. The results are consistent with the formation of robust M–N bonds. The inertness of compound **7a** to further reaction also may reflect an orientation of the coordinated COD ligand that is unfavorable for insertion into either the metal–carbon or metal–nitrogen bonds.

Experimental Section

All operations were carried out under nitrogen using either standard Schlenk techniques or an inert-atmosphere box. All solvents were reagent grade and dried by standard procedures. 1,2-Bis(dicyclohexylphosphino)ethane (dcpe) and 1,2-bis(dimethylphosphino)methane (dmpe) were purchased from Strem Chemicals. COD = 1,5-cyclooctadiene. Chloroplatinic acid was supplied by Johnson Matthey, Inc. Difluoroacetamide and triflamide were made from difluoroacetyl chloride and trifluoromethanesulfonic anhydride, respectively. Deuterated amides were synthesized by exchange with methyl alcohol-*d*. $Pt(C_2O_4)(PEt_3)_2$,[6] *trans*-$PtH(CH_3)(PEt_3)_2$,[11] $PdMe_2(PEt_3)_2$,[14] *cis*-$PtMe_2(PEt_3)_2$,[15] and $PtMe_2(COD)$[16] were synthesized according to literature procedures. All other starting materials were obtained from Aldrich. Microanalyses were carried out by Galbraith, Inc., Knoxville, TN, and Desert Analytics, Tucson, AZ. In many cases excess amide was difficult to remove and may account for small impurities in some samples. All NMR spectra were obtained on either a JEOL FX-90Q, Bruker WP-200, Bruker WP-270, Varian VXR-300S, or Bruker AM-360 spectrometer. ^{31}P, ^{19}F, and ^{15}N NMR chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 in C_6D_6, $CFCl_3$, and liquid ammonia, respectively. Values upfield of the standard are defined as negative. ^1H and ^{13}C chemical shifts are referenced with the residual solvent as internal standard. Irradiations were performed by using a Hanovia 450-W medium-pressure mercury arc lamp. Light output was filtered through a water-cooled quartz jacket to remove the IR radiation.

Synthesis of ^{15}N-Trifluoroacetamide. To a refluxing solution of 3 mL of distilled water and 0.95 g of NaOH (23.8 mmol) was added dropwise 0.50 g (9.3 mmol) of $^{15}NH_4Cl$ (99%) in 5 mL of water. $^{15}NH_3$ gas was immediately generated and passed out of the top of the relux condenser through a KOH drying tube and into a round-bottom flask fitted with a dry-ice cold finger at −78 °C containing 0.66 mL of trifluoroacetic anhydride (4.7 mmol) in 20 mL of diethyl ether. After 20 min the gas flow was stopped and the round-bottom flask warmed to room temperature. The ether was evaporated by passing a steady stream of N_2 into the solution, resulting in the isolation of a white solid. The labeled amide was removed from $(^{15}NH_4)(CF_3CO_2)$ by sublimation, yielding 0.25 g of $CF_3CO^{15}NH_2$ (46%). ^1H NMR (CD_3CN): δ 7.17 (d, J_{H-N} = 92 Hz, $^{15}NH_{anti}$, 1 H), 6.79 (dq, J_{H-N} = 91 Hz, J_{H-F} = 2 Hz, $^{15}NH_{syn}$, 1 H). ^{19}F NMR: δ −70.6 (s). ^{15}N NMR: δ 99.0 (t, J_{N-H} = 91 Hz).

Synthesis of ^{15}N-Triflamide. The same procedure as above was used, with trifluoromethanesulfonic anhydride as the starting material. Yield: 80%. ^1H NMR (CD_3CN): δ 6.61 (d, J_{H-N} = 89 Hz, 2 H).

Synthesis of $Pd(C_2O_4)(PEt_3)_2$. The following procedure is an adaptation of a literature procedure described by Trogler et al.[6] A mixture of 0.34 g of *cis*-$PdCl_2(PEt_3)_2$ (0.82 mmol) and 1.3 equiv of $Ag_2(C_2O_4)$ (0.21 g) in 20 mL of CH_2Cl_2 was refluxed for 1 h and then stirred for 18 h at room temperature. The solution was filtered and the CH_2Cl_2 removed in vacuo, resulting in a quantitative yield of product. ^1H NMR ($CDCl_3$): δ 2.0–1.8 (m, PCH_2, 12 H), 1.2–1.0 (m, PCH_2CH_3, 18 H). $^{31}P\{^1H\}$ NMR: δ 33.7 (s).

Synthesis of $Pd(C_2O_4)$(dcpe). The same procedure as above was used except the solution was stirred for 18 h at room temperature without reflux. Yield: 96%. ^1H NMR ($CDCl_3$): δ 2.4–2.2 (m, PCH_2, 4 H), 1.8–1.0 (br m, PC_6H_{11}, 44 H). $^{31}P\{^1H\}$ NMR: δ 94.0 (s).

Synthesis of $PdMe_2$(dcpe) (5). The following procedure is an adaptation of the procedure described by Calvin and Coates.[14] To a flask was added 0.55 g of $PdCl_2$(dcpe) in 20 mL of ether at −78 °C. Then, 3 equiv of ethereal 1.4 M MeLi was added. The solution was brought to room temperature and worked up by adding 5 mL of H_2O. The ether and aqueous layers were both filtered off, leaving a gray solid. The solid was washed with 2 × 5 mL portions of water and then dried in vacuo for 1 h at 60 °C. Yield: 0.47 g (90%). ^1H NMR (benzene-d_6): δ 2.3–1.9 (br m, PCH_2, 4 H), 1.8–1.0 (br m, PC_6H_{11}, 44 H), 0.95 (t, J_{H-P} = 6 Hz, Pd–C_{H3}, 3 H). $^{31}P\{^1H\}$ NMR: δ 56.9 (s).

Synthesis of $PdMe_2$(dmpe) (6).[17] The same procedure as above was used, except the product was recovered from the ether layer. Yield: 47%. ^1H NMR (CD_3CN): δ 1.7–1.5 (m, PCH_2, 4 H), 1.3–1.2 (m, PCH_3, 12 H), −0.14 ("t", J_{H-P} = 7 Hz, Pd–CH_3, 3 H). $^{31}P\{^1H\}$ NMR: δ 26.3 (s).

Formation of *trans*-$PtH(HNSO_2CF_3)(PEt_3)_2$ (1a). Method 1. A UV quartz cell containing 11.0 mg (0.02 mmol) of $Pt(C_2O_4)(PEt_3)_2$ (1), 1.0 equiv of triflamide (3.0 mg), and 0.9 mL of CD_3CN was irradiated for 45 min, turning from clear to light yellow. The solution was then filtered into an NMR tube. (Attempts to do this photolysis on a larger than NMR scale for purposes of product isolation resulted in the formation of impurities which could not be removed by recrystallization.) ^1H NMR (CD_3CN): δ 3.0 (br s, NH, 1 H), 1.9–1.7 (m, PCH_2CH_3, 12 H), 1.2–1.0 (m, PCH_2CH_3, 18 H), −19.0 (t, J_{H-P} = 15 Hz, J_{H-Pt} = 1127 Hz, Pt–H). $^{31}P\{^1H\}$ NMR: δ 27.2 (s). ^{19}F NMR: δ −70.5 (s). ^{15}N-**1a**: ^1H NMR δ 3.0 (d, J_{H-N} = 66 Hz), −19.0 (dt, J_{H-N} = 22 Hz, J_{H-P} = 15 Hz).

Formation of *trans*-$PtH(HNCOCF_3)(PEt_3)$ (1b). Method 1. The same photolysis procedure as above was used, with trifluoroacetamide as the starting material. ^1H NMR (CD_3CN): δ 5.2 (br s, NH, 1 H), 1.9–1.7 (m, PCH_2CH_3, 12 H), 1.2–1.0 (m, PCH_2CH_3, 18 H), −16.1 (t, J_{H-P} = 15 Hz, J_{H-Pt} = 975 Hz, Pt–H). $^{31}P\{^1H\}$ NMR: δ 27.3 (s, J_{P-Pt} = 2727 Hz). $^{31}P\{^1H$ off-resonance$\}$ NMR: δ 27.3 (d, J_{P-H} = 10 Hz). ^{19}F NMR: δ −68.4 (s). ^{15}N-**1b**: ^1H NMR: δ −16.1 (dt, J_{H-N} = 21 Hz, J_{H-P} = 15 Hz), 5.2 (br d, J_{H-N} = 60 Hz). $^{31}P\{^1H\}$ NMR: δ 27.3 (d, J_{P-N} = 2 Hz).

Formation of 1a. Method 2. To a flask containing 40.0 mg of *trans*-$PtHMe(PEt_3)_2$ (2; 0.09 mmol) in 5 mL of degassed benzene was added 2.0 equiv of triflamide (26.8 mg). The mixture was heated at 60 °C for 1 h. The solution was then filtered, and the light yellow filtrate was evaporated in vacuo and pumped on for 3 h at 60 °C to sublime away any excess amide, yielding at first an oil and then a pale yellow solid. Yield: 46 mg (90%). NMR data were identical with those of **1a** prepared by method 1. Anal. Calcd for $C_{13}H_{32}F_3NO_2P_2PtS$: C, 26.90; H, 5.56; N, 2.41. Found: C, 27.57; H, 5.51; N, 2.63.

Formation of 1b. Method 2. The same procedure as for **1a** (method 2) was used. Yield: 82%. NMR data were identical with those of **1b** prepared by method 1.

Photolysis of $Pd(C_2O_4)(PEt_3)_2$ with Triflamide. The same photolytic conditions as for **1a** (method 1) were employed, using a 2-fold excess of triflamide. ^1H NMR (CD_3CN): δ 3.2 (br s, NH, 2 H), 1.9–1.7 (m, PCH_2CH_3, 12 H), 1.2–1.0 (m, PCH_2CH_3, 18 H). $^{31}P\{^1H\}$ NMR δ 26.0 (s).

Formation of *trans*-$PdMe(HNSO_2CF_3)(PEt_3)_2$ (3a). To a flask containing 0.80 g of $PdMe_2(PEt_3)_2$ (10:1 cis/trans mixture; **3** ; 2.15 mmol) in 50 mL of benzene was added 0.38 g (1.2 equiv)

(17) This complex has previously been prepared by a different synthetic route: Tooze, R.; Chiu, K. W.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1025.

of triflamide. Gas immediately evolved from the solution. The mixture was stirred at room temperature for 20 min to ensure complete reaction. The solution was then filtered and the solvent removed in vacuo, resulting in a brown oil. The oil was redissolved in 50 mL of petroleum ether and filtered through decolorizing charcoal and Celite. The Celite and charcoal were washed with 2 × 25 mL portions of petroleum ether and the filtrates combined. The solvent was then removed in vacuo, resulting in a light yellow solid; mp 41 °C. Yield: 0.87 g (80%). ^{1}H NMR (benzene-d_6): δ 1.7 (br s, N*H*, 1 H), 1.5–1.4 (m, PCH_2CH$_3$, 12 H), 0.9–0.8 (m, PCH_2CH$_3$, 18 H), 0.1 (t, J_{H-P} = 6 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 16.0 (s). ^{15}*N*-**3a**: ^{1}H NMR: δ 1.7 (br d, J_{H-N} = 66. Hz). ^{13}C{^{1}H}: δ −9.4 (dt, J_{C-N} = 10 Hz, J_{C-P} = 4 Hz, Pd-*C*H$_3$).

Formation of *trans*-PdMe(HNCOCF$_3$)(PEt$_3$)$_2$ (3b). The same procedure as for **3a** was used, with trifluoroacetamide as the starting material. Yield: 72%. ^{1}H NMR (CD$_3$CN): δ 2.1 (br s, N*H*, 1 H), 1.6–1.4 (m, PCH_2CH$_3$, 12 H), 1.2–1.0 (m, PC-H_2CH_3, 18 H), −0.13 (t, J_{H-P} = 6 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 21.8 (s).

Formation of *trans*-PdMe(HNCOCF$_2$H)(PEt$_3$)$_2$ (3c). Into an NMR tube was placed 10.0 mg of **3** (0.027 mmol), 0.6 mL of benzene-d_6, and 1.5 equiv of difluoroacetamide (3.8 mg). Gas immediately evolved, and the NMR spectrum was then acquired. No attempt was made to isolate this compound. ^{1}H NMR (benzene-d_6): δ 4.0 (t, J_{H-F} = 51 Hz, *H*CF$_2$, 1 H), 2.3 (br s, N*H*, 1 H), 1.5–1.4 (m, PCH_2CH$_3$, 12 H), 0.9–0.8 (m, PCH$_2$CH_3, 18 H), 0.03 (t, J_{H-P} = 6 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 16.3 (s).

Formation of *trans*-PdMe(H^{15}NCOC$_6$H$_5$)(PEt$_3$)$_2$ (3d). The same procedure as for **3c** was used, with benzamide as the starting material, but the sample had to be heated at 60 °C for 2 h. ^{1}H NMR (benzene-d_6: δ 7.5–7.0 (m, C$_6H_5$CO, 5 H), 4.35 (d, J_{H-N} = 67 Hz, N*H*, 1 H), 1.5–1.4 (m, PCH_2CH$_3$, 12 H), 0.9–0.8 (m, PCH$_2$CH_3, 18 H), 0.1 (t, J_{H-P} = 6 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 16.7 (d, J_{P-N} = 3 Hz).

Formation of *trans*-PtMe(HNSO$_2$CF$_3$)(PEt$_3$)$_2$ (4a). To a flask containing 0.125 g of *cis*-PtMe$_2$(PEt$_3$)$_2$ (**4**; 0.27 mmol) and 15 mL of benzene was added 1.3 equiv of triflamide (54 mg). The solution was heated at 55 °C and monitored by ^{31}P{^{1}H} NMR spectroscopy. After 30 min, the solution contained a 3:1 cis/trans mixture of products. After an additional 3 h of heating, the solution contained 100% trans product. The solution was filtered and the benzene removed in vacuo, leaving a clear oil, which was then washed with 1 mL of diethyl ether and pumped on in vacuo for 3 h, resulting in a white solid. Yield: 0.10 g (62%). Anal. Calcd for C$_{14}$H$_{34}$F$_3$NO$_2$P$_2$PtS: C, 28.28; H, 5.76; N, 2.36. Found: C, 27.83; H, 5.87; N, 2.22. ^{1}H NMR (benzene-d_6): δ 1.97 (br s, N*H*, 1 H), 1.6–1.4 (m, PCH_2CH$_3$, 12 H), 1.0–0.8 (m, PCH$_2$CH_3, 18 H), 0.3 (t, J_{H-P} = 6.5 Hz, J_{H-Pt} = 75 Hz, Pt–CH_3, 3 H). ^{31}P{^{1}H} NMR: δ 15.7 (s, J_{P-Pt} = 2827 Hz). ^{15}*N*-**4a**: ^{1}H NMR δ 1.97 (br d, J_{H-N} = 72 Hz).

Formation of *trans*-PtMe(HNCOCF$_3$)(PEt$_3$)$_2$ (4b). The same procedure as for **4a** was used. Yield: 55%. ^{1}H NMR (benzene-d_6): δ 4.7 (br s, N*H*, 1 H), 1.6–1.4 (m, PCH_2CH$_3$, 12 H), 1.0–0.8 (m, PCH$_2$CH_3, 18 H), 0.3 (t, J_{H-P} = 6 Hz, J_{H-Pt} = 70 Hz, Pt–CH_3, 3 H). ^{31}P{^{1}H} NMR: δ 15.9 (s, J_{P-Pt} = 2811 Hz).

Formation of PdMe(HNSO$_2$CF$_3$)(dcpe) (5a). To a flask containing 350.0 mg of PdMe$_2$(dcpe) (**5**; 0.63 mmol) and 100 mL of benzene was added 1.6 equiv of triflamide (150.0 mg). Gas evolved immediately, and the solution was stirred at room temperature for 30 min to ensure complete reaction. After filtration, the solvent was removed in vacuo, leaving behind a light brown solid, which was pumped on for an additional 3 h at 50 °C to sublime excess amide. The solid was then redissolved in 100 mL of benzene and filtered through Celite to remove finely divided palladium metal. The Celite was washed with 2 × 30 mL portions of benzene, and the colorless benzene filtrates were combined. The benzene was then removed in vacuo, yielding a white solid. Yield: 140.0 mg (32%). Anal. Calcd for C$_{28}$H$_{52}$F$_3$NO$_2$P$_2$PdS: C, 48.57; H, 7.58; N, 2.02; Pd, 15.38. Found: C, 49.23; H, 7.19; N, 1.97; Pd, 14.67. ^{1}H NMR (benzene-d_6): δ 3.0 (br s, N*H*, 1 H), 2.25–2.45 (br m, PCH_2, 4 H), 1.9–0.85 (br m, PC$_6H_{11}$, 44 H), 0.49 (dd, $J_{H-P(trans)}$ = 7 Hz, $J_{H-P(cis)}$ = 3 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 73.8 (d, J_{P-P} = 19 Hz), 59.70 (d, J_{P-P} = 19 Hz). ^{19}F NMR: −76.6 (s). ^{15}*N*-**5a**: ^{1}H NMR δ 3.0 (d, J_{H-N} = 75 Hz), 0.5 (m, Pd–CH_3); ^{31}P{^{1}H} NMR 73.8 (dd, $J_{P-N(trans)}$ = 41 Hz, Hz, $J_{P-P(cis)}$ = 19 Hz), 59.7 (dd, $J_{P-P(cis)}$ = 19 Hz, $J_{P-N(cis)}$ = 3 Hz).

Formation of PdMe(HNCOCF$_3$)(dcpe) (5b). The same procedure as for **5a** was used, except only ∼50% reaction had occurred at room temperature (as monitored by NMR); therefore, the solution was heated at 55 °C for 2 H. Yield: 75%. ^{1}H NMR (benzene-d_6): δ 5.7 (s, N*H*, 1 H), 2.4–2.2 (br m, PCH_2, 4 H), 1.9–0.85 (m, PC$_6H_{11}$, 44 H), 0.56 (dd, $J_{H-P(trans)}$ = 7 Hz, $J_{H-P(cis)}$ = 3 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 71.0 (d, J_{P-P} = 18 Hz), 62.0 (d, J_{P-P} = 18 Hz). ^{19}F NMR: δ −81.0 (s). ^{15}*N*-**5b**: ^{1}H NMR δ 5.7 (d, J_{H-N} = 71 Hz), 0.56 (m); ^{31}P{^{1}H} NMR δ 71.0 (dd, $J_{P-N(trans)}$ = 46 Hz, $J_{P-P(cis)}$ = 18 Hz), 62.0 (dd, $J_{P-P(cis)}$ = 18 Hz, $J_{P-N(cis)}$ = 3 Hz).

Formation of PdMe(HNC$_6$H$_5$)(dcpe) (5c). The same procedure as for **5a** was used, except no reaction occurred at room temperature; therefore, the mixture was heated at 60 °C for 12 h, resulting in complete conversion to product. The compound was recrystallized from benzene/hexane. Yield: 65%. ^{1}H NMR (benzene-d_6): δ 7.5–7.0 (m, C$_6H_5$CO, 5 H), 5.9 (br s, N*H*, 1 H), 0.7 (dd, $J_{H-P(trans)}$ = 6 Hz, $J_{H-P(cis)}$ = 2 Hz, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 69.8 (d, J_{P-P} = 18 Hz), 63.0 (d, J_{P-P} = 18 Hz). ^{15}*N*-**5c**: ^{1}H NMR δ 5.88 (d, J_{H-N} = 69 Hz), 0.7 (m); ^{31}P{^{1}H} NMR δ 69.8 (dd, $J_{P-N(trans)}$ = 48 Hz, $J_{P-P(cis)}$ = 18 Hz), 63.0 (dd, $J_{P-P(cis)}$ = 18 Hz), 63.0 (dd, $J_{P-P(cis)}$ = 18 Hz, $J_{P-N(cis)}$ = 3 Hz).

Formation of PdMe(H^{15}NSO$_2$CF$_3$)(dmpe) (6a). This complex was prepared pure in solution in an NMR tube by reacting 8.0 mg of PdMe$_2$(dmpe) (**6**; 0.03 mmol) with 1.0 equiv of ^{15}*N*-trilamide (4.2 mg) in 0.6 mL of CD$_3$CN. Gas evolved as the amide was added, and NMR spectrosocpy at this juncture showed complete reaction. No attempt was made to isolate the compound on a larger scale. ^{1}H NMR (CD$_3$CN): δ 3.2 (d, J_{H-N} = 75 Hz), 2.0–1.5 (br m, PCH_2, 4 H), 1.53 and 1.45 (d, J_{H-P} = 10 Hz, PC*H*), 0.1 (br m, Pd–CH_3). ^{31}P{^{1}H} NMR: δ 44 (br m), 30.0 (br d, J_{P-P} = 23 Hz). ^{19}F NMR: δ −77.5 (s). *T* = −40 °C: ^{1}H NMR δ 0.05 (br ddd, $J_{H-P(trans)}$ = 8 Hz, $J_{H-P(cis)}$ = 3 Hz, J_{H-N} = 2 Hz); ^{31}P{^{1}H} NMR δ 45.0 (dd, $J_{P-N(trans)}$ = 48, $J_{P-P(cis)}$ = 24 Hz), 30.0 (d, $J_{P-P(cis)}$ = 24 Hz).

Formation of PtMe(HNSO$_2$CF$_3$)(COD) (7a). To a flask containing 80.0 mg of PtMe$_2$(COD) (**7**; 0.24 mmol) in 5 mL of chloroform was added an excess of triflamide (110 mg). The solution was then heated at 65 °C for 24 h. After filtration, the solvent was removed in vacuo and the resulting tan solid pumped on for 5 h at 50 °C to remove the excess amide by sublimation. Yield: 55 mg (49%). Anal. Calcd for C$_{10}$H$_{16}$F$_3$NO$_2$SPt: C, 25.75; H, 3.46; N, 3.00. Found: C, 26.37; H, 3.65; N, 2.41. ^{1}H NMR (CDCl$_3$): δ 5.95 (m, J_{H-Pt} = 34 Hz, C*H* cis to N, 2 H), 4.4 (m, J_{H-Pt} = 71 Hz, C*H* trans to N, 2 H), 4.2 (br s, N*H*, 1 H), 2.6–2.1 (m, CH_2, 8 H), 0.57 (s, J_{H-Pt} = 68 Hz, Pt–(CH_3). ^{15}*N*-**7a**: ^{1}H NMR δ 4.2 (d, J_{H-N} = 88 Hz), 0.56 (d, J_{H-N} = 2 Hz, J_{H-Pt} = 68 Hz).

Formation of PtMe(HNCOCF$_3$)(COD) (7b). The same procedure as for **7a** was used. Yield: 40%. ^{1}H NMR (CDCl$_3$): δ 6.28 (m, J_{H-Pt} = 37 Hz, C*H* cis to N, 2 H), 5.5 (br s, N*H*, 1 H), 4.5 (m, J_{H-Pt} = 63 Hz, C*H* trans to N, 2 H), 2.6–2.1 (m, CH_2, 8 H), 0.60 (s, J_{H-Pt} = 70.2 Hz, Pt–CH_3).

Acknowledgment. We gratefully acknowledge the support of this research by the NIH. We also wich to thank Isabel Treichel for the mass spectral analyses of isotopically labeled methane and Prof. Chuck Casey for stimulating discussions.

OM9106589