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Synthesis and Study of Heterobimetallic Complexes Supported by a Ferrocene-Based Bisphosphine−Diamine Ligand

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The difunctional bisphosphine−diamine ligand **1**, the racemate of (*S*)-*N*-[2-(dimethylamino)ethyl]-*N*-methyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine, has been used to prepare several novel heterobimetallic complexes for potential catalysis applications based on cooperative interactions between two reactive metal centers. The complexes were characterized by electron ionization mass spectrometry (ESI-MS) and multinuclear NMR spectroscopy. Specifically, ^{31}P NMR spectroscopy was used to characterize the binding modes of the ligand. The X-ray crystal structure of **10** (containing Pt and Cu) confirms a (P,P)-binding mode for Pd and an (N,N)-binding mode for Cu. The distance between Pt and Cu metal centers was 4.528(3) Å. Palladium complexes of **1** exist as an equilibrium mixture of isomers involving (P,P)- and (P,N)-coordination modes for palladium ($K_{eq} = 1.90$ at 22 °C; $\Delta H = -4.3(4)$ kcal/mol and $\Delta S = -13(1)$ eu). This isomerization process can be suppressed by the addition of $(Et_2O)MgBr_2$ to **1**, which forms the (N,N)-bound Mg complex **4**. This complex reacted with *trans*-$(PPh_3)_2PdBr_2$ to form the bimetallic complex **5**, in which Pd is (P,P)-bound.

Introduction

Recently, considerable interest has focused on the potential of heterobimetallic complexes to offer novel catalytic processes by way of dual activation of substrates.[1] Although several effective bimetallic catalysts are known for homogeneous systems, the two metals are typically not a part of the same complex and play separate, complementary roles.[2,3] In the case of the Wacker oxidation reaction, for example, the transformation of the olefin to the organic carbonyl product occurs at the palladium center, while the copper cocatalyst serves to mediate the oxidation of Pd(0) to the active Pd(II) species by molecular oxygen.[3] We are interested in developing a system in which the two metals, brought into close proximity by an appropriately selected ligand, act in a *cooperative* manner. The targeted catalysts are heterobimetallic complexes in which both metals are capable of activating small-molecule substrates. This mode of reactivity appears to be operative in metalloenzymes that utilize two or more different metals, such as nitrogenase or cytochrome *c* oxidase.[4] Indeed, the distinctive catalytic properties of these biological metal complexes emphasize the potential value of synthetic heterobimetallics.

Given these considerations, it seemed that complexes containing palladium and copper would represent ideal targets for synthesis and study. In monometallic systems, each of these metals has a rich, well-developed chemistry with small-molecule substrates. While palladium catalysts have found great utility in a variety of organic transformations involving olefins and other unsaturated organic molecules,[5] copper-containing complexes have been used extensively in biomimetic systems that activate dioxygen.[6] A properly designed complex incorporating both of these metals may make it possible to perform these activation processes in a cooperative fashion, leading to the discovery of novel oxidation processes. In addition, we sought to prepare Pt−Cu heterobimetallic complexes. Platinum generally forms stronger bonds with substrates than palladium, leading to a greater chance of isolating or at least observing putative intermediates in processes of interest.[7]

In designing the framework for preparing complexes with two different metal ions that would be sufficiently

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(1) (a) Wheatley, N.; Kalk, P. *Chem. Rev.* **1999,** *99*, 3379. (b) Severin, K. *Chem. Eur. J.* **2002**, *8*, 1515.

(2) See, for example: (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Shibasaki, M.; Boden, C. D. J.; Kojima, A. *Tetrahedron* **1997**, *53*, 7371.

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(6) For a recent review, see: Que, L. Tolman, W. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 1114.

(7) Cotton, F. A.; Wilkinson, J.; Murillo, C. A. *Advanced Inorganic Chemistry;* Wiley-VCH: Weinheim, Germany, 1999; p 1077.

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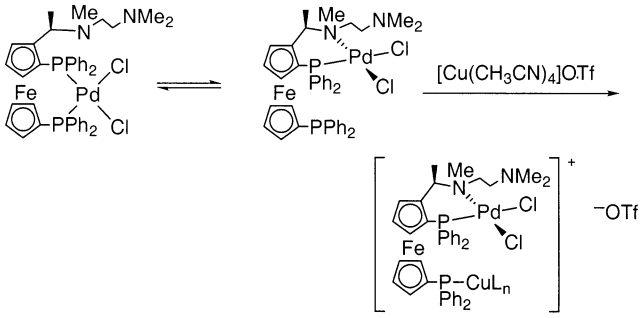
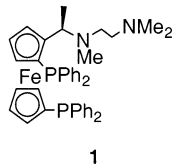
Scheme 1



close to ensure an interaction between coordinated substrates, our attention was drawn to Kumada's ferrocene-based ligand **1**.[8] This ligand has been used in



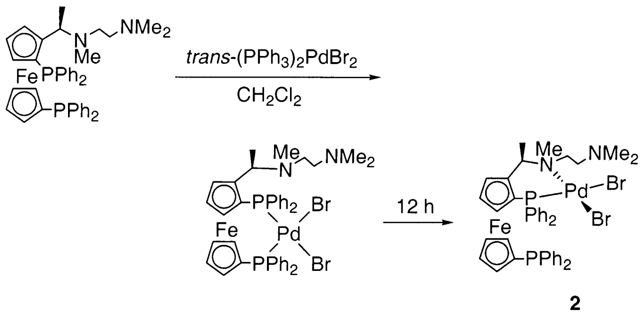
1

the gold-catalyzed asymmetric synthesis of oxazolidines, which involves complexation of Au(I) by the diphosphine moiety and binding of the substrate by the pendant diamine arm.[9] In addition, related ligand systems containing macrocyclic pendant groups have been proposed to serve as scaffolds for palladium−potassium bimetallic complexes, which were used as bifunctional catalysts for the enantioselective allylation of β-diketones and nitro-substituted carbonyl compounds.[10,11] We reasoned that bimetallic complexes supported by **1** might be readily synthesized in a stepwise fashion via the initial formation of a bisphosphine−Pd or −Pt complex and subsequent chelation of Cu(I) by the diamine moiety. Herein, we describe relevant aspects of the coordination chemistry of the bisphosphine−diamine ligand **1** and the preparation of heterobimetallic Pt−Cu complexes.

Results

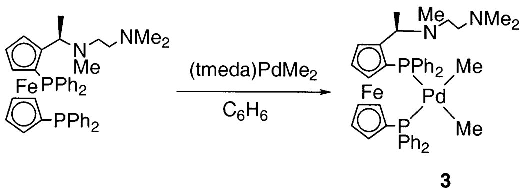
Pd(II) Complexes of 1. Ligand **1** was prepared as a racemic mixture from (±)-(α-(dimethylamino)ethyl)-ferrocene following the procedures of Kumada and coworkers, with minor modifications.[7] In reactions of **1** with various Pd(II) precursors such as *trans*-$(PPh_3)_2PdCl_2$, $(COD)PdCl_2$ (COD = cyclooctadiene), and *trans*-$(MeCN)_2PdCl_2$ in C_6D_6 or CD_2Cl_2, the desired (P,P)-Pd complex was observed as the initial product by ^{31}P NMR spectroscopy. However, over the course of approximately 30 h an equilibrium was established in which the (P,N) isomer was the major component (Scheme 1). To extract thermodynamic parameters for this process, the isomer-

Scheme 2



ization reaction was conducted in *o*-dichlorobenzene at 22, 30, 40, 50, and 62 °C, with *trans*-$(MeCN)_2PdCl_2$ as the source of Pd(II). To eliminate potential complications associated with free MeCN generated in the course of the reaction, equimolar amounts of **1** and *trans*-$(MeCN)_2PdCl_2$ were initially mixed in dichloromethane and all volatile species were immediately removed. The resulting residue was then redissolved in *o*-dichlorobenzene. The loss of MeCN was confirmed by ^{1}H NMR spectroscopy, and reaction progress was monitored by ^{31}P NMR spectroscopy. The (P,P) isomer gives rise to two downfield-shifted resonances that exhibit P−P coupling (26.26 and 35.02 ppm, $J_{P-P} = 14.2$ Hz), while the resonances for the (P,N) isomer show no P−P coupling and occur at −18.60 ppm (free phosphine) and 12.71 ppm (bound phosphine). From the measurements of equilibrium ratios of the (P,P) and (P,N) components at the indicated temperatures, the values $\Delta H = -4.3(4)$ kcal/mol and $\Delta S = -13(1)$ eu were obtained using the van't Hoff equation.

Conversion from the (P,P) to the (P,N) isomer was also observed in the reaction of **1** with *trans*-$(PPh_3)_2PdBr_2$ in CD_2Cl_2 (Scheme 2). In comparison to the reaction with the dichloride analogue, the isomerization was more rapid (12 h, as monitored by ^{31}P NMR spectroscopy) and proceeded to completion. The resulting complex **2**, isolated in 89% yield, features resonances at −20.02 ppm (free phosphine) and 13.74 ppm (bound phosphine) in its ^{31}P NMR spectrum. In contrast to the behavior observed with the dihalides, a reaction of **1** and $(tmeda)PdMe_2$ (tmeda = tetramethylethylenediamine) in C_6D_6 led to the quantitative formation of the (P,P) complex **3**, as judged by ^{31}P NMR spectroscopy (eq 1).



(1)

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No evidence of isomerization was observed in solution for several days, and **3** was isolated in 85% yield and fully characterized. The presence of resonances at 15.79 and 19.47 ppm ($J_{P-P} = 20.1$ Hz) in its ^{31}P NMR spectrum confirms bisphosphine ligation at Pd.

Bimetallic Pd−Cu and Pd−Mg Complexes of 1. To further understand the coordination chemistry of **1**, the effect of a Cu(I) additive on the (P,P)−(P,N) equilibrium was studied by ^{31}P NMR spectroscopy. Addition of $[Cu(CH_3CN)_4]OTf$ to the equilibrium mixture shown

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[8] Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, M.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

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[10] (a) Sawamura, M.; Nagata, H.; Sakamoto, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2586. (b) Sawamura, M.; Nakayama, Y.; Tang, W.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 9090.

[11] For related work, see: Landis, C. R.; Sawyer, R. A.; Somsook, E. *Organometallics* **2000**, *19*, 994 and references therein.

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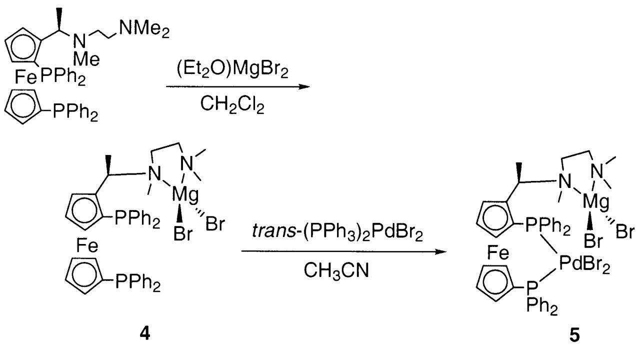
Scheme 3



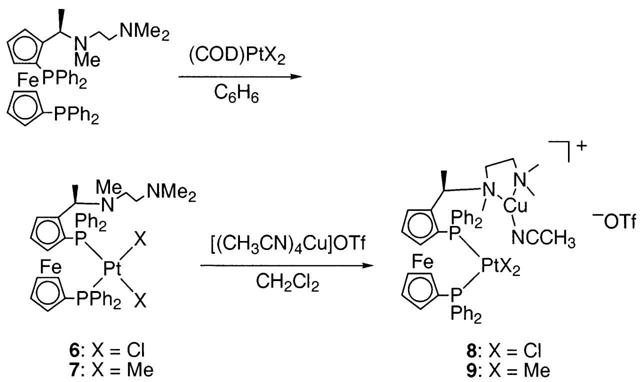
in Scheme 1 in CD_2Cl_2 solvent led to complete disappearance of the resonances associated with the (P,P)− and (P,N)−Pd isomers and the appearance of new resonances at −3.81 and 20.29 ppm, which exhibit no P−P coupling. No changes were observed by NMR spectroscopy when this mixture was heated at 45 °C. Moreover, the same resonances are seen if *trans*-$(MeCN)_2PdCl_2$ and $[Cu(CH_3CN)_4]OTf$ are simultaneously added to a CD_2Cl_2 solution of **1**. It is therefore proposed that Cu(I) induces a complete shift of the equilibrium to the (P,N) form by binding to the free phosphine of the (P,N)−Pd complex (Scheme 1).

Ligation of the diamine fragment of **1** by a different metal would represent a straightforward means of suppressing the (P,P)−(P,N) isomerization process observed in its reactions with Pd(II). It was thought that Mg(II), a hard metal ion, would bind preferentially to the diamine fragment, leaving the bisphosphine moiety available for complexing Pd. Indeed, reaction of **1** with $(Et_2O)MgBr_2$ in CH_2Cl_2 provided complex **4** in 92% yield (Scheme 3). Assignment of the structure of **4** is based on the downfield shifts of the ^{1}H NMR resonances for the NMe and NMe_2 groups relative to those of the free ligand. In the ^{1}H NMR spectrum of **1** taken in CD_2Cl_2, the NMe and NMe_2 resonances appear at 1.64 and 1.99 ppm, respectively, while in the ^{1}H NMR spectrum of complex **4** taken in the same solvent the corresponding resonances appear at 2.35 ppm (NMe) and 2.14 ppm (NMe_2).[12] In addition, the signals in the ^{31}P NMR spectrum of **4** (−28.90, −17.44 ppm) shift slightly relative to those of the free ligand (−23.32, −16.93 ppm), confirming the fact that the phosphines remain unbound in the Mg complex.

Bimetallic Pd−Mg complex **5** was prepared in 81% yield by a reaction of **4** with *trans*-$(PPh_3)_2PdBr_2$ in CH_2Cl_2 (Scheme 3). The use of a palladium dibromide starting material was crucial, as reactions of **4** with $(COD)PdCl_2$ or *trans*-$(PPh_3)_2PdCl_2$ led to the formation of several products, most likely resulting from halide redistribution. Bisphosphine ligation at Pd in complex **5** was confirmed by the presence of resonances at 27.12 and 35.56 ppm, which exhibit P−P coupling (J_{P-P} = 25.9 Hz), in its ^{31}P NMR spectrum.

Reactions of 1 with Pt(II) Complexes. In contrast to the behavior of Pd(II) dichloride precursors toward **1**, the binding of the $PtCl_2$ fragment by **1** occurs exclusively via the bisphosphine moiety to give complex

Scheme 4



6, which was isolated from a reaction of **1** with (COD)-$PtCl_2$ in benzene in 96% yield (Scheme 4). The ^{31}P NMR spectrum of **6**, which exhibits two signals at 9.50 and 16.25 ppm (J_{P-P} = 9.7 Hz) with coupling to Pt (J_{Pt-P} = 3726 and 3870 Hz, respectively), confirmed that both phosphorus atoms are bound to the platinum center. Similarly, the dimethyl analogue **7** was prepared in 95% yield by the reaction of **1** with $(COD)PtMe_2$ in benzene (Scheme 4). Bisphosphine ligation at Pt was again confirmed by ^{31}P NMR spectroscopy, with the signals appearing at 19.37 ppm (d, J_{P-P} = 13.0 Hz, J_{Pt-P} = 1828 Hz) and 25.86 ppm (d, J_{P-P} = 13.0 Hz, J_{Pt-P} = 1888 Hz). In addition, the ^{1}H NMR spectrum of **7** features two inequivalent methyl groups at 1.22 and 1.42 ppm, which appear as pseudotriplets due to coupling to the two phosphorus atoms (J_{P-H} = 8.8 and 8.6 Hz, respectively) and also exhibit coupling to Pt (J_{Pt-H} = 70.4 and 68.0 Hz, respectively).

Syntheses of Heterobimetallic Pt−Cu Complexes. A reaction of complex **6** with $[Cu(CH_3CN)_4]OTf$ in methylene chloride, followed by recrystallization of the crude product from acetone/diethyl ether, provides the desired bimetallic complex **8** as an analytically pure yellow powder in 76% yield (Scheme 4). Chelation of Cu(I) by the diamine functionality is confirmed by the changes in the chemical shifts of the methylene protons in the backbone of the diamine moiety of the ligand. In the ^{1}H NMR spectrum of the monometallic precursor **6**, these methylene protons appear as two complex multiplets at 2.17 and 2.73 ppm. In the bimetallic product, however, these signals are resolved into four complex multiplets (2.54, 2.66, 2.91, and 3.26 ppm) due to their proximity to the chiral nitrogen center. The overall downfield shift of these signals is also consistent with binding of a metal by the diamine.[13] In addition, characterization of **8** by electrospray ionization mass spectrometry (ESI-MS) indicated the presence of a molecular ion at *m*/*z* 1011, which corresponds to the mass of the bimetallic cation after the loss of 1 equiv of MeCN. Observed and simulated isotope patterns for this ion were identical.[14]

Bimetallic complex **9**, based on the dimethylplatinum fragment, was prepared in a manner similar to that

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(12) Similar changes were observed in (tmeda)$MgBr_2$ relative to free tmeda: Allan, J. F.; Clegg, W.; Henderson, K. W.; Horsburgh, L.; Kennedy, A. R. *J. Organomet. Chem.* **1998**, *559*, 173.

(13) Similar changes were observed in Cu(I)−diamine complexes reported by Stack and co-workers: (a) Mahadevan, V.; Hou, Z.; Cole, A. P.; Root, D. E.; Lal, T. K.; Solomon, E. I.; Stack, T. D. P. *J. Am. Chem. Soc.* **1997**, *119*, 11996. (b) Mahadevan, V.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. P. *J. Am. Chem. Soc.* **1999**, *121*, 5583.

(14) See the Supporting Information.

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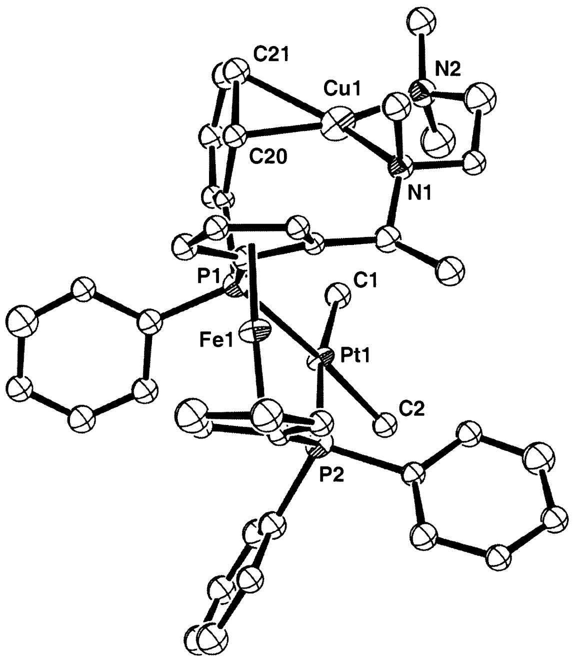


Figure 1. ORTEP diagram for the bimetallic cation of **10**. Hydrogen atoms were omitted for clarity.

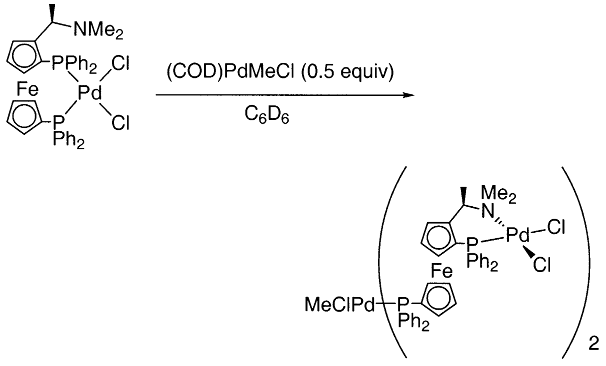
used to synthesize the dichloride analogue **8** (Scheme 4). The monometallic precursor **7** was reacted with $[Cu(CH_3CN)_4]OTf$ in methylene chloride, and analytically pure **9** was obtained in 73% yield after recrystallization of the crude product from acetonitrile/diethyl ether. This complex was characterized by ^1H and ^{31}P NMR spectroscopy, as well as by ESI-MS. The molecular ion peak at m/z 971 in its ESI-MS spectrum corresponds to the mass of the bimetallic cation after the loss of 1 equiv of MeCN, and the simulated pattern for this ion agrees with the observed pattern.

Heating complex **9** under vacuum at 40 °C leads to the loss of the MeCN molecule coordinated to the Cu center and formation of the new arene complex **10**, whose structure was confirmed by X-ray crystallography (Figure 1). Single crystals of **10** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution of the complex. The ORTEP diagram for the cation of **10** indicates the coordination of one of the phenyl rings on the "upper-ring" phosphine to the Cu center in an η^2 fashion. Difficulties with carrying out the absorption corrections for the crystal prevented anisotropic refinement of C and N atoms, resulting in a fairly high R value of 7.25 and preventing accurate determination of individual bond lengths and angles. Nevertheless, the structure is useful in that it provides information about the distance between Pt and Cu in this complex, which is found to be 4.528(3) Å.

Reactivity of Heterobimetallic Pt−Cu Complexes. Preliminary studies have been conducted in order to examine the feasibility of activating the Pt center in complexes **8** and **9** toward binding of organic substrates such as olefins. Attempts to abstract the chlorides in **8** with AgOTf in various solvents led to formation of intractable materials, likely resulting from oxidation of Cu(I) by the Ag(I) salt. The alkali-metal salts LiOTf and KOTf did not react with **8** under various conditions, while reactions of **8** with TlOTf and Me_3SiOTf in CD_3CN, CD_2Cl_2, and acetone-d_6 yielded mixtures of products. Attempts to substitute methyl groups in **9** by protonolysis with HOTf or CF_3COOH also led to intractable product mixtures. However, complex **9** reacted with 2 equiv of N,N-dimethyltoluidinium triflate in CD_2Cl_2 over the course of several days at 65 °C to give a mixture of three new products by ^{31}P NMR spectroscopy in an approximate ratio of 3:1:1, none of which contain Pt−Me groups, as judged by ^1H NMR spectroscopy.

Discussion

Chiral ferrocene-based ligands featuring the 1,2,1′-substitution pattern are used extensively in asymmetric catalysis.[9,10,15] In many applications, metal complexes of these ligands are formed in situ and are not isolated, with a few notable exceptions.[16,17] One example of a structurally characterized complex of a chiral ferrocene-based ligand involves Pd binding to (S,R)-N,N-dimethyl-1-(1′,2-bis(diphenylphosphino)ferrocenyl)ethylamine, which is closely related to the ligand used in this study.[16a] The crystal structure of this complex, which is formed in nearly quantitative yield using *trans*-$(MeCN)_2PdCl_2$ as the source of Pd(II), indicates bisphosphine ligation at Pd. It has recently been shown, however, that (P,P)−(P,N) isomerization in this complex can be induced by the addition of $^1/_2$ equiv of (COD)-PdMeCl, with the phosphine on the monosubstituted ring binding the added Pd (eq 2).[17] The authors argue that this observation indicates the presence of a small amount of a (P,N) isomer in equilibrium with the bisphosphine complex.



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The fact that, in the case of a ligand with a diamine substituent, isomerization occurs without additives suggests that a different mechanism is operative. At present, we believe that the (P,P)−(P,N) isomerization is initiated by the displacement of a chloride ion from Pd by the distal amine substituent, followed by a rearrangement in the coordination sphere of Pd and reassociation of the chloride ion (Scheme 5). Such a pathway is unavailable in the analogous complex with

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(15) For a general reference, see: *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995.

(16) (a) Hayashi, T.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Organomet. Chem.* **1987**, *334*, 195. (b) Togni, A.; Pastor, S. D.; Rihs, G. *J. Organomet. Chem.* **1990**, *381*, C21. (c) Blumer, R. E.; Lianza, F.; Pregosin, P. S.; Rüegger, H.; Togni, A. *Inorg. Chem.* **1993**, *32*, 2663.

(17) Manzano, B. R.; Jalon, F. A.; Gomez-de la Torre, F.; Lopez-Agenjo, A. M.; Rodriguez, A. M.; Mereiter, K.; Weissensteiner, W.; Sturm, T. *Organometallics* **2002**, *21*, 789.

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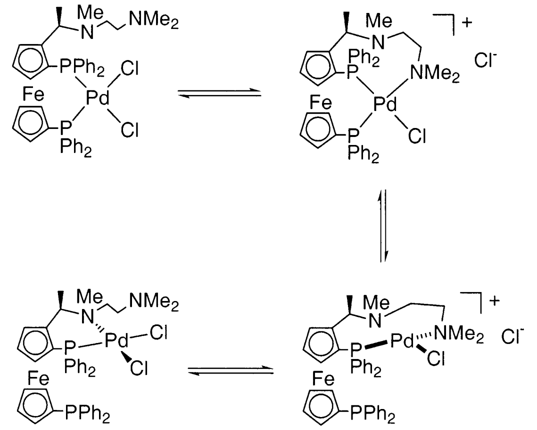
Scheme 5



a pendant monoamine, since association of the nitrogen to the Pd center in this case would lead to a highly strained intermediate. Increase in the rate of isomerization observed when a $PdBr_2$ source is used instead of $PdCl_2$ can then be explained by the greater lability of the Pd−Br bond. Moreover, we have been able to show that the dimethyl complex **3** is bisphosphine-bound and does not isomerize, suggesting that labile ligands on the Pd center are necessary for the (P,P)−(P,N) conversion. It is also possible, however, that the softer character of the $PdMe_2$ fragment leads to a thermodynamic preference for its ligation by the bisphosphine fragment.

Effects of Cu(I) and Mg(II) on the interaction of ligand **1** with Pd(II) provide further insight into its coordination chemistry. Cu(I) affects the (P,P)−(P,N) equilibrium in this system in a manner similar to that observed by Weissensteiner et al. for the reaction shown in eq 2.[16] In both cases, the exogenous ion drives the (P,P)−(P,N) equilibrium exclusively to the (P,N) form, while itself being bound by the remaining phosphine (Scheme 1). With Mg(II), an (N,N) complex of ligand **1** is selectively formed. This allows for the preparation of Pd−Mg heterobimetallic complex **5**, in which Pd is bound by the bisphosphine moiety.

Under the conditions in which (P,P)−(P,N) isomerization of a Pd adduct of **1** has been shown to occur, the analogous bisphosphine adduct of Pt, complex **6**, is formed exclusively and does not isomerize. The difference in reactivity between Pd and Pt can be explained with simple hard−soft acid−base theory arguments.[18] Pt(II), which is softer than Pd(II), prefers the softer (P,P) ligation, while Pd(II) prefers the somewhat harder (P,N) ligation. Incidentally, Mg(II), which is the hardest of the three ions, exhibits the hardest binding mode, (N,N).

The selective formation of bisphosphine-bound Pt complexes of **1** enabled successful preparation of heterobimetallic Pt−Cu complexes **8** and **9** by the addition of a Cu(I) salt to the monometallic precursors. Removal of coordinated MeCN in **9** leads to the formation of the η^2-arene complex **10**, whose structure was determined by X-ray crystallography. Interconversion between a MeCN adduct and an intramolecular η^2-arene complex of Cu(I) has recently been documented by Osako et al., who have utilized a bis(pyridylamine) ligand with a pendant phenyl group.[19]

The information on the distance and spatial orientation of the two metal centers in complex **10** provides a useful insight about the possibility of cooperative interactions between the two metal centers. In Collman's synthetic analogues of the Fe_{a3}/Cu_B center of cytochrome *c* oxidase (C*c*O), which performs the reduction of dioxygen, the separation between the metal centers is calculated by molecular modeling studies to be in the range of 4.5−5.5 Å.[20] Given the conformational flexibility of the diamine moiety in our bimetallic complexes, the crystallographically determined distance of about 4.53 Å between Pt and Cu probably indicates the lower limit for the metal−metal separation. The similarity in distances between the reactive metal centers in the structural analogues of C*c*O and the bimetallic cation **10** suggests that our complex may also engage in cooperative bimetallic reactivity. Investigations of the catalytic activities of such complexes will be aided by molecular modeling studies, which should reveal the possible combinations of substrates that may be activated by Pt and Cu.

Conclusion

In the context of our attempts to prepare heterobimetallic Pd−Cu and Pt−Cu complexes of the tetradentate bisphosphine−diamine ligand **1**, significant differences in reactivity between Pd and Pt were discovered. While the kinetically formed bisphosphine−Pd adduct was shown to isomerize to the more stable (P,N) product in various solvents, the analogous bisphosphine−Pt complex does not isomerize. The selective formation of this complex allowed the preparation of heterobimetallic Pt−Cu complexes containing the bisphosphine-bound $PtCl_2$ fragment. The analogous Pt−Cu bimetallic complex with the $PtMe_2$ fragment was also prepared. These complexes represent rare examples of Pt−Cu heterobimetallics in which Pt and Cu are not halide-bridged and may possess unique reactivity properties involving small-molecule activation by the two metal centers.[21]

Experimental Section

General Procedures. All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox unless otherwise noted. Dry, oxygen-free solvents were used throughout. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and saturated $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4 Å molecular sieves, and distilled over potassium benzophenone ketyl under a nitrogen atmosphere. Thiophene impurities were removed from benzene by treatment with H_2SO_4 and saturated $NaHCO_3$. Benzene was then dried over $MgSO_4$ and distilled from potassium metal under

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a nitrogen atmosphere. Reagent-grade acetone was vacuum-transferred from $CaSO_4$ and stored over activated 4 Å molecular sieves. Acetonitrile was distilled from CaH_2. Spectrophotometric grade diethyl ether was distilled over sodium benzophenone ketyl under a nitrogen atmosphere. Benzene-d_6 was purified and dried by vacuum distillation from sodium/potassium alloy. Methylene chloride-d_2 was dried by vacuum distillation from CaH_2.

NMR spectra were recorded using a Bruker DRX-500 spectrometer operating at 500.12 MHz (^1H), 125.77 MHz (^{13}C), and 202.45 MHz (^{31}P). ^1H NMR and ^{13}C NMR spectra were referenced internally by the residual solvent signal relative to tetramethylsilane. $^{31}P\{^1H\}$ spectra were referenced relative to 85% H_3PO_4 external standard. All spectra were recorded at room temperature unless otherwise noted. FT-infrared spectra were recorded as KBr pellets using a Mattson FTIR 3000 spectrometer at a resolution of 4 cm^{-1}. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. ESI-MS spectra were recorded on a Micromass BioQ/Quattro triple-quadrupole instrument equipped with an electrospray ionization source.

All chemicals were purchased from Aldrich or Strem Chemicals and used without further purification. The racemate of ligand **1**,[7] (COD)$PtCl_2$,[22] (COD)$PtMe_2$,[22] (COD)$PdCl_2$,[23] (tmeda)$PdMe_2$,[24] and $[Cu(CH_3CN)_4]OTf$[25] were prepared as reported in the literature.

Procedure for the Determination of Equilibrium Ratios of (P,P)- and (P,N)$PdCl_2$. To a vial containing 0.0181 g (0.0266 mmol) of **1** and 0.0069 g (0.0266 mmol) of $(MeCN)_2PdCl_2$ was added 0.5 mL of CH_2Cl_2. After the solids were dissolved, an immediate color change to red was observed. The volatiles were removed in vacuo, and the resulting solid was then redissolved in *o*-$C_6H_4Cl_2$ for a total solution volume of 0.5 mL. The solution was transferred to a J-Young tube and placed into an NMR probe preheated to the desired temperature. The isomerization reaction was monitored by ^{31}P NMR spectroscopy until the ratios of the two isomers remained constant over the course of 2 h.

(P,N)$PdBr_2$ (2). To a solution of 0.093 g (0.118 mmol) of *trans*-$(PPh_3)_2PdBr_2$ in 3 mL of CH_2Cl_2 was added **1** (0.080 g, 0.117 mmol) as a solid. The reaction mixture was stirred for 12 h, filtered, concentrated to 1 mL, and treated with 5 mL of pentane, leading to the precipitation of **2** as a red solid. The solvent was removed by decantation, and the solid was washed with benzene (2 × 3 mL) and dried in vacuo (0.099 g, 89%). ^1H NMR (CD_2Cl_2): δ 1.45 (d, 3H, $^2J = 5.5$ Hz, Cp CMe), 2.35 (s, 3H, NMe), 2.61 (m, 2H, NCH_2CH_2N), 2.69 (s, 3H, NMe), 3.04 (m, 1H, NCH_2CH_2N), 3.17 (m, 1H, NCH_2CH_2N), 3.20 (s, 3H, NMe), 3.66 (s, 1H, Cp H), 4.12 (s, 1H, Cp H), 4.19 (s, 1H, Cp H), 4.31 (s, 1H, Cp H), 4.36 (s, 1H, Cp H), 4.48 (s, 1H, Cp H), 4.50 (s, 1H, Cp H), 6.98 (q, 1H, $^2J = 5.5$ Hz, Cp CH), 7.22−8.28 (m, 20H, Ph). IR (cm^{-1}): 2917, 1642, 1434, 1107, 743, 692. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −20.02, 13.74. Anal. Calcd for $C_{41}H_{44}N_2Br_2FeP_2Pd$: C, 51.90; H, 4.67; N, 2.95. Found: C, 52.26; H, 4.72; N, 3.34.

(P,P)$PdMe_2$ (3). To a solution of 0.080 g (0.317 mmol) of (tmeda)$PdMe_2$ in 4 mL of C_6H_6 was added 0.220 g (0.322 mmol) of **1** as a solid. The resulting orange-brown solution was stirred for 12 h. Then, the reaction volume was concentrated to 1 mL and the reaction mixture was treated with 10 mL of pentane, leading to the precipitation of **3** as an orange-brown powder. The supernatant was removed by decantation, and the solid was washed with pentane (2 × 2 mL) and dried in vacuo (0.225 g, 85%). ^1H NMR (C_6D_6): δ 1.16 (t, 3H, $J_{P-H} = 7.0$ Hz, Pd−Me), 1.25 (t, 3H, $J_{P-H} = 7.5$ Hz, Pd−Me), 1.38 (d, 3H, $^2J = 6.5$ Hz, Cp CMe), 2.25 (s, 6H, NMe_2), 2.33 (m, 2H, NCH_2CH_2N), 2.40 (s, 3H, NMe), 3.04 (m, 2H, NCH_2CH_2N), 3.47 (s, 1H, Cp H), 3.68 (s, 1H, Cp H), 3.73 (s, 1H, Cp H), 3.78 (s, 1H, Cp H), 3.93 (s, 1H, Cp H), 4.24 (s, 1H, Cp H), 4.27 (s, 1H, Cp H), 5.95 (q, 1H, $^2J = 6.5$ Hz, Cp CH), 6.87−8.28 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 15.79 (d, $J_{P-P} = 20.1$ Hz), 19.47 (d, $J_{P-P} = 20.1$ Hz). IR (cm^{-1}): 2940, 1641, 1434, 1093, 1027, 775, 697. Anal. Calcd for $C_{43}H_{50}N_2FeP_2Pd$: C, 63.05; H, 6.15; N, 3.42. Found: C, 63.13; H, 6.33; N, 3.15.

(N,N)$MgBr_2$ (4). To a stirred suspension of 0.028 g (0.108 mmol) of $(Et_2O)MgBr_2$ in 3 mL of CH_2Cl_2 was added 0.075 g (0.110 mmol) of **1** as a solid. Stirring was continued for 8 h, and the reaction mixture was then filtered, concentrated to 1 mL, and treated with 10 mL of pentane, leading to the precipitation of **4** as a yellow powder. The supernatant was removed by decantation, and the solid was washed with pentane (2 × 2 mL) and dried in vacuo (0.088 g, 92%). ^1H NMR (C_6D_6): δ 1.81 (d, 3H, $^2J = 6.5$ Hz, Cp CMe), 1.95 (m, 2H, NCH_2CH_2N), 1.97 (s, 6H, NMe_2), 2.11 (s, 3H, NMe), 2.50 (m, 2H, NCH_2CH_2N), 3.40 (s, 1H, Cp H), 3.63 (s, 1H, Cp H), 3.72 (s, 1H, Cp H), 4.05 (s, 1H, Cp H), 4.17 (s, 1H, Cp H), 4.26 (s, 1H, Cp H), 4.38 (s, 1H, Cp H), 4.39 (s, 1H, Cp H), 5.05 (q, 1H, $^2J = 6.5$ Hz, Cp CH), 7.04−7.68 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −30.07, −19.05. IR (cm^{-1}): 2366, 1654, 1437, 164, 1091, 818, 753, 694, 543. Anal. Calcd for $C_{43}H_{50}N_2Br_2FeMgP_2$: C, 56.81; H, 5.12; N, 3.23. Found: C, 56.68; H, 5.48; N, 3.10.

(P,P)$PdBr_2$(N,N)$MgBr_2$ (5). To a solution of **4** (0.127 g, 0.146 mmol) in 3 mL of CH_2Cl_2 was added *trans*-$(PPh_3)_2PdBr_2$ (0.116 g, 0.146 mmol) as a solid. After it was stirred for 2 days, the mixture was filtered and the resulting solution was treated with 10 mL of pentane, leading to the precipitation of **5** as a red solid. The solvent was removed by decantation, and the solid was washed with benzene (2 × 5 mL) and dried in vacuo (0.134 g, 81%). ^1H NMR (CD_2Cl_2): δ 1.53 (d, 3H, $^2J = 6.4$ Hz, Cp CMe), 2.22 (s, 3H, NMe), 2.55 (s, 3H, NMe), 2.79 (m, 1H, NCH_2CH_2N), 2.87 (s, 3H, NMe), 3.19 (m, 2H, NCH_2CH_2N), 3.35 (s, 1H, Cp H), 3.42 (s, 1H, Cp H), 3.62 (m, 1H, NCH_2CH_2N), 4.21 (s, 2H, Cp H), 4.32 (s, 1H, Cp H), 4.76 (s, 1H, Cp H), 4.43 (s, 1H, Cp H), 4.64 (s, 1H, Cp H), 5.95 (q, 1H, $^2J = 6.8$ Hz, Cp CH), 7.02−8.39 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 27.06 (d, $J_{P-P} = 27.5$ Hz), 35.46 (d, $J_{P-P} = 27.5$ Hz). IR (cm^{-1}): 1653, 1476, 1352, 1096, 748, 695. Anal. Calcd for $C_{41}H_{44}N_2Br_4FeMgP_2Pd$: C, 43.48; H, 3.91; N, 2.47. Found: C, 43.51; H, 4.07; N, 2.28. ESI-MS: *m*/*z* 1053.

(P,P)$PtCl_2$ (6). To a stirred suspension of 0.200 g (0.530 mmol) of (COD)$PtCl_2$ in 10 mL of C_6H_6 was added **1** (0.370 mg, 0.540 mmol) as a solid. The resulting yellow slurry was stirred at room temperature for 3 h. Then, the reaction volume was reduced to 3 mL and the reaction mixture was treated with 20 mL of pentane. The supernatant was removed by decantation, and the solid was washed with pentane (2 × 5 mL) and dried in vacuo, yielding pure **6** as a yellow powder (0.494 g, 96%). ^1H NMR (CD_2Cl_2): δ 1.37 (d, 3H, $^2J = 6.8$ Hz, Cp CMe), 2.14 (s, 3H, NMe), 2.17 (m, 2H, NCH_2CH_2N), 2.27 (s, 6H, NMe_2), 2.73 (m, 2H, NCH_2CH_2N), 3.42 (s, 1H, Cp H), 3.49 (s, 1H, Cp H), 4.14 (s, 1H, Cp H), 4.16 (s, 1H, Cp H), 4.26 (s, 1H, Cp H), 4.43 (s, 1H, Cp H), 4.64 (s, 1H, Cp H), 5.82 (q, 1H, $^2J = 6.8$ Hz, Cp CH), 7.05−8.31 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 9.50 (d, $J_{P-P} = 9.7$ Hz, $J_{Pt-P} = 3726$ Hz), 16.25 (d, $J_{P-P} = 9.7$ Hz, $J_{Pt-P} = 3870$ Hz). IR (cm^{-1}): 2936, 1436, 1094, 747, 695. Anal. Calcd for $C_{41}H_{44}N_2Cl_2FeP_2Pt$: C, 51.91; H, 4.67; N, 2.95. Found: C, 51.62; H, 4.86; N, 2.57.

(P,P)$PtMe_2$ (7). To a solution of 0.080 g (0.240 mmol) of (COD)$PtMe_2$ in 5 mL of C_6H_6 was added **1** (0.164 g, 0.240 mmol) as a solid. The resulting brown solution was stirred for 12 h. Then, the reaction volume was reduced to 1 mL and the reaction mixture was treated with 10 mL of pentane, leading to the precipitation of **7** as a brown powder. The solvent was removed by decantation, and the solid was washed with pentane (2 × 3 mL) and dried in vacuo (0.207 g, 95%). ^1H NMR

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(C_6D_6): δ 1.22 (t, 3H, J_{P-H} = 8.8 Hz, J_{Pt-H} = 70.4 Hz, Pt−Me), 1.30 (d, 3H, ^2J = 6.4 Hz, Cp CMe), 1.42 (t, 3H, J_{P-H} = 8.6 Hz, J_{Pt-H} = 68.0 Hz, Pt−Me), 2.16 (s, 6H, NMe_2), 2.24 (m, 1H, NCH_2CH_2N), 2.33 (s, 3H, NMe), 2.39 (m, 1H, NCH_2CH_2N), 2.93 (m, 2H, NCH_2CH_2N), 3.36 (s, 1H, Cp H), 3.52 (s, 1H, Cp H), 3.65 (s, 1H, Cp H), 3.66 (s, 1H, Cp H), 3.76 (s, 1H, Cp H), 4.12 (s, 1H, Cp H), 4.16 (s, 1H, Cp H), 6.24 (q, 1H, ^2J = 6.4 Hz, Cp CH), 6.76−8.21 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 19.37 (d, J_{P-P} = 13.0 Hz, J_{Pt-P} = 1828 Hz), 25.86 (d, J_{P-P} = 13.0 Hz, J_{Pt-P} = 1888 Hz). IR (cm^{-1}): 2927, 1435, 1095, 744, 697. Anal. Calcd for $C_{43}H_{50}N_2FeP_2Pt$: C, 56.89; H, 5.55; N, 3.09. Found: C, 56.86; H, 5.24; N, 2.74.

[(P,P)PtCl$_2$(N,N)Cu(CH$_3$CN)]OTf (8). To a solution of **6** (0.200 g, 0.211 mmol) in 4 mL of CH_2Cl_2 was added [Cu(CH_3CN)$_4$]OTf (0.080 g, 0.212 mmol) as a solid. The cloudy reaction mixture was stirred for 15 min and filtered, and the solvent was evaporated. The resulting residue was redissolved in 2 mL of acetone, and the resulting solution was treated with 15 mL of diethyl ether, leading to the precipitation of a yellow powder. The solvent was removed by decantation, and the resulting solid was washed with diethyl ether (2 × 5 mL) and dried in vacuo (0.193 g, 76%). ^1H NMR (CD_2Cl_2): δ 1.77 (d, 3H, ^2J = 6.4 Hz, Cp CMe), 2.07 (s, 3H, coordinated MeCN), 2.13 (s, 6H, NMe_2), 2.22 (s, 3H, NMe), 2.54 (m, 1H, NCH_2CH_2N), 2.66 (m, 1H, NCH_2CH_2N), 2.91 (m, 1H, NCH_2CH_2N), 3.26 (m, 1H, NCH_2CH_2N), 3.67 (s, 1H, Cp H), 3.74 (s, 1H, Cp H), 4.33 (s, 1H, Cp H), 4.36 (s, 1H, Cp H), 4.56 (s, 1H, Cp H), 4.61 (s, 1H, Cp H), 4.99 (s, 1H, Cp H), 6.68 (q, 1H, ^2J = 6.4 Hz, Cp CH), 7.03−8.29 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 10.14 (d, J_{P-P} = 8.4 Hz, J_{Pt-P} = 4052 Hz), 17.62 (d, J_{P-P} = 8.4 Hz, J_{Pt-P} = 4174 Hz). IR (cm^{-1}): 2280, 1479, 1436, 1279, 1168, 1093, 1031, 751, 697, 638. Anal. Calcd for $C_{44}H_{47}N_3Cl_2CuF_3FeO_3P_2PtS$: C, 43.96; H, 3.94; N, 3.51. Found: C, 43.78; H, 3.70; N, 3.12. ESI-MS: *m/z* 1011.

[(P,P)PtMe$_2$(N,N)Cu(CH$_3$CN)]OTf (9). To a solution of **7** (0.120 g, 0.132 mmol) in 3 mL of CH_2Cl_2 was added [Cu(CH_3CN)$_4$]OTf (0.050 g, 0.133 mmol) as a solid. The cloudy reaction mixture was stirred for 15 min and then filtered, and the solvent was evaporated. The resulting residue was redissolved in 2 mL of acetonitrile, and the resulting solution was treated with 20 mL of diethyl ether, leading to the precipitation of an orange-brown powder. The solvent was removed by decantation, and the resulting solid was washed with diethyl ether (2 × 5 mL) and dried in vacuo (0.112 g, 76%). ^1H NMR (CD_2Cl_2): δ 0.63 (t, 3H, J_{P-H} = 8.0 Hz, J_{Pt-H} = 67.2 Hz, Pt−Me), 0.85 (t, 3H, J_{P-H} = 8.6 Hz, J_{Pt-H} = 67.2 Hz, Pt−Me), 1.21 (d, 3H, ^2J = 6.0 Hz, Cp CMe), 2.07 (s, 3H, coordinated MeCN), 2.10 (m, 1H, NCH_2CH_2N), 2.13 (s, 6H, NMe_2), 2.21 (m, 1H, NCH_2CH_2N), 2.31 (s, 3H, NMe), 2.48 (m, 1H, NCH_2CH_2N), 2.69 (m, 1H, NCH_2CH_2N), 3.66 (s, 1H, Cp H), 3.95 (s, 1H, Cp H), 4.15 (s, 1H, Cp H), 4.31 (s, 1H, Cp H), 4.40 (s, 1H, Cp H), 4.41 (s, 1H, Cp H), 4.64 (s, 1H, Cp H), 5.75 (q, 1H, ^2J = 6.4 Hz, Cp CH), 7.15−7.83 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.03 (d, J_{P-P} = 14.2 Hz, J_{Pt-P} = 1959 Hz, broad), 21.31 (d, J_{P-P} = 13.4 Hz, J_{Pt-P} = 2114 Hz). IR (cm^{-1}): 2267, 1437, 1267, 1160, 1096, 1030, 752, 697, 638. Anal. Calcd for $C_{46}H_{53}N_3CuF_3FeO_3P_2PtS$: C, 47.57; H, 4.60; N, 3.61. Found: C, 47.73; H, 4.56; N, 3.30. ESI-MS: *m/z* 971.

[(P,P)PtMe$_2$(N,N)Cu]OTf (10). A 0.050 g (0.043 mmol) sample of **9** was heated to 40 °C and exposed to vacuum for 16 h, yielding **10** (0.047 g, 97%) as an orange-brown powder. ^1H NMR (CD_2Cl_2): δ 0.52 (t, 3H, J_{P-H} = 8.0 Hz, J_{Pt-H} = 76.4 Hz, Pt−Me), 0.61 (t, 3H, J_{P-H} = 7.6 Hz, J_{Pt-H} = 83.2 Hz, Pt−Me), 1.27 (d, 3H, ^2J = 6.0 Hz, Cp CMe), 2.17 (s, 3H, NMe), 2.22 (s, 6H, NMe_2), 2.31 (m, 2H, NCH_2CH_2N), 2.66 (m, 2H, NCH_2CH_2N), 3.44 (s, 1H, Cp H), 3.65 (s, 1H, Cp H), 4.01 (s, 1H, Cp H), 4.12 (s, 1H, Cp H), 4.21 (s, 1H, Cp H), 4.22 (s, 1H, Cp H), 4.52 (s, 1H, Cp H), 5.83 (q, 1H, ^2J = 6.04 Hz, Cp CH), 7.04−7.95 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.97 (d, J_{P-P} = 14.2 Hz, J_{Pt-P} = 1908 Hz), 24.89 (d, J_{P-P} = 17.4 Hz, J_{Pt-P} = 1966 Hz, broad). IR (cm^{-1}): 1472, 1436, 1267, 1093, 1031, 751, 698, 637. Anal. Calcd for $C_{44}H_{50}N_2CuF_3FeO_3P_2PtS$: C, 47.17; H, 4.50; N, 2.50. Found: C, 46.99; H, 4.53; N, 2.24.

Table 1. Crystal Data and Structure Refinement for Compound 10

formula	$C_{44}H_{50}N_2CuF_3FeO_3P_2PtS$
fw	1120.34
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.935(1)
b, Å	14.020(2)
c, Å	15.432(2)
α, deg	85.079(2)
β, deg	85.860(2)
γ, deg	76.096(2)
V, Å^3	2075.8(4)
Z	2
D_{calcd}, g/cm^3	1.79
T, °C	−110
F(000)	1116
cryst dimens, mm	0.30 × 0.17 × 0.02
μ(Mo Kα), cm^{-1}	43.9
2θ_{max}, deg	49.8
no. of rflns measd	10 754
no. of unique rflns	6680
no. of rflns obsd	3476 ($I > 3.0\sigma(I)$)
no. of variables	298
R	0.072
R_w	0.084
GOF	1.34

X-ray Crystallography. The single-crystal X-ray analysis of compound **10** was carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker SMART CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. Structures were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the teXsan crystallographic software package. Details of the data collection and refinement are given in Table 1.

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Supporting Information Available: A van't Hoff plot for the equilibrium constant determination and tables giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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