Synthesis and Characterization of Chiral Platinum(II) Sulfonamides: (dppe)Pt(NN) and (dppe)Pt(NO) Complexes

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Received November 6, 1998

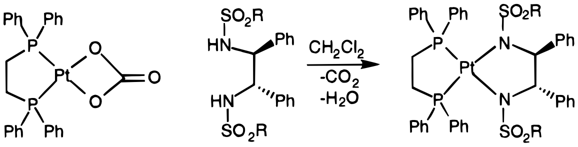
Reaction of (dppe)Pt(CO_3) with (1*S*,2*S*)-HN(R)CHPhCHPhNH(R) (R = SO_2CF_3, **1a**; SO_2-4-^{t}BuC_6H_4, **1b**) and (1*S*,2*R*)-HN(R)CHPhCHPhOH (R = SO_2CF_3, **3a**; SO_2-4-^{t}BuC_6H_4, **3b**) leads to well-behaved chiral (dppe)Pt[N(R)CHPhCHPhN(R)] (R = SO_2CF_3, **2a**; SO_2-4-^{t}BuC_6H_4, **2b**) and (dppe)Pt[N(R)CHPhCHPhO] (R = SO_2CF_3, **4a**; SO_2-4-^{t}BuC_6H_4, **4b**) complexes. X-ray structural analysis of **2a** and **4b** reveal that the Pt−N bond lengths are long with the triflamide bond lengths being slightly longer than the aryl sulfonamide bond lengths (~2.12 and 2.06 Å, respectively). Solid-state (X-ray) and solution (^{1}H NMR) structural analysis indicates that the phenyl groups α to the sulfonamide nitrogen adopt an axial conformation, as characteristic $^3J_{Pt-H}$ coupling constants are observed for equatorial, but not axially disposed hydrogens in the heterocycle. Relative binding affinities of **1a/b** and **3a/b** to the (dppe)Pt fragment were determined through pairwise ligand exchange reactions: Tf > SO_2Ar and NN > NO.

Introduction

In the context of a broader program aimed at developing transition metal catalysts whose selectivity has a controllable outer-sphere component, our laboratory has recently become interested in exploring the interaction of chiral ligands across the square plane of d^8 metal complexes.[1,2] As part of these efforts, we report the synthesis and characterization of several chiral platinum(II) diamine and amino alcohol complexes wherein the amine ligand is fitted with a sulfonamide electron withdrawing group. These compounds represent a relatively rare class of chiral late metal hard−soft mismatched complexes.[3−5]

Results and Discussion

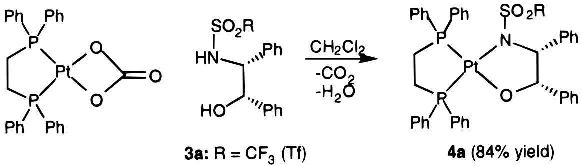
The desired air and water stable Pt complexes were prepared in good yields (55−85%) from the versatile dppePt(CO_3) precursor by the method of Andrews (eqs 1 and 2).[6,7] In the case of the triflamide ligands (**1a**/**3a**), reactions were generally complete in 12 h at room temperature, however, the less acidic sulfonamide ligands (**1b**/**3b**) took several days to go to completion.



(1)

1a: R = CF_3 (Tf)
1b: R = 4-C_6H_4-C(CH_3)$_3$

2a (73% yield)
2b (55% yield)



(2)

3a: R = CF_3 (Tf)
3b: R = 4-C_6H_4-C(CH_3)$_3$

4a (84% yield)
4b (85% yield)

To determine the effect of the chiral ligands (one symmetric and the other asymmetric) on the solid state conformation of the diphosphine ligands, compounds **2a** and **4b** were subjected to X-ray crystallographic analysis. Suitable white crystals were grown at room temperature from a saturated CH_2Cl_2 solution with slow diffusion of diethyl ether. ORTEP representations of these structures are shown in Figures 1 and 2, along with selected bond lengths and angles. A comparison of the Pt−N bond lengths in **2a** and **4b** reveal that the triflamide bond lengths are each ~0.07 Å longer than the aryl sulfonamide lengths, presumably reflecting the poorer donor properties of the CF_3-substituted ligand. The Pt−N bond lengths are unsurprisingly on the long side of characterized Pt-amides,[8−13] and, moreover, show only a slight distortion from planarity at the nitrogen center (Σ bond angles are 358.1 and 358.4° for **2a** and 358.6° for **4b**).

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(1) Brunkan, N. M.; White, P. S.; Gagné, M. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1579−1582.

(2) Brunkan, N. M.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 11002−11003.

(3) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188.

(4) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1−40.

(5) (a) For an example of Zn-sulfonamides, see: Denmark, S. E.; O'Connor, S. P.; Wilson, S. R.; *Angew. Chem., Int. Ed.* **1998**, *37*, 1149−1151. (b) For an example of a Cu-bissulfonamide, see: Nanthakumar, A.; Miura, J.; Diltz, S.; Lee, C.-K.; Aguirre, G.; Ortega, F.; Ziller, J. W.; Walsh, P. J. *Inorg. Chem.*, in press. We thank Prof. Walsh for communication prior to publication.

(6) Andrews, M. A.; Gould, G. L.; Klooster, W. T.; Koenig, K. S.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5478−5483.

(7) Andrews, M. A.; Voss, E. J.; Gould, G. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 5730−5740.

(8) Chan, D.; Cronin, L.; Duckett, S. B.; Hupfield, P.; Perutz, R. N. *New J. Chem.* **1998**, 511−516.

(9) Deacon, G. B.; Gathouse, B. M.; Ireland, J. *Aust. J. Chem.* **1991**, *44*, 1669−1681.

(10) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750−4761.

(11) Parkin, I. P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 58−59.

(12) Roundhill, D. M.; Park, S.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3972−3974.

(13) Ittel, S. D.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 2290−2295.

10.1021/ic981287s CCC: $18.00

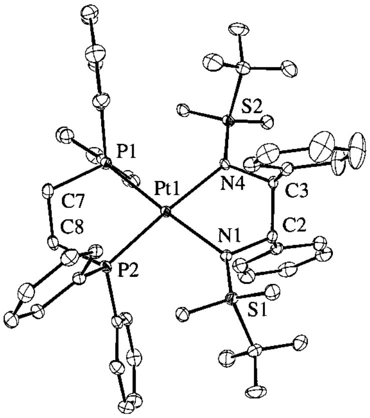

Figure 1. ORTEP representation of **2a**. Selected bond distances (Å) and bond angles (deg): Pt1−P1 = 2.2581(8), Pt1−P2 = 2.2620(8), Pt1−N1 = 2.1186(23), Pt1−N4 = 2.1251(24), P1−Pt1−P2 = 84.38(3), N1−Pt1−N4 = 78.39(10), P1−Pt−N4 = 98.82(7), P2−Pt−N1 = 98.35(8).

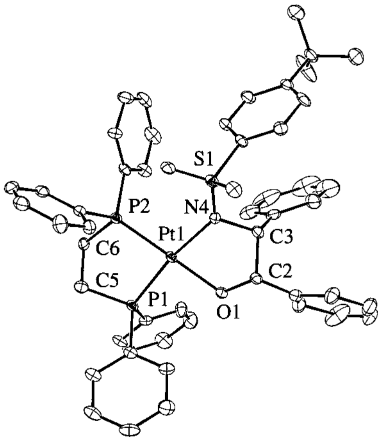

Figure 2. ORTEP representation of **4b**. Selected bond distances (Å) and bond angles (deg): Pt1−P1 = 2.2277(18), Pt1−P2 = 2.2355(14), Pt1−N4 = 2.062(6), Pt1−O1 = 2.038(4), P1−Pt1−P2 = 85.62(10), O1−Pt1−N4 = 81.5(3), P1−Pt1−O1 = 90.46(20), P2−Pt1−N4 = 102.85(18).

The Pt−O bond length in **4b** is also similar to previously reported chelating Pt-diolate structures.[7] The larger size of the sulfonamide nitrogen versus alkoxide group is also apparent in the cisoid P−Pt−(O/N) bond angles. In **2a** the P−Pt−N angles are reasonably symmetric (98.82(7) and 98.35(8)°) while in **4b** the P−Pt−N and P−Pt−O bond angles are 102.85(18) and 90.46(20)°, respectively, and reflect the closer approach of the alkoxide oxygen to the phosphine.

More interesting in these structures is the conformation of the substituents on the diamine and amino alcohol backbone. In particular, the phenyl rings in **2a** are diaxially disposed, while in **4b**, the phenyl rings α to nitrogen and oxygen are axial and equatorial, respectively. This unusual axial preference may reflect unfavorable interactions of the phenyl ring with the SO_2R group when in the equatorial position, the latter group tending to orient the SO_2 portion trans to the α substituent.

An additional peculiarity of **4b** is the close contact between a C−H group on the sulfonamide aromatic and one of the dppe phenyl rings. The ortho C−H···centroid distance of 2.43 Å (θ = 164°), represents a significant interaction[14,15] that distorts the relative orientation of the two phenyl groups attached to P2 (Figure 2). It is this combination of interactions and the steric bulk of the SO_2 portion of the ligand that forces the dppe ligand to adopt the λ conformation. The latter interaction is doubled in **2a** and since the C2/C3 centers have the opposite absolute stereochemistry as C3 in **4b**, they enforce a δ conformation in the dppe backbone.

The ^{31}P NMR data of these complexes are diagnostic of ligand symmetry as compounds **2a** and **2b** give rise to singlets at 38.8 ($J_{\mathrm{Pt-P}}$ = 3614 Hz) and 38.5 ($J_{\mathrm{Pt-P}}$ = 3520 Hz) ppm, respectively. The unsymmetrical compounds **4a** and **4b**, on the other hand, give two sets of doublets at 36.6 ($J_{\mathrm{Pt-P}}$ = 3703 Hz) and 34.5 ($J_{\mathrm{Pt-P}}$ = 3197 Hz) ppm for **4a**, and 36.1 ($J_{\mathrm{Pt-P}}$ = 3512 Hz) and 34.1 ($J_{\mathrm{Pt-P}}$ = 3244 Hz) ppm for **4b**. On the basis of the $J_{\mathrm{Pt-P}}$ coupling constant similarities, the downfield resonances are assigned to the phosphine trans to nitrogen.[16−19] Triflamide groups tend to impart the highest $J_{\mathrm{Pt-P}}$ (3600−3700 Hz), with aryl sulfonamides (~3500 Hz) and alkoxides (3200−3250 Hz) inducing smaller values in this series of chelating complexes.

Additional data that can be ascribed to conformational effects is found in the ^{1}H NMR of these complexes, as unusual $^{3}J_{\mathrm{Pt-H}}$ coupling to the backbone CHs are observed. For **2a**/**b**, the backbone hydrogens appear as a doublet ($^{4}J_{\mathrm{P-H}}$ = 4.3 (**2a**), 5.6 Hz (**2b**)) with broadened Pt-satellites (30.8 (**2a**), 35.8 Hz (**2b**)). As expected for **4a**/**b**, two mutually coupled doublets are observed (^{31}P decoupled); however, only the upfield CH resonance that is α to nitrogen displays Pt-satellites. It has been observed that Karplus-type relationships correlating the conformation of a β-CH with $^{3}J_{\mathrm{Pt-H}}$ exists in five- and six-membered platinum-containing chelates.[20−25] In general, equatorial hydrogens have greater three-bond coupling than axial hydrogens. In compounds **2a**/**b** Pt coupling is observed for the single CH resonance, suggesting that in solution both hydrogens are in the equatorial position or at least are able to achieve this conformation a reasonable fraction of the time. Consistent with this observation is the solid-state structure of **2a** wherein both backbone hydrogens are equatorial (Pt−N−C−H = 159.3 and 150.5°). A similar analysis for **4a**/**b**, suggests that since the carbinol hydrogen is not coupled to ^{195}Pt, the phenyl group must be equatorially disposed, as seen in the crystal structure of **4b** (Pt−N−C−H = 149.4°; Pt−O−C−H = 81.5°). NMR evidence therefore supports the notion that the solid-state structures of **2a** and **4b** actually represent reasonable solution structures as well.

The relative binding affinities of **1a**/**b** and **3a**/**b** to Pt were determined through a variety of pairwise ligand exchange reactions (40 °C), e.g. eq 3. Equilibration kinetics depended on the identities of the partners, but generally reflected the acidity of the nitrogen ligand (Tf > SO_2Ar), with NO ligands being

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(14) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669−2672.

(15) Steiner, T.; Starikov, E. B.; Amado, A. M.; Teixeira-Dias, J. J. C. *J. Chem. Soc., Perkins Trans. 2* **1995**, 1321−1326 and references therein.

(16) Schaad, D. R.; Landis, C. R. *Organometallics* **1992**, *11*, 2024−2029.

(17) Cenini, S.; Porta, F.; Pizzotti, M. *J. Organomet. Chem.* **1985**, *296*, 291−300.

(18) Parkin, I. P.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1990**, 519−523.

(19) Consistent with this assignment, (dppe)Pt(stilbenediolate) displays a singlet at 29.0 ppm ($J_{\mathrm{Pt-P}}$ = 3329 Hz). Becker, J. J.; Brunkan, N. M.; Gagné, M. R. Unpublished results.

(20) Cerasino, L.; Williams, K. M.; Intini, F. P.; Cini, R.; Marzilli, L. G.; Natile, G. *Inorg. Chem.* **1997**, *36*, 6070−6079.

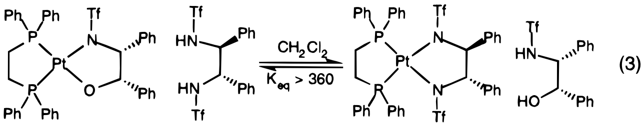
(21) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1971**, *10*, 1717−1725.

(22) Erickson, L. E.; McDonald, J. W.; Howie, J. K.; Clow, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 6371−6382.

(23) Sarneski, J. E.; Erickson, L. E.; Reilley, C. N. *Inorg. Chem.* **1981**, *20*, 2137−2146.

(24) Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007−3017.

(25) Yano, S.; Tukada, K.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1978**, *17*, 2520−2526.



4a **1a** **2a** **3a**

faster than NN. Monitoring the ratio of products by ^{31}P NMR to equilibrium, afforded information about the relative binding strengths of **1a**/**b** and **3a**/**b** to the (dppe)Pt fragment. When **1a** and **4a** were allowed to equilibrate in CH$_2$Cl$_2$ the diamine complex was clearly favored ($K_{eq} > 360$).[26] Similarly, when **1b** and **4b** were reacted the diamine was favored with a $K_{eq} > 360$. The combinations of **1a** and **2b**, and **3a** and **4b** led to product distributions that reflected the enhanced stability of triflamide complexes ($K_{eq} > 360$).[27] We reason that the better the ability of the substituent to stabilize the basic nature of the Pt-heteroatom, the more stable the complex (i.e. NTf > NSO$_2$-Ar > OR).

In summary, we have described the synthesis and structure of two classes of chiral PtNN and PtNO complexes. The amine ligands in these complexes adopt unique conformations wherein the phenyl group α to nitrogen is axially oriented. This stereogenic center also appears to control the λ/δ conformation of the dppe ligand.

Experimental Details

General. Starting materials (cod)PtCl$_2$, (dppe)PtCl$_2$, (dppe)PtCO$_3$, **1a**/**b**, and **3a**/**b** were prepared according to literature protocols.[6,28−31] ^{1}H and ^{13}C NMR spectra were recorded in CD$_2$Cl$_2$ at ambient temperature on a Bruker AMX 400 spectrometer. ^{31}P spectra were recorded on a Varian Gemini 2000 spectrometer (300 MHz, ^{1}H) with 85% H$_3$PO$_4$ as an external reference. Optical rotation measurements were obtained on a Jasco DIP-1000 digital polarimeter. Elemental Analyses were performed by E+R Microanalytical Laboratory, Inc. (Parsippany, NJ).

Crystallography. Crystals of **2a** and **4b** suitable for X-ray crystallography were grown at room temperature from a saturated CH$_2$Cl$_2$ solution with slow diffusion of diethyl ether. Single crystals were mounted in oil on the end of a fiber. Intensity data were collected on a Siemens SMART diffractometer with CCD detection using Mo Kα radiation of wavelength 0.710 73 Å (ω scan mode). The structure was solved by direct methods and refined by least squares techniques on F using structure solution programs from the NARCVAX System.[32] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C−H = 0.96 Å) and allowed to ride on the atoms to which they were bonded. Crystal data, data collection, and refinement parameters are listed in Table 1.

Table 1. Crystallographic Data for **2a** and **4b**

	2a·CH$_2$Cl$_2$	**4b**·(C$_2$H$_5$)$_2$O
empirical formula	PtP$_2$S$_2$C$_{43}$H$_{38}$F$_6$N$_2$O$_4$Cl$_2$	PtP$_2$SC$_{50}$H$_{49}$O$_3$N·(C$_2$H$_5$)$_2$O
fw	1152.83	1065.07
space group	$P2_12_12_1$	$P2_1$
a, Å	13.5266(8)	8.9041(6)
b, Å	14.9709(9)	19.6838(12)
c, Å	21.9952(13)	14.3184(9)
β, deg	−	106.523(1)
V, Å^3	4454.1(5)	2405.9(3)
Z	4	2
T, °C	−100	−100
D_c, g/cm^3	1.719	1.470
λ, Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	3.49	3.06
R_f[a]	0.029	0.034
R_w[b]	0.025	0.036

[a] $R_f = \Sigma(F_o - F_c)/\Sigma F_o$. [b] $R_w = [\Sigma\omega(F_o - F_c)^2/\Sigma\omega F_o^2]^{1/2}$.

(dppe)Pt[N(Tf)CHPhCHPhN(Tf)] (2a). To a solution of (dppe)PtCO$_3$ (300 mg, 0.46 mmol) in 10 mL of CH$_2$Cl$_2$ was added 219 mg (0.46 mmol) of **1a**. The reaction was stirred at room-temperature open to the atmosphere to allow CO$_2$ escape. By ^{31}P NMR the reaction was complete after 8 h. The solvent was evaporated in vacuo, and the white solid recrystallized from CH$_2$Cl$_2$/Et$_2$O, yielding 387 mg of **2a** (73%). ^{31}P NMR (121.5 MHz, CD$_2$Cl$_2$): δ 38.8 ($^1J_{P-Pt} = 3614$ Hz). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.19 (br s, 4H, Ar), 7.71 (m, 14 H, Ar), 7.48 (m, 10 H, Ar), 7.36 (m, 2 H, Ar), 4.93 (d, $^4J_{P-H} = 4.3$ Hz, (s with ^{31}P decoupling), $^3J_{Pt-H} = 30.8$ Hz, 2 H, CH), 2.16 (m, 2 H, CH$_2$), 1.55 (br s, 2 H, CH$_2$). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 141.7, 135.4, 133.0, 132.5, 131.9, 129.9, 129.0 (t, $J = 5.8$ Hz), 128.8 (t, $J = 6.0$ Hz), 128.2, 127.9, 127.7, 127.5 (Ar), 119.8 (q, $^1J_{C-F} = 327$ Hz, CF$_3$), 74.2 (CH), 32.7 (CH$_2$).[33] $[\alpha]_D^{25.2} = -20.1$ ($c = 1.002$ in CH$_2$Cl$_2$). Anal. Calcd for C$_{42}$H$_{36}$F$_6$N$_2$O$_4$P$_2$S$_2$Pt·CH$_2$Cl$_2$: C, 44.80; H, 3.32; N, 2.43. Found: C, 44.79; H, 3.43; N, 2.37.

(dppe)Pt[N(SO$_2$-4-^{t}BuC$_6$H$_4$)CHPhCHPhN(SO$_2$-4-^{t}BuC$_6$H$_4$)] (2b). To a solution of (dppe)PtCO$_3$ (236 mg, 0.36 mmol) in 10 mL of CH$_2$Cl$_2$ was added 219 mg (0.36 mmol) of **1b**. The reaction was stirred at 40 °C open to the atmosphere to allow CO$_2$ escape. By ^{31}P NMR the reaction was complete after 44 h. The solvent was evaporated in vacuo, and after several recrystallizations (CH$_2$Cl$_2$/Et$_2$O), 232 mg of white crystals of **2b** were obtained (55% yield). ^{31}P NMR (121.5 MHz, CD$_2$Cl$_2$): δ 38.5 (s, $^1J_{P-Pt} = 3520$ Hz). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.33 (m, 4H, Ar), 7.99 (m, 4H, Ar), 7.63 (m, 6H, Ar), 7.51 (m, 6H, Ar), 7.43 (m, 4 H, Ar), 7.10 (m, 6 H, Ar), 6.75 (d, $J = 8.5$ Hz, 4 H, Ar), 6.51 (d, $J = 8.5$ Hz, 4 H, Ar), 4.81 (d, $^4J_{P-H} = 5.6$ Hz, (s with ^{31}P decoupling), $^3J_{Pt-H} = 35.8$ Hz, 2 H, CH), 2.21 (m, 2 H, CH$_2$), 1.58 (m, 2 H, CH$_2$), 1.16 (s, 18 H, CH$_3$). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 153.0, 143.5, 138.5, 137.0, 136.7, 135.2 (t, $J = 5.3$ Hz), 133.2 (t, $J = 5.3$ Hz), 131.7, 131.0, 130.6, 129.9, 128.9, 128.6 (t, $J = 5.8$ Hz), 128.3 (t, $J = 6.0$ Hz), 128.0, 127.2, 127.1, 126.5, 126.3, 124.6 (Ar), 73.7 (CH), 34.7 (C(CH$_3$)), 33.3 (CH$_2$), 31.2 (C(CH$_3$)).[33] $[\alpha]_D^{24.4} = -15.3$ ($c = 1.004$ in CH$_2$Cl$_2$). Anal. Calcd for C$_{60}$H$_{62}$N$_2$O$_4$P$_2$S$_2$Pt: C, 60.24; H, 5.22; N, 2.34. Found: C, 60.47; H, 5.22; N, 2.21.

(dppe)Pt[N(Tf)CHPhCHPhO] (4a). To a solution of (dppe)PtCO$_3$ (301 mg, 0.46 mmol) in 10 mL of CH$_2$Cl$_2$ was added 159 mg (0.46 mmol) of **3a**. The reaction was stirred at room temperature open to the atmosphere to allow CO$_2$ escape. By ^{31}P NMR the reaction was complete after 4 h. The solvent was evaporated in vacuo, and the yellow solid recrystallized from CH$_2$Cl$_2$/Et$_2$O, yielding 362 mg of **4a** (84%). ^{31}P NMR (121.5 MHz, CD$_2$Cl$_2$): δ 36.6 (br s, $^1J_{P-Pt} = 3703$ Hz), 34.5 (d, $J_{P-P} = 12.5$ Hz, $^1J_{P-Pt} = 3197$ Hz). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.15 (m, 2H, Ar), 8.00 (m, 2H, Ar), 7.89 (m, 2H, Ar), 7.78 (m, 2H, Ar), 7.48 (m, 14 H, Ar), 7.05 (m, 8 H, Ar), 5.71 (d, $J = 4.2$ Hz, 1 H, CH), 4.70 (br s, (d, $J = 4.2$ Hz with ^{31}P decoupling), $^3J_{Pt-H} = 38.1$, 1 H, CH), 2.49 (m, 2 H, CH$_2$), 2.23 (m, 1 H, CH**H**), 1.92 (m, 1 H, C**H**H). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 144.6 (d, $J = 6.1$ Hz), 140.4, 134.9, 134.1 (d, $J = 10.3$ Hz), 133.6 (d, $J = 10.9$ Hz), 133.4 (d, $J = 11.1$ Hz), 132.3 (d, $J = 2.4$ Hz), 131.9, 131.6 (d, $J = 2.3$ Hz), 130.0, 129.5, 129.4, 129.3 (d, $J = 11.1$ Hz), 129.2, 128.7 (d, $J = 11.4$ Hz), 128.5, 128.3, 128.0, 127.8, 127.6, 127.0, 126.6, 126.3 (Ar), 121.3 (q, $^1J_{C-F} = 327$ Hz, CF$_3$), 89.6, 73.3 (CH), 33.9, 25.7 (CH$_2$).[33] $[\alpha]_D^{26.2} = -39.8$ ($c = 1.016$ in CH$_2$Cl$_2$). Anal. Calcd for C$_{41}$H$_{36}$F$_3$NO$_3$P$_2$SPt: C, 52.57; H, 3.87; N, 1.50. Found: C, 52.47; H, 3.92; N, 1.43.

(dppe)Pt[N(SO$_2$-4-^{t}BuC$_6$H$_4$)CHPhCHPhO] (4b). To a solution of (dppe)PtCO$_3$ (299 mg, 0.46 mmol) in 10 mL of CH$_2$Cl$_2$ was added 187 mg (0.46 mmol) of **3b**. The reaction was stirred at room-

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(26) Since **4a** was unobservable in the ^{31}P NMR, and we conservatively assume that a relative concentration of 5% would be detectable, this places a lower limit on the equilibrium constant at 360.

(27) In all cases the reverse experiments (e.g. **2a** + **3a**) did not lead to any detectable (<5%) quantities of the thermodynamically disfavored complex.

(28) Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta* **1977**, *24*, 277−280.

(29) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521−6527.

(30) Pikul, S.; Corey, E. J. *Org. Synth.* **1992**, *71*, 30−37.

(31) Li, G.; Chang, H.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 451−454.

(32) Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384−387.

(33) Not all aromatic carbons were observed in the ^{13}C NMR spectra.

temperature open to the atmosphere to allow CO_2 escape. By ^{31}P NMR the reaction was complete after 26 h. The solvent was evaporated in vacuo, and the white solid recrystallized from CH_2Cl_2/Et_2O, yielding 436 mg of **4d** (85%). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 36.1 (d, $J_{P-P} = 12.5$ Hz, $^1J_{P-Pt} = 3512$ Hz), 34.1 (d, $J_{P-P} = 12.5$ Hz, $^1J_{P-Pt} = 3244$ Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.26 (m, 2H, Ar), 8.00 (m, 4H, Ar), 7.88 (m, 2H, Ar), 7.46 (m, 12 H, Ar), 7.16 (d, $J = 7.1$ Hz, 2 H, Ar), 6.91 (m, 12 H, Ar), 5.59 (d, $J = 4.5$ Hz, 1 H, CH), 4.27 (m, (d, $J = 4.5$ Hz with ^{31}P decoupling), $^3J_{Pt-H} = 32.9$ Hz, 1 H, CH), 2.57 (m, 2 H, CH_2), 2.15 (m, 1 H, CH**H**), 1.81 (m, 1 H, C**H**H), 1.20 (s, 9 H, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 153.5, 135.3 (d, $J = 11.5$), 134.1 (d, $J = 11.1$), 133.6 (d, $J = 11.2$ Hz), 133.2 (d, $J = 10.8$ Hz), 131.9 (d, $J = 2.2$ Hz), 131.8 (d, $J = 2.4$ Hz), 131.5 (d, $J = 1.9$ Hz), 131.1 (d, $J = 2.6$ Hz), 130.6, 130.5, 130.0, 129.9, 129.6, 129.4, 129.3 (d, $J = 8.1$ Hz), 129.2 (d, $J = 7.8$ Hz), 129.0, 128.9, 128.6, 128.5 (d, $J = 8.0$ Hz), 128.4 (d, $J = 8.3$ Hz), 127.6, 127.3, 127.1, 126.4, 125.8, 125.7, 124.8, (Ar), 90.5, 72.4 (CH), 34.9 ($C(CH_3)_3$), 34.5 (CH_2), 31.3 ($C(CH_3)_3$), 25.6 (CH_2).[33] $[\alpha]_D^{24.9} = -82.4$ ($c = 1.014$ in CH_2Cl_2). Anal. Calcd for $C_{50}H_{49}NO_3P_2SPt\cdot(C_4H_{10}O)\cdot0.5(CH_2Cl_2)$: C, 58.57; H, 5.41; N, 1.25. Found: C, 58.25; H, 5.20; N, 1.25.

Typical Equilibration Experiment. To a solution of **4a** (22.8 mg, 24.3 μmol) in 0.5 mL of CD_2Cl_2 was added **1a** (11.6 mg, 24.3 μmol). The NMR tube was sealed and was allowed to equilibrate at 40 °C. Periodic monitoring by ^{31}P NMR over the course of days indicated that **4a** slowly disappeared while **2a** appeared. After 21 days, **4a** could no longer be detected in the mixture.

Acknowledgment. This work was partially supported by the NSF, under the auspices of a CAREER Development Award to M.R.G. (CHE-9624852), the Petroleum Research Fund, administered by the ACS, and the DuPont Company for a Grant in Aid.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **2a** and **4b** are available free of charge via the Internet at http://pubs.acs.org.

IC981287S