Protonolysis of Cationic Pt−C Bonds with Mild Acids: Can Ligand Torsional Effects Speed Associative Processes?

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Received December 14, 2005

Summary: Tridentate phosphine pincer ligands facilitate the protonolysis of cationic Pt−CH_3 compounds (to Pt dications and CH_4) with the ammonium acid $Ph_2NH_2{\cdot}BF_4$. Large rate enhancements over nonpincer analogues (>50 000) are observed. A mechanism is proposed wherein ring strain present in the planar ground-state arrangement of three phosphine ligands is released in putative five-coordinate intermediates and transition states.

The goal of selectively functionalizing alkane C−H bonds continues to drive efforts to understand the coordination behavior of alkanes, especially in the context of the Shilov oxidation. To this end, Pt−alkane adducts have been generated and studied by the protonation of Pt−alkyl complexes. General observations are that neutral Pt(II) alkyls are relatively easy to protonolyze[1] but cationic complexes are much more resistant,[2,3] so much so that some are stable to superacid conditions.[4] This may be rationalized by the less favorable protonation (i.e. oxidation) of an electron-deficient metal or Pt−C bond.[5,6] Such vigorous conditions are incompatible with most reactants,[7] and so milder protocols for protonating cationic Pt−C bonds would be beneficial. We report herein a family of pincer-ligated Pt cations that undergo protonolysis with unusually high rates and present a possible reason for this acceleration that may be of general utility.[8]

Initial investigations into the protonolysis of model cationic Pt−CH_3 complexes with mild acids were not encouraging. Test complexes that combined a bidentate and a monodentate phosphine, [$(P_2)(PMe_3)$Pt−CH_3][BF_4] (P_2 = dppe, dppp, dppf, dppb, dippf, DPEPhos, BINAP), and [(dppe)(PR_3)Pt−CH_3][BF_4] (R_3 = Ph_3, Ph_2Me, $PhMe_2$, Me_3), were completely inert to 10 equiv of [Ph_2NH_2][BF_4] (**AA**; pK_a = 0.8[9]),[10] with C_6F_5CN as the dication trap.[11] Despite variations in ligand basicity and bite angle, no reaction was observed over a 4−5 day period at room temperature (<5% conversion by ^{31}P NMR).[12]

Scheme 1

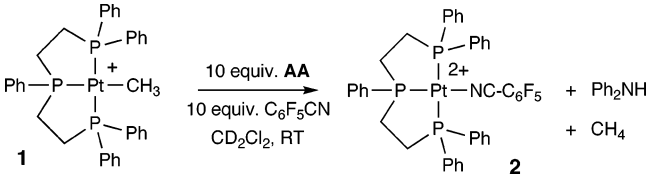
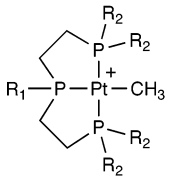


Chart 1. Tridentate PPP Ligand Variants



PPP,	R_1= R_2= Ph (**1**)
PPP-tol,	R_1= Ph, R_2= 4-Me-C_6H_4
PPP-xy,	R_1= Ph, R_2= 3,5-Me_2-C_6H_3
PPP-Cy,	R_1= Ph, R_2= Cy
PPP-Et,	R_1= Ph, R_2= Et
Et-PPP,	R_1= Et, R_2= Ph (**3**)
Et-PPP-Et,	R_1= R_2= Et
Cy-PPP,	R_1= Cy, R_2= Ph
***t*Bu-PPP**,	R_1= *t*Bu, R_2= Ph
***t*Bu-PPP-Et**,	R_1= *t*Bu, R_2= Et

More encouraging, however, were protonolysis experiments on compounds containing the triphos ligand, [(PPP)Pt−CH_3]-[BF_4] (**1**).[3,13] Under a standard set of conditions (Scheme 1), this complex was found to undergo protonolysis at room temperature to generate methane and the nitrile adduct **2**, with a time to 50% conversion of ∼8 h, a significant improvement over the conversion rate for the mixed bidentate/monodentate ligand systems initially tested.[14]

Additional enhancements in the rate of protonolysis were achieved with ligand variants that replaced the P−Ph of **PPP** with more electron donating P−Et substituents (Chart 1). These ligands were reliably constructed using the free-radical methods developed by DuBois.[15]

(1) For recent examples, see: (a) Qian, H.; Han, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 9536−9537. (b) Liu, C.; Han, X.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 3700−3701. (c) Helfer, D. S.; Atwood, J. D. *Organometallics* **2004**, *23*, 2412−2420.

(2) (a) Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 6366−6367. (b) Thorn, D. L. *Organometallics* **1998**, *17*, 348−352.

(3) Annibale, G.; Bergamini, P.; Cattabriga, M. *Inorg. Chim. Acta* **2001**, *316*, 25−32.

(4) See for example: (a) Butikofer, J. L.; Hoerter, J. M.; Peters, R. G.; Roddick, D. M. *Organometallics* **2004**, *23*, 400−408. (b) Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493−4499 and references therein.

(5) For careful evaluations of the mechanism, see: Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471−2526.

(6) For explicit discussions of metal vs alkyl/aryl protonation at Pt, see: (a) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116−12117. (b) Kalberer, E. W.; Houlis, J. F.; Roddick, D. M. *Organometallics* **2004**, *23*, 4112−4115. (c) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966−4968. (d) Jawad, J. K.; Puddephatt, R. J.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332−337. and references therein.

(7) For an example where turnover by protonation of a cationic Pt−C bond would be beneficial, see: Koh, J. H.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 3459−3461.

(8) For a recent intramolecular hydroamination of alkenes involving protonolysis of an intermediate (PNP)Pd−R^+ complex, see: Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 4246−4247.

(9) Stewart, R.; Dolman, D. *Can. J. Chem.* **1967**, *45*, 925−928.

(10) This acid was chosen because it only slowly reacts with trisubstituted alkenes.[7]

(11) Becker J. J.; Van Orden, L. J.; White, P. S.; Gagné, M. R. *Org. Lett.* **2002**, *4*, 727−730.

(12) Protonations are also sluggish with HOTf, which give 40−50% conversions in this time.

(13) The parent triphos (**PPP**) is commercially available (Strem).

(14) Protonation reactions with HOTf are nearly instantaneous at room temperature,[3] again, many times faster than with [(P_2P)Pt−CH_3][BF_4].[12]

(15) DuBois, D. L.; Miedaner, A.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 8753−8764.

10.1021/om051066b CCC: $33.50
Publication on Web 05/25/2006

Table 1. Ligand Effects on the Rate of [(L)Pt−CH_3][BF_4] Protonolysis (see Chart 1) by [Ph_2NH_2][BF_4] (AA) (C_6F_5CN Trap)[a]

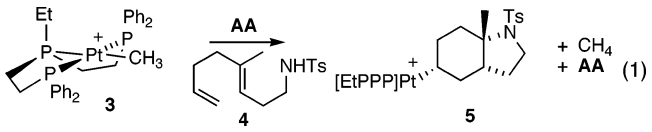
ligand	$t_{50\%}$ (min)[b]	ligand	$t_{50\%}$ (min)[b]
Et-PPP-Et	<5	PPP-xy	250
PPP-Et	10	Cy-PPP	345
*t*Bu-PPP-Et	50	PPP−Cy	435
Et-PPP	195	PPP	445
PPP-tol	220	*t*Bu-PPP	610

[a] Conditions: $[Pt]_0$= 0.01 M; 10 equiv of **AA**; 10 equiv of C_6F_5CN in CH_2Cl_2; 25(2)°C. Monitored by ^{31}P NMR. [b] Although the reactions were carried out under pseudo-first-order conditions in **AA**, the times are intended to be semiquantitative only.

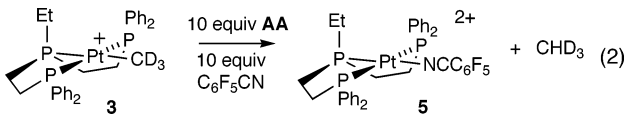
Table 1 contains times for 50% consumption of the Pt−CH_3 under the standard nitrile trapping conditions. Most notable are the increases in rate for the smaller basic ethyl substituent. Steric bulk in both the central and terminal positions slowed the rate, the former being significant, since R_1 orients nearly perpendicular to the square plane.[16]

The fastest ligand, **Et-PPP-Et**, reacted *>50 000-times faster than any of the [(P_2P)Pt−CH_3][BF_4] complexes*, which show no signs of reacting over 4−5 days under identical conditions (they do react with stronger acids such as HOTf). The triphos ligand thus engenders a unique reactivity to the Pt−CH_3^+ fragment.

To begin generating an explanation for this phenomenon, more detailed kinetics on the protonolysis of **3** were obtained. By measurement of the initial rates the reaction was determined to be first order in **AA** and zero order in the nitrile trap. Over multiple half-lives the consumption of **3** slows with conversion (see inset of Figure S6 in the Supporting Information), though it otherwise cleanly converts to the nitrile adducts with no detectable intermediates. Confirming an inhibitory role for the generated Ph_2NH were kinetic runs with added Ph_2NH, which slow the overall rate of protonolysis (Figure S6).[17] This inhibition could be removed by using a trap that generated an acid capable of reprotonating the liberated amine. With the diene−sulfonamide **4** (eq 1), the expected product of bicyclization was obtained[7] and well-behaved pseudo first-order kinetics resulted;[18] the rate is thus $\alpha = [Pt]^1[\mathbf{AA}]^1[trap]^0$.



To investigate the possibility of a *σ*-methane adduct occurring prior to the first irreversible step, protonation of the d_3 analogue of **3** was investigated (eq 2). On the basis of ^1H NMR analysis,

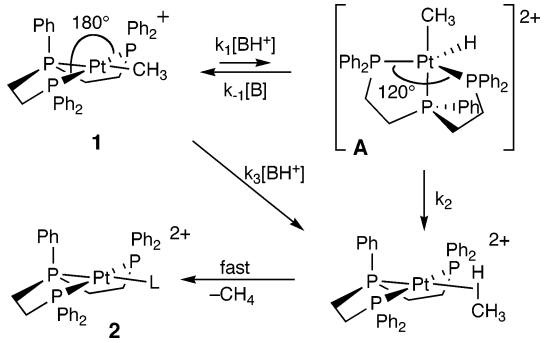


(16) (a) Bernatis, P. R.; Miedaner, A.; Haltiwanger, R. C.; DuBois, D. L. *Organometallics* **1994**, *13*, 4835−4843. (b) Annibale, G.; Bergamini, P.; Bertolasi, V.; Cattabriga, M.; Ferreti, V. *Inorg. Chem. Commun.* **2000**, *3*, 303−306. (c) Aizawa, S.; Sone, Y.; Kawamoto, T.; Yamada, S.; Nakamura, M. *Inorg. Chim. Acta* **2002**, *338*, 235−239.

(17) The kinetics with added amine were complicated by the presence of homoconjugate base pairs (Supporting Information); see for example: Papish, E. T.; Rix, F. C.; Spetseris, N.; Norton, J. R.; Williams, R. D. *J. Am. Chem. Soc.* **2000**, *122*, 12235−12242.

(18) The product cycloalkyl is stable to the protonation conditions and does not react further.

Scheme 2. Possible Pathways for Methane Loss



the only methane isotopologue detected was CD_3H (>95%), indicating that if a *σ*-methane intermediate forms, it does so irreversibly.[19] No significant kinetic isotope effect was noted (k_H/k_D = 1.2).

The data are thus consistent with two mechanistic scenarios. The first invokes a rate-determining protonation of the Pt−CH_3 bond or the methyl group to directly give the *σ*-methane adduct, which is rapidly displaced by the nitrile or alkene trap (Scheme 2). The second possibility generates the *σ*-methane adduct via a stepwise, reversible protonolysis at Pt to generate the five-coordinate Pt(IV) dication **A** (Scheme 2),[20] followed by rate-determining reductive coupling (k_2).[21,22] The zero-order behavior in the traps is indicative of a fast methane displacement step.[23]

Attempts to detect intermediate **A** by the low-temperature protonation of **1** or **3** using strong acids (HOTf and $HNTf_2$) were not successful. Triflic acid reacts quickly even at −78 °C (<10 min), and no intermediates are observed while monitoring the slower protonolysis with $HNTf_2$ (∼2 h at −65 °C). The very fast protonolysis rates at these low temperatures are in contrast with those observed in the (P_2P)Pt−CH_3^+ complexes described earlier, which were only partially complete after 5 days at room temperature.

What the data clearly show is that a relatively mild acid can protonolyze (PPP)Pt−CH_3^+ complexes much more easily than non-tridentate ligand structures. Since there is no obvious a priori reason the (P_2P)Pt−CH_3^+ and (PPP)Pt−CH_3^+ complexes could not each follow the direct protonolysis pathway (k_3[BH^+]), the striking lack of reactivity for the P_2P complexes suggests that another mechanism is operative, at least for the PPP cases. In contrast to the direct protonolysis pathway, the stepwise mechanism has features capable of distinguishing these two classes of complexes. Particularly relevant to the analysis are the relative energies of the four- (**1**) and five-coordinate (**A**) complexes in Scheme 2. The heightened reactivity of the (PPP)-Pt−CH_3^+ complexes suggested that the torsional strain inherent in the bicyclic PPP coordination mode might be the key differentiating feature. This strain results from enforcing a constrained bicyclic architecture onto an sp^3-hybridized center

(19) In contrast, model systems for Shilov chemistry experience extensive isotope scrambling, and this is often used as a diagnostic for *σ*-alkane formation.[5]

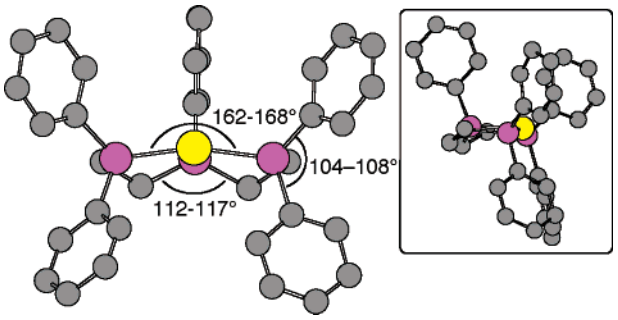
(20) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219*−*221*, 157−185.

(21) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442−9456.

(22) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739−740.

(23) Henderson has shown that protonation of (PPP)Ni−CH_3^+ is second-order in HCl, which led to the hypothesis that the first proton adds to the metal (detectable by NMR), while the second adds to the Ni−CH_3 bond. No hydride signals are observed at ambient or low temperatures (−78 °C) using **AA** and **1**, **AA** and **3**, HOTf and **3**, or $HNTf_2$ and **3**; see: Henderson, R. A.; Oglieve, K. E. *Chem. Commun.* **1999**, 2271−2272.

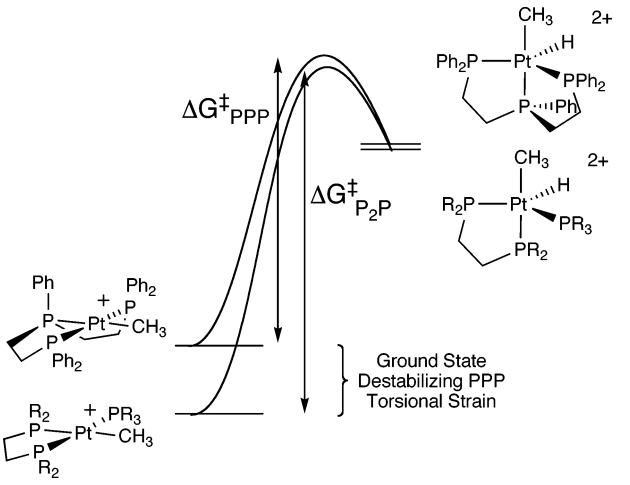
Chart 2. Representative C−P−C and P−Pt−P Bond Angles in Square-Planar Bicyclic Pt−triphos Complexes[27]



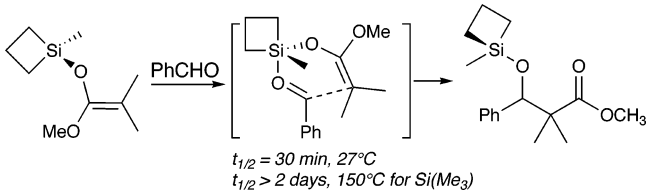
ligand[24] (idealized P−M−P ∼180°, Scheme 2) and is manifested in a number of ground-state structural distortions.[25] Most obvious are the transoid P−Pt−P bond angles, which are typically compressed in the direction that would seemingly reduce the imposed torsional strain (from ∼180° in non-triphos structures to 162−168°; Chart 2). Also, and in contrast to the terminal C−P−C bond angles, which are normal for an sp^3-hybridized ligand (104−108°), these same angles in the bridgehead phosphine are typically expanded to 112−117°, which minimizes bicyclic torsional strain at the expense of angle strain (Chart 2).[26]

In contrast to the case for square-planar structures, the geometry of a five-coordinate intermediate[28] (and structurally related transition states) reduces the C−P−C torsional and angle strain, since the arms of the central P now favorably project to accommodate the natural P−M−P projection (∼120° for a tbp, e.g. **A**).[29] Relieving torsional strain in the five-coordinate intermediates would thus lower the overall activation energy for Pt−CH_3 protonolysis (via the protonation and associative ligand substitution steps) (Scheme 3). Since this *differential torsional strain* is absent in $(P_2P)Pt-CH_3^+$, these compounds are comparatively less reactive. This analysis therefore suggests that a generic acceleration of 4−5−4 coordination number changes is responsible for the fast rates of protonolysis and that it is ultimately due to a differential ground-state destabilization of the square-planar geometry.[30]

Scheme 3. Differential Angle Strain in the Four- and Five-Coordinate States



Scheme 4



Conceptually related are the ring-strain enhancements of Lewis acidity achieved by silacyclobutanes. Their higher electrophilicity is proposed to be a result of ground-state angle strain (C−Si−C natural bond angle of 109°) being released in the hypervalent tbp geometry of the activated complex (C−Si−C natural bond angles of 90°; Scheme 4).[31,32] Strain within multicyclic aluminum alkoxide cages (cubes etc.), which is released upon valence expansion, is the purported source of their "latent" Lewis acidity.[33] This enhanced electrophilicity has been utilized in Ziegler−Natta catalyst activation, and it is speculated that a similar effect is operative in the ill-defined MAO formulations.

In summary, tridentate PPP ligands provide a mechanistic pathway for the protonolysis of cationic Pt−CH_3 bonds under conditions much milder than possible with mixtures of bi- and monodentate ligands of similar basicity. We present the notion that the observed rate accelerations may represent a subset of a more general phenomenon, namely acceleration of associative processes by differentially affecting torsional strain in the square-planar and five-coordinate geometries.[34] Current studies seek

(24) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229−266.

(25) Enhanced off-rates of one of the arms have also been documented; see: Sevillano, P.; Habtemariam, A.; Parsons, S.; Castiñeiras, A.; García, M. E.; Sadler, P. J. *J. Chem. Soc., Dalton Trans.* **1999**, 2861−2870.

(26) This torsional strain has previously been proposed to account for large downfield chemical shifts in the central P atom ($\Delta\delta$ ∼130−140 ppm). In comparison, the more flexible trimethylene ligands have significantly smaller coordination shifts,[24] as do tetrahedral (PPP)Pd^0 complexes, which would have similarly reduced torsional strain; see: DuBois, D. L.; Miedaner, A. *J. Am. Chem. Soc.* **1987**, *109*, 113−117.

(27) The source of these data are (PPP)Pt X-ray structures that we and others have obtained; they are meant to be illustrative and not exhaustive.

(28) For examples of stable five-coordinate Ni(II), Pd(II), and Pt(II) PPP complexes, see: (a) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076−3083. (b) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *J. Am. Chem. Soc.* **1981**, *103*, 4947−4948. (c) DuBois, D. L.; Miedaner, A. *Inorg. Chem.* **1986**, *25*, 4642−4650. (d) Petöcz, G.; Jánosi, L.; Wissensteiner, W.; Csók, Z.; Berente, Z.; Kollár, L. *Inorg. Chim. Acta* **2000**, *303*, 300−305. (e) López-Torres, M.; Fernández, A.; Fernández, J. J.; Suárez, A.; Pereira, M. T.; Ortigueira, J. M.; Vila, J. M.; Adams, H. *Inorg. Chem.* **2001**, *40*, 4583−4587. (f) Fernández, D.; Sevillano, P.; García-Seijo, M. I.; Castiñeiras, A.; Jánosi, L.; Berente, Z.; Kollár, L.; Garcia-Fernández, M. E. *Inorg. Chim. Acta* **2001**, *312*, 40−52.

(29) Structurally characterized five-coordinate structures are typically described as distorted tbp or distorted square pyramids. The central P−M−P angles in such cases are typically reduced to 125−150°. See ref 28e for representative examples.

(30) A reviewer suggested the possibility that protonolysis of an arm-off form of the complex could facilitate the reaction. Such putative intermediates are not observed on monitoring low-temperature reactions (^{31}P and ^1H NMR) with strong acids (above).

(31) (a) Myers, A. G.; Kephart, S. E.; Chen, H. *J. Am. Chem. Soc.* **1992**, *114*, 7923−7924. (b) Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 7026−7043.

(32) For examples of its use in synthesis, see: (a) Sunderhaus, J. D.; Lam, H.; Dudley, G. B. *Org. Lett.* **2003**, *5*, 4571−4573. (b) Wang, X.; Meng, Q.; Nation, A. J.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 10672−10673. (c) Franz, A. K.; Woerpel, K. A. *Acc. Chem. Res.* **2000**, *33*, 813−820. (d) Young, D. G. J.; Hale, M. R.; Hoveyda, A. H. *Tetrahedron Lett.* **1996**, *37*, 827−830.

(33) (a) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465−6474. (b) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5514−5518. See also: (c) Richter, B.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2166−2169.

(34) For cases where this effect may be contributing to heightened rates of exchange and/or catalysis, see: (a) Dockter, D. W.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1996**, *118*, 4846−4852. (b) Reference 16b. (c) Müller, T. E.; Berger, M.; Grosche, M.; Herdtweck, E.; Schmidtchen, F. P. *Organometallics* **2001**, *20*, 4384−4393. (d) Schneffknecht, C.; Peringer, P. *J. Organomet. Chem.* **1997**, *535*, 77−79. (e) Reference 16a.

to document this phenomenon in a variety of stoichiometric and catalytic applications.

Acknowledgment. We warmly thank the National Institutes of Health (Grant No. GM-60578) and the Department of Energy, Office of Basic Energy Sciences, each for partial support of this research.

Supporting Information Available: Text and figures giving synthetic and experimental procedures for ligand and complex synthesis and kinetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051066B