

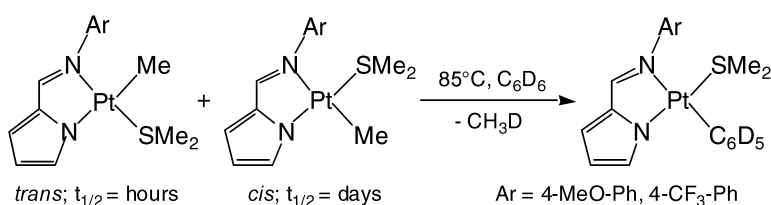
Communication

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C–H Bond Activation by Unsymmetrical 2-(*N*-Arylimino)pyrrolide Pt Complexes: Geometric Effects on Reactivity

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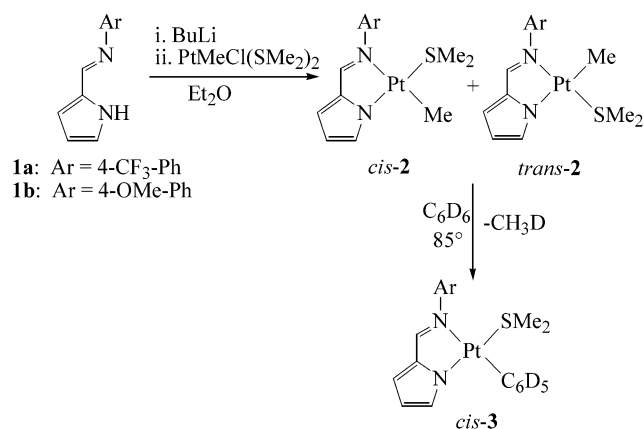
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N-Ligated chelate complexes of Pt(II) provide useful models for the C–H bond activation step in selective oxidation of alkanes by aqueous solutions of chloroplatinate salts (the Shilov system)¹ and are effective catalysts for methane oxidation by sulfuric acid.² Cationic complexes of the form [(*N*–*N*)PtMeL]⁺, where (*N*–*N*) is a neutral bidentate ligand, have been extensively studied.³ Our mechanistic picture of the Shilov system⁴ suggests that C–H activation followed by oxidation to Pt(IV) could provide a pathway to catalytic alkane oxidation by dioxygen. However, in contrast to neutral Pt dimethyl complexes (*N*–*N*)PtMe₂,⁵ recent experimental evidence suggests cationic methyl complexes can be resistant to oxidation by dioxygen to Pt(IV).⁶ Alkane activation by Pt(II) and a monoanionic bidentate *N*–*N* ligand would lead to a neutral complex (*N*–*N*)PtRL that might be more readily oxidized; several such complexes have been shown to be capable of C–H bond activation.⁷ We report here on neutral Pt(II) complexes of unsymmetrical 2-(*N*-arylimino)pyrrolide ligands, which are easily synthesized,⁸ and also present two types of nitrogen ligation with widely different steric and electronic attributes, leading to dramatic geometric effects on C–H bond activation chemistry.

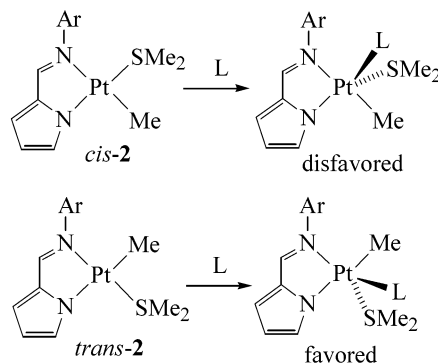
Treatment of (*N*-arylimino)pyrroles **1a,b** with *n*-BuLi followed by *trans*-PtMeCl(SMe₂)₂ affords (*N*–*N'*)PtMe(SMe₂) as a mixture of *cis* and *trans* isomers⁹ of **2**. Structures are assigned on the basis of NMR^{10,11} coupled with a crystal structure of *cis*-**2c** (*vide infra*). On heating in C₆D₆ at 85 °C, both isomers react to give the *cis* isomer of the corresponding phenyl complex **3** along with CH₃D, but at quite different rates: approximate half-lives are 1 and 4 h for *trans*-**2a** and *trans*-**2b** and 3 and 14 d for *cis*-**2a** and *cis*-**2b**, respectively (Scheme 1). We suggest that rate-determining associative displacement of SMe₂ by benzene accounts for these differences.¹² The greater electronegativity of the ligand in **2a** would tend to favor associative displacement. Furthermore, the trigonal bipyramidal intermediate for such displacement in *trans*-**2** would have the better π-acceptor imine ligand equatorial and the better σ-donor pyrrolide axial, the strongly preferred conformation¹³ (Scheme 2). Slower displacement in the *cis* isomer must pass through a higher-energy intermediate and is accompanied by isomerization to the thermodynamically preferred *cis* isomer of **3**. In agreement, *trans*-**2a** undergoes rapid exchange ($\tau_{1/2} \approx 5$ min) with S(CD₃)₂ at room temperature, whereas *cis*-**2a** is only partly exchanged after 2 d, during which time *trans*-**2a** is completely isomerized to *cis*-**2a**.¹⁴

In principle, methyl complexes **2** could be prepared directly from **1** and [PtMe₂(μ-SMe₂)₂] (**4**) by protonolysis of one methyl group by the pyrrole proton. Indeed, **1a–c** react with **4** in benzene at ambient temperature over several days to form *cis*-**2a–c** with methane evolution. The structure of *cis*-**2c** has been confirmed by

Scheme 1



Scheme 2



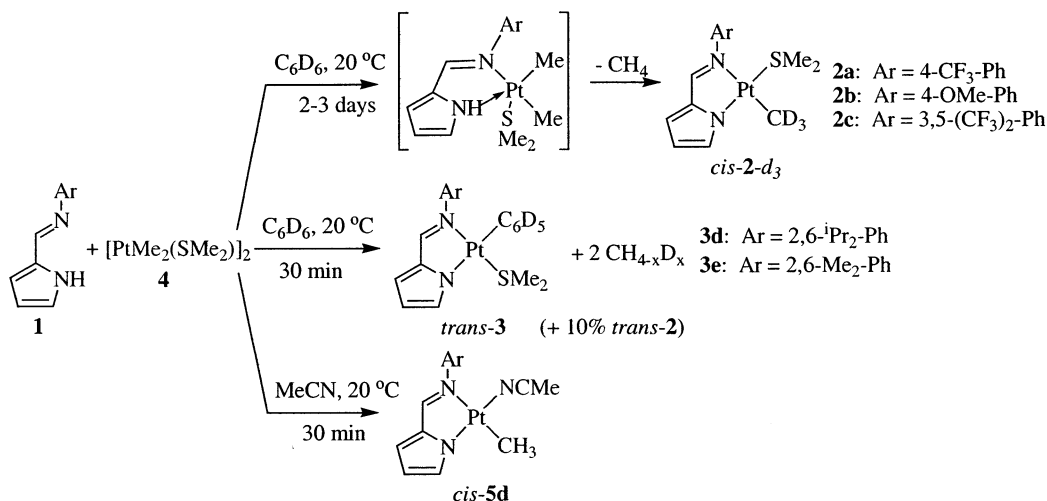
X-ray crystallography.¹¹ For **1a,b**, an intermediate may be observed by NMR at earlier stages; spectral parameters^{11,15} suggest the agostic structure shown in Scheme 3. Remarkably, when the reaction is carried out in C₆D₆, the remaining Pt–methyl group is about 90% deuterated, whereas the liberated methane is completely undeuterated.

Bulkier ligands **1d,e** with ortho-disubstituted aryl groups behave completely differently: reaction in benzene leads rapidly and directly to the C–H activation products *trans*-**3d,e**,¹¹ along with 2 equiv of liberated methane (Scheme 3). Significant deuteration of the methane is observed in C₆D₆,¹⁶ for **3d**, the methyl groups of the isopropyl substituents are partially deuterated as well.¹⁷ In contrast, reaction of **1d** with **4** in acetonitrile leads smoothly to the MeCN–methyl complex *cis*-**5d**; the assigned geometry has been confirmed by a crystal structure.¹¹ **5d** does not react with benzene even at reflux.

It appears that the C–H activation of benzene, whether leading all the way to phenyl products as in **3d,e** or just to H/D exchange

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Scheme 3



as in **2a,b**, must precede chelation, because preformed complexes **2** react with benzene only under considerably more stringent conditions. The fact that only CH₄ is produced in the reactions of **1a,b** with **4** further suggests that protonolysis by the pyrrole proton precedes any benzene activation, implying that the pyrrolide–Pt bond is formed while the imine N is not coordinated and hence that the intermediate observed in these reactions must be formed reversibly. The fact that only *trans*-**3d,e** are observed is presumably a consequence of strong steric interactions between the ortho-aryl substituents and a *cis*-SMe₂ ligand, disfavoring the *cis* geometry which otherwise appears preferred. Indeed, reaction of **1d** with *trans*-PtMeCl(SMe₂)₂ affords only *trans*-**2d**. A more complete mechanistic interpretation of the observations of Scheme 3 is not possible at this time; yet it is clear that C–H activation chemistry in these Pt(II) systems is highly dependent upon ligand electronic and steric properties, as well as subtle geometric factors. Exploitation of this behavior for the design of alkane functionalization catalysts is the subject of ongoing investigation in our labs.

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Supporting Information Available: Preparative details and NMR data for all new compounds; X-ray crystallographic results for *cis*-**2c** and *cis*-**5d** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim. (Engl. Transl.)* **1972**, *46*, 785. (b) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Boston, 1984.
- (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560–564.
- (a) Holtcamp, M. H.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848–849. (b) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974–1975. (c) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846–10855. (d) Johansson, L.; Ryan, O. B.; Romming, C.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 6579–6590. (e) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378–1399.
- (a) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horvath, I. T.; Eller, K. *Organometallics* **1993**, *12*, 895. (b) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004. (c) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1994**, *13*, 755. (d) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75. (e) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371–9372. (f) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961–5976.
- (a) Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4530–4531. (b) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608–3619.
- Scollard, J. D.; Day, M.; Labinger, J. A.; Bercaw, J. E. *Helv. Chim. Acta* **2001**, *84*, 3247–3268.
- Several reports relating C–H bond activation chemistry of neutral platinum–methyl complexes utilizing monoanionic bi- or tridentate ligands have recently appeared: (a) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (b) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6579–6590. (c) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804–6805. (d) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100–5101. (e) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724–12725. (f) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2001**, *20*, 1709–1712. (g) Lo, H. C.; Haskel, A.; Kapon, M.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 3226–3228. (h) Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7041–7054.
- Tanaka, T.; Yamauchi, O. *Chem. Pharm. Bull.* **1961**, *9*, 588.
- The *cis*:*trans* ratio of the products is 1:1 for **2a** and 1:4 for **2b**. We arbitrarily label the geometries *cis* and *trans* according to the relationship of the anionic (methyl or phenyl) group and the pyrrolide arm of the chelating ligand.
- Coupling constants in ¹⁹⁵Pt satellites appear to be reliably diagnostic, with ²J_{PH} for Pt–Me (79–80 Hz vs 73 Hz) and ³J_{PH} for SMe₂ (51 Hz vs 58 Hz), for *cis* (Me *cis* to pyrrolide) versus *trans* isomers, respectively.
- Synthetic details, full NMR spectroscopic characterization of all new compounds, and X-ray crystallographic results are presented in the Supporting Information.
- Hydrocarbon substitution of labile ligands in C–H bond activation studies has been observed previously. See, for example, refs 3b, 3e, and 7a.
- See, for example: Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Addison-Wesley Longman: New York, 1999; pp 101–103.
- Thermolysis of the isolable, more stable isomer, *cis*-**2**, in C₆D₆ results only in the activation of benzene solvent, and we do not observe *trans*-**2** in the reaction solution. However, given the difference in qualitative rates, it is possible that *cis*-**2** isomerizes to *trans*-**2** and then undergoes C–H bond activation.
- Interaction between the pyrrole N–H and the platinum metal center is suggested by a substantial downfield shift of the signal for the former, to δ 13.9 and J_{Pt–H} = 24 Hz. This is the lowest value observed for this coupling, however, and another possibility may be an H-bonding interaction with the sulfur.
- Added SMe₂ decreases the amount of methane deuteration, increases the amount of *trans*-**2** formed, and slows the rate of the reaction.
- Similar exchange has been observed in a related system: Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804–6805.

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