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

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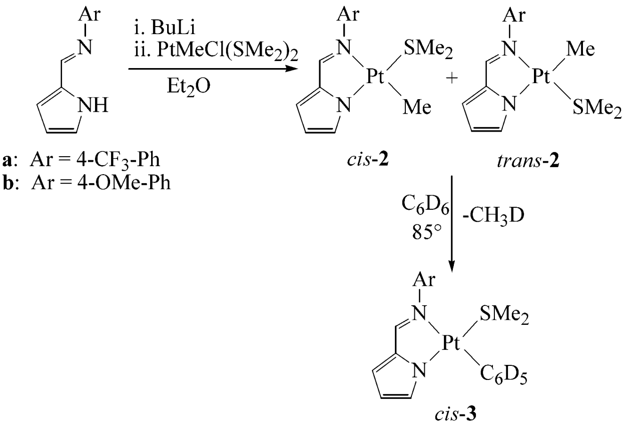
N-Ligated chelate complexes of Pt(II) provide useful models for the C−H bond activation step in selective oxidation of alkanes by aqueous solutions of chloroplatinate salts (the Shilov system)[1] and are effective catalysts for methane oxidation by sulfuric acid.[2] Cationic complexes of the form [(N−N)PtMeL]$^+$, where (N−N) is a neutral bidentate ligand, have been extensively studied.[3] Our mechanistic picture of the Shilov system[4] 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)PtMe$_2$,[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.

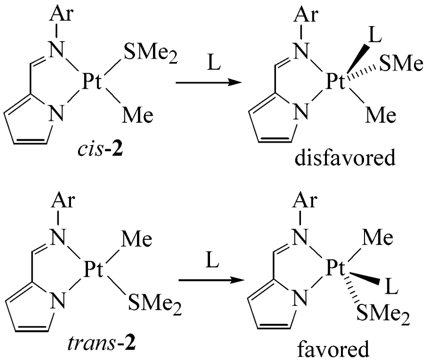
Treatment of (*N*-arylimino)pyrroles **1a**,**b** with *n*-BuLi followed by *trans*-PtMeCl(SMe$_2$)$_2$ affords (N−N′)PtMe(SMe$_2$) as a mixture of cis and trans isomers[9] of **2**. Structures are assigned on the basis of NMR[10,11] coupled with a crystal structure of *cis*-**2c** (*vide infra*). On heating in C$_6$D$_6$ at 85 °C, both isomers react to give the cis isomer of the corresponding phenyl complex **3** along with CH$_3$D, 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 SMe$_2$ 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 conformation[13] (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(CD$_3$)$_2$ 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 [PtMe$_2$(μ-SMe$_2$)]$_2$ (**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 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 C$_6$D$_6$, the remaining Pt−methyl group is about 90% deuterated, whereas the liberated methane is *completely undeuterated*.

Scheme 1



Scheme 2



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 C$_6$D$_6$;[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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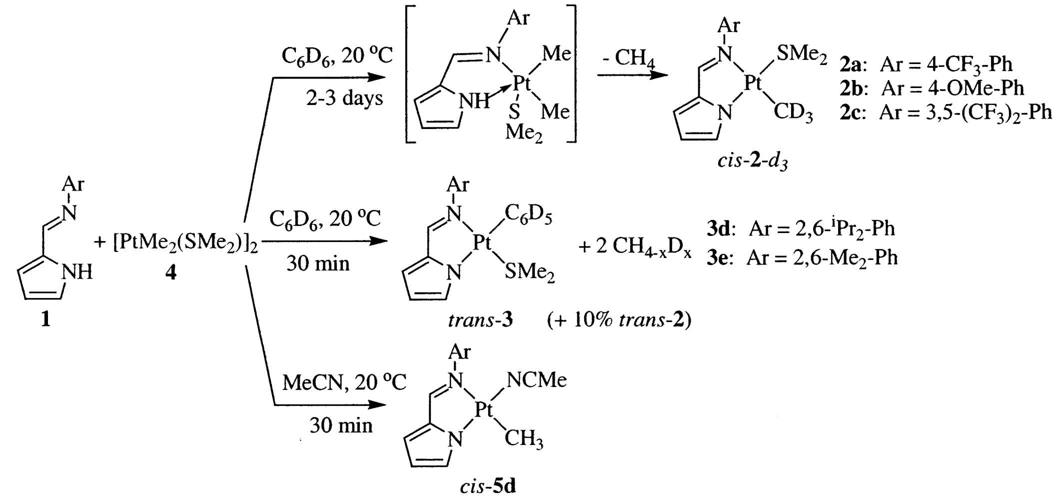
10.1021/ja036511d CCC: $25.00

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 CH_4 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*-SMe_2 ligand, disfavoring the cis geometry which otherwise appears preferred. Indeed, reaction of **1d** with *trans*-$PtMeCl(SMe_2)_2$ 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.

Acknowledgment. Parts of this work were supported by Akzo-Nobel; a joint DOE-OIT grant; the Los Alamos LDRD program; and BP. We thank Ulrich Fekl and Dave Thorn for helpful discussions. J.D.S. thanks Larry Henling and the X-ray Crystallography Facility of the Beckman Institute at Caltech for assistance with crystal structure determinations.

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.

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(9) 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.

(10) Coupling constants in ^{195}Pt satellites appear to be reliably diagnostic, with $^2J_{PtH}$ for Pt−Me (79−80 Hz vs 73 Hz) and $^3J_{PtH}$ for SMe_2 (51 Hz vs 58 Hz), for cis (Me cis to pyrrolide) versus trans isomers, respectively.

(11) Synthetic details, full NMR spectroscopic characterization of all new compounds, and X-ray crystallographic results are presented in the Supporting Information.

(12) Hydrocarbon substitution of labile ligands in C−H bond activation studies has been observed previously. See, for example, refs 3b, 3e, and 7a.

(13) See, for example: Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Addison-Wesley Longman: New York, 1999; pp 101−103

(14) Thermolysis of the isolable, more stable isomer, *cis*-**2**, in C_6D_6 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.

(15) 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.

(16) Added SMe_2 decreases the amount of methane deuteration, increases the amount of *trans*-**2** formed, and slows the rate of the reaction.

(17) Similar exchange has been observed in a related system: Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804−6805.

JA036511D