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N–Pt^{IV}–H/N–H…Pt^{II} intramolecular redox equilibrium in a product of H–C(sp^2) cleavage and unusual alkane/arene C–H bond selectivity of ([2.1.1]pyridinophane)Pt^{II}(CH$_3$)$^+$†

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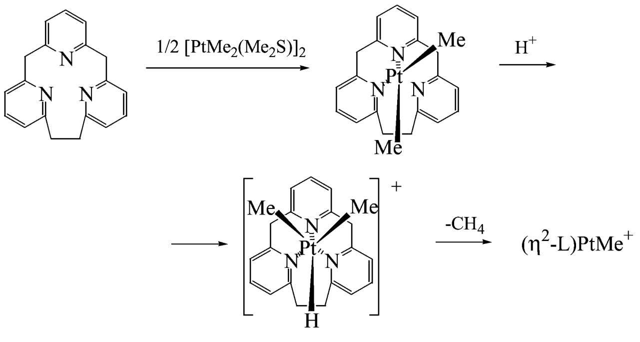
Received (in Purdue, IN, USA) 8th August 2002, Accepted 15th October 2002
First published as an Advance Article on the web 6th January 2003

T-shaped 14 valence electron (η^2-L)PtMe$^+$ (based on DFT geometry optimization, L = [2.1.1]-2,6-pyridinophane) reacts with benzene to give (η^3-L) Pt^{IV}(Ph)$_2$H$^+$ and methane; the latter cation is in thermal equilibrium with the N-protonated Pt^{II} tautomer (η^2-L-H)Pt(Ph)$_2$$^+$, and these complexes react with ethane or cyclopentane to produce benzene and (L)PtH(olefin)$^+$.

We have shown[1] a synthetic route to [2.1.1]-2,6-pyridinophanes ('L'), a class of nearly threefold symmetric ligands (Scheme 1). When attached to PdCl$_2$ or Pt(CH$_3$)$_2$, this ligand is bound $^2\eta$, but the pendant pyridine N is constrained to be nearby, and in fact this N binds to Pt when the metal in LPtMe$_2$ is protonated (*i.e.* oxidized to Pt^{IV}). The constrained η^3 binding imposed by a slightly 'oversized' macrocycle leads to facile methane reductive elimination (Scheme 1), and then to a transient (L)Pt^{II}Me$^+$ species[2] which shows the ability, at and below 25 °C, to effect oxidative addition of the C–H bonds of methane, ethane, propane, n-butane, cyclopentane and cyclohexane.[3]

We report here the DFT-calculated structure of (η^2-L)PtMe$^+$, together with its reactivity towards benzene and the results of some alkane–arene competition experiments. Taken together, these give an expanded view of the potential energy surface accessible, at and below 25 °C, to the species (L)Pt(R)$_2$H$^+$ and (L)PtR$^+$ + RH, and thus the *reversibility* of such a hydrocarbon attack system. Deuterium isotope labeling studies also indicate the presence of methane and arene complexes of (η^2-L)Pt(R)$^+$.

DFT calculations (program package Priroda,[4] PBE functional,[5] SBK basis set[6]) reveal a T-shaped three-coordinate 14 electron structure (Fig. 1) for the [PtMe(L)]$^+$ cation rather than a 4-coordinated pseudotetrahedral geometry. Due to the *trans*-effect of the methyl ligand the Pt–N(25) bond is 0.18 Å longer than the Pt–N(5) bond. The location of the C$_2$H$_4$ linker allows the third ligand donor, N(14), to be situated at a non-bonding position, slightly more than 3 Å from platinum. As a result, the platinum atom is intermolecularly accessible and forms a third Pt–N bond in the course of hydrocarbon substrate addition, thereby improving the reaction energetics.



Scheme 1

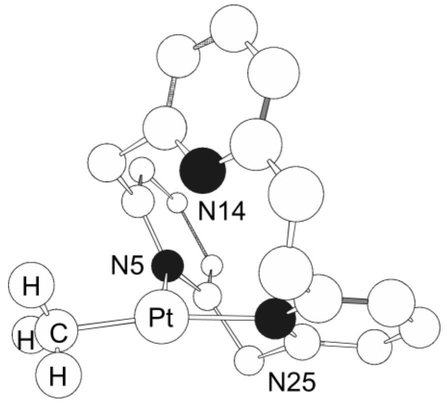
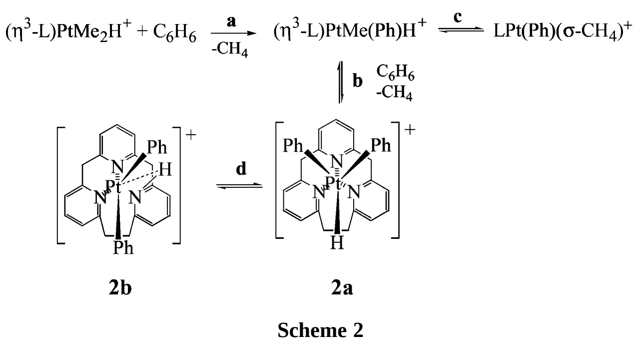


Fig. 1 DFT-optimized structure of (L)PtMe$^+$ cation. Hydrogen atoms of L are omitted. Selected bond lengths and angles: Pt–N(5), 1.993 Å; Pt–N(14), 3.026 Å; Pt–N(25), 2.171 Å; Pt–C(41), 2.042 Å; N(5)–Pt–N(25), 85.3; N(5)–Pt-C(41), 100.5; N(25)–Pt–C(41), 171.3.

Reaction of [PtMe$_2$H(L)]BAr^F$_4$ (BAr^F$_4$ is B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$) in the presence of benzene (10 equiv.) in dichloromethane solution at RT leads (Scheme 2, **a**) to the appearance of new ^{1}H NMR signals in both high- and low-field regions, 1.50 (J_{PtH} = 68 Hz, 3H, Pt-Me), −19.42 (J_{PtH} = 1370, 1H, Pt-H) which can be attributed to the formation of [(L)PtMe(Ph)H]X, **1** (X = BAr^F$_4$) (6% *vs.* BAr^F$_4$ in 30 min). Subsequently, a peak at −18.42 (J_{PtH} = 1350 Hz) appears with simultaneous disappearance of the signals of **1**, due to the formation of the diphenylhydrido complex, [(L) PtPh$_2$H]X, **2a**, (Scheme 2, **b**). Such a spontaneous alkyl for aryl ligand exchange at a Pt(IV) center has not been observed earlier, though it can occur in the presence of tris(pentafluorophenyl)boron in neat benzene.[7,8] It is interesting to note that the hydride complex **2a** exists *in equilibrium* (**d**)[9] with its platinum(II)-hydrogen bonded NH-tautomer, [PtPh$_2$(H-L)]X, **2b**, with a very characteristic low-field signal at 17.32 ppm (br, J_{PtH} = 86 Hz) for the N–H proton. The observed NH/Pt coupling suggests hydrogen bonding between H and Pt.[10,11] Complex **2a**, of mirror symmetry according to ^{1}H and ^{13}C NMR spectroscopy, shows one AX pattern for the pyridinophane ligand methylene bridges and only two triplet signals for the *para*-protons of its pyridine rings in a 1 : 2 ratio. In contrast, its platinum(II) tautomer, **2b**, has no symmetry as proven by NMR data, and platinum is thus



Scheme 2

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b207797n/

DOI: 10.1039/b207797n

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coordinated to two nitrogen atoms of non-equivalent pyridine rings of the pyridinophane. Its spectrum exhibits two AX patterns due to two non-equivalent methylene bridges, three triplets corresponding to the *para*-protons of three non-equivalent pyridine rings in a 1 : 1 : 1 ratio and two sets of signals of nonequivalent phenyls.

The methyl-to-phenyl exchange is almost quantitative ($\geq$98% *vs*. BAr^F_4) and the redox-isomeric diphenyl products **2a** : **2b** are present in molar ratio 1 : 9 and are stable in dichloromethane solution at 25 °C for at least several days. This mixture of the tautomeric diphenyl platinum complexes **2** *of the same composition* has been obtained independently from HOTF and $(L)PtPh_2$, then $NaBAr^F_4$.

A similar picture is observed for the reaction of $[(L)PtMe_2H]X$ in C_6D_6 solution but isotopomers of methane are formed: CH_4, CDH_3 and CD_2H_2 and CD_3H in 1 : 0.6 : 0.4 : 0.4 mol ratio (NMR integration). The formation of CD_2H_2 and CD_3H is consistent with *reversibility* of the R/H reductive coupling,[12,13] and the intermediacy of methane η^2- complexes (Scheme 2 **c**), *e.g.* $[LPtPh(\eta^2\text{-}CDH_3)]^+$ and the benzene complex $[LPt(CH_2D)(\eta^2\text{-}HC_6D_5)]^+$. The structure of $[\kappa^2(HTp')Pt(H)(\eta^2\text{-}C_6H_6)]^+$, and its ability to be in equilibrium with $[\kappa^2\text{-}(HTp')PtPh(H)_2]^+$, has been described recently.[14]

The equilibrating system **d** in Scheme 2 shows *alkane* C–H cleavage chemistry. Recently we reported[3] facile alkane dehydrogenation using $[PtMe_2H(L)]^+$ and have shown that formation of the corresponding hydridoplatinum(II) *olefin* complex is thermodynamically favorable. Now we demonstrate that this driving force is enough to overcome the expected higher affinity of $[PtR(L)]^+$ species for arene C–H bonds as compared with alkane C–H bonds in the course of reversible oxidative addition. An equilibrium mixture of tautomers **2a** : **2b**, reacts in CD_2Cl_2 with cyclopentane (3 M) at 25 °C (RT) over 3 days to produce $[PtH(cyclo\text{-}C_5H_8)(L)]BAr^F_4$ and two moles of benzene in 80% yield *vs*. BAr^F_4 (eqn. 1).

$$[(L)PtPh_2H]X + cyclo\text{-}C_5H_{10} \rightarrow \{(L)PtH(\eta^2\text{-}cyclo\text{-}C_5H_8)]X + 2\ PhH \qquad (1)$$

This observation proves the *reversibility* of *arene* C–H bond oxidative addition to the $[(L)PtR]^+$ species and shows its *unusual* alkane–arene C–H bond selectivity in favor of an alkane C–H bond caused by the high thermodynamic preference[15–18] for a cationic hydridoplatinum(II) *olefin* complex over its 14 electron alkylplatinum(II) isomer.

An alkane–arene competition experiment has been conducted when both substrates were present in comparable concentrations. A solution of benzene and ethane taken at 1.6 : 1 mol ratio reacts with $[PtMe_2H(L)]^+$ at RT in the course of 8 h to produce, with 100% yield *vs*. BAr^F_4, the tautomeric mixture (1 : 9) of $[PtPh_2H(L)]^+$ and $[PtPh_2(H\text{-}L)]^+$. Then, in the course of several days, the slow accumulation of the hydridoplatinum(II) ethene complex (analogous to eqn. 1) has been observed so that in 4 days the yield of the ethene complex reached 10%. The slow *rate* of alkane consumption indicates that benzene at high concentration significantly inhibits alkane oxidative addition, presumably due to formation of a π-complex with transient $[(L)PtR]^+$ species.

The observed chemistry can be related both to the ability of L to not 'overstabilize' $PtR_2H(L)^+$,[13] and also to the electrophilicity of platinum in the described complexes. Thus, the presence of two electron-withdrawing aryl (*vs*. methyl, since **1** does not show an N–H isomer) ligands decreases metal basicity to a degree sufficient to match that of the nitrogen in the ligand L and as a result to make observable for the first time the redox–prototropic equilibrium $PtR_2H(L)^+$ with $PtR_2(H\text{-}L)^+$. On the other hand, transformation of $PtAlk(L)^+$ into $PtH(olefin)(L)^+$ helps to stabilize an electrophilic platinum by the electron donating olefin to such an extent that it overcomes the energy losses when going from $PtAr_2H(L)^+$ to $PtAlk(Ar)H(L)^+$ and then to $PtAlk(L)^+$. These features of the described C–H bond cleavage system open new perspectives in arene functionalization and clarify the energy balance and mechanism of competition between electrophilic and oxidative addition pathways in hydrocarbon activation with platinum(II) complexes.

This work was supported by the Department of Energy. We thank Dr D. N. Laikov for the use of his software. ANV is on leave from the Chemical Faculty, Kazan State University, Kazan, Russia. This work has been made possible in part due to support from Russian Foundation for Basic Research (grant #01.03.32692).

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