[2.1.1]-(2,6)-Pyridinophane(L)-controlled alkane C–H bond cleavage: (L)$PtMe_2H^+$ as a precursor to the geometrically "tense" transient (L)$PtMe^+$ †

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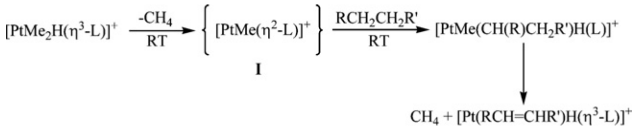
(η^2-L)$PtMe_2$ {L = [2.1.1]-(2,6)-pyridinophane} is protonated at Pt to give (η^3-L)$PtHMe_2^+$, where three pyridine ligands of the macrocycle L bind to Pt in a *facial* manner. This cation eliminates methane at a rate convenient for trapping of the T-shaped, 14-valence electron (η^2-L)$PtMe^+$ (based on DFT geometry optimization) by ethane, propane, *n*-butane, cyclopentane and cyclohexane to give (η^3-L)Pt(olefin)H^+ and CH_4. The crystal structure of (η^3-L)Pt(cyclohexene)H^+ as its BAr_4^{F-} salt is reported.

Mild transition metal catalyzed hydrocarbon functionalization is the focus of much research work.[1–12] Despite many metal complexes able to effect alkane CH bond oxidative addition, producing alkyl hydrido species, the potential of this fundamental reaction in elaboration of new catalytic hydrocarbon transformations remains still unused; few examples of catalysis involving this step are known.[13,14,15] To serve such a catalytic role, metal alkyl hydrides should be sufficiently transient ("unstable") under catalytic conditions but this makes their characterization more difficult.[16] Particular examples include platinum(IV) alkyl hydrido species,[17] which are supposed to be responsible for so-called Shilov-type chemistry,[18] and recently for methane transformation into methylhydrosulfate[19] and some other reactions involving hydrocarbon CH bond cleavage.[17] Both moderately persistant[20,21] and even quite persistant ("stable") platinum(IV) alkyl hydrides[22–24] permit testing the intermediacy of platinum(IV) alkyl hydrides in alkane functionalization and to reveal some factors controlling their reactivity.[17] Moreover, alkane oxidative addition to the presumably 14-electron platinum(II) transient species Tp*PtMe[8] has proven this is a feasible process. However, *use* of platinum(IV) hydrocarbyl hydrides in alkane activation, the simplest example of which is hydrocarbyl ligand exchange, has been demonstrated only recently.[25]

Thus, platinum(IV) alkyl hydrides of *intermediate* thermodynamic and kinetic stability would be of special interest precisely because they could be convenient sources of the reactive unsaturated fragment L_nPt^{II}. Recently we have developed an approach to designing new ligands and complexes that optimize the reactivity of 14-electron d^8 metal complexes.[26] We report here our observations of hydrocarbon CH bond oxidative addition to a cationic, presumably 14-electron transient platinum(II) complex resulting (**I**, Scheme 1) from methane elimination from a dimethyl hydrido platinum(IV) species $[PtMe_2H(L)]^+$ supported with the [2.1.1]-(2,6)-pyridinophane ligand [27] shown in Fig. 1(a). This ligand is shown here to allow unusually fast room temperature CH bond cleavage of aliphatic hydrocarbons RH (RH = C_2H_6, C_3H_8, *n*-butane, cyclo-C_5H_{10}, cyclo-C_6H_{12}).



Scheme 1

According to DFT calculations (program package Priroda,[28] functional PBE,[29] basis set SBK[30]), the cationic hydrido dimethyl platinum(IV) complex $[PtMe_2H(L)]^+$ is expected to allow facile ($\Delta G^{\neq}_{298}$ = 16 kcal mol^{-1}) and thermodynamically only slightly unfavorable (ΔG°_{298} = +11 kcal mol^{-1}) methane elimination to produce $[PtMe(\eta^2\text{-L})]^+$, **I**. Due to the tridentate ligand constraints, its three nitrogen donor atoms cannot be arranged in one plane with the Pt–C bond, thus preventing formation of a stable (*i.e.*, less reactive) 16-electron *square planar* complex.

The new cationic hydridodimethyl platinum(IV) complex $[PtMe_2H(L)]^+$ can be obtained by protonation of the corresponding $[PtMe_2(\eta^2\text{-L})]^{27,31}$ with a suitable Brønsted acid according to the known method.[20–23] To preserve the reactivity of the platinum(II) species **I**, we have used the anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, BAr_4^{F-} and a solvent of low donicity, dichloromethane. This is accomplished by one-pot protonation of the corresponding dimethylplatinum(II)

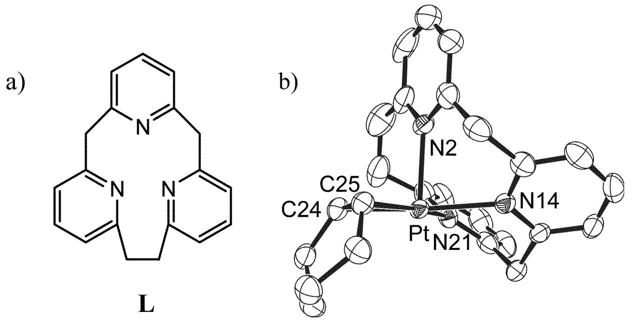


Fig. 1 (a) Ligand **L**. (b) ORTEP diagram of [PtH(cyclohexene)(η^3-L)]$^+$ ion in its BAr_4^{F-} salt. Hydrogen atoms are omitted. The hydride ligand presumably located trans to N2 was not located. Selected bond lengths (Å) and angles (°): Pt–C24, 2.098(3); Pt–C25, 2.077(3); C24–C25, 1.443(5); Pt–N2, 2.198(3); Pt–N14, 2.221(3); Pt–N21, 2.221(3); N2-Pt–N14, 84.9(1); N2–Pt–N21, 90.1(1); N14–Pt–N21, 82.1(1); N2–Pt–C24, 93.3(1); N2–Pt–C25, 91.5(1).

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† Electronic supplementary information (ESI) available: complete experimental and characterization data. See http://www.rsc.org/suppdata/nj/b3/b302055j/.

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complexes with triflic acid [eqn. (1), > 95% yield] and anion exchange with solid $NaBAr^F_4$ in dichloromethane at −60 °C ([eqn. (2), > 98% yield].

$$[PtMe_2(\eta^2\text{-L})] + HOTf \rightarrow [PtMe_2H(\eta^3\text{-L})]OTf \qquad (1)$$

$$[PtMe_2H(\eta^3\text{-L})]OTf + NaBAr^F_4 \rightarrow [PtMe_2H(\eta^3\text{-L})]BAr^F_4 + NaOTf \qquad (2)$$

The $[PtMe_2H(L)]X$ complexes in both cases (X = OTf, BAr_4^{F-}) exhibit almost identical ^1H NMR resonances (−20.65, J_{PtH} = 1354 Hz in CD_2Cl_2, X = BAr_4^{F-}) and possess mirror symmetry, showing one signal of equivalent methyl groups at 1.27 ppm (J_{PtH} = 70 Hz), one set of signals of two equivalent pyridine rings and one set of AX resonances for protons of the methylene bridges. The solid tetraarylborate salt decomposes completely during one week at RT.

Both Pt(IV) complexes synthesized undergo methane reductive elimination at room temperature.[32] Saturated hydrocarbons, both acyclic and cyclic, introduced into dichloromethane solutions of the $[PtMe_2H(L)]BAr^F_4$ complex prepared according to eqns (1) and (2), react at room temperature with one and the same rate constant [$k_{295\ K} = (1.55 \pm 0.03) \times 10^{-4} s^{-1}$, hence identical rate-determining steps] to produce C–H bond activation products in high yield after 8 h.

Ethane (2 M) reacts, with methane elimination, to produce (95 ± 2% *vs.* BAr_4^{F-} signals) $[PtH(\eta^2\text{-}C_2H_4)(L)]X$ with a hydride ligand chemical shift of −27.49 (J_{PtH} = 1093 Hz) at −40 °C, which has been completely characterized by ^1H and ^{13}C NMR spectroscopy [see Electronic supplementary information (ESI) for this and other adducts].

Higher alkanes, propane (3 M), *n*-butane (3 M), cyclopentane and cyclohexane (all the liquids are in 1:1 volume ratio) react similarly (≥95% yield) to produce platinum hydrido η^2-olefin complexes. This behavior resembles closely the properties of $[Cp^*IrMe(PMe_3)(ClCH_2Cl)]^+$, with the difference that the latter is more sensitive to the steric accessibility of the alkane CH bond.[33] In the case of propane, two diastereomers of $[PtH(\eta^2\text{-}C_3H_6)(L)]X$ in almost 1:1 ratio have been observed with Pt–H resonances at −27.59 (J_{PtH} = 1158 Hz) and −27.50 (J_{PtH} = 1141 Hz) at −30 °C. *n*-Butane gives rise to five isomeric products (1:0.7:0.1:0.1:0.2 ratio) with hydride ligand δ values (−30 °C) of −27.57 ($^1J_{PtH}$ = 1137 Hz), −27.69 ($^1J_{PtH}$ = 1143 Hz), −27.69 ($^1J_{PtH}$ = 1207 Hz), −27.88 ($^1J_{PtH}$ = 1150 Hz) and −28.34 ($^1J_{PtH}$ = 1163 Hz). The first two contain 1-butene coordinated to the platinum center while the third is an adduct of 2-*cis*-butene; alkyl groups are *cis*- to the Pt–H fragment in all three compounds, as established by 1D NOE experiments. The two last hydride resonances, which are very broad at RT, are attributed to 2 diastereomeric *trans*-2-butene complexes. This olefin was liberated when the mixture of adducts was exposed to 1 atm CO at room temperature; conditions under which other adducts remained intact. The mixture of isomeric butene complexes decomposes when heated at 100 °C in CD_2Cl_2 solution in a sealed NMR tube, gradually liberating metallic Pt, LH^+ salt and *cis*- and *trans*-2-butenes while the 1-butene complexes *persist* in the same 1:0.7 ratio. Thus, no fast equilibration between isomeric butene complexes occurs even at 100 °C and the initial olefin complex ratio reflects purely kinetic selectivity of *n*-butane dehydrogenation by transient $PtMe(L)^+$.

Cyclopentane and cyclohexane each give a single isomer of $[PtH(\eta^2\text{-olefin})(\eta^3\text{-L})]X$ (olefin = C_5H_8, C_6H_{10}) characterized with one Pt–H resonance at −27.20 (olefin = C_6H_{10}, −30 °C; J_{PtH} = 1181 Hz) or at −26.97 (olefin = C_5H_8, −30 °C; J_{PtH} = 1171 Hz). Formation of $[PtH(\eta^2\text{-}C_5H_8)(L)]^+$ has been confirmed by electrospray ionization MS (M^+ = 551.2 for the ^{195}Pt isotopomer). The structure of the cyclohexene complex, established by X-ray crystallography‡ [Fig. 1(b)], shows a *five*-coordinated platinum with the pyridinophane ligand coordinated unsymmetrically (unsym) relative to the Pt–H fragment and the cyclohexene ring *cis* to the hydride. Noteworthy in the structure are the *three* nearly identical Pt–N distances.

The mild conversion effected by $(\eta^2\text{-L})PtMe^+$ of alkane to coordinated *olefin* and hydride offers new possibilities for subsequent functionalization of an alkane compared to previous conversions to coordinated *alkyl* and hydride. This is a special advantage of slightly "oversized" ligands like [2.1.1]-(2,6)-pyridinophane, which form *constrained* octahedral d^6 complexes and therefore can more easily change from η^3 to η^2 than does Tp or does the corresponding ring slippage occur for C_5R_5.

A new alkane CH bond cleavage reagent has been designed and synthesized that possesses an unusually high [for Pt(II)/Pt(IV)] *room temperature* reactivity in hydrocarbon *oxidative addition/reductive elimination*. The latter properties might be used to design new catalytic alkane-to-olefin conversions.

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References

1 A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879.
2 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352.
3 W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562.
4 W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1984, **106**, 1650.
5 S. E. Bromberg, H. Yang, M. C. Asplund, T. Lian, B. K. McNamara, K. T. Kotz, J. S. Yeston, M. Wilkens, H. Frei, R. G. Bergman and C. B. Harris, *Science*, 1997, **278**, 260.
6 B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154.
7 C. Wang, J. W. Ziller and T. C. Flood, *J. Am. Chem. Soc.*, 1995, **117**, 1647.
8 D. D. Wick and K. I. Goldberg, *J. Am. Chem. Soc.*, 1997, **119**, 10 235.
9 H. Heiberg, L. Johansson, O. Gropen, O. B. Ryan, O. Swang and M. Tilset, *J. Am. Chem. Soc.*, 2000, **122**, 10 831.
10 L. Johansson, M. Tilset, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2000, **122**, 10 846.
11 M. W. Holtcamp, L. M. Henling, M. W. Day, J. A. Labinger and J. E. Bercaw, *Inorg. Chim. Acta*, 1998, **270**, 467.
12 A. E. Shilov and G. B. Shulpin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Dordrecht, Boston, 2000.
13 (*a*) T. Sakakura and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1987, 758; (*b*) T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada and M. Tanaka, *J. Am. Chem. Soc.*, 1990, **112**, 7221; (*c*) G. P. Rosini, K. M. Zhu and A. S. Goldman, *J. Organometal. Chem.*, 1995, **504**, 115.
14 (*a*) K. Nomura and Y. Saito, *J. Chem. Soc., Chem. Commun.*, 1988, 161; (*b*) F. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, *J. Am. Chem. Soc.*, 1999, **121**, 4086.
15 (*a*) K. M. Waltz, C. N. Muhoro and J. F. Hartwig, *Organometallics*, 1999, **18**, 3383; (*b*) K. Kawamura and J. F. Hartwig, *J. Am. Chem. Soc.*, 2001, **123**, 8422.
16 S. R. Klei, T. D. Tilley and R. G. Bergman, *J. Am. Chem. Soc.*, 2000, **122**, 1816.
17 R. J. Puddephatt, *Coord. Chem. Rev.*, 2001, **219–222**, 157 and references therein.
18 N. F. Gol'dshleger, V. V. Es'kova, A. E. Shilov and A. A. Shteinman, *Russ. J. Phys. Chem.*, 1972, **5**, 785.
19 R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, **280**, 560.

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‡ CCDC reference number 205619. See http://www.rsc.org/suppdata/nj/b3/b302055j/ for crystallographic data in CIF or other electronic format.

20 V. De Felice, A. De Renzi, A. Panunzi and D. Tesauro, *J. Organomet. Chem.*, 1995, **488**, C13.

21 S. S. Stahl, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1995, **117**, 9371.

22 S. A. O'Reilly, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1996, **118**, 5684.

23 A. J. Canty, A. Dedieu, H. Jin, A. Milet and M. K. Richmond, *Organometallics*, 1996, **15**, 2845.

24 E. M. Prokopchuk, H. A. Jenkins and R. J. Puddephatt, *Organometallics*, 1999, **18**, 2861.

25 A. N. Vedernikov and K. G. Caulton, *Angew. Chem., Int. Ed.*, 2002, **41**, 4102.

26 A. N. Vedernikov, G. A. Shamov and B. N. Solomonov, *Russ. J. Gen. Chem.*, 1999, **69**, 1102.

27 A. N. Vedernikov, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 2002, **41**, 6867.

28 (*a*) Y. A. Ustynyuk, L. Y. Ustynyuk, D. N. Laikov and V. V. Lunin, *J. Organomet. Chem.*, 2000, **597**, 182; (*b*) D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.

29 (*a*) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3038; (*b*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

30 (*a*) W. J. Stevens, H. Basch and M. Krauss, *J. Chem. Phys.*, 1984, **81**, 6026; (*b*) W. J. Stevens, H. Basch, M. Krauss and P. Jasien, *Can. J. Chem.*, 1992, **70**, 612; (*c*) T. R. Cundari and W. J. Stevens, *J. Chem. Phys.*, 1993, **98**, 5555.

31 J. D. Scott and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1643.

32 Methane elimination from $[HN(CH_2pyridyl)_2]PtHMe_2^+$ was proposed to require cleavage of one Pt–N(pyridyl) bond. U. Fekl, A. Zahl and R. van Eldik, *Organometallics*, 1999, **18**, 4156.

33 P. Burger and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 10 462.