Oxidative Dehydrogenation of Tris(*o*-isopropylphenyl)phosphines by Platinum Complexes

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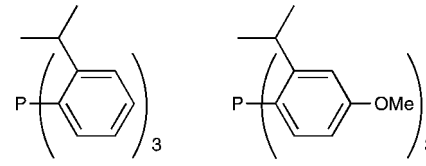
Received May 1, 2008

The binuclear cyclometalates $[Pt_2Cl_2\{2\text{-}CMe_2C_6H_4P(C_6H_4(2\text{-}^iPr))_2\}_2]$ (**1a**) and $[Pt_2Cl_2\{2\text{-}CMe_2C_6H_3(4\text{-}OMe)P(C_6H_3(2\text{-}^iPr)(4\text{-}OMe))_2\}_2]$ (**1b**) react with $CHCl_2CHCl_2$ to give the corresponding mononuclear phosphine-alkene chelates $[PtCl_2\{2\text{-}CH_2{=}CMeC_6H_4P(C_6H_4(2\text{-}^iPr))_2\}]$ (**2a**) and $[PtCl_2\{2\text{-}CH_2{=}CMeC_6H_3(4\text{-}OMe)P(C_6H_3(2\text{-}^iPr)(4\text{-}OMe))_2\}]$ (**2b**). The product **2a** can also be formed directly from $[PtCl_2(NC^tBu)_2]$ and $\mathbf{L_a}$ in $CHCl_2CHCl_2$ or by addition of SO_2Cl_2 to **1a**. Addition of an excess of SO_2Cl_2 to **1b** gave $[PtCl_2\{2\text{-}CH_2{=}CMeC_6H_3(4\text{-}OMe)P(C_6H_2(2\text{-}^iPr)(4\text{-}OMe)(5\text{-}Cl))_2\}]$ (**3b**), a derivative of **2b** featuring *meta*-chlorine substituents on the terminal P groups as a result of electrophilic aromatic substitution. A mechanism for the conversion of **1a**,**b** to **2a**,**b** is proposed involving an electrophilic alkyl C−H activation by a coordinatively unsaturated platinum(IV) species. The mechanism is supported by the isolation of the diplatinum(IV) cyclometalate $[Pt_2Cl_2\{2\text{-}CH_2C_6H_3(4\text{-}OMe)P(C_6H_3(2\text{-}Me)(4\text{-}OMe))_2\}]$ as a mixture of *syn* and *anti* isomers **5b** and **5b′**. The crystal structures of **2a** and **3b** have been determined.

Introduction

Understanding the factors involved in the activation of alkyl C−H bonds by transition metal complexes is a topic of fundamental interest because of the prospect and importance of selectively functionalizing alkanes.[1,2] Ever since Shilov's pioneering work[1] on alkane activation with platinum(II)/(IV) systems in the 1970s, much effort has been directed at using precious metal complexes for homogeneous functionalization of alkanes.[3−7] Efficient homogeneous catalysts have been reported for transfer dehydrogenation[4] and acceptorless dehydrogenation of alkanes[5] but not for the oxidative dehydrogenation of alkanes,[8] which is potentially a very attractive process.[2] One of the most promising strategies for homogeneous, oxidative, alkane dehydrogenation involves electrophilic C−H activation by late transition metal complexes and especially with platinum(II)/(IV) systems, for which stoichiometric dehydrogenations have been reported.[6,7]

Cyclometalation is a common form of intramolecular C−H activation, and the reactivity of the resulting M−C bonds has been well documented.[9] We reported[10] rare examples of tertiary carbon−metal bonds formed upon cycloplatination of $\mathbf{L_a}$ and $\mathbf{L_b}$, and here we report that the C−H bonds of the methyl groups in the isopropyl substituents are activated upon oxidation of the complex, resulting in the formation of a coordinated alkene. Overall the reaction constitutes an oxidative dehydrogenation of a tertiary phosphine.



$\mathbf{L_a}$ $\mathbf{L_b}$

Results and Discussion

It was previously reported[10] that treatment of $[PtCl_2(NCBu^t)_2]$ with $\mathbf{L_a}$ or $\mathbf{L_b}$ in refluxing toluene gave the binuclear cyclometalated complexes **1a** and **1b**, which contain tertiary C−Pt

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(1) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(2) For reviews see: (a) Marks, T. J.; et al. *Chem. Rev.* **2001**, *101*, 953. (b) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (c) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (d) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (e) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550. (f) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(3) (a) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340. (b) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560. (c) Periana, R. A.; Mironov, O.; Taube, D. J.; Bhalla, G.; Jones, C. J. *Science* **2003**, *301*, 814. (d) Sen, A.; Benvenuto, M. A.; Lin, M.; Hutson, A. C.; Basickes, N. *J. Am. Chem. Soc.* **1994**, *116*, 998. (e) Lin, M.; Shen, C.; Garcia-Zayas, E. A.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 1000. (f) Mukhopadhyay, S.; Bell, A. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 2990.

(4) (a) Jensen, C. M. *Chem. Commun.* **1999**, 2443, and references therein. (b) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086. (c) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788. (d) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083. (e) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (f) Gupta, M.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1997**, 461. (g) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816. (h) Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Lin, Y. *Tetrahedron Lett.* **1985**, *26*, 1999. (i) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (j) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706. (k) Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. *J. Organomet. Chem.* **1996**, *518*, 55. (l) Renkema, K. B.; Kissin, Y. V.; Goldman, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 7770. (m) Gottker-Schnetmann, I.; White, P. S.; Brookhart, M *J. Am. Chem. Soc.* **2004**, *126*, 1804, and references therein.

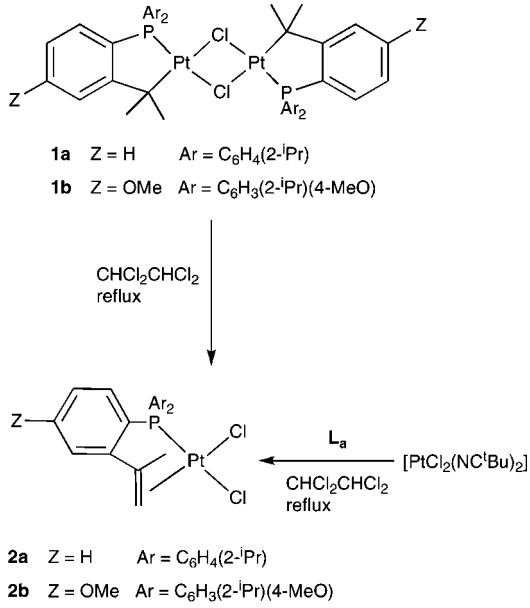
(5) Liu, F.; Goldman, A. S. *Chem. Commun.* **1999**, 655.

(6) (a) Fekl, U.; Kaminsky, W.; Goldberg, K. *J. Am. Chem. Soc.* **2003**, *125*, 15286. (b) Fekl, U.; Goldberg, K. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (c) Fekl, U.; Goldberg, K. *J. Am. Chem. Soc.* **2001**, *123*, 6423.

(7) (a) Vedernikov, A. N.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, *27*, 665. (b) Kostelansky, C. N.; MacDonald, M. G.; White, P. S.; Templeton, J. L. *Organometallics* **2006**, *25*, 2993. (c) Khaskin, E.; Zavalij, P. Y.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2006**, *128*, 13054.

10.1021/om800382m CCC: $40.75
Publication on Web 10/08/2008

Scheme 1



bonds. We now find that when **1a** or **1b** is refluxed in $CHCl_2CHCl_2$, a single P-containing complex was observed in each case. The complex products are assigned the phosphine-alkene chelate structures **2a** and **2b** on the basis of elemental analysis, NMR spectroscopy, and the X-ray crystal structure of **2a** (see below). The ^1H and ^{13}C NMR spectra of **2a** and **2b** show peaks characteristic of a coordinated alkene (see Experimental Section). Complex **2a** was also formed by heating $[PtCl_2(NC^tBu)_2]$ with $\mathbf{L_a}$ in $CHCl_2CHCl_2$ (Scheme 1).

Crystals of **2a** were grown from its $CDCl_3$ solution, and the X-ray crystal structure of **2a**, as a chloroform solvate, was determined (see Figure 1). The molecular structure confirms that assigned above, with a conventional square-planar Pt(II) coordination geometry. The conformation of the diaryl portion of the chelating ligand is of the g^+g^+ type,[10] and only one pair of (enantiomeric) diastereoisomers is seen in the unit cell; that

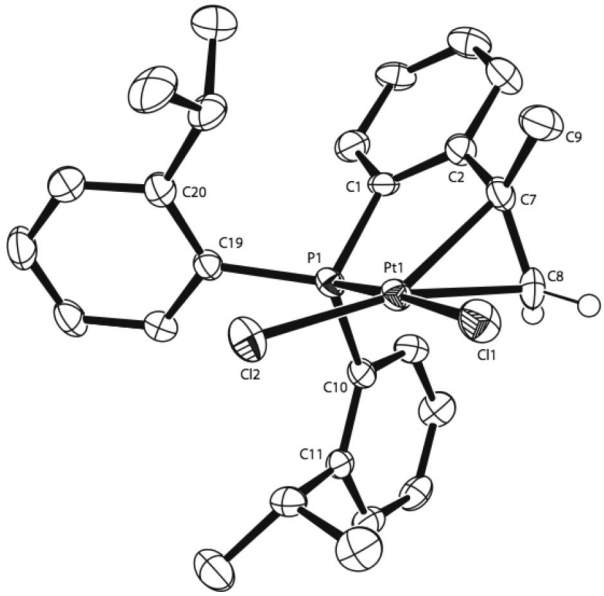


Figure 1. Structure of **2a** with hydrogen atoms removed for clarity (except those on C8). Important geometric parameters include Pt1−P1 2.2426(14), Pt1−C7 2.207(5), Pt1−C8 2.135(5), Pt1−Cl1 2.3651(14), Pt1−Cl2 2.3201(15), C7−C8 1.402(7) Å.

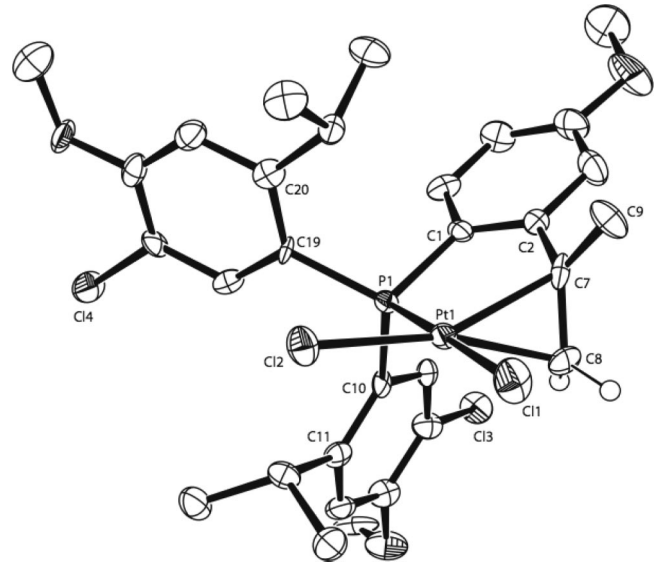


Figure 2. Structure of **3b** with hydrogen atoms removed for clarity (except those on C8). Important geometric parameters include Pt1−P1 2.242(3), Pt1−C7 2.199(13), Pt1−C8 2.114(13), Pt1−Cl1 2.369(3), Pt1−Cl2 2.310(3), C7−C8 1.404(18) Å.

is, there is no molecule with the same configuration at the sterogenic carbon C7 and a g^-g^- diaryl conformation. The chelating phosphino-alkene ligands in **2a**,**b** are related to those in complexes of (*o*-vinylphenyl)diphenylphosphine reported by Bennett et al.[11]

The transformation of **1a**,**b** into **2a**,**b** must involve reaction with the solvent and, since the Cl:Pt ratio has increased from 1:1 to 1:2 (see Scheme 1), an abstraction of a Cl atom has taken place. Two stoichiometries were considered plausible, where $CHCl_2CHCl_2$ acts as the source of HCl (eq 1) or Cl_2 (eq 2).[12] The modest yields of **2a**,**b** in the $CHCl_2CHCl_2$ reactions were accompanied by significant decomposition to metallic platinum and other brown insoluble products, and therefore a more selective route to **2a**,**b** was sought. To investigate the feasibility of the reactions shown in eqs 1 and 2, more accessible sources of HCl and Cl_2 than $CHCl_2CHCl_2$ were investigated.

$$0.5\ \mathbf{1a,b} + HCl \rightarrow \mathbf{2a,b} + H_2 \quad (1)$$

$$0.5\ \mathbf{1a,b} + Cl_2 \rightarrow \mathbf{2a,b} + HCl \quad (2)$$

No reaction was observed by ^{31}P NMR spectroscopy upon treatment of **1a** in toluene with a large excess of HCl in diethyl ether at ambient temperature or at reflux. However **1a** reacted

(8) Cu systems that catalyze the oxidative dehydrogenation of cycloalkanes with turnover numbers of less than 10 have been described; see: Vedernikov, A. N.; Caulton, K. G. *Chem. Commun.* **2004**, 162.

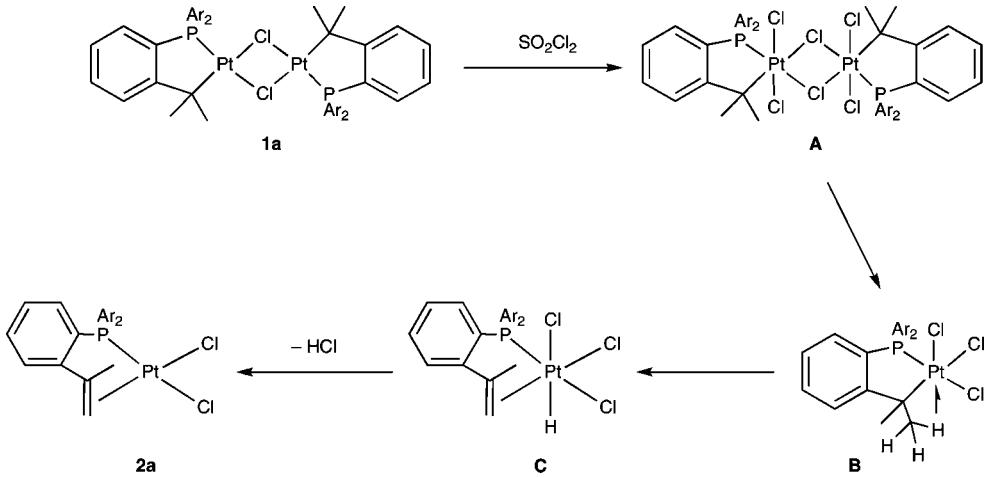
(9) Omae, I. *Organometallic Intramolecular Coordination Compounds*; Elsevier, Amsterdam, 1986.

(10) Baber, R. A.; Orpen, A. G.; Pringle, P. G.; Wilkinson, M. J.; Wingad, R. L. *Dalton Trans.* **2005**, 659.

(11) (a) Bennett, M. A.; Nyholm, R. S.; Saxby, J. D. *J. Organomet. Chem.* **1967**, *10*, 301. (b) Bennett, M. A.; Chiraratvatana, C.; Robertson, G. B.; Tooptakong, U. *Organometallics* **1988**, *7*, 1394. (c) Bennett, M. A.; Chiraratvatana, C.; Robertson, G. B.; Tooptakong, U. *Organometallics* **1988**, *7*, 1403.

(12) The mechanism by which the $CHCl_2CHCl_2$ delivers the chlorine to **1a**,**b** is not clear but probably involves Cl radicals. If it were a sequence of oxidative addition/reductive elimination, then the byproducts would be CHCl=CHCl or $CHCl{=}CCl_2$, but neither was detected by GC/MS analysis of the final product solution of the reaction of **1a** with $CHCl_2CHCl_2$. Instead, several chlorocarbons (including significant amounts of C_2Cl_6) were detected, consistent with radicals being involved in the reaction.

Scheme 2

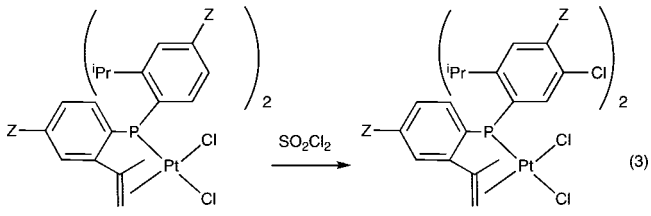


rapidly with SO_2Cl_2 (as a source of Cl_2) in CH_2Cl_2 at ambient temperatures to give **2a**, showing that the stoichiometry of eq 2 is viable.

The reaction between SO_2Cl_2 and **1a** was monitored by ^{31}P NMR spectroscopy. At low conversions to **2a**, the only P-containing species observed were **1a** and **2a**; that is, no intermediates were detected. At higher conversions, it was noticed that a minor species (up to 10%) formed with ^{31}P NMR parameters (δ_P 19.0, $^1J_{PtP}$ 3202 Hz) similar to those for **2a** (δ_P 17.5, $^1J_{PtP}$ 3279 Hz). The likely structure of this impurity (**3a**, see eq 3) emerged only after the reaction of **1b** with SO_2Cl_2 had been investigated.

Reaction of **1b** with an excess of SO_2Cl_2 initially gave two products in the ratio 1:1 with similar ^{31}P NMR parameters.[13] After 4 h, a single product was present, for which crystals were grown from its $CDCl_3$ solution and the X-ray crystal of **3b**, as a chloroform solvate, was determined (see Figure 2). The crystal structure revealed that *meta* chlorination of the terminal aryl substituents had occurred in the reaction of **1b** with SO_2Cl_2. The conformation of the diaryl portion of the chelating ligand in **3b** is again of the g^+g^+ type, and the configuration at C7 is also as in **2a**. The details of the molecular structure around the metal in **3b** are less precisely determined than for **2a** but are otherwise very similar.

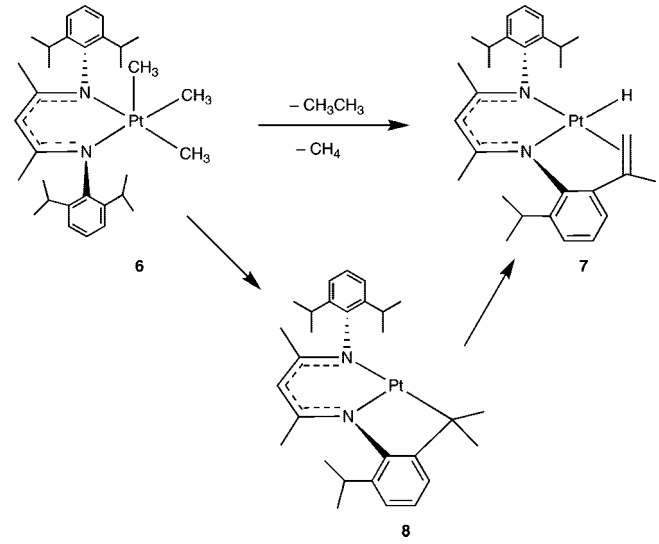
Thus it appears that **2b** readily undergoes electrophilic aromatic substitution by chlorine to afford **3b**. This was confirmed by addition of 2 equiv of SO_2Cl_2 to **2b**, which gave **3b** quantitatively (eq 3). The activation by the *ortho*-directing methoxy substituents would explain why the electrophilic aromatic substitution occurs more readily with **2b** than with **2a** (eq 3). Notably, it appears that the terminal aryl groups are more activated to the chlorination than the aryl group that is part of the chelate.



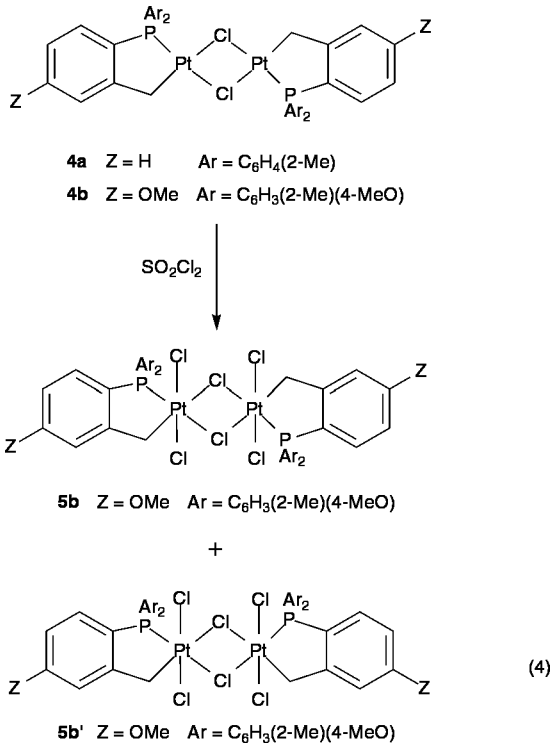
2a Z = H
2b Z = OMe
3a Z = H
3b Z = OMe

A mechanism for the conversion of **1a** into **2a** is proposed in Scheme 2. Oxidative addition of Cl_2 to **1a** would give the diplatinum(IV) intermediate **A**. Dissociation to give a five-coordinate mononuclear species **B** would be promoted by the bulky phosphine. Intermediate **B** may have an agostic C−H interaction in the ground state (as depicted in Scheme 2) or in the transition state of the β-hydrogen elimination step to give **C**. Reductive elimination of HCl from **C** would give the observed **2a**. This mechanism is reminiscent of Shilov's proposal[1] to explain the formation of hexene from hexane using $[PtCl_6]^{2-}$ in aqueous solution: β-hydrogen elimination from the five-coordinate platinum(IV) species $[RCH_2CH_2PtCl_4]^-$ to give $[(\eta\text{-RCH=CH})Pt(H)Cl_4]^-$ followed by HCl loss to give $[(\eta\text{-RCH=CH})PtCl_3]^-$.

Scheme 3



The previously reported[10] complexes **4a**,**b** are analogues of **1a**,**b** but have *ortho*-methyl rather than *ortho*-isopropyl substituents, and therefore do not have the potential to be dehydrogenated in the same way as **1a**,**b**. The lack of solubility of **4a** precluded a study of its reactions with SO_2Cl_2. However treatment of **4b** with SO_2Cl_2 smoothly gave a 1:1 mixture of two species with closely similar ^{31}P NMR parameters (δ 29.6, J_{PtP} 2870 Hz, 28.1, J_{PtP} 2824 Hz). The diplatinum(IV) isomers **5b** and **5b′** (eq 4) are assigned to the products on the basis of elemental analysis, mass spectrometry, and ^1H and ^{31}P NMR spectroscopy (see Experimental Section for the data). Complexes **5b/5b′** are close analogues of the proposed intermediate **A**, and their formation supports the mechanism given in Scheme 2.



(4)

Goldberg et al.[6] have shown that one of the isopropyl groups in the five-coordinate organoplatinum(IV) complex **6** is dehydrogenated at elevated temperatures to give **7** via three-coordinate cycloplatinate(II) intermediate **8** (Scheme 3), which was formed by elimination of ethane and methane. Complex **6** has some similarities to the organoplatinum(IV) intermediate **B** proposed in Scheme 2, although the Pt in **6** is more electron-rich, and therefore **6** would be less electrophilic than **B**. The alkane dehydrogenation mechanisms in Schemes 2 and 3 differ significantly in that the crucial step involves β-hydrogen migration to platinum(IV) in Scheme 2 and to platinum(II) in Scheme 3.

Conclusion

The oxidative alkane dehydrogenation reported here is stoichiometric and intramolecular and uses a source of Cl_2 as the oxidant with HCl as the byproduct. This is a long way from the sought-after catalytic, intermolecular alkane dehydrogenation using O_2 as the oxidant with H_2O as the byproduct.[2] Nevertheless the great facility with which the putative platinum(IV) activates the alkyl C−H bonds described here suggests that functionalization of alkanes mediated by electrophilic transition metal complexes has great potential.

Experimental Section

General Considerations. Unless otherwise stated, all work was carried out under a dry nitrogen atmosphere, using standard Schlenk line techniques. Dry N_2-saturated solvents were collected from a Grubbs system[14] in flame- and vaccuum-dried glassware. Complexes **1a**,**b** and **4b** were made by the previously reported method.[10]

(13) Presumably the monochloroaryl complex [$PtCl_2$\{2-CH_2=$CMeC_6H_3$(4-OMe)P(C_6H_2(2-^{i}Pr)(4-OMe)(5-Cl))(C_6H_2(2-^{i}Pr)(4-OMe))\}] intermediate must also be formed, but this was not detected in the ^{31}P NMR spectrum either because it is formed in only small quantities or its signals are masked by those for **3b**.

(14) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Table 1. Crystallographic Data for 2a·2CHCl$_3$ and 3b

	2a·2CHCl$_3$	**3b**
color, habit	colorless, block	colorless, block
size (mm)	0.15 × 0.1 × 0.1	0.2 × 0.18 × 0.18
formula	$C_{29}H_{33}C_{l8}$PPt	$C_{30}H_{35}C_{l4}O_3$PPt
M	891.21	811.47
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	11.281(3)	13.348(3)
b (Å)	12.104(2)	15.743(3)
c (Å)	13.133(3)	15.330(3)
α (deg)	89.331(15)	90.00
β (deg)	76.72(2)	109.57(3)
γ (deg)	75.780(19)	90.00
V (Å^{-3})	1689.8(7)	3035.4(11)
Z	2	4
μ (mm^{-1})	4.851	5.059
T (K)	173(2)	100(2)
reflns: total/indep/R_{int}	18 174/7680/0.0574	34 003/6966/0.1058
final R_1	0.0422	0.0951
largest peak, hole (e Å^{-3})	1.256, −0.912	4.729, −4.792
ρ_{calc} (g cm^{-3})	1.752	1.776

NMR spectra were measured on a Jeol Eclipse 300, Jeol Eclipse 400, or Jeol GX 400. Unless otherwise stated, ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 300, 100, and 121 MHz, respectively, at +23 °C. Mass spectra were recorded on a MD800. Elemental analyses were carried out by the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

Synthesis of [$PtCl_2$\{2-CH_2=$CMeC_6H_4P(C_6H_4$(2-^{i}Pr))$_2$\}] (2a). Method a. [Pt_2Cl_2\{2-$CMe_2C_6H_4PAr_2$\}$_2$] (**1a**) (0.094 g, 0.076 mmol) was suspended in $CHCl_2CHCl_2$ (5 cm^3) and heated at reflux for 4 h to give a yellow solution and some metallic Pt deposit. The solvent was removed under reduced pressure, and the resulting residue was dissolved in $CDCl_3$. The solution was filtered through Florisil to remove the metallic deposit, and the solvent was removed under reduced pressure to give an off-white solid, **2a** (0.054 g, 55%). Colorless crystals were obtained by slowly evaporating the $CDCl_3$ solution in a NMR tube.

Method b. [Pt_2Cl_2\{2-$CMe_2C_6H_4PAr_2$\}$_2$] (**1a**) (0.094 g, 0.076 mmol) was suspended in CH_2Cl_2 (2 cm^3), and an excess of SO_2Cl_2 (0.1 cm^3) was added. The mixture was stirred for 4 h. The volatiles were then removed under reduced pressure. The resultant yellow solid was washed with toluene (3 × 2 cm^3) and hexane (3 × 1 cm^3) and then filtered off. The white solid **2a** was then dried under reduced pressure (0.091 g, 92%). Anal. Found (calc for $C_{27}H_{31}Cl_2$PPt): C, 49.64 (49.70); H, 4.71 (4.79). Mass spectrum (FAB): m/z 652 (M$^+$). NMR ($CDCl_3$): ^{31}P\{^{1}H\}, δ 17.5, J_{PtP} 3279 Hz; ^{1}H, δ 7.66−7.08 (m, 10H, C_6H_4), 6.79−6.73 (m, 2H, C_6H_4), 4.97 (s, J_{PtH} 48 Hz, 1H, CCH_2), 4.07 (m, 1H, CH(CH$_3$)$_2$), 3.89 (m, 1H, CH(CH$_3$)$_2$), 3.29 (s, J_{PtH} 42 Hz, 1H, CCH_2), 2.49 (s, J_{PtH} 36 Hz, 3H, CCH_3), 1.36 (d, 6H, CH(CH_3)$_2$), 1.22 (d, 3H, CH(CH_3)$_2$), 0.22 (d, 3H, CH(CH_3)$_2$); ^{13}C\{^{1}H\}, δ 163.3 (d, J_{PC} 5 Hz) 163.0 (s), 162.9 (d, J_{PC} 5 Hz), 156.4 (d, J_{PC} 12 Hz) 156.2 (d, J_{PC} 12 Hz), 154.0 (d, J_{PC} 18 Hz), 135.9 (d, J_{PC} 5 Hz), 135.3 (d, J_{PC} 11 Hz), 134.8 (d, J_{PC} 13 Hz), 122.1 (d, J_{PC} 69 Hz), 115.8 (d, J_{PC} 70 Hz), 115.0 (d, J_{PC} 10 Hz), 114.5 (d, J_{PC} 6 Hz), 114.3 (d, J_{PC} 7 Hz), 112.5 (d, J_{PC} 5 Hz), 112.1 (d, J_{PC} 12 Hz), 111.4 (d, J_{PC} 14 Hz), 110.6 (d, J_{PC} 13 Hz), 74.2 (s), 70.4 (J_{PtC} 151), 33.1 (d, J_{PC} 6 Hz), 32.8 (d, J_{PC} 9 Hz), 27.8 (s), 24.7 (s), 24.1 (s), 23.6 (s), 22.8(s).

Synthesis of [$PtCl_2$\{2-CH_2=$CMeC_6H_3$(4-OMe)P(C_6H_3(2-^{i}Pr)(4-OMe))$_2$\}] (2b). [Pt_2Cl_2\{2-$CMe_2C_6H_3$(4-OMe)PAr_2\}$_2$] (**1b**) (0.100 g, 0.070 mmol) was suspended in $CHCl_2CHCl_2$ (5 cm^3) and heated at reflux for 4 h to give a yellow solution and some metallic Pt deposit. The solvent was removed under reduced pressure, and the resulting residue was dissolved in $CDCl_3$. The solution was filtered through Florisil to remove the metallic deposit, and the solvent was removed under reduced pressure to give an off-white solid, **2b** (0.047 g, 45%). Anal. Found (calc for $C_{30}H_{37}Cl_2O_3$PPt): C, 47.90 (48.52); H, 5.38 (5.02). Mass spectrum (ESI): m/z 742 (M$^+$). NMR ($CDCl_3$): ^{31}P\{^{1}H\}, δ 12.0, J_{PtP} 3249; ^{1}H, δ 7.27−6.65 (m, 9H,

C_6H_3), 4.99 (t, J_{PtH} 48 Hz, 1H, CCH_2), 4.13 (t, 3.74, 2H, $CH(CH_3)_2$), 3.89 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.35 (s, J_{PtH} 72 Hz, 1H, CCH_2), 2.51 (s, J_{PtH} 42 Hz, 3H, CCH_3), 1.42 (d, 6H, $CH(CH_3)_2$), 1.30 (d, 3H, $CH(CH_3)_2$), 0.38 (d, 3H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ (CD_2Cl_2), δ 163.6 (s), 163.4 (d, J_{PC} 2 Hz), 163.3 (d, J_{PC} 2 Hz), 158.5 (d, J_{PC} 10 Hz), 156.2 (d, J_{PC} 13 Hz), 155.2 (d, J_{PC} 9 Hz), 154.9 (d, J_{PC} 10 Hz), 154.2 (d, J_{PC} 12 Hz), 153.9 (d, J_{PC} 11 Hz), 135.9 (s), 135.2 (d, J_{PC} 11 Hz), 134.5 (d, J_{PC} 11 Hz), 121.4 (d, J_{PC} 38 Hz) 119.4 (d, J_{PC} 14 Hz), 115.5 (d, J_{PC} 10 Hz), 115.3 (d, J_{PC} 11 Hz), 112.4 (d, J_{PC} 12 Hz), 111.6 (d, J_{PC} 12 Hz), 74.3 (s), 70.6 (J_{PtC} 102 Hz), 33.3 (d, J_{PC} 9 Hz), 32.8 (d, J_{PC} 8 Hz), 27.4 (s), 24.5 (s), 23.6 (s), 23.2 (s), 22.3 (s).

Synthesis of [$PtCl_2${2-CH_2=$CMeC_6H_3$(4-OMe)P(C_6H_2(2-^{i}Pr)(4-OMe)(5-Cl))$_2$}] (3b). [Pt_2Cl_2{2-$CMe_2C_6H_3$(4-OMe)PAr_2}$_2$] (**1b**) (0.100 g, 0.070 mmol) was suspended in toluene (10 cm^3), and an excess of SO_2Cl_2 (0.2 cm^3) was added. The mixture was stirred for 4 h. The volatiles were removed under reduced pressure. The resulting off-white solid was washed with hexane (3 × 10 cm^3) to give **3b** (0.076 g, 67%). Colorless crystals of **3b** were obtained from a toluene solution layered by hexane. Anal. Found (calc for $C_{30}H_{35}Cl_4O_3PPt$): C, 45.61 (44.77); H, 4.75 (4.35). Mass spectrum (ESI): *m*/*z* 811 (M^+). NMR ($CDCl_3$): $^{31}P\{^1H\}$, δ 11.29, J_{PtP} 3278 Hz; ^1H, δ 7.27−6.79 (m, 7H, C_6H_3, C_6H_2), 5.03 (s, 1H, J_{PtH} 54 Hz, CCH_2), 4.04 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.87 (br, 3.74, 2H, $CH(CH_3)_2$), 3.36 (s, 1H, J_{PtH} 66 Hz, CCH_2), 2.52 (s, 3H, J_{PtH} 42 Hz, CCH_3), 1.42 (d, 6H, $CH(CH_3)_2$), 1.31 (d, 3H, $CH(CH_3)_2$), 0.38 (d, 3H, $CH(CH_3)_2$).

Synthesis of the Diplatinum(IV) Complexes 5b/5b′. [Pt_2Cl_2{2-$CH_2C_6H_3$(4-OMe)PAr_2}$_2$] (**4b**) (0.25 g, 0.20 mmol) was dissolved in CH_2Cl_2 (3 cm^3), and SO_2Cl_2 (0.064 cm^3, 0.8 mmol) added dropwise to give a dark orange solution. Et_2O (12 cm^3) was added after 20 min, and the resulting precipitate collected on a frit and dried under reduced pressure to give a bright yellow powder, **5b/5b′** (0.24 g, 86%). Anal. Found (calc for $C_{48}H_{52}Cl_6O_6P_2Pt_2$): C, 41.46 (41.48); H, 3.92 (3.77). High-resolution ESI mass spectrum (calc for M^+): *m*/*z* 1386.06603 (1386.06660). NMR (CD_2Cl_2): $^{31}P\{^1H\}$ (1:1 mixture of isomers), δ 29.6, J_{PtP} 2870 Hz, 28.1, J_{PtP} 2824 Hz; ^1H (recorded at −80 °C), δ 7.25−6.48 (m, 18H, C_6H_3), 3.79 (br s, 18H, OCH_3), 1.98 (br m, 2H, CH_2), 1.85 (s, 3H, CH_3), 1.82 (s, 3H, CH_3); $^{13}C\{^1H\}$, δ 163.1 (s), 162.8 (d, J_{PC} 4 Hz), 155.8 (d, J_{PC} 12 Hz), 144.6 (br m), 131.4 (t, J_{PC} 7.5 Hz), 121.1 (s), 120.0 (s), 117.8 (br m), 113.3 (m), 111.4 (m), 55.7 (s), 55.5 (s), 55.4 (s), 41.7 (br m), 23.3 (s).

X-ray Crystal Structure Analyses. X-ray diffraction experiments on **2a** as its chloroform solvate were carried out at 173 K on a Bruker SMART diffractometer and on **3b** at 100 K on a Bruker SMART APEX diffractometer, using Mo Kα X-radiation (λ = 0.71073 Å) and a CCD area detector, on single crystals coated in paraffin oil and mounted on a glass fiber. Intensities were integrated[15] from several series of exposures, each exposure covering 0.3° in ω. Absorption corrections were based on equivalent reflections using SADABS V2.10,[16] and structures were refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL[17] Crystal and refinement data are given in Table 1. Data for **3b** were of low intensity and poor quality, leading to high R_{int} and R_1 values and a final difference map with large electron density features within 1 Å of the platinum atom but otherwise reasonable refinement characteristics.

Acknowledgment. We thank ORSAS and EPSRC for support, Johnson Matthey for a loan of $K_2[PtCl_4]$, The Leverhulme Trust for a Research Fellowship (to P.G.P.), and Claire McMullin for help with the presentation of the X-ray material. D.W.N. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) and The Royal Society for Postdoctoral Fellowships.

Supporting Information Available: X-ray crystal data, atomic coordinates, bond lengths and angles, and thermal displacement parameters for compounds **2a**·2$CHCl_3$ and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800382M

(15) *SAINT integration software*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.
(16) Sheldrick, G. M. *SADABS V2.10*; University of Göttingen, 2003.
(17) *SHELXTL program system version 5.1*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.