The Mechanism of Carbon−Carbon Bond Activation in Cationic 6-Alkylcyclohexadienyl Ruthenium Hydride Complexes

Christina M. Older and Jeffrey M. Stryker*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 Canada

Received August 17, 1999

Abstract: Carbon−carbon bond activation in cationic 6-*endo*-methyl-η^5-cyclohexadienyl and 6-*exo*-methyl-η^5-cyclohexadienyl ruthenium hydride complexes has been investigated. Contrary to expectations, it is the 6-*exo*-methyl complex and not the stereoisomeric 6-*endo*-methyl complex that undergoes selective carbon−carbon bond activation under exceptionally mild conditions, quantitatively converting the 6-*exo*-methyl substituent and the hydride ligand to methane. The mechanism of the activation reaction involves dissociation of protic acid from the agostic starting complex by reaction with a weak base (typically water), followed by protolytic activation of the alkyl group, with "back-side" assistance from the nucleophilic metal center. Under the same conditions, the corresponding 6-*endo*-methyl isomer undergoes selective dehydrogenation rather than demethylation, despite the proximity of the *endo*-methyl substituent to the metal center. For both *exo* and *endo* isomers, the cationic ruthenium hydride intermediates were determined by spectroscopic analysis to adopt fluxional agostic structures. The agostic complexes are kinetically stable at room temperature under rigorously anhydrous conditions but convert quantitatively to cationic η^6-arene products in the presence of a Brønsted base. The rates of both carbon−carbon bond activation and dehydrogenation are dependent on the identity and concentration of the base and suppressed in the presence of excess acid. The protolytic mechanism for carbon−carbon bond activation is supported by deuterium-labeling studies and by the reactivity of the neutral complexes toward Lewis acids and one-electron oxidants. This mechanism is shown to be relevant to carbon−carbon bond activation reactions observed in less-substituted 6-*exo*-methyl-η^5-cyclohexadienyl complexes and in a steroid-derived 6,6-disubstituted-η^5-cyclohexadienyl complex, representative of previously reported cases of dealkylative ligand aromatization. The low kinetic barrier for the protolytic dealkylation mechanism is contrasted to the comparatively high activation barriers reported for carbon−carbon bond activation reactions that occur in structurally related systems that cannot access a protolytic pathway. This investigation provides a consistent basis for rationalizing this potentially important but poorly understood class of metal-mediated reactions.

Introduction

Although the direct activation of alkane carbon−carbon bonds by soluble transition metal complexes remains elusive, transition metals mediate the activation of carbon−carbon bonds in a range of contexts.[1] Both oxidative and nonoxidative processes are relatively common, typically driven by a combination of kinetic and thermodynamic factors such as release of ring strain[2] and coordination-induced proximity. Proximity effects function to overcome the generally higher kinetic barrier for carbon−carbon bond activation over competitive carbon−hydrogen bond activation and promote selectivity in both oxidative[3] and nonoxidative reactions, the latter of which can generally be classified as β-alkyl elimination reactions.[4−9]

Ligand aromatization provides the driving force for one general class of β-alkyl elimination processes, in which alkylated η^4-cyclopentadiene and η^5-cyclohexadienyl complexes are converted into dealkylated η^5-cyclopentadienyl and η^6-arene complexes, respectively.[8,9] Similar reactions of η^5-cyclohexadienyl intermediates are presumably also involved in coordina-

(1) General reviews: Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1048. Merola, J. S. *Curr. Org. Chem.* **1997**, *1*, 235. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(2) Oxidative activation driven by relief of ring strain. Recent reviews: (a) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241. Hirao, T. *Top. Curr. Chem.* **1996**, *178*, 99. Recent lead references: (b) Yeh, W.-Y.; Hsu, S. C. N.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1998**, *17*, 2477. (c) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016. Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.

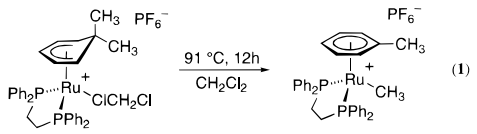
(3) Oxidative carbon−carbon activation: (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679 and references therein. Jun, C.-H. *Organometallics* **1996**, *15*, 895. Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880. (b) Rybtchinski, B.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528. Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. van der Boom, M. E.; Ben- David, Y.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1998**, 917. Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1998**, 687. van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415. Gandelman, M.; Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3981. Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406 and references therein.

(4) β-Alkyl elimination by "low-electrophilicity" late transition metals (selected recent references): (a) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11244. Hartwig, J. A.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, *16*, 1106. (b) Takemori, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 4346. Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779 and references therein. (c) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795. Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634. (d) Thompson, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068. Ankianiec, B. C.; Christou, V.; Hardy, D. T.; Thomson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963. (e) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893.

10.1021/ja992987e CCC: $19.00
Published on Web 03/14/2000

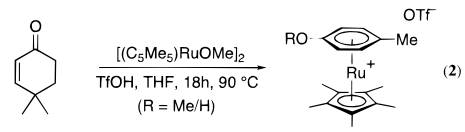
tion-induced hexaalkylbenzene dealkylation, a process mediated by aluminum trichloride and proceeding only in the presence of the transition metal.[10]

The mechanisms of 6-alkyl-η^5-cyclohexadienyl dealkylation reactions remain elusive. In the most rigorous previous investigation, Dimauro and Wolczanski[9d] clearly demonstrated that generation of a coordinatively unsaturated metal center is required[11] to induce β-methyl activation in phosphine-supported 6,6-dimethyl-η^5-cyclohexadienyl complexes of ruthenium (eq 1). Despite the presence of the highly labile dichloromethane



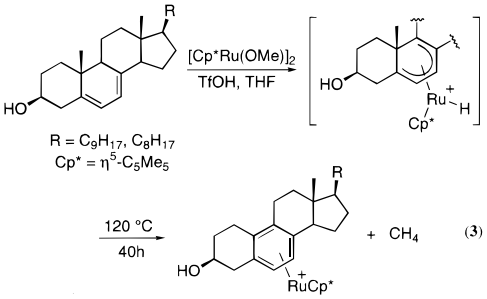
(1)

ligand, however, the demethylation proceeds slowly even at elevated temperature. In this investigation, it was not possible to determine whether it is the *endo*- or *exo*-methyl substituent that is activated in the reaction. Chaudret and co-workers[9a] demonstrated a similarly high activation barrier for the demethylation of 4,4-dimethyl-2-cyclohexenone, using an unsaturated cationic ruthenium complex to effect dehydrogenation and aromatization (eq 2). The formation of the 4-methylanisole



(2)

complex is presumed to arise from reaction with the methanol liberated upon protonation of $[(C_5Me_5)Ru(OMe)]_2$ with trifluorosulfonic acid. The methyl fragment is released principally as methane, although a minor amount of ethane is also formed. On the basis of this observation, the dealkylation was proposed to proceed by extrusion of methyl radical from a cationic η^5-cyclohexadienyl hydride intermediate. The ruthenium fragment also aromatizes unsaturated steroid substrates upon prolonged thermolysis at high temperature (e.g., eq 3); a partially characterized intermediate was observed in these reactions, spectroscopically consistent with the proposed η^5-cyclohexadienyl hydride complex.[9a,b] The high activation barrier for demethylation was attributed to the stereochemistry of ruthenium binding: the reaction clearly proceeds by activation of a methyl group on the *exo* face of the coordinated ring.



(3)

In contrast, the groups of both Chaudret and Itoh have reported closely related dealkylation reactions that proceed under surprisingly mild conditions, although the dealkylations occur only as minor reaction pathways (Scheme 1). Thus, the aromatization of 3-methylcyclohexene proceeds under Chaudret's conditions to yield a minor fraction of the η^6-benzene complex along with the major η^6-toluene product *at room temperature*.[9a] Itoh observes demethylation as a minor pathway in ruthenium-mediated diene/alkyne cycloaddition at low temperature, a reaction that leads principally to the formation of double alkyne adducts.[9c] Both reactions were rationalized by proposing the formation of stereoisomeric η^5-cyclohexadienyl intermediates **1**-*exo* and **1**-*endo*, with the dealkylation pathway arising from the sterically less favorable minor *endo*-methyl intermediate. It is attractive to attribute the difference in activation barriers between this system and Wolczanski's

(5) β-Alkyl elimination by electrophilic lanthanide and early transition metals: (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6471. Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (b) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. Bercaw, J. E. *Pure Appl. Chem.* **1990**, *62*, 1151. Burger, B. J.; Thompson, M.; Cotter, D.; Bercaw, J. *J. Am. Chem. Soc.* **1990**, *112*, 1566. (c) Horton, A. D. *Organometallics* **1996**, *15*, 2675. Etienne, M.; Mathieu, R.; Donnadieu, B. *J. Am. Chem. Soc.* **1997**, *119*, 3218. β-Carbon elimination in olefin polymerization catalysis: (d) Eshuis, J.; Tan, Y.; Teuben, J. *J. Mol. Catal.* **1990**, *62*, 277. Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (e) Mise, T.; Kageyama, A.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1991**, 1525. (f) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (g) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565. (h) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424. (i) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (j) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147. (k) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392.

(6) Carbon−carbon bond activation by electrophilic late metal complexes: (a) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891. (b) Nicholls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781. Cracknell, R. B.; Nicholls, J. C.; Spencer, J. L. *Organometallics* **1996**, *15*, 446. (c) Dzwiniel, T. D.; Etkin, N.; Stryker, J. M., *J. Am. Chem. Soc.* **1999**, *121*, 10640.

(7) Activation reactions driven by a combination of factors: (a) Murakami, M.; Amii, H.; Kunji, S.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285. Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540. (b) Kondo, T.; Kodoi, K.; Nishinaga, E.; Okada, T.; Morisaki, Y.; Watanabe, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **1998**, *120*, 5587.

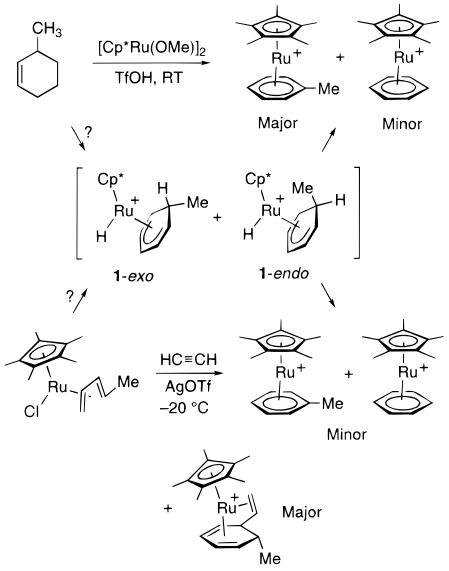
(8) Carbon−carbon bond activation driven by ligand aromatization. Alkylated η^4-cyclopentadiene conversions: (a) Kang, J. W.; Maitlis, P. M. *J. Am. Chem. Soc.* **1968**, *90*, 3259. Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773. King, R. B.; Douglas, W. M.; Efraty, A. *J. Organomet. Chem.* **1974**, *69*, 131. (b) Eilbracht, P. *Chem. Ber.* **1976,** *109*, 1429, 3136. Eilbracht, P. *J. Organomet. Chem.* **1976**, *120*, C37. Eilbracht, P.; Dahler, P. *J. Organomet. Chem.* **1977**, *125*, C23. Eilbracht, P.; Dahler, P. *J. Organomet. Chem.* **1977**, *127*, C48. Eilbracht, P.; Mayser, U. *J. Organomet. Chem.* **1977**, *135*, C26. Eilbracht, P.; Dahler, P. *Chem. Ber.* **1980**, *113*, 542. Eilbracht, P.; Dahler, P.; Mayser, U.; Henkes, E. *Chem. Ber.* **1980**, *113*, 1033. Eilbracht, P.; Mayser, U.; Tiedtke, G. *Chem. Ber.* **1980**, *113*, 1420. Eilbracht, P.; Mayser, U. *Chem. Ber.* **1980**, *113*, 2211. (c) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. Barretta, A.; Cloke, F. G., N.; Feigenbaum, A.; Green, M. L. H.; Gourdon, A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1981**, 156. Baretta, A.; Chong, K. S.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1983**, 861. Green, M. L. H.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1984**, 1442. Gladyz, J. A.; Fulcher, J. G.; Ugolick, R. C.; Hanlan, A. J. L.; Bocarsly, A. B. *J. Am. Chem. Soc.* **1979**, *101*, 3388. Fu, Y.-T.; Chao, P.-C.; Liu, L.-K. *Organometallics* **1998**, *17*, 221. (d) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260. Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. H. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (e) Hemond, R. C.; Hughes, R. P.; Locker, M. B. *Organometallics* **1986**, *5*, 2392. (f) Jones, W. D.; Maguire, *Organometallics* **1987**, *6*, 1301.

(9) Carbon−carbon bond activation driven by ligand aromatization. η^5-Cyclohexadienyl conversions: (a) Rondon, D.; Chaudret, B.; He, X.-D.; Labroue, D. *J. Am. Chem. Soc.* **1991**, *113*, 5671. Urbanos, F.; Halcrow, M. A.; Fernandez-Baeza, J.; Dahan, F.; Labroue, D.; Chaudret B. *J. Am. Chem. Soc.* **1993**, *115*, 3484. Chaudret, N. *Bull. Soc. Chim. Fr.* **1995**, *132*, 268. (b) Chaudret, B.; Halcrow, M. A.; Urbanos, F. *Organometallics* **1993**, *12*, 955. (c) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *Organometallics* **1993**, *12*, 2221. (d) Dimauro, P. T.; Wolczanski, P. T. *Polyhedron* **1995**, *1*, 149.

(10) (a) Fischer, E. O.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162. (b) Roman, E.; Astruc, D. *Inorg. Chim. Acta* **1979**, *37*, L465. Astruc, D. *Tetrahedron* **1983**, *39*, 4027.

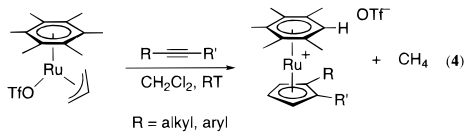
(11) The reaction of 1,1-dimethylcyclohexane with $[L_2Ir(acetone)_2]^+$ [L = $(p\text{-}FC_6H_4)_3P$], for example, leads to the coordinatively saturated [(6,6-dimethyl-η^5-cyclohexadienyl)$Ir(H)L_2]^+$, which does not undergo subsequent demethylation, even under harsh reaction conditions.[8d]

Scheme 1



presumed *endo*-dealkylations to the possibility of a concerted extrusion of methane from the coordinatively saturated and sterically crowded intermediate **1**-*endo*. This rationalization is inconsistent, however, with Chaudret's high-temperature demethylation of 4,4-dimethyl-2-cyclohexenone, which is proposed to proceed via an analogous intermediate.

Our interest in the aromatization of η^5-cyclohexadienyl complexes was engendered by the serendipitous discovery of a general new class of arene dealkylation reactions that converts coordinated hexamethylbenzene into pentamethylbenzene in high yield under exceptionally mild conditions (eq 4).[12] The



dealkylation is integrated into an overall [3 + 2] cycloaddition that converts (η^6-hexamethylbenzene)ruthenium η^3-allyl complexes and disubstituted alkynes into (η^6-*penta*methylbenzene)-ruthenium η^5-dialkylcyclopentadienyl complexes and methane. Allyl/alkyne [3 + 2] cycloaddition reactions have been previously reported for η^5-cyclopentadienyl,[13] η^5-pentamethylcyclopentadienyl,[14] and η^6-arene[13] complexes of the late transition metals, but the process normally proceeds via "oxidative" extrusion of dihydrogen. While no mechanistic investigations have been reported, the transformation can be rationalized by proposing the intermediacy of a cationic η^4-cyclopentadiene hydride complex **I** (Figure 1). This intermediate can, in principle, undergo dehydrogenation to give the expected η^5-cyclopentadienyl product **II** or demethylation of the ancillary hexamethylbenzene ligand, as observed. A satisfying mechanistic rationale for the dealkylation pathway, however, is problematic. Migration

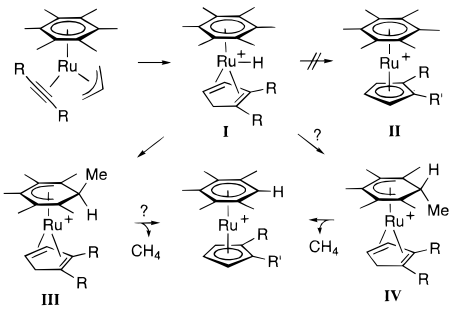


Figure 1.

of the hydride ligand to the η^6-arene is adequately precedented,[15] but this leads to a 6-*exo*-methyl-η^5-cyclohexadienyl intermediate **III** that appears to be a poor candidate for low-temperature carbon−carbon bond activation. While the 6-*endo*-methyl stereoisomer **IV** constitutes an attractive precursor to demethylation, it is not at all obvious how such an intermediate might arise.[16]

In this report, the synthesis and aromatization reactions of a series of stereochemically unambiguous ruthenium 6-methyl-η^5-cyclohexadienyl complexes are described. The low-temperature carbon−carbon bond activation is shown to proceed by an unexpected mechanistic pathway that considerably clarifies prior investigations into the dealkylation of η^5-cyclohexadienyl complexes and our own report of hexamethylbenzene demethylation.

Results and Discussion

Synthesis of 6-Methyl-η^5-cyclohexadienyl Ruthenium Complexes. To evaluate stereochemical effects on carbon−carbon bond activation in 6-methyl-η^5-cyclohexadienyl aromatization reactions, a stereochemically unambiguous synthesis of cationic ruthenium complexes modeling putative intermediates **III** and **IV** was required. This was accomplished by protonation of the neutral (η^5-cyclopentadienyl)ruthenium η^5-cyclohexadienyl precursors, which in turn were prepared by regioselective nucleophilic addition to the corresponding cationic η^6-arene complexes. Such reactions generally proceed by stereoselective alkylation of the *exo*-face of the coordinated arene.[17,18]

Thus, the known[19] cation [(η^5-C_5Me_5)Ru(η^6-hexamethylbenzene)]$^+BF_4^-$ (**2**) was prepared from [(η^5-C_5Me_5)RuCl]$_4$ and converted to the η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl complex **3** in moderate yield by treatment with lithium triethylborohydride in tetrahydrofuran at low temperature (Scheme 2). The addition was confirmed by the presence of a high-

(12) (a) Preliminary communication: Older, C. M.; Stryker, J. M. *Organometallics* **1999**, *17*, 5596. (b) Synthetic and mechanistic details will be presented in a complete account: Older, C. M.; Stryker, J. M., manuscript in preparation.

(13) (a) Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Yu. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349. (b) Lutsenko, Z. L.; Petrovskii, P. V.; Bezrukova, A. A.; Rubezhov, A. Z. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1988**, *37*, 735; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 855.

(14) (a) Iridium: Schwiebert, K. E.; Stryker, J. M. *Organometallics* **1993**, *12*, 600. (b) Cobalt: Nehl, H. *Chem. Ber.* **1993**, *126*, 1519.

(15) (a) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 1730. (b) Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745. (c) Kowalski, A. S.; Ashby, M. T. *J. Am. Chem. Soc.* **1995**, *117*, 12639.

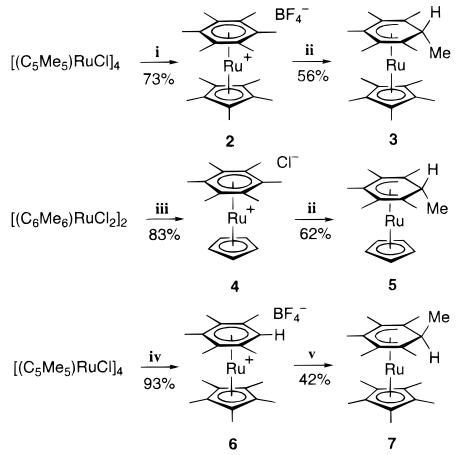
(16) It is possible to propose a pathway involving protonation of a neutral η^6-arene intermediate on the *exo* face of the arene ligand to give a 6-*endo*-methyl complex. This requires deprotonation of a cationic η^4-cyclopentadiene intermediate by a catalytic amount of an adventitious base to generate the neutral substrate. It is also possible to consider an unprecedented unimolecular mechanism involving a 1,2-methyl migration on the *exo*-face of the 6-methyl-η^5-cyclohexadienyl intermediate, leading to the formation of a 6,6-dimethyl-η^5-cyclohexadienyl intermediate that undergoes activation of the *endo* substituent. These rationales, along with synthetic and mechanistic investigations specifically relevant to hexamethylbenzene dealkylation, will be more completely discussed in a subsequent report.[12b]

(17) Alkylation of [(η^5-cyclopentadienyl)Ru(η^6-benzene)]$^+$: Vol'kenau, N. A.; Bolesova, I. N.; Shul'pina, L. S.; Kitaigorodskii, A. N. *J. Organomet. Chem.* **1984**, *267*, 313.

(18) Alkylation of [(η^5-cyclopentadienyl)Fe(η^6-$R_nC_6H_{6-n}$)]$^+$: (a) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. (C)* **1968**, 2257. (b) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. (C)* **1969**, 2024.

(19) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

Scheme 2[a]



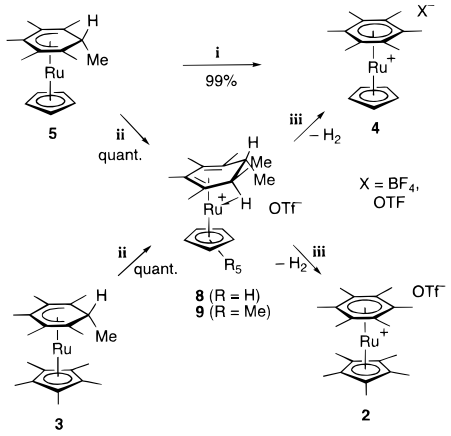
[a] Conditions: (i) C_6Me_6, $AqBF_4$, CH_2Cl_2, 35 °C; (ii) $LiEt_3BH$, THF, 0 °C → room temperature; (iii) C_5H_6, Na_2CO_3, EtOH, Δ; (iv) C_6Me_5H, $AgBF_4$, CH_2Cl_2, 35 °C; (v) MeLi, THF, −78 °C → room temperature.

field[18,20] methyl doublet (δ 0.95) in the ^{1}H NMR spectrum, accompanied by a quartet resonance for the methine position (δ 2.44). While structurally related complexes bearing a similar *exo*-methine hydrogen generally show an anomalously low-frequency C−H stretch in the infrared spectrum (ca. 2750−2820 cm^{-1}),[20] the lowest frequency C−H absorption in the infrared spectrum of complex **3** appears at 2847 cm^{-1}, only marginally lower in energy than the 2852 cm^{-1} absorption observed for the stereoisomeric complex **7** (vide infra). The corresponding cyclopentadienyl complex **5** was similarly prepared from [(η^5-C_5H_5)Ru(η^6-hexamethylbenzene)]$^+$Cl$^-$ (**4**),[21] which was itself synthesized from [(η^6-hexamethylbenzene)-$RuCl_2$]$_2$[22a] and cyclopentadiene using a modification of a literature procedure (Scheme 2).[22] The off-white solid was characterized spectroscopically and used for subsequent transformations without further purification.

Stereoisomeric η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl complex **7** was prepared from [(η^5-C_5Me_5)Ru(η^6-pentamethylbenzene)]$^+$$BF_4^-$ (**6**)[19] by regioselective alkylation with methyllithium at low temperature (Scheme 2). The selective addition to the single unsubstituted position on the pentamethylbenzene ligand is remarkable but consistent with the results reported by Pauson et al. for alkylation of the analogous pentamethylbenzene complexes of iron.[18] Complex **7** was purified by chromatography on neutral alumina and isolated as a crystalline solid in moderate yield. The 6-*exo*-methyl substituent in complex **7** is strongly shielded by the ruthenium center, resonating at δ 0.11 in the ^{1}H NMR spectrum.

Protonation of 6-*endo*-Hexamethylcyclohexadienyl Complexes. The reactivity of the 6-*endo*-methyl complexes **3** and **5** was first investigated. Contrary to expectations, protonation of cyclopentadienyl complex **5** with tetrafluoroboric acid in acetone-d_6 at room temperature leads to the rapid regeneration of the cationic η^6-hexamethylbenzene complex **4**, presumably via loss of dihydrogen (Scheme 3). The reaction is clean and quantitative, as determined both by in situ spectroscopic analysis and by product isolation. Protonation using trifluoromethanesulfonic acid (triflic acid) in rigorously anhydrous dichloromethane-d_2, however, leads to the quantitative formation of an intermediate, identified spectroscopically as the cationic agostic hydride complex [(C_5H_5)Ru(η^4-1,2,3,4,5-*exo*-6-*endo*-hexamethylcyclohexadiene)]$^+$OTf$^-$ (**8**). The complex exhibits an upfield doublet of septets at δ −4.81 (J = 13.3, 2.6 Hz, respectively), characteristic of a fluxional agostic hydride ligand, rapidly equilibrating between the ends of the unsaturated moiety via a symmetric η^5-cyclohexadienyl ruthenium hydride transition state or intermediate. The large vicinal coupling constant confirms the *trans* disposition of the methyl substituents, supporting a mechanism involving direct protonation at the ruthenium center. Consistent with this fluxional structure, the complex shows time-averaged symmetry in both the ^{1}H and ^{13}C NMR spectra at room temperature and a methyl resonance (δ 1.67, d, 6H) coupled to the agostic hydride by an unusually small vicinal coupling constant (J = 2.7 Hz), as established by homonuclear decoupling experiments. This dynamic behavior and the low barrier to the 1,5-intraligand hydride transfer are closely analogous to several extensively investigated agostic complexes formed by protonation of ruthenium η^5-pentadienyl complexes.[23,24] Attempted isolation of this intermediate results in the development of product mixtures, and no further characterization was pursued.

Scheme 3[a]



[a] Conditions: (i) HBF_4·Et_2O, acetone-d_6, 20 °C, 10 min; (ii) HOTf, CH_2Cl_2 (anhydrous), −35 °C → room temperature; (iii) MeOH (anhydrous), room temperature, 3 h (**8**) or 5 d (**9**).

Protonation of the corresponding pentamethylcyclopentadienyl complex **3** with triflic (or tetrafluoroboric) acid in dichloromethane-d_2 under strictly anhydrous conditions provides the isostructural fluxional agostic hydride complex **9** (Scheme 3), as deduced by analysis of the closely analogous spectroscopic data. The agostic hydride resonance in the ^{1}H NMR spectrum is shifted to higher field (δ −5.82), consistent with the greater shielding induced by the pentamethylcyclopentadienyl ring. This signal shows the expected large vicinal coupling constant to the 6-*exo* proton, but the coupling to the flanking methyl substituents is unresolved at room temperature, despite the

(20) See: Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857 and references therein.

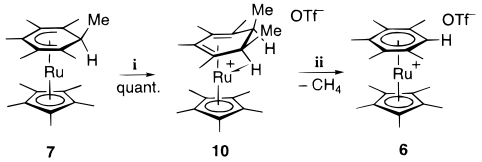
(21) Complex **2** was previously prepared by the treatment of [(η^6-hexamethylbenzene)$RuCl_2$]$_2$ with (C_5H_5)Tl: Baird, M. C. Zelonka, R. A. *J. Organomet. Chem.* **1972**, *44*, 383.

(22) (a) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74. (b) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1978**, *153*, C25.

(23) (a) Cox, D. N.; Roulet R. *J. Chem. Soc., Chem. Commun.* **1988**, 951. (b) Cox, D. N.; Roulet R. *J. Chem. Soc., Chem. Commun.* **1989**, 175. (c) Lumini, T.; Cox, D. N.; Roulet R.; Chapuis, G.; Nicolo, F. *Helv. Chim. Acta* **1990**, *73*, 1931. (d) Lumini, T.; Cox, D. N.; Roulet R.; Schenk, K. *J. Organomet. Chem.* **1992**, *434*, 363. (e) Cox, D. N.; Lumini, T.; Roulet R. *J. Organomet. Chem.* **1992**, *438*, 195.

(24) (a) Gleiter, R.; Hyla-Kryspin, I.; Ziegler, M. L.; Sergeson, G.; Green, J. C.; Stahl, L.; Ernst, R. D. *Organometallics* **1989**, *8*, 298. (b) Newbound, T. D.; Stahl, L.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1990**, *9*, 2962. (c) Trakarnpruk, W.; Hyla-Kryspin, I.; Arif, A. M.; Gleiter, R.; Ernst, R. D. *Inorg. Chim. Acta* **1997**, *259*, 197. (d) Bosch, H. W.; Hund, H.-U.; Nietlispach, D.; Salzer, A. *Organometallics* **1992**, *11*, 2087.

Scheme 4[a]



[a] Conditions: (i) HOTf, CH_2Cl_2 (anhydrous), room temperature; (ii) H_2O, room temperature, 1 h.

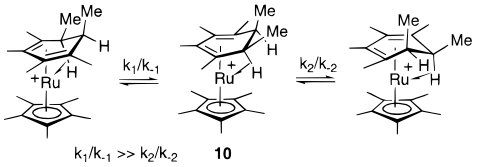
appearance of resolved coupling (J = 2.4 Hz) in the corresponding methyl resonance.

Complexes **8** and **9** persist indefinitely in solution, so long as anhydrous conditions are maintained. Upon addition of water or methanol (5−7 equiv), however, both complexes extrude hydrogen and convert to the corresponding η^6-hexamethylbenzene complexes **2** and **4** (Scheme 3). The reaction of cyclopentadienyl complex **8** with water is quantitative and complete within minutes at room temperature, but the alcohol is a much less effective catalyst: upon treatment with methanol, the dehydrogenation of complex **8** and pentamethyl complex **9** requires hours and days, respectively, to go to completion. As determined in a series of qualitative experiments, both dehydrogenation reactions are inhibited by excess acid and suppressed when the molar amount of protic acid exceeds the amount of base present in or added to the system.

Protonation of the 6-*exo*-Hexamethylcyclohexadienyl Complex. Carbon−Carbon Bond Activation. Consistent with the reactivity observed in the 6-*endo* series, but contrary to our initial assumptions, protonation of 6-*exo*-hexamethylcyclohexadienyl complex **6** with either triflic acid or tetrafluoroboric acid leads to exclusive activation of the *exo*-methyl carbon−carbon bond. Similar to the *endo*-methyl derivatives, an intermediate complex can be prepared and characterized spectroscopically under rigorously anhydrous conditions. Thus, treatment of complex **7** with a slight excess of triflic acid in anhydrous dichloromethane-d_2 at room temperature results in the formation of the cationic agostic hydride complex [(C_5Me_5)Ru(η^4-1,2,3,4,5-*exo*-6-*exo*-hexamethylcyclohexadiene)]$^+$OTf$^-$ (**10**) (Scheme 4). Spectroscopic analysis of this material at room temperature is relatively uninformative: the complex exhibits resolved but very broad resonances in the ^{1}H NMR spectrum. The broad signal at δ −5.83 nonetheless suggests the presence of an agostic hydride ligand. The ^{13}C NMR spectrum at room temperate is even less informative, with only the pentamethylcyclopentadienyl resonances evident above the baseline. Reacquisition of the data at low temperature (−80 °C) resolves the (nonagostic) 6-*endo*-hydrogen signal at δ 2.53 (br q, J = 6.6 Hz) coupled to the 6-*exo*-methyl resonance at δ 0.22 (d, J = 6.5 Hz, 3H), which is shifted considerably further upfield from the 6-*endo*-methyl resonances[20] in either complex **8** or **9** (δ 1.12 and 1.21, respectively). The agostic hydride signal, however, remains an unresolved multiplet even at low temperature, reflecting both the small vicinal coupling constant to the 6-*endo*-hydrogen and the persistent fluxionality arising from the fast 1,5-intraligand hydride transfer. Both the ^{1}H and ^{13}C NMR spectra at −80 °C reflect the higher symmetry structure that results from this fluxional process.

At higher temperatures in 1,1,2,2-tetrachloroethane-d_2, the agostic and free methine signals further broaden, as do the arene methyl resonances, coalescing at approximately 80 °C. The higher temperature fluxional process was further probed by irradiation of the agostic hydride resonance at room temperature, which results in spin saturation transfer to the broad *endo*-hydrogen resonance at δ 2.59 and complete suppression of this signal. Similarly, irradiation of the upfield 6-*exo*-methyl resonance leads to saturation transfer to the remaining (broad) methyl signals at δ 2.25 and 1.71. Taken together, the spectroscopic data are consistent with the occurrence of two distinct fluxional processes operating at very different rates: facile 1,5-intraligand transfer of the agostic hydrogen, similar to that observed in the *endo*-methyl series, and a higher activation energy process that shifts the agostic interaction to the adjacent *endo*-methine hydrogen (Scheme 5). The latter process is slow below room temperature but at higher temperature provides a mechanism for complete equilibration of the cyclohexadiene methyl groups and methine hydrogen atoms. Structurally similar but nonfluxional *exo*-methyl intermediates have been previously observed spectroscopically by Chaudret et al., although the complexes were described as classical cationic η^5-cyclohexadienyl ruthenium hydrides.[9a,b]

Scheme 5



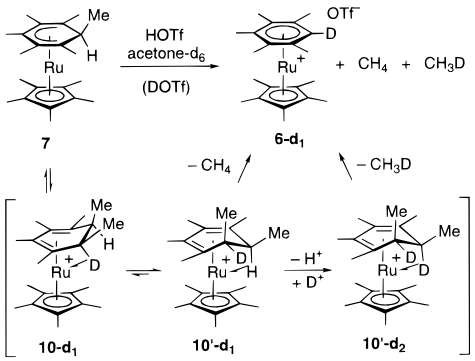
Agostic *exo*-methyl cyclohexadiene complex **10** persists indefinitely in solution under strictly anhydrous conditions. Upon addition of distilled water (6 equiv) to a solution of the agostic complex prepared from the protonation using 1 equiv of acid, quantitative conversion to the cationic η^6-pentamethybenzene complex **6** and methane (δ 0.2 in CD_2Cl_2, 22 °C) is observed within 1 h at room temperature (Scheme 4). As observed in the 6-*endo*-methyl complex, this extrusion is also suppressed in the presence of excess acid, provided that the amount of acid is sufficient to scavenge all of the base present in solution.[25] No other organic or organometallic intermediates or byproducts are detected by spectroscopic analysis.

Isotopic Labeling Studies. Two deuterium labeling experiments confirm the exchange equilibria suggested by variable-temperature NMR spectroscopy and provide additional insight into the mechanism of carbon−carbon bond activation in this system. Treatment of 6-*exo*-hexamethylcyclohexadienyl complex **7** with deuterium-labeled[26] triflic acid (CF_3SO_3D, 1.2 equiv) in nominally anhydrous acetone-d_6 leads to the instantaneous formation of the deuterium-labeled agostic cyclohexadiene complex **10**, as determined by analysis of the ^{1}H NMR spectrum. This reaction is followed by slow formation of deuterium-labeled η^6-pentamethylbenzene complex **6**-d_1 and evolution of methane over a period of 24 h (Scheme 6). To the limits of spectroscopic detection, the deuterium label is located exclusively in the η^6-pentamethylbenzene ligand methine position, although the methane produced also contains an unquantified but substantial amount of methane-d_1 (CH_3D, δ 0.13, 1:1:1 triplet). These results are consistent with a mechanism in which the kinetically formed cationic intermediate **10**-d_1, with a C−D agostic

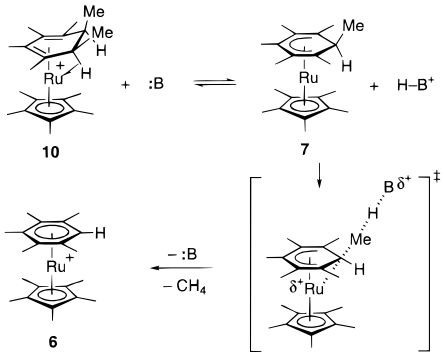
(25) The reaction of 6-*exo* complex **7** in dichloromethane with 2.7 equiv of triflic acid in the presence of 6.7 equiv of water, for example, proceeds 50% to completion after 48 h at room temperature, as monitored by NMR spectroscopy. Under otherwise identical conditions but in the presence of 6 equiv each of triflic acid and water, no detectable conversion is observed over the same time period. Upon addition of a further 5 equiv of water to this reaction mixture, however, the conversion to pentamethylbenzene complex **6** proceeds approximately 60% to completion after an additional 48 h.

(26) Deuterium-labeled triflic acid was prepared in situ by exchange of triflic acid and acetone-d_6. This exchange appears to be rapid at room temperature, in contrast to the isotopic exchange of tetrafluoroboric acid in the same medium, which proceeds only slowly.

Scheme 6

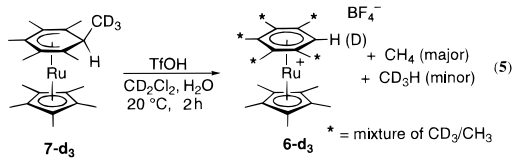


Scheme 7



interaction, equilibrates rapidly to form the thermodynamically more favored[27] intermediate **10′**-d_1 prior to activation of the 6-*exo* carbon−carbon bond. This proposal is supported by the absence of the signal assigned to the 6-*endo*-hydrogen (δ 2.7 in acetone-d_6) in the ^{1}H NMR spectrum acquired immediately after addition of the acid. The small amount of methane-d_1 can arise from methane loss from undetected **10**-d_1 or, more likely, from the formation of doubly labeled **10**-d_2 by incorporation of a second deuterium atom via exchange of the agostic protium in **10′**-d_1 with the slight excess of labeled triflic acid used in the experiment. This exchange requires that the agostic intermediate **10** be in equilibrium with the neutral hexamethylcyclohexadienyl complex **7** and free acid during the course of the demethylation reaction. Importantly, it also suggests an alternative mechanism for carbon−carbon bond activation of the *exo*-methyl complex **10** (vide infra).

The high-temperature exchange equilibria revealed by NMR spectroscopy were probed chemically by treatment of 6-*exo*-CD_3-pentamethylcyclohexadienyl complex **7**-d_3[28] with triflic acid in wet dichloromethane-d_2 (eq 5). This reaction provides



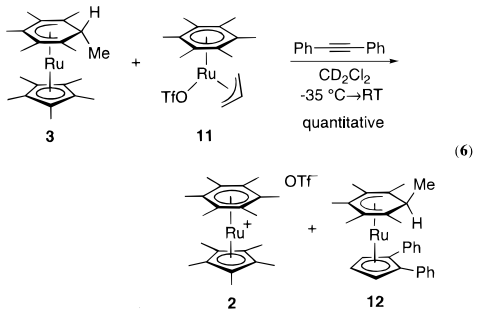
pentamethylbenzene complex **6** with equivalent deuterium incorporation into all arene methyl positions, confirming complete *endo*-hydrogen scrambling in this system. Consistent with this observation, the methane released into solution is largely unlabeled, accompanied by a minor fraction of the tentatively identified CD_3H (δ 0.12, br s). Repetition of this experiment using tetrafluoroboric acid in acetone-d_6 also provides equivalent incorporation of the labeled methyl group into all arene positions. In addition, however, a small amount of deuterium appears in the unsubstituted arene position, presumably a result of the slow H/D exchange between the acid and acetone-d_6.[26]

Mechanism of the Carbon−Carbon Bond Activation. Taken together, our experimental observations strongly suggest that the mechanism for low-temperature carbon−carbon bond activation of 6-alkylcyclohexadienyl ligands involves a ruthenium-assisted protolytic dealkylation by Brønsted acid with complete selectivity for activation of the *exo* substituent (Scheme 7). The acid is liberated from the intermediate agostic cyclohexadiene cation in a preequilibrium induced by a base, the source of which can be the solvent, adventitious or added water, or, perhaps, the weakly basic counterion. In addition to accommodating the stereoselectivity of the activation process, this mechanistic rationale is consistent with and strongly supported by all of the experimental evidence. The thermal stability of the 6-*exo* and 6-*endo* agostic η^4-methylcyclohexadiene cations **8**−**10** under strictly anhydrous conditions is inconsistent with a mechanism involving thermal radical scission of an *exo*-methyl substituent or any pathway invoking direct metal-mediated activation of an *endo*-methyl substituent or concerted extrusion of methane from a classical hydrido 6-*endo*-methyl-η^5-cyclohexadienyl intermediate. Standard steady-state or preequilibrium kinetic analysis of the mechanism proposed in Scheme 7 predicts that the rate of dealkylation will be first-order dependent on the concentration of base and independent of the concentration of acid above that required to produce the agostic complex **10**, as observed experimentally. The inhibition of the reaction observed in the presence of excess strong acid thus arises from the efficient scavenging of the available base. Inhibition by excess acid equally eliminates from consideration pathways involving protonolysis of an already cationic precursor. Also consistent with an acid/base mechanism is the qualitative observation of rate differences for both dealkylation and dehydrogenation as a function of the Brønsted base (water vs methanol) and the significantly slower dehydrogenation rate observed for the more strongly basic pentamethylcyclopentadienyl ligand system in complex **8** over the parent cyclopentadienyl complex **9**.

The deuterium labeling experiment (Scheme 6) suggests that protonation of the neutral hexamethylcyclohexadienyl complex is reversible under the reaction conditions. To confirm that protic acid is liberated from the cationic intermediate and to probe for the intervention of alternative dealkylation mechanisms, a crossover experiment was designed in which no external source of acid is provided. Thus, the [3 + 2] cycloaddition of (η^6-hexamethylbenzene)Ru(η^3-allyl)OTf (**11**) and diphenylacetylene was conducted in the presence of the neutral 6-*endo*-hexamethylcyclohexadienyl complex **3** (eq 6). Without intervention, the diphenylacetylene cycloaddition proceeds slowly and quantitatively to yield methane and (η^5-1,2-diphenylcyclopentadienyl)-ruthenium(η^6-pentamethylbenzene)$^+$OTf$^-$ under the reaction conditions, presumably via an intermediate analogous to 6-*exo* complex **10**.[12] The use of the 6-*endo*-hexamethylcyclohexadienyl complex **3** in this experiment was based on its established efficiency as an acid scavenger. In the event, the reaction proceeds quantitatively to give the crossover products, [(η^5-C_5Me_5)Ru(η^6-C_6Me_6)]$^+$OTf$^-$ (**2**-OTf) and the neutral (η^5-1,2,3,4,5,6-

(27) The thermodynamic preference for CH over CD agostic interactions has been documented: (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(28) The 6-*exo*-CD_3-pentamethylcyclohexadienyl complex **7**-CD_3 was prepared by alkylation of cationic η^6-pentamethybenzene complex **6** with CD_3Li, under conditions otherwise identical to those described for the synthesis of the unlabeled material.



exo-hexamethylcyclohexadienyl)ruthenium η^5-1,2-diphenylcyclopentadienyl (**12**),[29] unambiguously establishing the presence of a Brønsted acid in the medium.[30] This reaction also confirms the competency of *exo*-methyl complex **12** as an intermediate in the dealkylative [3 + 2] cycloaddition reaction.[12b] A related electrophilic abstraction of an *exo* carbon−carbon bond was recently postulated for acid-mediated cyclopropane ring opening of (η^4-spirobicyclo[2.4]hepta-4,6-diene)Fe(CO)$_3$.[31]

The specificity and low activation barrier for cleavage of the *exo* carbon−carbon bond can be rationalized by considering that significant stabilization of the transition state may be provided from interaction of a filled metal-centered (or mixed metal/cyclohexadienyl)[32] molecular orbital with the σ^*-orbital of the activating carbon−carbon bond (Figure 2a). This bonding interaction transforms without discontinuity into a metal−arene bonding orbital as the bent cyclohexadienyl ring[32] converts into the planar arene ligand. A similar molecular orbital interaction is considered to be responsible for the low-frequency C−H vibrational mode observed for the *exo* carbon−hydrogen bond in the infrared spectra of other η^5-cyclohexadienyl complexes[20] and is consistent with the shielding experienced by the *exo*-methyl substituent in the ^{1}H NMR spectrum of complex **7**. The metal is, in effect, displacing the methyl substituent by a concerted nucleophilic substitution with electrophilic assistance from the proton, which functions to stabilize the anionic alkyl leaving group. The high activation barrier for direct metal-mediated *endo* activation can be attributed to the strong metal ↔ alkyl antibonding interaction experienced by the *endo* substituent as the η^5-cyclohexadienyl ligand distorts to position the substituent in proximity to the metal (Figure 2b).[32] This four-electron repulsion is mitigated by unsaturation at the metal, but as demonstrated by Dimauro and Wolczanski,[9d] the barrier to carbon−carbon bond activation remains high.

Dealkylation Using Lewis Acids. Additional support for the protolytic mechanism for carbon−carbon bond activation in 6-*exo*-methylcyclohexadienyl ruthenium complexes is provided by the reactions of the neutral precursor with Lewis acids. Although carbon−carbon bond activation is, indeed, observed under mild conditions, surprising differences are found in the mechanistic detail. Thus, the reaction of η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl complex **7** with tris(perfluorophenyl)borane[33] at low temperature under strictly anhydrous conditions leads to instantaneous and quantitative *hydride* abstraction from a methyl substituent, providing the 5-methylene-1,3-cyclohexadiene complex **13**, as determined by in situ NMR spectroscopic analysis (Scheme 8). This complex could not be isolated without suffering partial further conversion, but spectroscopic analysis strongly supports the structural assignment. The exocyclic methylene moiety is defined by the appearance of two downfield resonances for the inequivalent methylene hydrogen atoms (δ 4.33 and 3.54), bonded directly to an sp^2-hybridized carbon (δ 76.2, $^1J_{C-H}$ = 161 Hz), as determined by ^{13}C−^{1}H heteronuclear correlated NMR spectroscopy. The chemical shifts of the remaining quaternary carbon centers suggest strongly that the *s-cis*,*s-trans*-triene fragment is η^6-coordinated to the metal.[34] The 6-*exo*-methyl and 6-*endo*-hydrogen resonances remain relatively unperturbed at δ 0.66 (d, J = 6.7 Hz) and δ 1.84 (q, J = 6.7 Hz), respectively. Although the hydride abstraction may be reversible under the reaction conditions, tris(perfluorophenyl)borane does not activate the carbon−carbon bond until protic acid is present, typically as a result of the introduction of water. Complex **13** thus persists indefinitely at room temperature under anhydrous conditions but converts slowly to η^6-pentamethylbenzene cation **6** and methane in the presence of even a trace of moisture; the reaction with added water (7.5 equiv) is complete within a few hours at room temperature. The counterion produced in this reaction is tentatively identified as the known borate anion $(C_6F_5)_3BOH$,[35] on the basis of the broad hydroxyl absorption at 3670 cm^{-1} in the infrared spectrum.

In contrast, the reaction of hexamethylcyclohexadienyl complex **7** with aluminum tribromide under otherwise identical conditions proceeds directly to η^6-pentamethylbenzene complex **6** without evidence of intermediate hydride abstraction (Scheme 8). The counterion in this complex is tentatively identified as $MeAlBr_3^-$ on the basis of a characteristic broad singlet at δ 0.00 (3H) in the ^{1}H NMR spectrum.[36] It is interesting to consider these results in the context of the partial dealkylation of

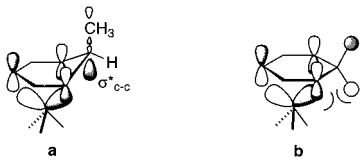
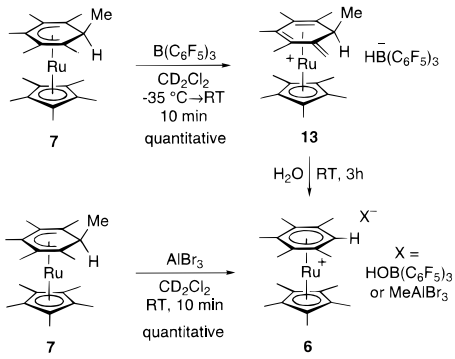


Figure 2.

Scheme 8



(29) The identity of this complex was confirmed by independent synthesis starting from [(η^5-1,2-diphenylcyclopentadienyl)Ru(η^6-pentamethylbenzene)]-OTf[12a] and MeLi in tetrahydrofuran at low temperature, similar to the synthesis of complex **7**. See Experimental Section.

(30) It is, of course, reasonable to propose that the cationic agostic complex itself acts as the Brønsted acid to mediate dealkylation or dehydrogenation of the neutral precursor. In the dealkylation reaction, however, at least some neutral intermediate must be formed in solution by loss of the proton to the medium.

(31) Fu, Y.-T.; Chao, P.-C.; Liu, L.-K. *Organometallics* **1998**, *17*, 221.

(32) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *82*, 598.

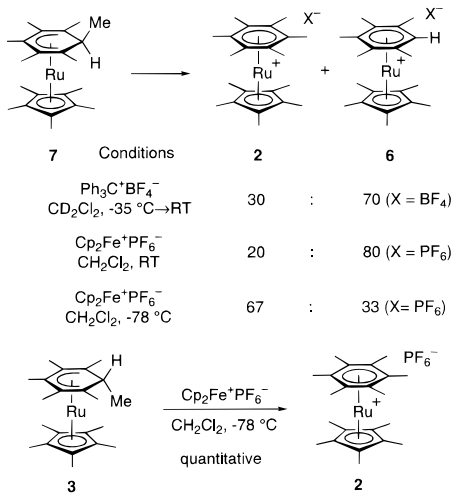
(33) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc*. **1991**, *113*, 3623. Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc*. **1994**, *116*, 10015.

(34) A similar cyclic *s-cis*,*s-trans* triene complex, but embedded in a steroid framework, has been reported by Chaudret et al.[9a]

(35) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M. *Organometallics* **1993**, *12*, 1491. Schaefer, W. P.; Quan, R. W.; Bercaw, J. E. *Acta Crystallogr. C* **1993**, *49*, 878.

(36) $MeAlBr_3^-$ appears to be unknown; the aluminate $MeAlCl_3^-$ has been described: Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H. *J. Crystallogr. Spectrosc. Res.* **1990**, *20*, 53.

Scheme 9



hexaalkylbenzenes observed during aluminum trichloride-induced exchange reactions with ferrocene and ruthenocene.[10] The highest fraction of dealkylated arene complex is reported from reactions mediated by wet $AlCl_3$; little or no dealkylation is obtained with highly purified reagent.[10b] Although no mechanistic details were determined, the dealkylations were attributed to the presence of residual protic acid in the Lewis acid, a result of contamination by water.

Activation by One-Electron Oxidants. Dimauro and Wolczanski have established that the kinetic barrier to carbon−carbon bond activation in 6,6-dimethylcyclohexadienyl ruthenium(II) complexes is significantly reduced upon one-electron oxidation.[9d] It has also been shown that one-electron oxidation of 5-*exo*-alkyl-η^4-cyclohexadiene complexes of iron leads to activation of the alkyl substituent at room temperature, although in this case the substituents (benzyl, dithiane) are activated toward radical extrusion.[37] Oxidation of the same iron complexes, however, at low temperature (−50 °C) instead affords exclusive abstraction of an *endo*-hydrogen rather than carbon−carbon bond scission. To evaluate the potential relevance of one-electron oxidation to the 6-*exo*-methylcyclohexadienyl dealkylation mechanism, the reactions of *exo*- and *endo*-ruthenium complexes **3** and **7** with one-electron oxidants were investigated. The reactivities of both triphenylmethyl (trityl) and ferricinium cations were evaluated, the former because it can react as either an outer-sphere oxidant or an alkyl abstraction agent, and the latter because it functions exclusively as an outer-sphere oxidant.[38]

The addition of stoichiometric trityl cation to a solution of (η^5-C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**7**) in dichloromethane at −35 °C, followed by warming to room temperature, results in rapid conversion to a mixture of η^6-*hexa*methylbenzene and η^6-pentamethylbenzene ruthenium complexes **2** and **6**, derived from carbon−hydrogen and carbon−carbon bond activations, respectively (Scheme 9). The products are formed in a ratio of 30:70 favoring carbon−carbon bond cleavage and are accompanied by the formation of a mixture of 3-benzhydrylidene-6-triphenylmethyl-1,4-cyclohexadiene[39] (trityl dimer) and 1,1,1-triphenylethane in the same 30:70 ratio. While the former byproduct clearly results from a one-electron oxidation of the ruthenium complex, the latter could arise either from direct abstraction of methyl anion by the trityl cation or from methyl radical abstraction following a one-electron oxidation. To constrain the mechanistic pathway to oxidation only, parallel experiments were performed using ferricinium (Scheme 9). The oxidation of 6-*exo*-methyl complex **7** with $Cp_2Fe^+PF_6^-$ at room temperature leads to the isolation of a mixture of dehydrogenation and dealkylation products **2** and **6** in a ratio of 20:80, similar to the product mixture obtained from trityl cation. As previously noted,[37] however, the product distribution is profoundly influenced by the reaction temperature: when the oxidation is conducted at −78 °C, the ratio of complexes **2** and **6** changes to 67:33, now favoring *endo*-hydrogen rather than *exo*-methyl abstraction.[40] For comparison, the oxidation of the corresponding *endo*-methyl complex **3** with ferricinium at low temperature leads to exclusive loss of the *exo*-hydrogen, providing the η^6-hexamethylbenzene complex **2** in quantitative yield (Scheme 9).

The quantitative demethylation observed in the thermal reaction of cationic agostic complex **10** at or below room temperature is thus inconsistent with a mechanistic pathway involving odd-electron intermediates. The experimental data converge on the conclusion that the mechanism of methane extrusion from such complexes proceeds via reversible deprotonation and direct methyl abstraction by the Brønsted acid.

6-Alkylcyclohexadienyl Aromatization by Carbon−Carbon Bond Activation. Literature Dealkylations Revisited. The relevance of this protolytic mechanism to the demethylation reactions reported by Chaudret et al.[9a,b] and Itoh et al.[9c] was addressed by extending our investigation to intermediates proposed for or observed in the course of these transformations. Thus, the otherwise unsubstituted 6-*exo*-methylcyclohexadienyl complex **14** was prepared from the known complex [(η^5-C_5Me_5)Ru(η^6-C_6H_6)]$^+PF_6^-$ (**16**)[41] by alkylation with methyllithium. Protonation of the ruthenium complex **14** with strong acid was then expected to provide the cationic (and presumably agostic) complex **1**-*exo* (Scheme **10**), the proposed intermediate in both the aromatization of 3-methylcyclohexene induced by the (C_5Me_5)Ru$^+$ fragment[9a] and the ruthenium-mediated [4 + 2] cycloaddition reaction of 1,3-pentadiene and acetylene.[9c]

The addition of tetrafluoroboric acid or triflic acid to a solution of 6-*exo*-methyl complex **14** in acetone results in rapid formation of aromatized products (Scheme **10**). The product mixture consists of a 91:9 ratio of the known[9] η^6-toluene and η^6-benzene complexes **15** and **16**, arising from competitive dehydrogenation and demethylation pathways, respectively. No evidence for the formation of a cationic agostic intermediate is observed in reactions run in dichloromethane under strictly anhydrous conditions, and neither the solvent nor the water content significantly impacts the product ratio. The proportion of dealkylation to dehydrogenation obtained is indistinguishable from that reported for the diene cycloaddition and only slightly higher than that observed in the methylcyclohexene aromatization.[9] It is thus unnecessary to propose the formation of a sterically unfavorable 6-*endo*-methylcyclohexadienyl intermediate to account for the minor fraction of dealkylated product: complex **1**-*exo* is *by itself competent to produce both of the* η^6*-arene products obtained in these prior investigations.* The product mixture is readily rationalized by assuming that the

(37) (a) Mandon, D.; Astruc, D. *Organometallics* **1989**, *8*, 2372. (b) For other oxidative carbon−carbon bond activations, see ref 17 and the following: Nesmeyanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S.; Petrakova, V. A. *J. Organomet. Chem.* **1975**, *85*, 365.

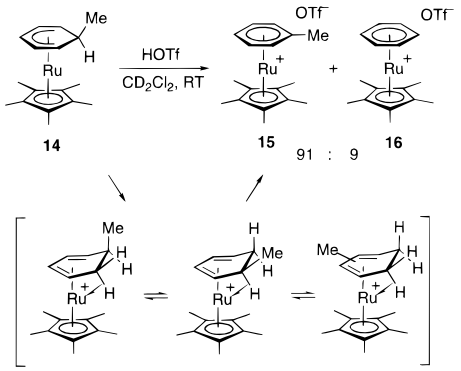
(38) (a) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. (b) Beck, W.; Sunkel, K. *Chem. Rev.* **1988**, *88*, 1405.

(39) Spectroscopic data: Volz, H.; Lotsch, W.; Schnell, H.-W. *Tetrahedron* **1970**, *26*, 5343.

(40) The oxidation reactions were not performed in sealed vessels; consequently, the composition of the volatile fractions remains undetermined.

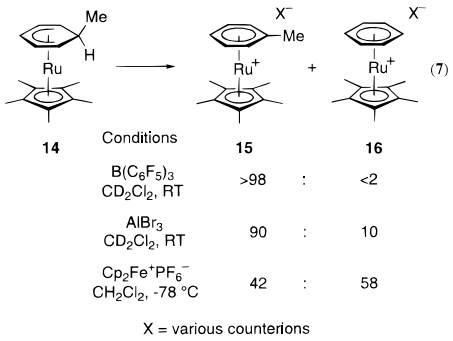
(41) Bosch, H. W.; Hund, H.-U.; Nietlispach, D.; Salzer, A. *Organometallics* **1992**, *11*, 2087.

Scheme 10



6-*exo*-methyl intermediate equilibrates rapidly by migration of the agostic hydride, analogous to the degenerate fluxionality determined for the agostic η^4-hexamethylcyclohexadiene complex **10**. The equilibration provides a mixture of agostic alkyl-η^4-cyclohexadiene complexes statistically and, perhaps, electronically favoring isomers in which the methyl substituent is positioned such that it cannot be activated (Scheme 10). Such equilibration is precedented by previously reported isomerizations of 6-*exo*-alkylcyclohexadienyl osmium hydride complexes.[42] In contrast to ruthenium, however, the η^5-cyclohexadienyl osmium cations assume a classical hydride structure and do not undergo ligand aromatization, both presumably a consequence of the greater basicity of the third row metal center.

The 6-*exo*-methylcyclohexadienyl complex **14** also aromatizes upon reaction with Lewis acids and one-electron oxidants, but the proportion of dealkylation observed strongly depends on the choice of reagent (eq 7). The reaction with tris(perfluo-

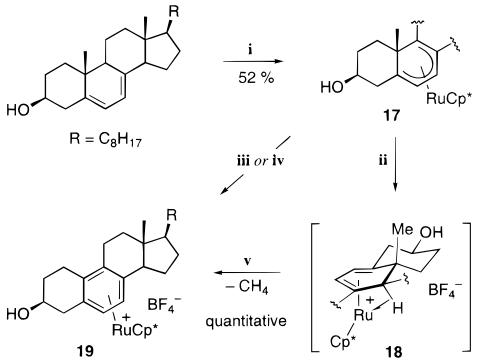


rophenyl)boron at room temperature, for example, provides η^6-toluene complex **15** with high (≥98:2) selectivity; only a trace of η^6-benzene complex **16** is detected in the crude product mixture. This result is consistent with the odd reluctance of tris(perfluorophenyl)boron to promote the demethylation of complex **7** under anhydrous conditions. In contrast, the reaction with aluminum tribromide proceeds to give a 90:10 ratio of hydrogen to methyl abstraction, closely comparable to the reaction mediated by protic acid. The highest selectivity for demethylation, however, is obtained upon one-electron oxidation with the ferricinium salt, providing the aromatized complexes in a 42:58 ratio favoring the η^6-benzene complex **16**.[43] Given these results, it is curious that oxidizing agents are generally selected for reactions requiring the abstraction of an *endo*-hydrogen.[17,18,37b]

(42) Werner, R.; Werner, H. *Chem. Ber.* **1984**, *117*, 161.

(43) The reaction of 6-*exo*-methylcyclohexadienyl complex **14** with $Ph_3C^+BF_4^-$ also favors methyl over hydrogen abstraction, but spectroscopic analysis of the crude mixture suggests that the major product formed in this reaction is an adduct resulting from trityl alkylation of the cyclohexadienyl ligand. This material has not been isolated in pure form and remains to be conclusively identified.

Scheme 11[a]



[a] Conditions: (i) $[(C_5Me_5)RuCl]_4$, THF; then Rieke Zn^0, room temperature, 12 h; (ii) $HBF_4{\cdot}Et_2O$, CD_2Cl_2, room temperature; (iii) $HBF_4{\cdot}Et_2O$ (2.2 equiv), H_2O (10 equiv), CH_2Cl_2, room temperature, 4d; (iv) $Ph_3C^+BF_4^-$, CH_2Cl_2, room temperature, 1 h; (v) H_2O (10 equiv), room temperature.

Finally, the question of steroid aromatization was addressed, to assess the relevance of protolytic activation mechanisms in this ruthenium-mediated demethylation reaction (eq 3).[9a,b] Steroid dealkylation proceeds unambiguously by coordination of the unsaturated metal fragment to the steroid α-face and activation of the *exo*-methyl substituent. Based on the high activation barrier for this reaction and the observation of trace amounts of ethane in certain A-ring aromatization reactions, a free radical mechanism was postulated involving homolytic scission of the carbon−carbon bond.

To address the mechanism of this reaction, the aromatization of ergosterol was reinvestigated, beginning with an independent synthesis of Chaudret's partially characterized hydridoruthenium intermediate.[9b] Thus, the complex formed in situ from the reaction of $[(C_5Me_5)RuCl]_4$ and ergosterol in tetrahydrofuran was treated with an excess of zinc dust to yield the neutral η^5-cyclohexadienyl complex, $(C_5Me_5)Ru(\eta^5$-9-dehydroergosterol) (**17**) in modest, unoptimized, yield (Scheme 11). Protonation of this complex with tetrafluoroboric acid in anhydrous dichloromethane-d_2 at room temperature leads to the quantitative formation of cationic agostic η^4-ergosterol complex **18**, identified and characterized by spectroscopic analysis but not isolated. The spectroscopic data are fully consistent with the intermediate proposed by Chaudret et al., but the hydride resonance at δ −5.00 in CD_2Cl_2 is closely analogous to the corresponding signals in agostic cyclohexadiene complexes **8**−**10**, strongly suggesting that this complex adopts an agostic structure rather than the previously assigned classical η^5-cyclohexadienyl hydride structure. In contrast to the fluxional character of complexes **8**−**10**, agostic ergosterol complex **18** is structurally rigid at room temperature on the NMR time scale, presumably a consequence of the structural dissymmetry of the steroid framework. The complex is stable indefinitely in solution at room temperature under anhydrous conditions.

Upon addition of water, however, the cationic ergosterol complex undergoes slow conversion to the η^6-arene complex $[(C_5Me_5)Ru(\eta^6$-neoergosterol)$]^+BF_4^-$ (**19**) and methane at room temperature. The reaction of η^5-dehydroergosterol complex **17** with tetrafluoroboric acid (2.2 equiv) in anhydrous dichloromethane containing 10 equiv of water, for example, is complete in 4 days at room temperature and provides the aromatized product in quantitative yield. The substantial increase in the rate of carbon−carbon bond activation obtained upon addition of water to the reaction medium is inconsistent with a free radical mechanism for activation of the carbon−carbon bond. The slow rate of carbon−carbon bond activation under

Chaudret's conditions (TfOH, 0.5 equiv of $[(C_5Me_5)Ru(OMe)]_2$), can be attributed to an anhydrous reaction medium containing only 1 equiv of methanol, a less effective Brønsted base for mediating protolytic demethylation (vide supra). The detection of a trace of ethane from some steroid demethylation reactions (but not in the case of ergosterol[9b]) can be rationalized, we believe, by considering that the active demethylation agent under Chaudret's reaction conditions is likely to be $CH_3OH_2^+$, formed from deprotonation of agostic complex **18** by methanol. In addition to the acidic protons, this reagent bears an electrophilic methyl group, which may participate in the abstraction of the angular methyl group as a minor pathway. Finally, we note that the *optimal* method for the demethylation of ergosterol involves neither Chaudret's conditions nor our own: the reaction of η^5-9-dehydroergosterol complex **17** with trityl cation proceeds quantitatively to demethylated complex **19** at room temperature in less than 1 h!

Conclusion. A novel mechanism for metal-mediated carbon−carbon bond activation has been defined for the dealkylation of cationic 6-*exo*-methylcyclohexadiene ruthenium hydride complexes at low temperature. The reaction has been determined to proceed by an acid/base mechanism, in which an exogenous Brønsted base deprotonates the agostic hydride complex and the resulting acid activates the *exo* carbon−carbon bond of the 6-*exo*-methylcyclohexadienyl complex by a protolytic mechanism. Protolytic demethylation is the exclusive pathway observed in the reactions of 1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl complexes and in a steroid-derived 6,6-disubstituted cyclohexadienyl complex. Under the same conditions, the stereoisomeric 1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl complexes undergo exclusive carbon−hydrogen bond activation, releasing hydrogen by a similar protolytic mechanism. The facile nature of the protolytic carbon−carbon bond activation contrasts dramatically with the previously reported dealkylations of 6,6-dimethyl-substituted cyclohexadienyl complexes,[9d] which activate what is presumed to be the 6-*endo*-methyl carbon−carbon bond by a concerted metal-mediated abstraction, but only by traversing a substantially higher activation barrier. In the protolytic mechanism, the transition metal still functions to stabilize the transition state for carbon−carbon bond scission, but it does so by a mechanism clearly distinct from typically invoked β-alkyl elimination pathways. On the basis of this investigation, the relevance of protolytic carbon−carbon bond activation to the dealkylation of coordinated hexaalkylbenzenes appears highly probable, in the context of both Lewis acid-mediated cyclopentadienyl/arene exchange reactions and the hexamethylbenzene demethylation we observed in the course of [3 + 2] allyl/alkyne cycloaddition.[12b]

For monosubstituted 6-*exo*-methylcyclohexadienyl complexes and their cationic conjugate acids, protolytic dealkylation is observed as a minor reaction pathway, consistent with the minor fraction of dealkylation product obtained from various previously reported metal-mediated cycloaddition and cyclohexene aromatization reactions. As such, cationic *exo*-substituted agostic η^4-cyclohexadiene complexes thus constitute competent intermediates in these poorly understood processes. While there remains a number of obvious opportunities for quantification of the kinetic relationships defined by this investigation, the metal-assisted protolytic pathway constitutes a simple and potentially exploitable alternative strategy for selective carbon−carbon bond activation.

Experimental Section

General. All manipulations of air-sensitive compounds were performed under prepurified nitrogen using standard Schlenk techniques or in a drybox. Toluene, benzene, tetrahydrofuran, diethyl ether, hexane, and pentane were distilled from sodium/benzophenone ketyl or from sodium/potassium alloy/benzophenone ketyl. Reagent-grade acetone was degassed and stored under nitrogen with no further purification. Dichloromethane, dichloromethane-d_2, and acetonitrile were distilled from calcium hydride and degassed. Unless stated otherwise, all reactions were carried out under a nitrogen atmosphere. IR spectra were recorded on a Nicolet Magna IR 750 or a Nicolet 20SX spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), a Bruker AM-360 (^{1}H, 360 MHz), a Bruker AM-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz), or a Varian Unity-Inova 300 (^{1}H, 300 MHz) spectrometer. High-resolution mass spectra were obtained on a Kratos MS-50 spectrometer, and elemental analyses were performed by the University of Alberta Microanalysis Laboratories. The following compounds were prepared according to published procedures: $[(C_5Me_5)RuCl]_4$,[19] $[(C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]^+PF_6^-$,[42] $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$,[22] $[Cp_2Fe]^+PF_6^-$,[37a] $[(\eta^5\text{-}C_5H_3Ph_2)Ru(\eta^6\text{-}C_6Me_5H)]^+OTf^-$,[12a] and $(C_6Me_6)Ru(C_3H_5)OTf$.[12a]

$[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+BF_4^-$ (2). A Schlenk flask equipped with a septum was charged with $[(C_5Me_5)RuCl]_4$ (0.100 g, 0.368 mmol/Ru), hexamethylbenzene (0.310 g, 1.90 mmol), and silver tetrafluoroborate (0.076 g, 0.390 mmol). Dichloromethane (6 mL) was added by syringe, and the reaction mixture immediately turned dark green. The reaction was then heated to a gentle reflux for 5 h, gradually turning to a light brown with a gray precipitate. The solution was then filtered over Celite and evaporated to dryness. The tan residue was rinsed with hexane to remove excess hexamethylbenzene and then dissolved in a minimum of dichloromethane, and the product was precipitated with diethyl ether. A white powder was collected (0.131 g, 73%), spectroscopically identical to the known $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+OTf^-$.[19]

$(C_5Me_5)Ru(\eta^5\text{-}1,2,3,4,5,6\text{-}endo\text{-}$hexamethylcyclohexadienyl) (3). A suspension of $[(C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+BF_4^-$ (**2**, 0.050 g, 0.103 mmol) in tetrahydrofuran (3 mL) was cooled to 0 °C, and $LiEt_3BH$ (1.0 M in THF, 0.11 mL, 0.110 mmol, 1.07 equiv) was added via syringe. After being stirred at 0 °C for 30 min, the reaction was warmed to room temperature for 1 h before the solvent was removed in vacuo. The residue was triturated with 2 × 3 mL of pentane, and the pentane extracts were filtered over Celite and dried to give a white solid. The crude product was then redissolved in pentane and filtered through a plug of alumina (5% H_2O). After evaporation of pentane, the product (0.023 g, 56%) was obtained as a white crystalline solid and used without further purification. IR (CH_2Cl_2 cast, cm^{-1}): 2967 (s), 2898 (s), 2870 (s), 2847 (s), 1375 (s), 1026 (m). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.44 (q, J = 7.1 Hz, 1H, *exo*-H), 2.07 (s, 3H, CH_3), 1.64 (s, 6H, CH_3), 1.61 (s, 15H, C_5Me_5), 1.05 (s, 6H, CH_3), 0.95 (d, J = 7.1 Hz, 3H, *endo*-CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 96.8, 89.9, 87.0, 41.1, 35.3, 17.4, 15.9, 15.3, 15.0, 10.0. MS *m*/*z* (relative intensity): calculated for $C_{22}H_{34}{}^{102}Ru$ (M^+), 400.1704; found, 400.1655 (28.08); calculated for $C_{22}H_{33}{}^{102}Ru$ (M − H), 399.1626; found, 399.1625 (100.00); calculated for $C_{21}H_{31}{}^{102}Ru$ (M − CH_3), 385.1469; found, 385.1464 (4.41).

$[(C_5H_5)Ru(\eta^6\text{-}C_6Me_6)]^+Cl^-$ (4). A small round-bottom flask equipped with nitrogen inlet, reflux condenser, and stir bar was charged with $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (0.080 g, 0.239 mmol/Ru), anhydrous sodium carbonate (0.100 g, 0.943 mmol), and ethanol (8 mL). Freshly cracked cyclopentadiene (1.0 mL, 14.9 mmol) was then added via syringe, and the reaction mixture was heated to reflux for 2 h, during which time the suspended dimer dissolved and the solution turned pale yellow. Afterward, the volatile liquids were removed in vacuo, and the crude product was extracted into dichloromethane (2 × 4 mL), which was then filtered over Celite. Addition of diethyl ether to the filtrate precipitated the product as a white powder (0.072 g, 83%) which was spectroscopically identical to the known $[(C_5H_5)Ru(\eta^6\text{-}C_6Me_6)]^+Cl^-$.[21]

$(C_5H_5)Ru(\eta^5\text{-}1,2,3,4,5,6\text{-}endo\text{-}$hexamethylcyclohexadienyl) (5). A suspension of $[(C_5H_5)Ru(\eta^6\text{-}C_6Me_6)]^+Cl^-$ (**4**, 0.055 g, 0.151 mmol) in tetrahydrofuran (3 mL) was cooled to 0 °C, and $LiEt_3BH$ (1.0 M in THF, 0.18 mL, 0.180 mmol, 1.2 equiv) was added via syringe. After being stirred at 0 °C for 30 min, the reaction was warmed to room temperature for another hour before the solvent was removed in vacuo. The residue was triturated with 2 × 3 mL of pentane, and the pentane extracts were filtered over Celite and dried to a white solid. The crude

product was redissolved in pentane and filtered through a plug of alumina (5% H_2O). After evaporation of pentane the product (0.031 g, 62%) was obtained as an off-white solid and used without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.36 (s, 5H, C_5H_5), 2.41 (s, 3H, CH_3), 2.21 (q, J = 7.1 Hz, 1H, *exo*-H), 1.94 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.12 (d, J = 7.1 Hz, 3H, *endo*-CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 91.9, 91.2, 78.3, 39.9, 37.0, 18.9, 17.6, 17.4, 17.1.

[(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+BF_4^-$ (6). A procedure similar to that described for complex **2** above was followed, except that pentamethylbenzene was used in place of hexamethylbenzene. Thus, a mixture of [(C_5Me_5)RuCl]$_4$ (0.300 g, 1.104 mmol/Ru), pentamethylbenzene (0.840 g, 5.66 mmol), and silver tetrafluoroborate (0.218 g, 1.12 mmol) in 12 mL of dichloromethane was maintained at a gentle reflux for 5 h. A bright white powder (0.483 g, 93%) was isolated after recrystallization from dichloromethane/diethyl ether. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.46 (s, 1H, C_6Me_5H), 2.10 (s, 6H, C_6Me_5H), 2.06 (s, 3H, C_6Me_5H), 2.03 (s, 6H, C_6Me_5H), 1.71 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 99.2, 99.1, 98.7, 93.1, 91.5, 17.9, 14.7, 14.2, 9.4. Anal. Calcd for $C_{21}H_{31}RuBF_4$: C, 53.51%; H, 6.63. Found: C, 53.38; H, 6.52.

(C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (7). A suspension of [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+BF_4^-$ (**6**, 0.165 g, 0.350 mmol) in 6 mL of tetrahydrofuran was cooled to −78 °C using a dry ice/acetone bath, and MeLi (1.4 M in diethyl ether, 0.75 mL, 1.050 mmol, 3.0 equiv) was added via syringe. The reaction was stirred at −78 °C for several hours before gradually being warmed to room temperature. The resulting yellow solution was then evaporated under low pressure, and the residue was triturated with several portions of pentane. The combined pentane extracts were filtered over Celite, and the yellow filtrate was concentrated to a solid. After thorough drying in vacuo, the yellow solid was dissolved in pentane and filtered through a plug of alumina (5% H_2O), giving a colorless filtrate. This filtrate was concentrated under low pressure to give 0.058 g (42%) of white crystalline material, which was used without further purification. IR (CH_2Cl_2 cast, cm^{-1}): 2959 (s), 2937 (s), 2902 (s), 2881 (s), 2852 (s), 1376 (m), 1265 (m), 1017(m), 740 (s). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.02 (s, 3H, CH_3), 1.94 (q, J = 6.3 Hz, 1H, *endo*-H), 1.60 (s, 21H, CH_3 and C_5Me_5), 1.31 (s, 6H, CH_3), 0.11 (d, J = 6.3 Hz, 3H, *exo*-CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 88.1, 86.7, 86.5, 50.2, 39.9, 20.3, 20.2, 15.3, 14.4, 10.0. MS *m/z* (relative intensity): calculated for $C_{22}H_{34}{}^{102}$Ru (M^+), 400.1704; found, 400.1687 (3.81); calculated for $C_{22}H_{33}{}^{102}$Ru (M − H), 399.1626; found, 399.1644 (6.55); calculated for $C_{21}H_{31}{}^{102}$Ru (M − CH_3), 385.1469; found, 385.1464 (100.00).

(C_5Me_5)Ru(η^5-1,2,3,4,5-pentamethyl-6-*exo*-CD_3-cyclohexadienyl) (7-d_3). A procedure similar to that described for complex **7** was followed. A cold (−78 °C) suspension of (C_5Me_5)Ru(η^6-C_6Me_5H)]$^+$-BF_4^- (**6**, 0.050 g, 0.106 mmol) in tetrahydrofuran was prepared, and CD_3Li (approximately 0.3 M in diethyl ether, 1.06 mL, 3.0 equiv) was added by syringe. The flask was then warmed to room temperature and the product isolated as described. Pale yellow crystals were collected (0.015 g, 37%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.02 (s, 3H, CH_3), 1.93 (br s, 1H, *endo*-H), 1.60 (s, 21H, CH_3 and C_5Me_5), 1.31 (s, 6H, CH_3).

Protonation of Complex 5 with HBF_4·Et_2O in Acetone-d_6. In the drybox, a solution of (C_5H_5)Ru(η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl) (**5**, 0.010 g, 0.030 mmol) in acetone-d_6 was placed into an NMR tube equipped with a rubber septum. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether) (0.004 mL, 0.045 mmol) was then added via microsyringe and the resulting solution analyzed by ^{1}H NMR spectroscopy. Clean conversion to [(C_5H_5)Ru(η^6-C_6Me_6)]$^+$-BF_4^- (**4**) was observed within 10 min at room temperature.

[(C_5H_5)Ru(η^4-1,2,3,4,5-*exo*-6-*endo*-hexamethylcyclohexa-1,3-diene)]$^+BF_4^-$ (8). In the drybox, a solution of (C_5H_5)Ru(η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl) (**5**, 0.016 g, 0.049 mmol) in anhydrous CD_2Cl_2 was placed into an NMR tube equipped with a rubber septum. Tetrafluoroboric acid (diethyl ether complex, 85%) was then added (0.008 mL, 0.064 mmol) via microsyringe and the resulting yellow solution analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.14 (s, 5H, C_5H_5), 2.82, (s, 3H, CH_3), 2.50 (dq, J = 13.2, 6.6 Hz, 1H, *exo*-H), 2.17 (s, 6H, CH_3), 1.67 (d, J = 2.7 Hz, 6H, CH_3), 1.31 (d, J = 6.7 Hz, 3H, *endo*-CH_3), −4.81 (d of sept, J = 13.3, 2.6 Hz, 1H, H_{ag}).

Addition of MeOH to 8. Methanol (0.008 mL, 6.5 equiv) was added via microsyringe to the solution of [(C_5H_5)Ru(η^4-1,2,3,4,5-*exo*-6-*endo*-hexamethylcyclohexa-1,3-diene)]$^+BF_4^-$ (**8**) prepared above and the reaction monitored spectroscopically. Complete conversion to [(C_5H_5)-Ru(η^6-C_6Me_6)]$^+BF_4^-$ (**4**) was observed within 4 h at room temperature, accompanied by a trace of decomposition products.

[(C_5Me_5)Ru(η^4-1,2,3,4,5-*exo*-6-*endo*-hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ (9). A solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl) (**3**, 0.030 g, 0.075 mmol) in anhydrous CD_2Cl_2 was placed into an NMR tube equipped with a rubber septum. Triflic acid (0.007 mL, 0.079 mmol) was then added via microsyringe and the resulting solution analyzed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.44 (dq, J = 13.0, 6.6 Hz, 1H, *exo*-H), 2.40 (s, 3H, CH_3), 1.85 (s, 6H, CH_3), 1.77 (s, 15H, C_5Me_5), 1.44 (d, J = 2.4 Hz, 6H, CH_3), 1.21 (d, J = 6.6 Hz, 3H, *endo*-CH_3), −5.82 (br d, J = 13.0 Hz, H_{ag}). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 101.9, 99.9, 96.8, 67.1, 42.1, 16.9, 16.0, 14.9, 14.2, 9.7 (triflate carbon not observed).

Addition of MeOH to 9. Methanol (0.011 mL, 6.0 equiv) was added via microsyringe to the CD_2Cl_2 solution of [(C_5Me_5)Ru(η^4-1,2,3,4,5-*exo*-6-*endo*-hexamethylcyclohexa-1,3-diene)]$^+$OTf$^-$ (**9**) prepared above and the reaction monitored spectroscopically. After 24 h, only 21% conversion to [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$OTf$^-$ (**2**) was observed. The reaction was complete after about 5 days at room temperature.

[(C_5Me_5)Ru(η^4-1,2,3,4,5-*exo*-6-*exo*-hexamethylcyclohexa-1,3-diene)]$^+OTf^-$ (10). A solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**7**, 0.015 g, 0.038 mmol) in CD_2Cl_2 was placed into an NMR tube equipped with a septum. Triflic acid (0.004 mL, 0.045 mmol) was added via syringe and the resulting solution analyzed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy at room temperature and at −80 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 2.59 (br s, 1H, *endo*-H), 2.37 (br s, 3H, CH_3), 1.79 (br s, 12H, CH_3), 1.77 (s, 15H, C_5Me_5), 0.33 (br s, 3H, *exo*-CH_3), −5.73 (br s, 1H, H_{ag}). ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C): δ 2.53 (br q, J = 6.6 Hz, 1H, *endo*-H), 2.25 (s, 3H, CH_3), 1.71 (s, 12H, CH_3), 1.67 (s, 15H, C_5Me_5), 0.22 (d, J = 6.5 Hz, 3H, *exo*-CH_3), −5.40 (br s, 1H, H_{ag}). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ 96.8, 9.8 (all other signals broadened into the baseline). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, -80 °C): δ 98.6, 96.1, 95.6, 74.0, 51.2, 22.4, 19.8, 14.0, 12.8, 9.2 (triflate carbon not observed). Qualitative spin saturation transfer experiments (400 MHz, CD_2Cl_2, 20 °C): irradiation of δ −5.73 (H_{ag}) ↔ suppression of the signal at 2.59 ppm (*endo*-H); irradiation of δ 0.33 (*exo*-CH_3) ↔ suppression of the signal at 1.79 ppm (12H, CH_3) and diminution of the signal at 2.37 ppm (3H, CH_3).

Addition of Water to 10. Excess distilled water (0.004 mL, 5.9 equiv) was added via microsyringe to the solution of [(C_5Me_5)Ru(η^4-1,2,3,4,5-*exo*-6-*exo*-hexamethylcyclohexa-1,3-diene)]$^+$OTf$^-$ (**10**) prepared above. The NMR tube was shaken for 1 min, after which time the reaction was monitored by ^{1}H NMR spectroscopy at 10-min intervals. After 50 min, the conversion to [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+$-OTf$^-$ (**6**) and methane (δ 0.20 ppm in CD_2Cl_2) was complete.

Protonation of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (7) with CF_3SO_3D (Prepared in Situ by Exchange with Acetone-d_6). In the drybox, a solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**7**, 0.015 g, 0.038 mmol) in acetone-d_6 was placed into an NMR tube equipped with a rubber septum and sealed. After removal of the solution from the drybox, triflic acid (0.004 mL, 0.045 mmol) was then added via syringe and the reaction monitored spectroscopically. After 20 min at room temperature, ^{1}H NMR showed complete conversion of starting material to [(C_5Me_5)Ru(η^4-1,2,3,4,5-*exo*-6-*exo*-hexamethylcyclohexa-1,3-diene)]$^+$OTf$^-$ (**10**) along with traces of [(C_5Me_5)Ru(η^6-C_6Me_5D)]$^+$OTf$^-$ (**6**-d_1). After 24 h at room temperature, conversion to complex **6**-d_1 was complete, accompanied by the formation of methane (δ 0.15 in acetone-d_6) and methane-d_1 (1:1:1 triplet at δ 0.13 in acetone-d_6).

Protonation of (C_5Me_5)Ru(η^5-1,2,3,4,5-pentamethyl-6-*exo*-CD_3-cyclohexadienyl) (7-d_3) with CF_3SO_3H. A dichloromethane solution of (C_5Me_5)Ru(η^5-1,2,3,4,5-pentamethyl-6-*exo*-CD_3-cyclohexadienyl) (**7**-d_3, 0.015 g, 0.037 mmol) was placed into an NMR tube and capped

with a rubber septum. The solution was frozen using liquid N_2 (−196 °C), and triflic acid (0.004 mL, 0.045 mmol) was added via microsyringe, followed quickly by the addition of excess distilled water (0.004 mL, 0.222 mmol, 6 equiv). The NMR tube was then warmed rapidly to room temperature and allowed to stand for a further 2 h. Subsequent spectroscopic analysis of the solution by ^{2}H NMR spectroscopy revealed the incorporation at deuterium at δ 2.07, 2.03, and 2.00 ppm in a ratio of 2:1:2, respectively, consistent with equal incorporation of CD_3 at each of the arene methyl positions. Also present is a broad upfield signal at approximately 0.12 ppm, consistent with the formation of a small amount of CD_3H. Similar results were obtained by protonation of **7**-d_3 using 1 equiv of tetrafluoroboric acid in acetone-d_6.

Reaction of (η^6-C_6Me_6)Ru(η^3-C_3H_5)OTf (11),[12a] (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl) (3), and Diphenylacetylene. Crossover Experiment. A solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl) (**3**, 0.014 g, 0.035 mmol) and diphenylacetylene (0.008 g, 0.045 mmol) in anhydrous CD_2Cl_2 was prepared and placed in an NMR tube capped with a rubber septum. The solution was cooled in the drybox freezer (−35 °C) for 20 min, after which time an orange solution of (C_6Me_6)Ru(η^3-C_3H_5)OTf (**11**, 0.017 g, 0.037 mmol) in ∼0.2 mL of CD_2Cl_2 was added. The reaction mixture was warmed to room temperature and the resulting yellow solution analyzed by ^{1}H NMR spectroscopy. The spectrum revealed quantitative formation of [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$OTf$^-$ (**2**) and (η^5-$C_5H_3Ph_2$)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**12**), confirmed by comparison to authentic material prepared by independent synthesis (see below). The solvent was then removed under reduced pressure, the residue triturated with 3 mL of pentane, and the pentane extract filtered over Celite and dried to afford a pale yellow solid (**12**, 0.012 g, approximately 71%; contaminated with a small amount of diphenylacetylene).

(η^5-$C_5H_3Ph_2$)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (12, Independent Synthesis). A suspension of [(η^5-$C_5H_3Ph_2$)Ru(η^6-C_6Me_5H)]$^+$OTf$^-$ [12a] (0.055 g, 0.089 mmol) in 4 mL of tetrahydrofuran was cooled to −78 °C using a dry ice/acetone bath, and MeLi (1.4 M in diethyl ether, 0.15 mL, 0.210 mmol, 2.36 equiv) was added via syringe. The reaction was stirred at −78 °C for several hours before being gradually warmed to room temperature. The resulting yellow solution was then evaporated under low pressure and the residue triturated with several portions of hexane (3 × 2 mL). The combined hexane extracts were filtered over Celite, and the yellow filtrate was concentrated to a solid. After thorough drying in vacuo the solid was then dissolved in pentane and filtered through a plug of alumina (5% H_2O). The filtrate was concentrated under low pressure to yield 0.016 g (37%) of pale yellow crystalline complex **12**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.19−7.10 (m, 10H, H_{Ph}, partially obscured), 4.70 (t, J = 2.5 Hz, 1H), 4.65 (d, J = 2.5 Hz, 2H), 2.23 (q, J = 6.4 Hz, 1H), 2.12 (s, 3H, CH_3), 1.63 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 0.15 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 137.2, 129.4, 128.0, 125.9, 94.4, 90.9, 88.3, 81.3, 78.4, 50.3, 43.2, 22.1, 20.8, 16.2, 15.4. MS *m*/*z* (relative intensity): calculated for $C_{29}H_{32}{}^{102}Ru$ (M^+), 482.1548; found, 482.1543 (1.54); calculated for $C_{29}H_{31}{}^{102}Ru$ (M − H), 481.1469; found, 481.1458 (2.80); calculated for $C_{28}H_{29}{}^{102}Ru$ (M − CH_3), 467.1313; found, 467.1325 (100.00).

[(C_5Me_5)Ru(η^6-1,2,3,4,6-*exo*-pentamethyl-5-methylenecyclohexa-1,3-diene)]$^+$HB(C_6F_5)$_3^-$ (13). An NMR tube was charged with a solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**7**, 0.012 g, 0.030 mmol) in anhydrous CD_2Cl_2 and the tube cooled to −35 °C. Immediately upon addition of tris(perfluorophenyl)borane (0.016 g, 0.031 mmol), the colorless solution turned bright yellow. Spectroscopic analysis (^{1}H, ^{13}C NMR, HMQC) of the reaction mixture showed quantitative formation of product (complex **13**) within 10 min. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.33 (s, 1H, $HC_6Me_5CH_2$), 3.54 (s, 1H, $HC_6Me_5CH_2$), 2.02 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.84 (q, J = 6.7 Hz, 1H, *endo*-H), 1.67 (s, 15H, C_5Me_5), 1.48 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 0.66 (d, J = 6.7 Hz, 3H, *exo*-CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, $^1J_{CH}$ values obtained from the HMQC spectrum): δ 106.4 (s, $HC_6Me_5CH_2$), 98.7 (s, $HC_6Me_5CH_2$), 96.3 (s, C_5Me_5), 94.5 (s, $HC_6Me_5CH_2$), 89.6 (s, $HC_6Me_5CH_2$), 76.2 (d, $^1J_{CH}$ = 161 Hz, $HC_6Me_5CH_2$), 55.7 (s, $HC_6Me_5CH_2$), 40.2 (d, $^1J_{CH}$ = 133 Hz, CH), 21.0 (q, $^1J_{CH}$ = 133 Hz, *exo*-CH_3), 18.9 (q, $^1J_{CH}$ = 129 Hz, CH_3), 14.9 (q, $^1J_{CH}$ = 130 Hz, CH_3), 13.4 (q, $^1J_{CH}$ = 130 Hz, CH_3), 13.0 (q, $^1J_{CH}$ = 129 Hz, CH_3), 9.7 (q, $^1J_{CH}$ = 127 Hz, C_5Me_5). HMQC (300 MHz, CD_2Cl_2): δ 76.2 (CH_2) ↔ δ 4.33, 3.54 (CH_2); δ 40.2 (CH) ↔ δ 1.84 (CH); δ 21.0 (CH_3) ↔ δ 0.66 (CH_3); δ 18.9 (CH_3) ↔ δ 1.39 (CH_3); δ 14.9 (CH_3) ↔ δ 1.48 (CH_3); δ 13.4 (CH_3) ↔ δ 1.88 (CH_3); δ 13.0 (CH_3) ↔ δ 2.02 (CH_3); δ 9.7 (C_5Me_5) ↔ δ 1.67 (C_5Me_5).

Addition of Water to 13. Excess distilled water (0.004 mL, 7.5 equiv) was added via microsyringe to the anhydrous CD_2Cl_2 solution of [(C_5Me_5)Ru(η^6-1,2,3,4,6-*exo*-pentamethyl-5-methylenecyclohexa-1,3-diene)]$^+$HB(C_6F_5)$_3^-$ (**13**) prepared above. The NMR tube was shaken for 1 min, and then the reaction was monitored by ^{1}H NMR spectroscopy. After 4 h the conversion of starting material to [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+$HOB(C_6F_5)$_3^-$ (**6**−B(Ar_f)$_3$OH) and methane (0.20 ppm in CD_2Cl_2) was complete. IR (CH_2Cl_2 cast, cm^{-1}): 3670 (br), 1644 (m), 1515 (s), 1465 (s), 1089 (s), 976 (s).

Reaction of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (7) with $AlBr_3$. A solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**7**, 0.010 g, 0.025 mmol) in CD_2Cl_2 was loaded into an NMR tube, and pure $AlBr_3$ (0.008 g, 0.030 mmol) was added. The NMR tube was capped and shaken for 1 min. After the solution was left to stand for 10 min at room temperature, ^{1}H NMR spectroscopic analysis indicated only a single product in quantitative yield, [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+$MeAlBr$_3^-$ (**6**−MeAlBr$_3$), based on spectroscopic comparison with the well-characterized triflate analogue. ^{1}H NMR (360 MHz, CD_2Cl_2): δ 5.37 (s, 1H, C_6Me_5H), 2.10 (s, 6H, C_6Me_5H), 2.06 (s, 3H, C_6Me_5H), 2.03 (s, 6H, C_6Me_5H), 1.71 (s, 15H, C_5Me_5), 0.00 (br s, 3H, MeAlBr$_3$).

Reaction of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (7) with $Ph_3C^+BF_4^-$. A solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**7**, 0.010 g, 0.025 mmol) in anhydrous CD_2Cl_2 was cooled to −35 °C and triphenylcarbenium tetrafluoroborate (0.009 g, 0.027 mmol) added. The solution immediately turned bright yellow and was placed into an NMR tube. Subsequent ^{1}H NMR analysis indicated the formation of a mixture of [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$BF$_4^-$ (**2**) and [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+$BF$_4^-$ (**6**); no intermediate formation is observed. The integrated ratio of **2**:**6** was 30:70 at long pulse delay. Also present are trityl dimer [^{1}H NMR, (300 MHz, CD_2Cl_2): δ 7.33−7.15 (m, 21H), 6.95 (dd, J = 8.1, 1.8 Hz, 4H), 6.23 (dd, J = 10.5, 2.0 Hz, 2H), 5.97 (dd, J = 10.5, 3.8 Hz, 2H), 5.13 (br s, 1H)] and Ph_3-CMe [^{1}H NMR, (300 MHz, CD_2Cl_2): δ 7.37−7.06 (m, 15H, H_{Ph}), 2.17 (s, 3H, Me)] in a ratio of 30:70.

Reaction of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (7) with [Cp_2Fe]$^+$$PF_6^-$. (i) At −78 °C. A blue suspension of [Cp_2Fe]$^+$$PF_6^-$ (0.009 g, 0.027 mmol) in 2 mL of dichloromethane was cooled to −78 °C in a dry ice/acetone bath, and a solution of (C_5Me_5)-Ru(η^5-1,2,3,4,5,6-*exo*-hexamethylcyclohexadienyl) (**7**, 0.011 g, 0.027 mmol) in 1 mL of dichloromethane was added slowly via syringe. The reaction mixture turned from blue to orange within 5 min, and the cold bath was removed. Upon warming to room temperature the reaction lightened to pale yellow; the solvent was then removed under reduced pressure. ^{1}H NMR analysis of the yellow residue revealed the formation of [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$$PF_6^-$ (**2**) and [(C_5Me_5)Ru(η^6-C_6Me_5H)]PF_6 (**6**) in a ratio of 67:33, along with ferrocene.

(ii) At 22 °C. The reaction was performed as described above, except that no cold bath was used. Upon addition of complex **7**, the reaction mixture immediately turned pale yellow as stirring was continued for a further 10 min. The solvent was then removed in vacuo and the residue analyzed by ^{1}H NMR spectroscopy. [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$$PF_6^-$ (**2**) and [(C_5Me_5)Ru(η^6-C_6Me_5H)]$^+$$PF_6^-$ (**6**) were formed in a ratio of 30:70, accompanied by ferrocene.

Reaction of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl) (3) with [Cp_2Fe]$^+$$PF_6^-$. To a blue suspension of $Cp_2Fe^+PF_6^-$ (0.009 g, 0.027 mmol) in 2 mL of dichloromethane cooled to −78 °C in a dry ice/acetone bath was added a solution of (C_5Me_5)Ru(η^5-1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl) (**3**, 0.011 g, 0.027 mmol) in 1 mL of dichloromethane slowly via syringe. The reaction mixture immediately faded from blue to pale yellow, and the cold bath was removed. After the mixture warmed to room temperature, the solvent was removed under reduced pressure. ^{1}H NMR spectroscopic analysis of the yellow residue revealed complete and quantitative conversion to [(C_5Me_5)Ru(η^6-C_6Me_6)]$^+$$PF_6^-$ (**2**) and ferrocene.

(C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (14). To a suspension of [(C_5Me_5)Ru(η^6-C_6H_6)]$^+PF_6^-$ (**16**,[39] 0.210 g, 0.457 mmol) in 20 mL of diethyl ether cooled to 0 °C using an ice bath was added MeLi (1.4 M in diethyl ether, 0.36 mL, 0.504 mmol, 1.1 equiv) via syringe. No reaction was observed until 3 mL of tetrahydrofuran was added. The reaction mixture was stirred at 0 °C for 1 h and gradually warmed to room temperature over another 4 h. The bright orange solution was evaporated under low pressure and the residue triturated with several portions of hexane (3 × 2 mL). The combined hexane extracts were filtered over Celite, and the orange filtrate was concentrated to an oily residue. After thorough drying in vacuo, the red residue was dissolved in pentane and filtered through a plug of alumina (5% H_2O), giving a nearly colorless filtrate. This filtrate was concentrated under reduced pressure to yield 0.086 g (57%) of a pale yellow crystalline complex **14**, which was used without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.13 (td, J = 4.7, 0.9 Hz, 1H), 3.89 (tt, J = 4.8, 1.3 Hz, 2H), 2.22−2.20 (m, 3H), 1.88 (s, 15H), 0.12 (d, J = 5.9 Hz). ^{13}C{1H} NMR (100 MHz, CD_2Cl_2): δ 89.2, 80.5, 79.3, 36.7, 34.6, 28.0, 11.5. MS *m*/*z* (relative intensity): calculated for $C_{17}H_{24}{}^{102}$Ru (M^+), 330.0922; found, 330.0906 (5.97); calculated for $C_{17}H_{23}{}^{102}$Ru (M − H), 329.0843; found, 329.0869 (8.77); calculated for $C_{16}H_{21}{}^{102}$Ru (M − CH_3), 315.0687; found, 385.0686 (100).

Protonation of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (14). A solution of (C_5Me_5)Ru(η^5-6-*exo*-$CH_3C_6H_6$) (**14**, 0.015 g, 0.046 mmol) in anhydrous CD_2Cl_2 was placed into an NMR tube and the tube capped with a rubber septum. Triflic acid (0.004 mL, 0.045 mmol) was added via microsyringe and the resulting solution analyzed by ^{1}H NMR spectroscopy. The reaction was complete within 10 min at room temperature, giving [(C_5Me_5)Ru(η^6-$CH_3C_6H_5$)]$^+$OTf$^-$ (**15**), spectroscopically identical to known compound[9] and the demethylated product, [(C_5Me_5)Ru(η^6-C_6H_6)]$^+$OTf$^-$ (**16**), also based on spectroscopic comparison to authentic material,[9] in a ratio of approximately 91:9. Comparable results were obtained from the analogous reaction of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (**14**) tetrafluoroboric acid in acetone-d_6.

Reaction of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (14) with $B(C_6F_5)_3$. A solution of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (0.020 g, 0.060 mmol) in anhydrous CD_2Cl_2 was loaded into an NMR tube and tris(perfluorophenyl)borane (0.035 g, 0.068 mmol) added in one portion. The NMR tube was then capped and shaken for 1 min. After 10 min at room temperature, ^{1}H NMR spectroscopic analysis of the colorless solution indicated the formation of the known cation [(C_5Me_5)Ru(η^6-$CH_3C_6H_5$)]$^+$ (**15**)[9] as the major product accompanied by only a trace of [(C_5Me_5)Ru(η^6-C_6H_6)]$^+$ (**16**)[9] in a ratio of >98:2. The counterions were not identified.

Reaction of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (14) with $AlBr_3$. A solution of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (**14**, 0.025 g, 0.076 mmol) in anhydrous CD_2Cl_2 was loaded into an NMR tube and $AlBr_3$ (0.021 g, 0.079 mmol) added. The NMR tube was then capped and shaken for 1 min. After 10 min at room temperature, ^{1}H NMR spectroscopic analysis of the colorless solution indicated the formation of a mixture of the known[9] cations [(C_5Me_5)Ru(η^6-$CH_3C_6H_5$)]$^+$ (**15**) and [(C_5Me_5)Ru(η^6-C_6H_6)]$^+$ (**16**) in a ratio of ca. 90:10, with no trace of the starting material. The counterions, presumably $HAlBr_3^-$ and $MeAlBr_3^-$, respectively, were not further characterized.

Reaction of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (14) with $Cp_2Fe^+PF_6^-$. A blue suspension of $Cp_2Fe^+PF_6^-$ (0.025 g, 0.076 mmol) in 2 mL of dichloromethane was prepared, and a solution of (C_5Me_5)Ru(η^5-6-*exo*-methylcyclohexadienyl) (0.025 g, 0.076 mmol) in 2 mL of dichloromethane was added slowly via cannula. The blue suspension immediately turned pale yellow and became homogeneous. After the suspension was stirred at room temperature for 30 min, the solvent was removed under reduced pressure. ^{1}H NMR spectroscopic analysis of the yellow residue indicated conversion to [(C_5Me_5)Ru(η^6-$CH_3C_6H_6$)]$^+PF_6^-$ (**15**)[9] and [(C_5Me_5)Ru(η^6-C_6H_6)]$^+PF_6^-$ (**16**)[9] in a ratio of 42:58, accompanied by the formation of ferrocene.

(C_5Me_5)Ru(η^5-9-dehydroergosterol) (17). In the drybox, a Schlenk flask was charged with [(C_5Me_5)RuCl]$_4$ (0.130 g, 0.478 mmol Ru content) and ergosterol (0.200 g, 0.504 mmol, 1.05 equiv). Tetrahydrofuran (6 mL) was added, and the reaction mixture was stirred at room temperature for 6 h, gradually turning deep green. Afterward, excess activated zinc (Rieke zinc,[44] 0.100 g) was added, and the reaction mixture was stirred for a further 10 h, during which time the green solution became nearly colorless. The solvent was then evaporated under reduced pressure, the residue triturated with several portions of hexanes (3 × 2 mL), and the combined extracts filtered over Celite. The filtrate was evaporated to give a brown foam and then redissolved in tetrahydrofuran and filtered through a plug of alumina (5% H_2O). The solvent was removed under reduced pressure to yield 0.157 g of ergosterol complex **17** (52%) as a tan solid, which was used without further purification. ^{1}H NMR (400 MHz, C_6D_6, selected assignments only): δ 5.28, 5.21 (AB quartet, J = 7.5 Hz, 2H, H_{22}/H_{23}), 5.11 (d, J = 4.8 Hz, 1H, H_6/H_7), 3.59 (d, J = 4.8 Hz, 1H, H_6/H_7), 3.97−3.85 (m, 1H, H_3) 1.70 (s, 15H, C_5Me_5), 1.10 (d, J = 6.6 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.90 (d, J = 6.7 Hz, 3H), 0.75 (s, 3H), 0.54 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 136.2 (C_{22}/C_{23}), 132.3 (C_{22}/C_{23}), 95.8 (C_5/C_8), 92.1 (C_5/C_8), 87.2 (C_5Me_5), 79.3 (C_6/C_7), 78.5, (C_6/C_7), 75.5 (C_9), 69.9 (C_3), 55.2, 51.4, 44.2, 42.4, 43.3, 41.0, 38.6, 37.7, 36.4, 33.4, 32.9, 29.8, 25.2, 23.7, 22.6, 21.3, 20.2, 19.9, 17.9, 11.3, 10.9 (C_5Me_5). MS *m*/*z* (relative intensity): calculated for $C_{38}H_{58}{}^{102}$RuO (M^+), 632.3534; found, 632.3405 (2.83); calculated for $C_{37}H_{55}{}^{102}$RuO (M − CH_3), 617.3297; found, 617.3288 (100.00).

[(C_5Me_5)Ru(η^4-ergosterol)]$^+BF_4^-$ (18). (i) From HBF_4·Et_2O. A solution of (C_5Me_5)Ru(η^5-9-dehydoergosterol) (**17**, 0.027 g, 0.043 mmol) in anhydrous dichloromethane-d_2 was placed into an NMR tube and capped with a rubber septum. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether, 0.008 mL, 0.064 mmol) was then added via microsyringe and the resulting yellow solution analyzed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. (Chemical shifts vary slightly depending on the concentration of excess acid.)

(ii) From HOTf. A solution of (C_5Me_5)Ru(η^5-dehydroergosterol) (**17**, 0.022 g, 0.035 mmol) in distilled diethyl ether (3 mL) was prepared in a small Schlenk flask. Triflic acid (0.004 mL, 0.045 mmol) was added via microsyringe and the resulting solution stirred for 1 h. Within 20 min an oily yellow residue deposited from the solution. The solution was decanted, and the residue was rinsed with several portions of diethyl ether and dried under vacuum. The resulting yellow foam was analyzed spectroscopically without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2, selected assignments only): δ 6.26 (d, J = 5.7 Hz, 1H, H_6/H_7), 4.65 (d, J = 5.7 Hz, 1H, H_6/H_7), 5.30, 5.14 (AB quartet, J = 7.2 Hz, 2H, H_{22}/H_{23}), 4.08−3.90 (m, 1H, H_3), 1.91 (s, 15H, C_5Me_5), 1.00 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H), 0.65 (s, 3H), 0.55 (s, 3H), −5.00 (br s, 1H, H_{ag}). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 134.9 (C_{22}/C_{23}), 133.4 (C_{22}/C_{23}), 103.8 (C_8), 97.6 (C_5Me_5), 88.7 (C_6/C_7), 88.6 (C_6/C_7), 81.6 (C_5), 79.7 (C_3), 68.1 (br C_9), 54.7, 51.0, 45.8, 42.2, 43.2, 40.5, 33.4, 39.2, 36.3, 31.0, 29.0, 24.9, 24.0, 26.1, 21.0, 20.0, 19.8, 17.6, 10.8 (C18), 10.6 (C_5Me_5). The triflate carbon was not observed.

Dealkylation of (C_5Me_5)Ru(η^5-9-dehydroergosterol) (17). (i) By Protic Acid. A solution of (C_5Me_5)Ru(η^5-9-dehydroergosterol) (0.044 g, 0.032 mmol) in dry dichloromethane (2 mL) was prepared in a small Schlenk flask. Tetrafluoroboric acid (diethyl ether complex, 85% in diethyl ether, 0.013 mL, 0.075 mmol) was added via syringe, and the reaction was stirred for 5 min before addition of distilled water (0.006 mL, 0.333 mmol, 10.4 equiv). After 4 days at room temperature, the solvent was removed under reduced pressure, leaving a solid tan residue. Analysis of the residue by ^{1}H NMR spectroscopy showed clean conversion to the known complex, [(C_5Me_5)Ru(η^6-neoergosterol)]$^+BF_4^-$ (**19**), which was spectroscopically consistent with the complex reported by Chaudret et al.[9b]

(ii) By Ph_3CBF_4. In the drybox, a solution of (C_5Me_5)Ru(η^5-dehydroergosterol) (0.015 g, 0.024 mmol) in 3 mL of tetrahydrofuran was placed in a Schlenk flask. A yellow slurry of triphenylcarbenium tetrafluoroborate (0.009 g, 0.027 mmol) was added dropwise over 5 min; the reagent rapidly dissolved and the solution turned light brown. The reaction was stirred for 1 h, and the solvent was then removed in

(44) Rieke, R. D.; Sell, M. S.; Klein, W. R.; Chen, T.; Brown, J. D.; Hanson, M. V. In *Active Metals*; Fürstner, A., Ed.; VCH: New York, 1996; Chapter 1.

vacuo. Analysis of the residue by ^{1}H NMR spectroscopy in acetone-d_6 revealed clean conversion to the known $[(C_5Me_5)Ru(\eta^6\text{-neoergosterol})]^+BF_4^-$ (**19**) and Ph_3CCH_3.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada and the University of Alberta is gratefully acknowledged. C.M.O. acknowledges the support of an NSERC Post-graduate Scholarship and a Dissertation Year Fellowship from the University of Alberta.

JA992987E