downfield shift for the adenine N1–thymine H3 H-bonding interaction.

The results presented above demonstrate that the nitrogen chemical shift for the adenine N1 in an A·T Watson–Crick base pair is influenced by the hydrogen isotope present in the H-bond. This is unequivocal observation by NMR of a through-space interaction between an imino nitrogen and the hydrogen to which it is H-bonded. This solvent isotope effect should be generally useful in probing the origin of ^{15}N chemical shifts observed in studying nucleic acid structure, particularly the structure of mismatched base pairs, as well as protein–nucleic acid and drug–nucleic acid interactions.

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Activation of Hydrocarbons by a Ruthenium(II) (Fluoroalkyl)phosphine Hydride Complex

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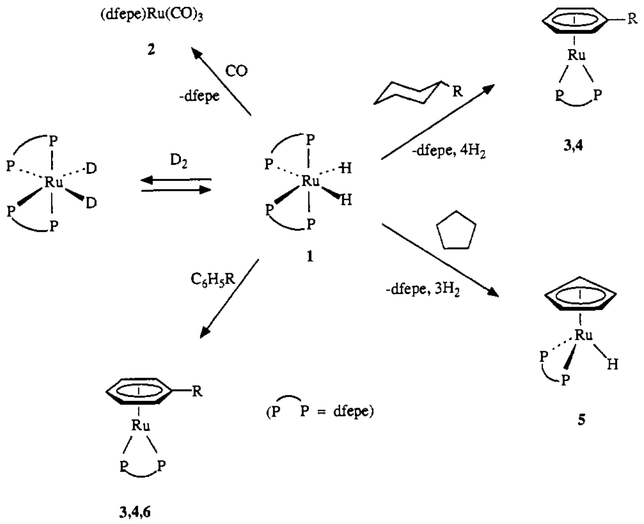
The selective functionalization of simple alkanes by transition-metal complexes in homogeneous media remains a goal of considerable practical and fundamental importance.[1] Substantial progress over the past decade has been made not only in the basic understanding of factors that influence the viability of the initial intra-[2] or intermolecular[1,3,4] addition of C–H bonds, but also in strategies for subsequent productive functionalization of unactivated hydrocarbons. In particular, catalytic photochemically driven systems for carbonylation of saturated[5] and unsaturated[6] hydrocarbons and dehydrogenation of cyclic[7] and acyclic[7c,8] alkanes have recently been demonstrated. Although these results are encouraging, a serious problem generally associated with these reactive systems that still needs to be overcome is catalyst deactivation via attack on ancillary ligand substituents.[1,7c,9]

Scheme I



We have recently begun to develop the (fluoroalkyl)phosphine chemistry of group VIII metals in an effort to design degradation-resistant electron-poor analogues to well-known $L_4M(R)_2$ (M = Fe, Ru, Os; L = PR_3, CO; R = H, alkyl) systems. C–H activation studies for this class of compounds to date have centered on electron-rich complexes such as $(dmpe)_2M(H)R$ (M = Fe, Ru; R = H, aryl)[10] and $(PMe_3)_4Os(H)R$,[11] with very little presently known concerning the comparable chemistry of electron-poor group VIII analogues.[12] Herein we report the synthesis of *cis*-$(dfepe)_2RuH_2$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$)[13] and some initial observations concerning ligand substitution reactions and the unusual direct thermal dehydrogenation of cyclic alkanes by this electrophilic complex to give well-characterized polyene complexes.

cis-$(dfepe)_2RuH_2$ (**1**) is prepared in 41% yield as an air-stable sublimable white solid from the reaction of $(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})Ru$[14] with 2 equiv of dfepe under 1 atm H_2 in methanol.[15] The reaction chemistry of **1** is summarized in Scheme I.[17] With the exception of H_2/D_2 exchange,[18] a common feature in the

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(1) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989. (c) Halpern, J. *J. Inorg. Chim. Acta* **1985**, *100*, 41. (d) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, Holland, 1984.

(2) (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Brookhart, M. O.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (d) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

(3) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (d) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (e) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620. (g) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*. 6491. (h) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (i) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425. (j) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 2825.

(4) (a) Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177. (b) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (c) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 6115. (d) Brown, C. E.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 2530.

(5) (a) Sakakura, T.; Sasaki, K.; Tokunaga, Y.; Wada, K.; Tanaka, M. *Chem. Lett.* **1988**, 155. (b) Sakakura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758.

(6) (a) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764. (b) Sakakura, T.; Tanaka, M. *Chem. Lett.* **1987**, 249.

(7) (a) Baudry, D.; Ephritikhine, M.; Felkin, H. Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 788. (b) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816. (c) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025.

(8) Sakakura, T.; Sodeyama, T.; Tokunaga, Y.; Tanaka, M. *Chem. Lett.* **1988**, 263.

(9) (a) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 606. (b) Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1987**, *6*, 696.

(10) (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080, 7577. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742. (d) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433, 7436. (e) Baker, M. V.; Field, L. D. *Organometallics* **1986**, *5*, 821. (f) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640.

(11) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915.

(12) A few examples of C–H activation by $M_3(CO)_{12}$ (M = Ru, Os) have been reported: (a) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1972**, *36*, C43. (b) Deeming, A. J.; Hasso, S.; Underhill, M.; Carty, A. J.; Johnson, B. F. G.; Jackson, W. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Chem. Commun.* **1974**, 1415. (c) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.

(13) Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1989**, *28*, 1624.

(14) Pertici, P.; Vitulli, G.; Pari, M.; Pori, L. *J. Chem. Soc.*; *Dalton Trans.* **1980**, 1961.

(15) Spectroscopic data for **1**: ^1H NMR (50 °C, C_6D_6) δ 2.39 (m, 4 H, PCH_2), 1.38 (br s, 4 H, PCH_2), −10.79 (AA′MM′XX′ pattern, $^2J_{PH}(cis) \approx 3$ Hz, $^2J_{PH}(trans) \approx 50$ Hz, 2 H, ReH_2); ^{31}P NMR (24 °C, $(CD_3)_2CO$) δ 109.4 (m), 91.2 (m); IR (Nujol) 1990 cm^{-1}. The crystal structure of **1** has been determined (see supplementary material) and shows that the coordination geometry about ruthenium is essentially equivalent to that reported for *cis*-$(dppe)_2RuH_2$.[16]

(16) Pertici, P.; Vitulli, G.; Porzio, W.; Zocchi, M. *Inorg. Chim. Acta* **1979**, *37*, L521.

(17) Thermolysis reactions of **1** were carried out in sealed NMR tubes or carius tubes fitted with Kontes Teflon high-vacuum valves. Cycloalkanes were treated with concentrated H_2SO_4 to remove traces of olefins, then distilled, and stored under N_2.

(18) H_2/D_2 exchange for **1** under 2 atm D_2 in benzene is quite slow, occuring to an appreciable extent only after several hours at 150 °C.

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chemistry observed is the loss of H_2 and one dfepe ligand to give products formally derived from a 12-electron (dfepe)Ru fragment. Thus, the reaction of **1** with CO is complete after 72 h at 90 °C to give (dfepe)Ru(CO)$_3$ (**2**) (ν_{CO} = 2068, 2019 (sh), and 1996 cm^{-1}), with no evidence under these conditions of partial substitution products (dfepe)$_2$Ru(CO) or (dfepe)Ru(CO)$_2$(H)$_2$, or the expected product of complete substitution, $Ru_3(CO)_{12}$. The reaction of **1** with neat benzene or toluene similarly occurs at more elevated temperatures to give not the anticipated C–H addition product, (dfepe)$_2$Ru(H)(Ar), but instead the arene complexes (η^6-C_6H_5R)Ru(dfepe) (R = H, **3**; R = Me, **4**) as yellow sublimable solids in essentially quantitative yield.[19]

The thermal behavior of **1** in neat cycloalkane solvents is of special interest. While completely unreactive at temperatures up to 150 °C, warming **1** to 180 °C for 5 days in neat cyclohexane yields the benzene complex **3** as the major (>90%) observed product.[20] No product arene ring exchange with neat C_6D_6, production of free benzene, or deuterium incorporation into the arene C–H bonds of **3** by D_2 is seen after prolonged heating at 180 °C, indicating that the formation of **3** from **1** and cyclohexane is stoichiometric and irreversible. Monitoring this process by ^{19}F and ^{31}P NMR reveals that **3** and free dfepe are the sole products during the early stages of the reaction. After prolonged heating, several uncharacterized minor side products begin to appear due to secondary reactions of **1** with released dfepe. No difference in reaction rate was noted between samples heated in the presence and absence of light; the reaction rate was similarly unaffected by the addition of metallic mercury.[21]

The generality of this transformation has been confirmed by the reactions of **1** with neat methylcyclohexane and cyclopentane at 180 °C to give (η^6-C_6H_5Me)Ru(dfepe) (**4**) and (η^5-C_5H_5)-Ru(dfepe)H (**5**), respectively, as the major (>90%) products. Complex **5** may also be quantitatively prepared from the reaction of **1** with cyclopentene or cyclopentadiene at 130 °C. A qualitative comparison of arene substitution and dehydrogenation rates run to partial completion gives the reactivity ordering for this system of cyclopentene $\gg$ arene > cyclopentane $\approx$ C_6H_{12}.[22] The greater apparent reactivity of **1** toward arenes versus cyclohexane is confirmed by the thermolysis of **1** with cyclohexylbenzene, which gives (η^6-C_6H_5Cy)Ru(dfepe) (**6**) as the exclusive product at a rate comparable to that observed for the formation of **4**. Some preliminary mechanistic information is provided by a comparison of the thermolysis reactions of **1** in the presence and absence of ambient H_2 and D_2. An approximately 2-fold inhibition in the thermolysis rate for **1** in both neat benzene and cyclopentane under 500 Torr H_2 is observed, consistent with a mechanism involving H_2 loss and the generation of a reactive (dfepe)$_2$Ru intermediate. In addition, no incorporation of deuterium into either the hydride or ring positions of **5** during the thermolysis of **1** in cyclopentane under 500 Torr D_2 is detected, indicating that there is no reversible dissociation of hydrogen in the dehydrogenation steps subsequent to the initial addition of the hydrocarbon substrate.

The thermal dehydrogenation reactions of **1** uniquely differ from most previously reported dehydrogenation systems[7,23] in that no hydrogen acceptor (*tert*-butylethylene) or photochemical conditions are required to drive the process. This difference in reactivity is presumably due to unusually strong Ru–(arene) binding in the systems examined compared to Rh and Ir analogues,[10b,24] as well as the thermal accessibility and surprising stability of reactive, highly unsaturated monochelate intermediates under the harsh conditions employed. It is particularly significant that no P–C cleavage products such as C_2F_5H have been detected in our system.[25] Furthermore, although activation of sp^2 and sp^3 C–H bonds by known thermal or photogenerated 16-electron $(\widehat{P\ P})_2M$ ($\widehat{P\ P}$ = dmpe, depe, dppe; M = Fe, Ru) intermediates is complicated by the competitive formation of inter- or intramolecular orthometalation products such as (dppe)Fe($C_6H_4PPh_2$)(H),[26] analogous "tuck-in" products derived from C–F bond addition from dfepe ligands have thus far not been identified in the reactions of **1**. In light of these observations, we believe that (fluoroalkyl)phosphine complexes offer considerable promise in the design of practical hydrocarbon activation systems. Currently our efforts are directed toward detailed mechanistic studies of the above dehydrogenation reactions and the extension of this work to more labile, potentially catalytic group VIII and IX systems.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1–6** and crystallographic data for complexes **1** and **3**, including ORTEP figures, collection and refinement parameters, and tables of positional parameters and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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[19] With the exception of **2**, which was obtained as an oil contaminated with ≈10% dfepe, all reported compounds were isolated in 69–81% yield as analytically pure crystalline solids; see supplementary material for full characterization data. Selected data for **3**: ^{1}H NMR (C_6D_6) δ 5.10 (s, 6 H, C_6H_6), 1.75 (m, 4 H, PCH_2); ^{13}C NMR ($(CD_3)_2CO$) δ 88.49 (d, $^1J_{CH}$ = 175 Hz, C_6H_6). For **5**: ^{1}H NMR (C_6D_6) δ 4.83 (s, 5 H, C_5H_5), 1.76 (m, 4 H, PCH_2), −13.58 (t, $^2J_{PH}$ = 35 Hz, 1 H, RuH); ^{13}C NMR (C_6D_6) δ 83.25 (dt, $^1J_{CH}$ = 179 Hz, $^2J_{CP}$ = 7 Hz, C_5H_5). The crystal structure of **3** has also been determined; details are included in the supplementary material.

[20] The production of H_2 in the conversion of **1** to **3** was qualitatively verified by GC.

[21] Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

[22] Preliminary kinetic experiments were run on 1.30 × 10^{-3} M solutions of **1** (0.5 mL) in sealed 5-mm NMR tubes and followed by ^{19}F NMR. The following approximate half-lives were obtained: C_5H_8 (164 °C, $t_{1/2}$ = 45 min), C_6H_6 (164 °C, $t_{1/2}$ = 12 h), C_5H_{10} (195 °C, $t_{1/2}$ = 35 h), C_6H_{12} (195 °C, $t_{1/2}$ = 60 h). At these concentrations, no inhibition by released H_2 was observed.

[23] Rhodium-catalyzed homogeneous dehydrogenation of cyclooctane under H_2 purge conditions has recently been reported: Fujii, T.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 757.

[24] Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1217.

[25] This observation is consistent with Hoffmann's prediction that electron-withdrawing phosphorous substituents should be less prone to P–C cleavage: Ortiz, J. V.; Havlas, J.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.

[26] Azizian, H.; Morris, R. H. *Inorg. Chem.* **1983**, *22*, 6.

Gemini Surfactants: Synthesis and Properties

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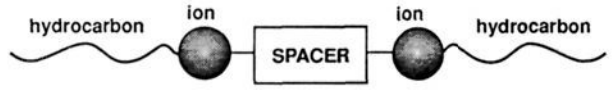
Single-chained amphiphiles (e.g., sodium dodecyl sulfate) form, in aqueous solution, spherical aggregates called micelles. Ionic head-groups of micelles lie near the water, whereas the hydrocarbon tails project inwardly.[1] Double-chained amphiphiles (e.g., didodecyldimethylammonium bromide) form bilayer sheets. These aggregates are also organized such that the ionic groups reside on the outside while the hydrocarbon tails extend into the bilayer away from the water.[2] We have synthesized and studied a new type of amphiphile, called gemini surfactants, which are intriguing because (unlike conventional surfactants) there is no way for them to aggregate without exposing hydrocarbon moieties to the water. The molecules possess, in sequence, a long hydrocarbon chain, an ionic group, a rigid spacer, a second ionic group, and another hydrocarbon tail. Initial concern that the compounds might not



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[1] Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982. Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1978. Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.

[2] Ostro, M. J. *Liposomes*; Marcel Dekker: New York, 1983.

0002-7863/91/1513-1451$02.50/0