Based on Scheme I[9] and neglecting the unknown product, the equation below is obtained in which f_3 is the fraction of product accounted for by **3**. The double reciprocal plot is shown in Figure

$$\frac{1}{f_3} = \left(\frac{1}{[N_3^-]}\right)\left(\frac{k_{H_2O}}{k_{az}}\right) + 1$$

2 and does have the correct form. The inverse of the slope gives a selectivity ratio k_{az}/k_{H_2O} of 7.5 M^{-1}. This value is some 6 orders of magnitude smaller than the selectivity observed for activation limited reactions with stable cations and can be interpreted as evidence that the reaction with azide ion is diffusion controlled.[10] Choosing a value for the rate constant for a diffusion-limited reaction, and thus for k_{az}, of 5×10^9 M^{-1} s^{-1} (limits 1-10 × 10^9),[11] the rate constant for the reaction with water is 7×10^8 s^{-1} (limits 1.3-13 × 10^8).[12]

Thus, for the hydroxylamine **1**, both the rearrangement reaction and the substitution reaction involving the powerful nucleophile azide occur via a short-lived but free nitrenium ion intermediate. From a biological point of view this study establishes that such electrophiles can form under aqueous conditions. However, the short lifetime indicates that little DNA modification is to be expected by the cation of this study unless it is formed in the immediate vicinity of the target. We are currently investigating the reactions of other nucleophiles with **1** and reactions of other phenylhydroxylamines to determine whether and how the selectivities of nitrenium ions change.

Acknowledgment. This material is based upon work supported by the North Atlantic Treaty Organization and by the National Institutes of Health under grants awarded in 1985-1987.

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(9) A control experiment shows that azide ion is likely acting only as a nucleophile, not as a base catalyst of hydration. Product analysis of five reactions with $[N_3^-]$ = .0544 M showed that **3**/**2** decreased by less than 5% as acetate buffer, $[HA]/[A^-]$ = 2.3, was varied from 0.19 to 0.98 M.

(10) Ta-Shma, R.; Rappoport, Z. *J. Am. Chem. Soc.* **1983**, *105*, 6089.

(11) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238.

(12) From k_{az}/k_{H_2O} = 7.5 M^{-1} and $k_{az} = 5 \times 10^9$ M^{-1} s^{-1}, $k_{H_2O} = 5 \times 10^9$ M^{-1} s^{-1}/7.5 M^{-1} = 7×10^8 s^{-1}.

Reaction of C-H Bonds in Alkanes with Bis(diphosphine) Complexes of Iron

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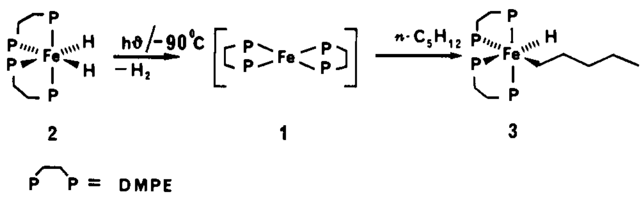
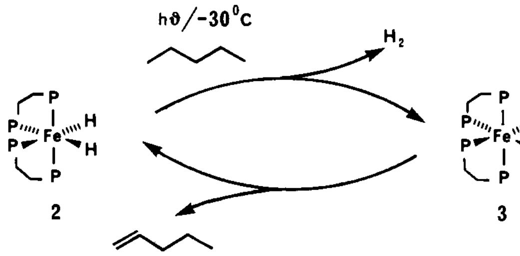
Oxidative addition of unactivated C-H bonds to transition-metal complexes has been an area of intense interest in organometallic chemistry over recent years. There have been numerous reports of complexes of second- and third-row transition metals (including Ir,[1] Rh,[2] Re,[3] and Os[4]), lanthanides,[5] and actinides,[6] which react intermolecularly with the C-H and C-C bonds in alkanes, but, to our knowledge, there have been no reports of alkane C-H activation involving complexes of first-row transition metals. In this paper we describe the reaction of alkanes with the species $Fe(DMPE)_2$ (**1**)[7] [DMPE = 1,2-bis(dimethylphosphino)ethane] in homogeneous solution.

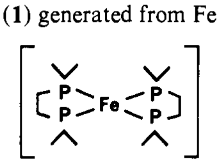
Scheme I



Scheme II



We recently reported[8] some reactions of the reactive intermediate $Fe(DMPE)_2$ (**1**) generated from $FeH_2(DMPE)_2$ (**2**) with sp^2 C-H bonds in alkenes and arenes at low temperature. In previous work, [7c-e] the species **1** has been generated by the reductive elimination of naphthalene from *cis*-FeH(Np)$(DMPE)_2$ (Np = 2-naphthyl); however, this limited the scope of reactions which could be studied to substrates with a reactivity greater than (or comparable to) that of naphthalene. In addition, to form **1** from FeH(Np)$(DMPE)_2$ necessarily required reaction temperatures close to room temperature, where any thermally labile products may not have been sufficiently stable to be observed. Generation of **1** by the photochemical elimination of dihydrogen from **2** has the advantage that **1** can be formed in the absence of compounds with which it can react readily.



1

When the dihydride **2** was irradiated[9] at low temperature (<-90 °C) in n-pentane solution, dihydrogen was eliminated and one major product was formed (70% yield after 60% conversion, by ^{31}P NMR) (Scheme I). We assign this as *cis*-(1-pentyl)Fe$(DMPE)_2$H (**3**). The complex **3** contains four nonequivalent phosphorus atoms and possesses a single phosphorus-coupled, iron-bound hydride which resonates at δ -13.283 in the ^1H NMR spectrum (Figure 1b).[10,11] The complex decomposed rapidly on warming to temperatures above -20 °C and could not be isolated.

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(1) See, for example: (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190-7191 and references cited therein. (b) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure App. Chem.* **1984**, *56*, 13-23 and references cited therein.

(2) See, for example: Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562-563.

(3) See, for example: (a) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856-4867. (b) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrewski, J. *Tetrahedron Lett.* **1984**, *25*, 1283-1286. (c) Klahn-Oliva, A. H.; Singer, R. D.; Sutton, D. *J. Am. Chem. Soc.* **1986**, *108*, 3107-3108.

(4) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81-91.

(5) See, for example: (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276-277. (b) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491-6493.

(6) See, for example: Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425-437 and references cited therein.

(7) For earlier studies on the chemistry of bidentate alkylphosphine complexes of iron, see: (a) Baker, M. V.; Field, L. D. *Organometallics* **1986**, *5*, 821-823. (b) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7436-7438. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080-4089. (d) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577-7585. (e) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742-1751. (f) Bergamini, P.; Sostero, S.; Traverso, O. *J. Organomet. Chem.* **1986**, *299*, C11-C14.

(8) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433-7434.

(9) Samples (2-10 mg/mL) were irradiated in Pyrex NMR tubes, positioned ca. 10 cm from a 125-W mercury vapor lamp. The tubes were supported within a quartz cylinder and cooled by a stream of nitrogen gas.

(10) ^{31}P NMR spectra were referenced to external, neat trimethyl phosphite, taken as 140.85 ppm, at the temperature quoted. ^1H NMR spectra were referenced to solvent resonances. P-P splittings were measured directly from spectra and signs of P-P couplings are not implied. In protonated solvents, some regions of ^1H spectra were obscured by solvent resonances.

(11) **3**: $^{31}P\{^1H\}$ NMR spectrum (pentane, -80 °C) δ 76.41, P_A; 75.04, P_B; 64.98, P_C; 63.18, P_D (J_{AB} = 125.4, J_{AC} = 22.7, J_{AD} = 33.2, J_{BC} = 27.0, J_{BD} = 25.1, J_{CD} = 11.3 Hz). ^1H NMR spectrum (pentane, -80 °C) δ -13.283, Fe-H (dddd, J = 38.4, 50.6, 60.8, 60.8 Hz); -0.190, -0.414, multiplets, $FeCH_2(CH_2)_3CH_3$.

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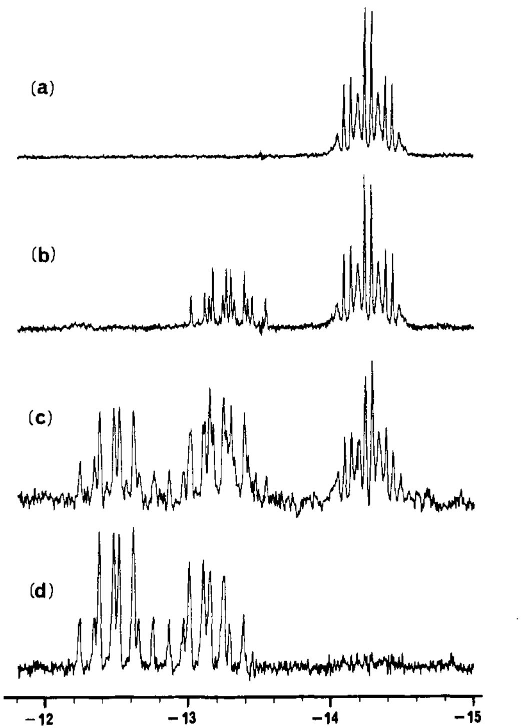
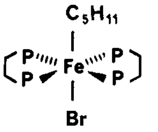


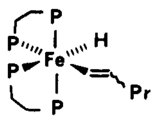
Figure 1. High-field (iron hydride) region of the ^{1}H NMR spectra (400 MHz, pentane solution, −50 °C): (a) *cis*-$Fe(DMPE)_2H_2$ (**2**); (b) solution of **2** after irradiation[9] in pentane for 70 min at −90 °C; (c) solution of **2** after irradiation[9] in pentane for 70 min at −30 °C; (d) mixture of (*E*)- and (*Z*)-1-pentenyl hydrides, **5a** and **5b**, obtained on irradiation of **2** in a solution (5%) of 1-pentene in pentane for 90 min at −80 °C.

Irradiation of **2** in cyclopentane (or other alkanes) at low temperature produced analogous but different alkyl metal hydrides.

When a solution containing **3** was allowed to react[12] with CH_2Br_2 at −78 °C and warmed to room temperature, *trans*-(1-pentyl)$Fe(DMPE)_2Br$ (**4**)[13] was formed. Treatment of a solution containing **3** with bromine in pentane at −78 °C resulted in formation of 1-bromopentane.[14] When a solution containing **3** was quenched at −78 °C with deuteriotrifluoroacetic acid, the ^{2}H NMR spectrum of pentane[14] which was recovered from the reaction mixture showed incorporation of deuterium at C1. There was no evidence for reaction of pentane at C2 or C3.

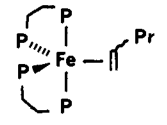


4



5a : E

5b : Z



5c

Irradiation of **2** in dilute pentane solution at higher temperatures (ca. −30 °C) produced 1-pentene[14] and a mixture containing the known[8] 1-pentenyl iron hydrides **5a** and **5b** and the π-complex **5c**, as well as **3** (Figure 1c). We have previously shown[8] that the complexes **5a–c** are formed when **2** is irradiated in the presence of 1-pentene (Figure 1d). We propose that on irradiation at -30 °C, the pentyl iron hydride **3** forms initially but is unstable at this temperature and decomposes by β-hydride elimination[15] to produce 1-pentene[16] and regenerate the starting dihydride **2** (Scheme II). While the scheme is cyclic, the 1-pentene formed is far more reactive than pentane and the reactive iron species **1** is trapped eventually by the alkene.

The major byproducts of the photolysis of **2** (in all solvents) showed resonances at ca. 62 and 10 ppm in the ^{31}P NMR spectrum, and these are close to those reported for the DMPE-bridged dimer, $Fe_2(DMPE)_5$.[7c] After short periods of irradiation, the resonances were reasonably sharp and showed some multiplicity; the resonances broadened significantly after prolonged irradiation. In more concentrated solutions, the byproducts formed in higher yield. These observations suggest that the byproducts are probably oligomeric or polymeric species arising via intermolecular attack of **1** on other iron complexes present in solution.

In this paper, we have clearly demonstrated for the first time that iron species can be made that are sufficiently reactive to add intermolecularly to the C–H bonds of alkanes, even at −100 °C. We are currently investigating the application of iron complexes to the functionalization of alkanes and alkyl groups.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme and the Australian Government for a Commonwealth Postgraduate Award (M. V. B.).

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[12] In a typical experiment, 2–4 equiv of a solution of CH_2Br_2 0.2 M in pentane) was added to a photolysis mixture containing the iron hydride at −78 °C. The sample was warmed to room temperature, stripped of solvent under vacuum, and extracted into deuteriobenzene. After they were quenched, the mixtures always contained *trans*-$Br_2Fe(DMPE)_2$ in varying amounts.

[13] **4**: $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 25 °C) δ 63.51. $^1H\{^{31}P\}$ NMR spectrum (C_6D_6, 25 °C) δ −1.672, $FeCH_2CH_2CH_2CH_2CH_3$; 0.488, $FeCH_2CH_2CH_2CH_2CH_3$; 0.902, $FeCH_2CH_2CH_2CH_2CH_3$; 1.118, $FeCH_2CH_2CH_2CH_2CH_3$; 1.278, $FeCH_2CH_2CH_2CH_2CH_3$; 1.102, 1.582, $P(CH_3)_2$; 1.545, 1.815, PCH_2CH_2P. This compound is also formed in the reaction of 1-pentylmagnesium bromide with *trans*-$Br_2Fe(DMPE)_2$ at 0 °C in THF.

[14] All quenching experiments were performed against appropriate (unirradiated) blanks. Formation of deuteriopentane was assayed by ^{2}H NMR spectroscopy of pentane recovered from the reaction mixture. Formation of 1-bromopentane was verified by ^{1}H NMR spectroscopy and GLC against an authentic sample. Formation of 1-pentene was verified by ^{1}H NMR spectroscopy and conversion to its dibromo derivative by reaction with Br_2.

[15] β-Elimination of the alkene from **3** would probably proceed with prior partial dissociation of one of the bidentate phosphine ligands to make available a coordination site on the metal. See, for example: (a) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640–5641. (b) Jones, W. D.; Libertini, E. *Inorg. Chem.* **1986**, *108*, 1794–1800.

[16] Alkane dehydrogenation reactions have been reported previously in complexes of iridium and rhenium. See, for instance: (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (b) Crabtree, R. H.; Mellea, M. F., Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (c) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1283. (d) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Common.* **1980**, 1243. (e) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235.

Oxidative Addition of Carbon Dioxide, Epoxides, and Related Molecules to $WCl_2(PMePh_2)_4$ Yielding Tungsten(IV) Oxo, Imido, and Sulfido Complexes. Crystal and Molecular Structure of $W(O)Cl_2(CO)(PMePh_2)_2$

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We have recently reported the first examples of complexes with both terminal oxo ligands and carbonyl or olefin groups: $W(O)Cl_2(L)(PMePh_2)_2$, L = CO (**2**), $CH_2{=}CH_2$ (**3**), $CH_2{=}CHMe$ (**4**), $CNCMe_3$ (**5**), etc.[2] We proposed that compounds **2–4** might be models for intermediates in olefin or carbon monoxide oxidation by metal oxides. These compounds do not, however, rearrange to epoxides, carbon dioxide, or other products of ligand oxidation. Ligand oxidation was suggested to be

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[1] (a) University of Washington. (b) University of Delaware.

[2] Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545–3547.