# Methane Activation by an Iron Phosphine Complex in Liquid Xenon Solution

**Leslie D. Field,* Adrian V. George and Barbara A. Messerle**

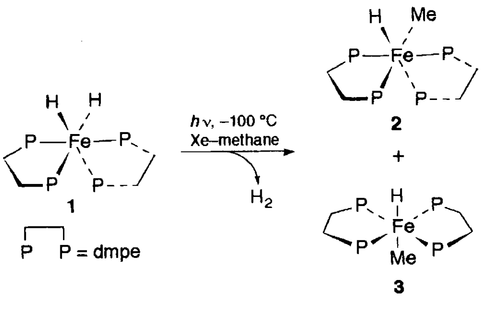
*Department of Organic Chemistry, University of Sydney, Sydney, NSW 2006, Australia*

Irradiation of $FeH_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] in a solution of methane in liquefied xenon at −100 °C affords a mixture of *cis*-$FeH(dmpe)_2Me$ and *trans*-$FeH(dmpe)_2Me$; the *cis* and *trans* isomers equilibrate photochemically at −100 °C but decompose thermally with elimination of methane at temperatures above *ca.* 0 °C following solvent exchange with toluene.

Alkane activation has been achieved with a number of soluble transition metal complexes,[1–3] however, there are very few well-characterised homogeneous reactions of methane with organometallic reagents.[3] Here we report the activation of methane with $FeH_2(dmpe)_2$ **1** [dmpe = 1,2-bis(dimethylphosphino)ethane] under photochemical conditions using liquified xenon as a reaction solvent.

We have previously reported the photochemical activation of C–H bonds in hydrocarbons (arenes, alkenes and alkanes) with $FeH_2(L)_2$ complexes (L = $R_2PCH_2CH_2PR_2$, R = Me, Et).[4] These reactions are thought to proceed *via* the photochemical elimination of dihydrogen from the organometallic complex to form the unsaturated $[Fe(L)_2]$ species which reacts with C–H bonds in the hydrocarbon substrate.[5] C–H activation of methane by organometallic complexes has been studied in the solid state under matrix isolation conditions.[6] Methane is, however, a technically difficult alkane substrate to study conveniently in solution because of its low boiling point (−161 °C) and generally poor solubility in solvents suitable for C–H activation. Bergman *et al.*[7] recently employed liquefied xenon as an inert solvent for studying reactive species in solution at low temperature. As well as acting as an unreactive supporting medium, liquefied xenon dissolves a variety of organic and organometallic compounds. It has been used in a number of spectroscopic studies but its potential as a useful solvent in organometallic synthesis is only now being realised.[8] With methane, xenon forms a solution (>30 mol% methane) at pressures and temperatures where C–H activation with homogeneous organometallic reagents and catalysts can be studied without recourse to the use of high pressures.

A mixture of methane and xenon (*ca.* 40 mol% methane) was condensed quantitatively from a vacuum line into a thick-walled NMR[9] tube containing $FeH_2(dmpe)_2$ (*ca.* 11



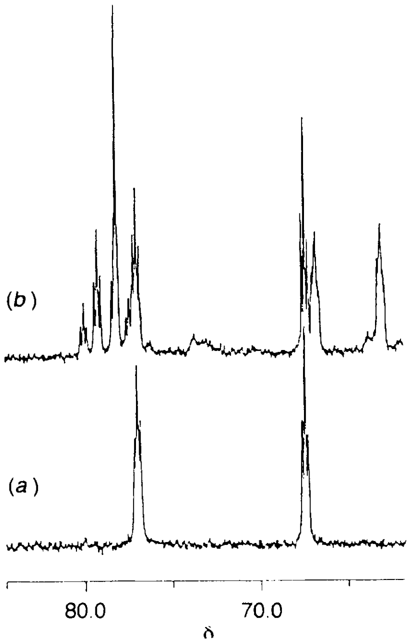
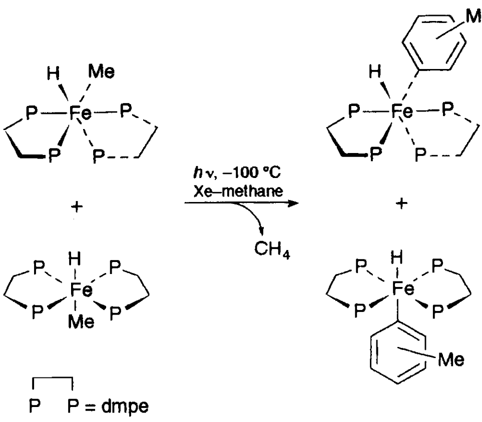


**Fig. 1** $^{31}P$ NMR spectrum (162.0 MHz) of $FeH_2(dmpe)_2$ **1** in a solution of methane in liquid xenon (40 mol% methane, −110 °C). (*a*) before irradiation; (*b*) after UV irradiation for 2 h

μmol) and $[^2H_8]$tetrahydrofuran (50 μl).† The tube was sealed with a pressure-release cap[9] which permitted escape of the gases if the pressure exceeded a preset level (*ca.* 8 atm.). The mixture was warmed to −98 °C (methanol–liquid nitrogen slush bath) and the solution mixed. The sample was irradiated, through Pyrex, with a 125 W medium pressure mercury lamp while the temperature was maintained at −100 °C. After irradiation for 15 min, $^{31}P$ and $^1H$ NMR spectra‡ indicated conversion of $FeH_2(dmpe)_2$ to *cis*-$FeH(dmpe)_2Me$ **2** and *trans*-$FeH(dmpe)_2Me$ **3**§ in a ratio of 5 : 2, respectively (approximately 32% conversion). Methane activation proceeded further with continued irradiation [approximately 74% conversion after 2 h, Fig. 1(*b*)] and the proportion of the *trans* isomer **3** increased as the irradiation progressed.¶



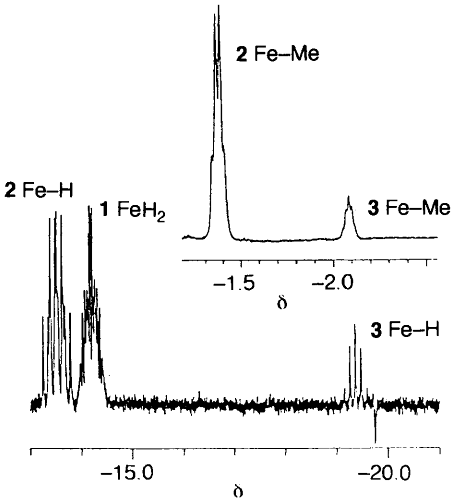


**Fig. 2** High field regions of the $^1H$ NMR spectrum (400.1 MHz) of $FeH_2(dmpe)_2$ **1** in a solution of methane in liquid xenon (40 mol% methane, −110 °C) after UV irradiation for 2 h

In the $^{13}C$ NMR spectrum, the metal bound carbon atoms of **2** and **3** appear to high field of $SiMe_4$ at δ − 14.02 and −18.95, respectively. The iron-bound hydrides for *cis*-$FeH(dmpe)_2Me$ **2** and *trans*-$FeH(dmpe)_2Me$ **3** resonate at δ −13.58 and −19.43 in the $^1H$ NMR spectrum and resonances due to the protons of the corresponding iron-bound Me groups appear at δ −1.37 and −2.08, respectively (Fig. 2).[10] The resonances assigned to *trans*-$FeH(dmpe)_2Me$ **3** correspond to those of an authentic sample of the compound formed by the reaction of dimethylmagnesium with $FeCl(dmpe)_2H$ in tetrahydrofuran (THF) at −30 °C.[10]

Under the conditions of the experiment, both the *cis* and *trans* isomers of $FeH(dmpe)_2Me$ are formed. In the early stages of the reaction, the *cis* isomer **2** is the major product in the mixture, however, over an extended period of irradiation the *trans* isomer **3** is formed almost exclusively. There is no change in the *cis* : *trans* ratio when the product mixture is allowed to stand at −110 °C in the dark for 14 h which indicates that the observed isomerization is a photochemical process at this temperature.

$[^2H_8]$Toluene was condensed into the reaction mixture and the xenon–methane solvent was removed by evaporation below −80 °C without any change in the product mixture. As the temperature of the toluene solution was increased to −15 °C, the *cis* isomer **2** isomerised completely to the *trans* isomer **3** *i.e.* the *cis* to *trans* isomerization also occurs thermally but at significantly higher temperatures than under conditions of irradiation. When a toluene solution of **2** and **3** was warmed to room temperature, methane was eliminated and a mixture of the known *cis*- and *trans*-tolyl hydrido complexes[5d] formed.|| The thermal elimination of methane

---

† $[^2H_8]$THF assists the dissolution of $FeH_2(dmpe)_2$ iron complexes and provides a deuterium lock signal for the NMR experiments. Identical reaction products are obtained in the absence of THF.

‡ NMR spectra were obtained at −110 °C using a Bruker AMX400 spectrometer. $^{31}P$ NMR spectra (162.0 MHz) were referenced to the shift of external, neat, trimethyl phosphite taken as 140.85 ppm (extrapolated to −110 °C). $^1H$ NMR spectra (400.1 MHz) were referenced to the resonance of methane in the solution, taken to be 0.23 ppm; $^{13}C$ NMR spectra were referenced to the highfield resonance of $[^2H_8]$THF in the solvent mixture, taken to be 26.7 ppm. Chemical shifts are sensitive to the concentration of xenon present.

§ *cis*-$FeH(dmpe)_2Me$, **2**, $^{31}P\{^1H\}$ NMR (xenon–methane solution, −110 °C) δ 63.8 (m, 1P, *J* 28, 28 and 13 Hz), 67.4 (m, 1P, *J* 28, 28 and 13 Hz), 78.2 (m, 1P, *J* 128, 28 and 28 Hz), 79.8 (m, 1P, *J* 128, 28 and 28 Hz); $^1H$ NMR δ −1.37 (m, 3H, $FeCH_3$), −13.58 (dddd, 1H, $^2J_{PH}$ 60.7, 60.7, 51.4 and 39.9 Hz FeH); $^{13}C\{^1H,^{31}P\}$ NMR δ −14.02 ($FeCH_3$) *trans*-$FeH(dmpe)_2Me$, **3** $^{31}P\{^1H\}$ NMR (xenon–methane solution, −110 °C) δ78.4 (s); $^1H$ NMR δ −2.08 (quintet, 3H, $^3J_{PH}$ 6.0 Hz, $FeCH_3$), −19.43 (quintet, 1H, $^2J_{PH}$ 43.0 Hz, FeH); $^{13}C\{^1H,^{31}P\}$ NMR δ −18.95 ($FeCH_3$)

¶ The only other product formed (*ca.* 7% after 2 h irradiation) exhibits a broad singlet resonance (δ 61.5) in the $^{31}P$ NMR spectrum. This unidentified product does not contain an activated methyl group and is also formed in photochemical activation of other substrates.[4]

|| *cis*- and *trans*-$FeH(dmpe)_2(C_6H_4Me)$ were obtained as a mixture of *meta* and *para* isomers.

from $FeH(L)_2(Me)$ complexes and subsequent trapping of the liberated $[Fe(L)_2]$ fragment by reactive arenes has been observed previously.[4,5,10]

The bonds in methane are amongst the strongest and least reactive C–H bonds, however, the addition of a photochemically generated coordinatively unsaturated iron phosphine species to a C–H bond of methane is a facile process in xenon solution and proceeds smoothly even at −100 °C. Xenon has proved to be an important supporting solvent for studying homogeneous reactions of reactive organometallic complexes with hydrocarbons which cannot be obtained conveniently as liquids and we are currently exploring the reactions of related iron phosphines with low-boiling alkanes in xenon solution.

We gratefully acknowledge support from the Australian Research Council and the University of Sydney for an H. B. and F. M. Gritton Postdoctoral Research Fellowship (B. A. M.).

*Received, 6th June 1991; Com. 1/02710G*

## References

1 For recent reviews of aspects of transition metal activation of alkanes see: *Activation and Functionalisation of Alkanes*, ed. C. L. Hill, Wiley, New York, 1989; *Selective Hydrocarbon Activation*, eds. J. A. Davies; P. L. Watson, J. F. Liebman and A. Greenberg, VCH, New York, 1990; R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245; A. E. Shilov, *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Riedel, Dodrecht, 1984; J. Halpern, *Inorg. Chim. Acta* 1985, **100**, 41; G. W. Parshall, *Chem. Tech.*, 1984, **14**, 628 and references cited therein.

2 See, for example: W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1984, **106**, 1650; W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562; W. A. G. Graham, *J. Organomet. Chem.*, 1986, **300**, 81; A. H. Klahn-Oliver, R. D. Singer and D. Sutton, *J. Am. Chem. Soc.*, 1986, **108**, 3107; A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 3929; A. J. Rest, I. Whitwell, W. A. G. Graham, J. K. Hoyano and A. D. McMaster, *J. Chem. Soc., Chem. Commun.*, 1984, 624; R. A. Periana and R. G. Bergman, *Organometallics*, 1984, **3**, 508; T. T. Wenzel and R. G. Bergman, *J. Am. Chem. Soc.*, 1986, **108**, 4856.

3 See, for example: P. L. Watson, *J. Am. Chem. Soc.*, 1983, **105**, 6491; M. J. Wax, J. M. Stryker, J. M. Buchanan, C. A. Kovac and R. G. Bergman, *J. Am. Chem. Soc.*, 1984, **106**, 1121; R. G. Bergman, P. F. Seidler and T. T. Wenzel, *J. Am. Chem. Soc.*, 1985, **107**, 4358; C. N. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 2214; C. K. Ghosh and W. A. G. Graham, *J. Am. Chem. Soc.*, 1987, **109**, 4726.

4 M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, 1987, **109**, 2825; M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, 1986, **108**, 7433; M. V. Baker and L. D. Field, *Organometallics*, 1986, **5**, 821.

5 (*a*) C. A. Tollman, S. D. Ittel, A. D. English and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 4080; (*b*) S. D. Ittel, C. A. Tollman, P. J. Krusic, A. D. English and J. P. Jesson, *Inorg. Chem.*, 1978, **17**, 3432; (*c*) C. A. Tollman, S. D. Ittel, A. D. English and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 7577; (*d*) C. A. Tollman, S. D. Ittel, A. D. English and J. P. Jesson, *J. Am. Chem. Soc.*, 1979, **101**, 1742; (*e*) P. Bergamini, S. Sostero and O. Traverso, *J. Organomet. Chem.*, 1986, **299**, C11; (*f*) H. Azizian and R. H. Morris, *Inorg. Chem.*, 1983, **22**, 6; (*g*) A. Maldotti, S. Sostero, O. Traverso and J. Sima, *Inorg. Chim. Acta*, 1981, **54**, L271.

6 A. McCamley, R. N. Perutz, S. Stahl and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1690; D. M. Hadderton, A. McCamley and R. N. Perutz, *J. Am. Chem. Soc.*, 1988, **110**, 1810; and references cited therein.

7 M. B. Sponsler, B. H. Weiller, P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 6841.

8 M. T. Haward, M. W. George, S. M. Howdle and M. Poliakoff, *J. Chem. Soc., Chem. Commun.*, 1990, 913; B. H. Weiller, E. P. Wasserman, R. G. Bergman, C. B. Moore and G. C. Pimentel, *J. Am. Chem. Soc.*, 1989, **111**, 8288; R. K. Upmacis, M. Poliakoff and J. J. Turner, *J. Am. Chem. Soc.*, 1986, **108**, 3645; S. A. Jackson, R. K. Upmacis, M. Poliakoff, J. J. Turner, J. K. Burdett and F.-W. Grevels, *J. Chem. Soc., Chem. Commun.*, 1987, 678; G. E. Gadd, M. Poliakoff and J. J. Turner, *Organometallics*, 1987, **6**, 391; S. Frith, W. E. Klotzbücher, M. Poliakoff and J. J. Turner, *Inorg. Chem.*, 1987, **26**, 3370; R. K. Upmacis, G. E. Gadd, M. Poliakoff, M. B. Simpson, J. J. Turner, R. Whyman and A. F. Simpson, *J. Chem. Soc., Chem. Commun.*, 1985, 27.

9 L. D. Field, A. V. George, B. A. Messerle and H. Ionn, *Anal. Chem.*, 1991, **63**, 184.

10 The $^1H$ chemical shifts of iron-bound methyl groups have been reported as $\delta$ −0.64 for $Fe(dmpe)_2(Me)_2$: G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 1339; $\delta$ −1.27 for *trans*-$FeH(dprpe)_2CH_3$ [dprpe = 1,2-bis(dipropylphosphino)ethane]; $\delta$ −0.94 for *cis*-$FeH(dprpe)_2Me$; $\delta$ −1.35 for *trans*-$FeH(depe)_2Me$ [depe = 1,2-bis(diethylphosphino)ethane]; $\delta$ −1.15 for *cis*-$FeH(depe)_2Me$, see M. V. Baker, Ph.D. Thesis, University of Sydney, Sydney, 1988.