1:10 mixture of acetonitrile/THF resulted in the clean formation of **4** in 64% isolated yield. Heating **1** to 50 °C under 600 torr of dihydrogen in pentane for 16 h gave dinuclear dihydride **5** in 80% isolated yield.

The isolation of **2a–c** enabled us to explore the possibility of regenerating the C–H activating intermediate (presumably complex X shown in Scheme I) by dissociation of a dative ligand from a dinuclear complex. In hopes of converting **2a** to X, the trimethylphosphine adduct was heated to 100 °C for 11.5 h in benzene. However, conversion back to **1** was not observed. Instead, intramolecular C–H insertion occurred, giving a mixture of two new organometallic complexes in a ratio of 10:1. The major product obtained was isolated in 52% yield, analytically pure after two crystallizations from toluene/hexane.[10] On the basis of spectral and analytical data[5] the new product is formulated as the diiridium complex **3** having a terminal hydride and bridging (CH_2PMe_2) ligand. Complex **3** arises from formal intramolecular oxidative addition of the C–H bond of the bound trimethylphosphine across the Ir–Ir bond; complexes having a μ-CH_2PMe_2 ligand are rare.[11]

Because of the intramolecular reaction observed with **2a**, generation of X from carbonyl complex **2b** was investigated. Heating to 165 °C gave no reaction in C_6D_6, but irradiation of **2b** in benzene-d_6 resulted in the generation of **1**-d_6 in 53–60% yield by ^{1}H NMR (ferrocene internal standard). Surprisingly (especially in view of the behavior of Brown's rhenium system[2a,b]), **2c** exhibits chemistry paralleling that of **2b**, with no addition to the C–H bonds of ethylene observed. Irradiation of **2c** in benzene-d_6 gave **1**-d_6 in 40–53% yields (ferrocene internal standard) along with several unidentified minor compounds.

Preliminary mechanistic information on the elimination of benzene from **1** has been obtained from crossover isotope labeling and kinetic studies. The crossover experiment was carried out by heating a 1:1 mixture of **1** and **1**-d_{10} (phenyl and allyl groups completely deuterated; prepared as described above using C_6D_6 in place of C_6H_6)[12] to 50 °C in pentane with added ethylene for 2.25 h. Only C_6D_6 and C_6H_6 were obtained from the volatile materials as determined by GC/mass spectroscopy, demonstrating that the benzene C–H reductive elimination reaction (and therefore, by the principle of miroscopic reversibility, the corresponding oxidative addition reaction) is cleanly intramolecular. Kinetic studies were carried out by following reactions of **1** in the presence of various ligands by ^{1}H NMR and UV spectroscopy. Clean pseudo-first-order kinetics were observed, providing the following data at 45 °C: $k_{\mathrm{obsd}}(C_6D_6) = 1.50 \times 10^{-4}\ \mathrm{s}^{-1}$; k_{obsd} (PMe_3, n-hexane) $= 2.41 \times 10^{-4}\ \mathrm{s}^{-1}$; no dependence on [$PMe_3$]; $k_{\mathrm{obsd}}(P(OCH_3)_3; C_6D_{12}) = 1.65 \times 10^{-4}\ \mathrm{s}^{-1}$. The isotope data and minimal influence of concentration or identity of entering ligand on k_{obsd} require intramolecular, rate-determining elimination of benzene to form an intermediate (presumably X in Scheme I). This is then followed by attack of ligand in a subsequent step.[13]

Complex **1** can be related conceptually to the analogous mononuclear hydrido phenyl complex, Cp*(PMe_3)Ir(Ph)(H), by replacing the phosphine group with a second iridium moiety and allowing the hydride to bridge both metal centers. Perhaps the most striking feature of the binuclear system is the fact that the temperature for reductive elimination of benzene from **1** is *at least* 150 °C lower than that required for the corresponding reductive elimination from the mononuclear complex, which is stable to nearly 200 °C.[14] We do not yet know whether the primary reaction step involves interaction of the C–H bond with one or two metal centers. Whatever the precise reaction mechanism, however, our results make it clear that a second metal attached to a center capable of C–H activation can have a profound effect on the energetics of the insertion process. On the basis of the results described here it seems reasonable to expect that attachment of other metals will retain this energetic effect but also return the ability of the iridium center to react with alkanes. We hope to be able to test this hypothesis in the near future.

Acknowledgment. This work was carried out under the auspices of a collaborative Lawrence Berkeley Laboratory/Industrial research project supported by the Chevron Research Co., Richmond, CA, and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098. W.D.M. acknowledges the Organic Division of the American Chemical Society for a predoctoral fellowship. We are also grateful for a generous loan of $IrCl_3 \cdot nH_2O$ from Johnson-Matthey, Inc. The crystal structure analysis was performed by Dr. F. J. Hollander, staff crystallographer at UC Berkeley X-ray crystallographic facility (CHEXRAY).

Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **1**-d_{10}, **2a–c**, and **3–5** and details of the structure determination of complex **1**, including experimental description, ORTEP drawings showing full atomic numbering scheme, crystal and data collection parameters, general temperature factor expressions (B's), positional parameters and their estimated standard deviations, and intramolecular distances and angles (23 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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(10) The minor product was also isolated and characterized as Cp*(η^2-$Me_2P{=}CH_2$)Ir(μ-$CH{=}CHMe$)IrCp*. Its formation will be discussed in a full account of this work.

(11) (a) See, for example: Graimann, C. E.; Green, M. L. H. *J. Organomet. Chem.* **1984**, *275*, C12. (b) Klein, H.-F.; Wemninger, J.; Schubert, J. Z. *Naturforsch, B* **1979**, *34B*, 1391. (c) Werner, H.; Zolk, R. *Organometallics* **1985**, *4*, 601. As pointed out by a referee, the formation of **3** suggests that both iridium atoms may be independently capable of C–H oxidative addition.

(12) **1**-d_{10} was characterized by ^{1}H NMR, ^{2}H NMR, and mass spectrometry.

(13) Preliminary isotope effect data suggest that a second intermediate (possibly an η^2-arene complex; cf.: Feher, F. J.; Jones, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1650) may intervene between **1** and X. This possibility will be discussed in a full paper.

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Rapid Measurement of Less Abundant and Low-γ Spin-$^1/_2$ Nuclei: $\delta(^{57}\mathrm{Fe})$, $^1J(^{57}\mathrm{Fe},^1\mathrm{H})$, and $^1J(^{57}\mathrm{Fe},^{31}\mathrm{P})$ from Reverse 2D $^1\mathrm{H}\{^{57}\mathrm{Fe}\}$ Spectroscopy

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Beside ^{187}Os the ^{57}Fe isotope is the most insensitive spin-$^1/_2$ nucleus in NMR spectroscopy,[1] and despite the extensive chemistry involving iron,[2] ^{57}Fe NMR studies of iron complexes are still rare.[1] Among the approaches made to improve the NMR detection of ^{57}Fe NMR parameters are isotopic enrichment of ^{57}Fe,[3] the application of steady-state techniques,[4] and the use of high magnetic

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(1) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981. Benn, R.; Rufińska, A. *Angew. Chem.*, in press, and references cited. While the ^{3}He nucleus is even more insensitive, this isotope has received no attention in chemistry.

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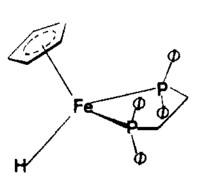

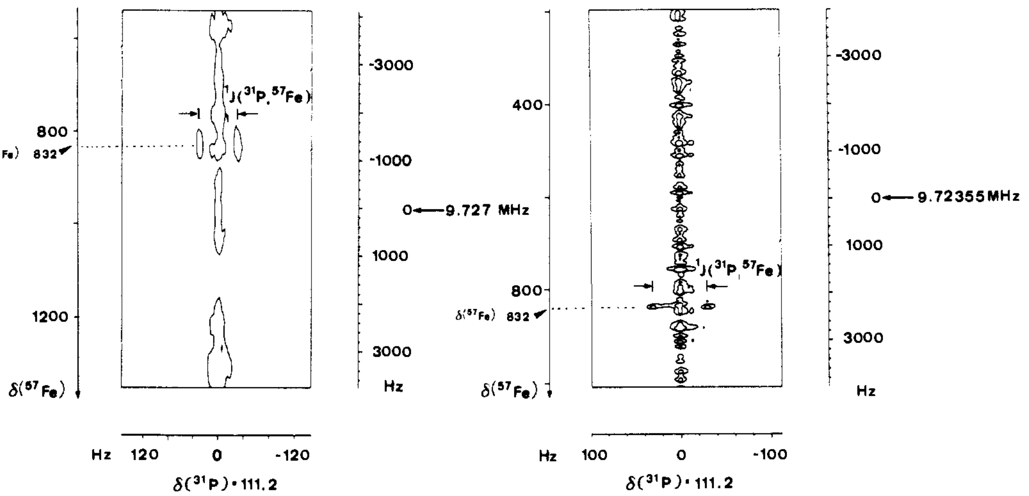

Figure 1. Reverse proton-decoupled 2D $^{31}P\{^{57}Fe\}$ spectra of **1** (10-mm sample, 10% solution in toluene-d_8) at 310 K recorded on a Bruker AM 300 spectrometer with sequence 2a at 121.51 MHz. The ^{57}Fe pulses were generated with a broad-band BSV 3 decoupler and a frequency synthesizer with computer-controlled phase-shift capabilities[6] (90°(^{57}Fe) = 40 μs, 90°(^{31}P) = 35 μs). A 10-mm probehead was used (X observation, ^{2}H lock, ^{1}H and ^{31}P decoupling). In experiments where the Fe carrier frequency was set to 9.727 MHz, 15 time increments were used in each of which 96 transients were added, with a repetition delay of 4 s, yielding a total measuring time of 1.8 h. When the Fe carrier frequency was set to 9.72355 MHz 104 increments and 48 scans were used with a repetition delay of 8s yielding a total measuring time of 11.4 h. In this experiment after zero filling the digital resolution in F_1 dimension was 7.8 Hz/Pt. The exact frequency for $Fe(CO)_5$ was 9.717 748 MHz. The δ(^{57}Fe) values are related to this standard.

fields which not only enhance the Boltzmann factor but may also shorten $T_1(^{57}Fe)$ due to chemical shift anisotropy (CSA).[5] Other investigations have involved polarization transfer techniques like INEPT.[6] In the following we report the first indirect two-dimensional measurements of ^{57}Fe NMR spectra via observation of the ^{1}H or ^{31}P nuclei taking (η^5-cyclopentadienyl)[1,2-ethanediylbis(diphenylphosphane)]hydridoiron (**1**)[7] as example. It is shown that δ(^{57}Fe) and ^1J(Fe,P) can be obtained from one indirect 2D $^1H\{^{57}Fe\}$ spectrum from a dilute 5-mm sample of **1** recorded in 2 h. In addition, the first example of J(Fe,H) was observed.

In order to observe ^{57}Fe NMR spectra indirectly there must be an observable scalar coupling from ^{57}Fe to a magnetically active nucleus X. Until now, only a few spin–spin couplings of ^{57}Fe to X = ^{31}P,[6,8] ^{13}C,[3,4,8] and ^{15}N[9] have been reported; all are smaller than 35 Hz. In **1** ^1J(Fe,P) is 61.6 Hz as was found by observing the ^{57}Fe satellites in the 1D $^{31}P\{^1H\}$ spectrum of **1** using a 1D spin–echo sequence, (1a),[10] or applying a 1D pulse scheme in-

$$90(X)–1/[2J(X,Fe)]–180(X)180(Fe)–1/[2J(X,Fe)]–FID(X) \quad (1a)$$

$$90(X)–1/[2J(X,Fe)]–90(Fe)180(X)90(Fe)–FID(X) \quad (1b)$$

volving multiquantum transitions, (1b).[11] In (η^4-butadiene)$_2$FePMe$_3$ (**2**) and (η^4-butadiene)$_2$FePEt$_3$ (**3**) ^1J(Fe,P) is 61.3 and 62.0 Hz, respectively. This indicates that ^1J(Fe,P) may in general be significantly larger than previously assumed. Apparently there is substantially more σ-character in the Fe,P bond in **1**–**3** than in (CO)$_4$FePEt$_3$.

Although the ^{57}Fe shifts of **1**–**3** could be roughly estimated via sequence 1a or 1b by varying the Fe carrier frequency and monitoring the intensity of the satellites, exact δ(^{57}Fe) values were obtained readily from indirect 2D $X\{^{57}Fe\}$ spectra by using sequence 2a[12] or 2b.[13] The highest efficiency is obtained if X is

$$90(X)–1/[2J(Fe,X)]–90(Fe)–t_1/2–180(X)–t_1/2–90(Fe)–FID(X,t_2) \quad (2a)$$

$$90(X)–1/[4J(Fe,X)]–180(X)180(Fe)–1/[4J(Fe,X)]–90(X)90(Fe)–t_1–90(Fe)90(X)–FID(X,t_2) \quad (2b)$$

a high-γ nucleus with 100% natural abundance like ^{31}P or ^{1}H. In Figure 1 the proton F_1,F_2 decoupled indirect 2D $^{31}P\{^{57}Fe\}$ spectra of **1** are shown. Besides confirmation of the ^1J(Fe,P) coupling, these spectra give δ(^{57}Fe) = +832 for **1**. Although the F_1 spectral width for ^{57}Fe in this experiment was 8000 Hz, a further measurement of similar type was performed, changing the spectral width and the Fe carrier frequency in order to confirm that the cross peaks are not folded.

Theoretically, the sensitivity gain via the indirect measurement compared to direct observation is given by $(\gamma_P/\gamma_{Fe})^3$. Even when compared to the direct observation using polarization transfer techniques the gain is still a factor of $(\gamma_P/\gamma_{Fe})^2$. As with INEPT or DEPT techniques the repetition rate for indirect 2D $^{31}P\{^{57}Fe\}$

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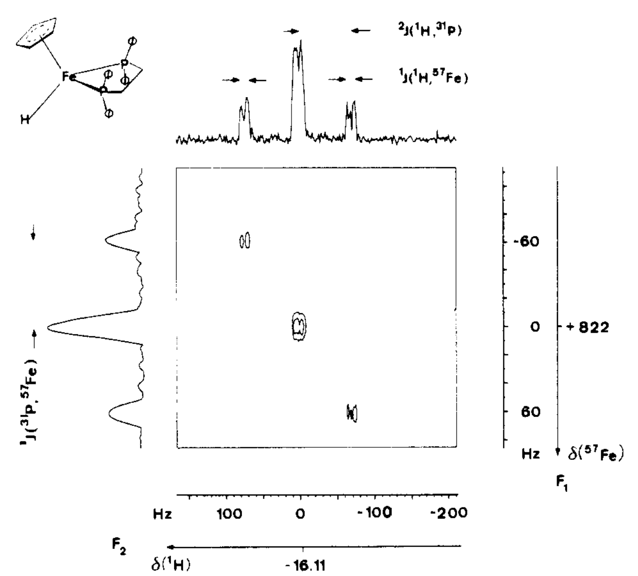

Figure 2. Reverse 2D $^1H\{^{57}Fe\}$ spectrum of **1** (5-mm sample, 8% solution in toluene-d_8) recorded at 295 K at 300.13 MHz using sequence 2a. The Fe carrier frequency was 9.725 735 MHz; $^1/_2{}^1J$(Fe,H) was set to 0.0568 s; the repetition delay was 4 s. 112 transients were collected and 32 (16) experiments for 400 Hz spectral width were carried out. Note that due to the lower temperature $\delta(^{57}Fe)$ is 10 ppm smaller than in the $^{31}P\{^{57}Fe\}$ experiment.

measurements is determined by $T_1(^{31}P)$ rather than by $T_1(^{57}Fe)$, which may be significantly longer.

To the best of our knowledge no J(Fe,H) couplings have previously been reported. The ^1J(Fe,H) coupling of **1** was obtained by using sequence 1b. By irradiation of the exact ^{57}Fe frequency as known from the previously described 2D $^{31}P\{^{57}Fe\}$ experiments, the $(1/2J)$ period was varied until a clear up–down iron satellite response was observed. Subsequently an indirect 2D $^1H\{^{57}Fe\}$ measurement was performed (cf. Figure 2). $\delta(^{57}Fe)$ and ^1J(Fe,P) can be extracted from the projection of the contour plot onto the F_1 dimension. Besides $\delta(^1H)$ and ^2J(P,H) (71.2 Hz) the projection onto the F_2 dimension also contains ^1J(Fe,H) (9.3 Hz). In addition, the positions of the cross peaks indicate that ^1J(P,Fe) is of opposite sign relative to ^2J(P,H) since the lowest frequency proton peak is correlated with the highest frequency iron line (The phosphorus spins were not excited in this experiment).[14] All this information characterizing the environment of the iron nucleus of **1** could be obtained in one experiment of only 2-h duration using an 8% (w/w) solution of **1** in a 5-mm NMR tube inserted into a 10-mm probe, which is not the best choice for optimum sensitivity. This indirect 2D NMR technique should be suitable for many iron complexes because phosphorus compounds are frequently used ligands in iron chemistry and J(Fe,P) may become large. However, this procedure can also be applied even when small J(Fe,H)[15] couplings are present, enabling the ^{57}Fe NMR parameters to be detected with the sensitivity of the protons. We therefore conclude that the indirect observation of insensitive spin-$^1/_2$ nuclei is the most efficient technique and opens new horizons for the NMR investigation of low-γ nuclei, which exhibit a scalar coupling to a sensitive nucleus.

Supplementary Material Available: ^{1}H and ^{31}P NMR spectra showing $^2J(^1H,^{31}P)$, $^1J(^1H,^{57}Fe)$, and $^1J(^{31}P,^{57}Fe)$ (2 pages). Ordering information is given on any current masthead page.

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(14) We are highly indebeted to a referee for drawing our attention to that point.

(15) In olefin–tungsten and –rhodium compounds ^2J(W,H) and ^2J(Rh,H) lie between 1 and 9 Hz. Corresponding indirect 2D $^1H\{^{183}W\}$ and $^1H\{^{103}Rh\}$ experiments for the rapid detection of ^{183}W and ^{103}Rh NMR parameters were found to be straightforward and posed no problems. It is likely that small ^2J(Fe,H) couplings are present in iron olefin complexes so that we feel optimistic that the 2D $^1H\{^{57}Fe\}$ technique can be applied to the large class of olefin iron compounds.

Variable-Temperature ^{13}C and ^{29}Si CPMAS NMR Studies of Poly(di-*n*-hexylsilane)

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Soluble high molecular weight substituted silane polymers are a new class of radiation-sensitive materials[1] which have demonstrated ceramic and lithographic applications.[2-4] Much of the recent scientific interest in these materials has centered around their unusual electronic spectra.[5,6] In this regard, substituted silane polymers all show an intense and molecular weight dependent absorption in the UV.[6] Recently, it has been shown that certain polysilanes are also thermochromic both in the solid state[7] and solution[8,9] state, a property which has tentatively been attributed to the formation of a trans backbone conformation at low temperatures. The present study was undertaken to investigate the dynamic characteristics of poly(di-*n*-hexylsilane) in the solid state by variable-temperature ^{13}C and ^{29}Si CPMAS NMR.[10-12]

Figure 1 shows the ^{29}Si and ^{13}C CPMAS NMR spectra of poly(di-*n*-hexylsilane). The ^{13}C peak assignments were based on comparisons to previously published spectra.[13,14] In addition, some assignments were confirmed by the synthesis of poly(di-*n*-hexylsilane-*1*-^{13}C) as part of a related study.[15] At 240 K, the ^{29}Si spectrum consists of a single peak. Between 304 and 310 K there is a sharp transition above which only a single high field peak is observed. It is assumed that at low temperatures the silicon backone exists predominantly in the all trans form.[7,16,17] Above the transition temperature of ca. 307 K the probability of gauche conformations is significant. Conformational mobility of the backbone results in a time-averaged resonance. This is consistent with recent empirical force field (EFF) calculations which suggest that the gauche conformer is less stable.[18] Figure 2 shows the all-trans content of the polymer as a function of temperature. This behavior mirrors thermal analysis data[7] and other temperature-dependent spectroscopic data.[17] The sharp transition at 305–310 K for the final 75% of the sample is particularly striking. The gradual decrease of about 25% of the all-trans fraction from 250 to 305 K is probably due to some local disorder, the molecular

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