

## <sup>57</sup>Fe NMR Study of Ligand Effects in Cyclopentadienyliron Complexes†

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Received December 28, 1995<sup>§</sup>

The first systematic <sup>57</sup>Fe NMR study of ligand effects in cyclopentadienyliron complexes is presented. Four series encompassing a total of 35 compounds have been studied. Among the compounds are five new ring-substituted complexes with the formula (C<sub>5</sub>H<sub>4</sub>Y)Fe(CO)-(PPh<sub>3</sub>)(Me), Y = Me, SiMe<sub>3</sub>, NEt<sub>2</sub>, I, and Ph. The crystal structure of (C<sub>5</sub>H<sub>4</sub>I)Fe(CO)(PPh<sub>3</sub>)(Me) (**32**) was determined. For the series CpFe(CO)<sub>2</sub>R (type **I**), <sup>57</sup>Fe shielding was found to decrease with the bulkiness of the alkyl ligand R and to correlate with the CO-insertion rate of the complex. In type **III** complexes CpFe(CO)(L)(COMe), L = PR<sub>3</sub>, and CO, it is again the steric requirement of the ligand L that dominates the <sup>57</sup>Fe chemical shift which increases with larger cone angles (θ). In contrast, a strong electronic effect was found for type **II** complexes CpFe(CO)(PPh<sub>3</sub>)X, X = H, Me, and I. Ligands with higher electronegativity induce a shift of the <sup>57</sup>Fe resonance to higher frequencies. In the complexes (C<sub>5</sub>H<sub>4</sub>Y)Fe(CO)(PPh<sub>3</sub>)(Me), Y = Me, H, SiMe<sub>3</sub>, NEt<sub>2</sub>, I, Ph, COOMe, and CO<sup>i</sup>Pr (type **IV**), again electronic effects are dominant, whereby electron acceptor substituents (e.g. Y = CO<sup>i</sup>Pr, COOMe) cause a deshielding of the iron nucleus, relative to complexes with electron donor substituents (e.g. Y = Me, H, SiMe<sub>3</sub>). Dominant electronic ligand effects in type **IV** complexes are also apparent from the correlation of δ(<sup>57</sup>Fe) with the electronic substituent parameter σ<sub>1</sub>. The <sup>57</sup>Fe chemical shift is shown to be very sensitive to changes in the ligand sphere, and the effects are discussed in terms of the paramagnetic shielding constant (σ<sub>para</sub>). The <sup>1</sup>J(<sup>57</sup>Fe, <sup>13</sup>C) coupling constants and longitudinal relaxation times T<sub>1</sub> of <sup>57</sup>Fe in selected complexes have been determined and ligand effects are discussed.

### Introduction

The performance of catalysts, e.g. of a homogeneous Ziegler–Natta type, depends critically on the nature of the metal-coordinated ligands. The catalytic activity has been shown to vary with the metal–alkyl bond stability, the metal–olefin coordination, and steric effects.<sup>2</sup> However, a more than qualitative characterization of ligand effects is often difficult. Ligand effects on structure and reactivity can be probed by transition metal NMR spectroscopy, as we have reported for a variety of cases: <sup>59</sup>Co,<sup>3,4</sup> <sup>103</sup>Rh,<sup>5–9</sup> <sup>55</sup>Mn,<sup>10,11</sup> and <sup>57</sup>Fe.<sup>12–14</sup>

Cyclopentadienyl complexes of group VIII transition metals are vital in several important stoichiometric and catalytic reactions,<sup>15</sup> and annually many synthetic applications are published.<sup>16,17</sup> Cyclopentadienyliron complexes in particular have attracted considerable interest as stoichiometric reagents in stereoselective reactions.<sup>18</sup> To date, no systematic <sup>57</sup>Fe NMR study of ligand effects in such complexes has been reported, but preliminary results have shown that <sup>57</sup>Fe shielding is a sensitive parameter reflecting both electronic and steric ligand effects.<sup>19</sup>

While metal NMR investigations are becoming more and more common,<sup>20,21</sup> the number of <sup>57</sup>Fe NMR studies is still limited<sup>22,23</sup> because the <sup>57</sup>Fe nucleus is one of the most insensitive nuclei in NMR spectroscopy owing to its small magnetic moment and low natural abundance (2.2%).<sup>24</sup> Therefore, direct detection of <sup>57</sup>Fe NMR

† Transition Metal NMR Spectroscopy. 31. Part 30: See ref 1.

§ Abstract published in *Advance ACS Abstracts*, April 15, 1996.

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Scheme 1

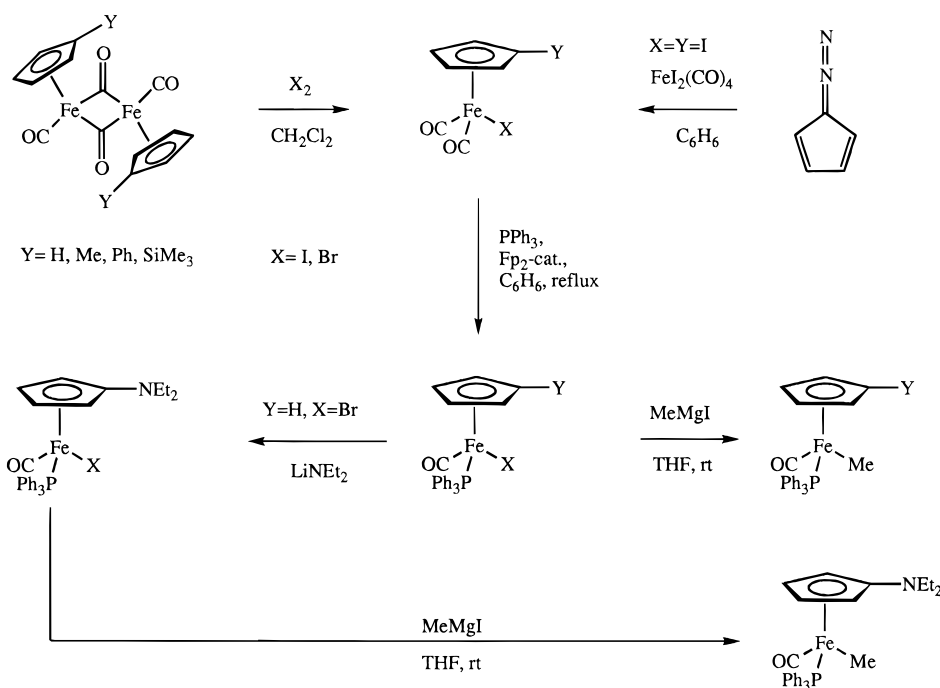
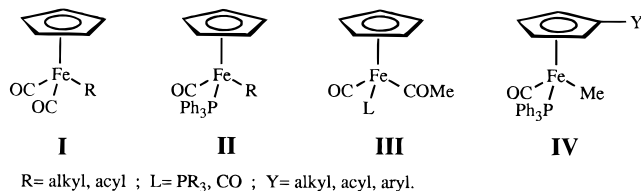


Chart 1



signals requires high sample concentrations,<sup>12</sup> high magnetic fields,<sup>13</sup> and long measurement times.<sup>20,22,25</sup> Koridze and co-workers overcame the sensitivity problem by synthesizing <sup>57</sup>Fe-enriched (80–90%) complexes.<sup>26</sup> More recently, the powerful method of indirect 2D HMQC (<sup>31</sup>P, <sup>57</sup>Fe){<sup>1</sup>H} NMR spectroscopy was introduced by Benn and Brevard,<sup>20,23,27–29</sup> which allows the determination of <sup>57</sup>Fe chemical shifts and <sup>1</sup>J(<sup>57</sup>Fe, <sup>31</sup>P) coupling constants with dilute 5-mm samples in recording times that permit systematic studies.

In the present work, we report results obtained on four closely related series of cyclopentadienyliron complexes of the type (C<sub>5</sub>H<sub>4</sub>Y)Fe(CO)LR.

## Results and Discussion

**Syntheses.** The cyclopentadienyliron complexes of four series with the general formula (C<sub>5</sub>H<sub>4</sub>Y)Fe(CO)LR were prepared for a systematic study of ligand effects (Chart 1). While the well-known complexes of type I,<sup>30,31</sup> type II,<sup>32</sup> and type III<sup>33</sup> were obtained according

to the literature, in group IV five new complexes (**29–33**) were synthesized and completely characterized for the first time. The selected synthetic path for these complexes is shown in Scheme 1. As starting materials, [(C<sub>5</sub>H<sub>4</sub>Y)Fe(CO)<sub>2</sub>]<sub>2</sub>, Y = H, Me, Ph, and SiMe<sub>3</sub>,<sup>34,35</sup> and diazocyclopentadiene<sup>36</sup> were used to form [(C<sub>5</sub>H<sub>4</sub>Y)Fe(CO)<sub>2</sub>X], X = hal.<sup>37,38</sup> Further reaction with PPh<sub>3</sub> in benzene, catalyzed by [CpFe(CO)<sub>2</sub>]<sub>2</sub><sup>39</sup> and followed by addition of MeMgI in THF, gave the desired type IV complexes **29**, **30**, **32**, and **33**. [(C<sub>5</sub>H<sub>4</sub>NEt<sub>2</sub>)Fe(CO)-(PPh<sub>3</sub>)Me] (**31**) was synthesized from CpFe(CO)(PPh<sub>3</sub>)Br<sup>35,39</sup> by ring substitution with LiNEt<sub>2</sub>, again followed by methylation with MeMgI. Two other complexes that have been synthesized (**34**, **35**) were previously reported by Abbott et al.,<sup>40</sup> but the authors gave no details about the syntheses and spectroscopic properties. We isolated them after deprotonation of the cyclopentadienyl ligand of CpFe(CO)(PPh<sub>3</sub>)(COR), R = <sup>i</sup>Pr, and OMe, with *n*-BuLi, followed by migration of the acyl ligand. Subsequent methylation of the anion with methyl iodide yielded the two corresponding substituted cyclopentadienyl complexes (**34**, **35**).

**<sup>57</sup>Fe NMR Spectroscopy of Complexes of Types I–IV.** The spectra of type I complexes were recorded

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**Table 1.**  $^{57}\text{Fe}$  NMR Data for Cyclopentadienyliron Complexes

no.	R, L, or Y	$\delta(^{57}\text{Fe})/\text{ppm}$	$^1J(^{57}\text{Fe}, ^{31}\text{P})/\text{Hz}$	$T_1/s$ (% CSA)	
				9.4 T	14.1 T
CpFe(CO) <sub>2</sub> R, Type I					
1	Me	684			
2	Et	696			
3	<sup>n</sup> Bu	716			
4	<sup>t</sup> Bu	727			
5	<sup>neo</sup> Pe	784			
6	<sup>i</sup> Pr	796			
7	<sup>s</sup> Bu	805			
8	COMe	959			
CpFe(CO)(PPh <sub>3</sub> )R, Type II					
9	H	536	54.4		
10	<sup>t</sup> Bu	1385	58.7		
11	<sup>n</sup> Bu	1386	58.8		
12	Me	1392	57.0		
13	<sup>t</sup> Bu	1425	58.1		
14	<sup>i</sup> Pr	1480	60.6		
15	<sup>neo</sup> Pe	1500	57.9		
16	I	2607	55.1		
17	CO <sup>n</sup> Bu	1525	59.3	4.5 (77)	2.3 (88)
18	CO <sup>t</sup> Bu	1531	59.5	4.0 (96)	1.8 (98)
19	COMe	1531	59.2	4.3 (91)	2.0 (96)
20	CO <sup>i</sup> Pr	1536	58.4		
21A	CO <sup>s</sup> Bu (A)	1543	58.9	4.5 (95)	2.1 (98)
21B	CO <sup>s</sup> Bu (B)	1545	58.5	4.0 (88)	1.9 (94)
22	CO <sup>neo</sup> Pe	1550	60.1	5.0 (100)	2.1 (100)
CpFe(CO)(L)COMe, Type III					
23	P(OMe) <sub>3</sub>	1159	93.9	12.2 (32)	8.8 (51)
24	P(O <sup>i</sup> Pr) <sub>3</sub>	1268	93.0		
25	PMe <sub>3</sub>	1374	58.3	13.7 (18)	11.2 (33)
26	PMe <sub>2</sub> Ph	1414	57.7		
27	PMePh <sub>2</sub>	1424	57.5		
19	PPh <sub>3</sub>	1531	59.2		
28	P <sup>i</sup> Pr <sub>3</sub>	1683	58.1		
(C <sub>5</sub> H <sub>4</sub> Y)Fe(CO)(PPh <sub>3</sub> )Me, Type IV					
29	Me	1367	56.4	3.8 (96)	1.8 (98)
30	SiMe <sub>3</sub>	1421	54.7		
31	NEt <sub>2</sub>	1437	56.6	4.0 (88)	1.9 (94)
32	I	1439	56.5	3.4 (79)	1.7 (90)
33	Ph	1500	55.8		
34	COOMe	1576	56.6		
35	CO <sup>i</sup> Pr	1580	55.9	3.7 (96)	1.7 (98)

by direct  $^{57}\text{Fe}$  observation at 19.4 MHz ( $B_0 = 14.1$  T). The  $^{57}\text{Fe}$  chemical shifts and the coupling constants  $^1J(^{57}\text{Fe}, ^{31}\text{P})$  of type II–IV complexes were measured at 12.9 MHz ( $B_0 = 9.4$  T) by inverse 2D ( $^{31}\text{P}, ^{57}\text{Fe}$ ){ $^1\text{H}$ } experiments.<sup>28</sup> This recording technique has the advantage that sample concentrations are more than ten times lower and recording times are at least three times shorter than for direct observation; however, coupling to an abundant spin- $1/2$  nucleus, such as  $^{31}\text{P}$  or  $^1\text{H}$ , is required. The  $^{57}\text{Fe}$  chemical shifts and  $^1J(^{57}\text{Fe}, ^{31}\text{P})$  coupling constants of all complexes studied in this work are summarized in Table 1.

The shielding constant  $\sigma$  which is responsible for the chemical shift  $\delta$  can be separated into diamagnetic ( $\sigma_{\text{dia}}$ ) and paramagnetic ( $\sigma_{\text{para}}$ ) components according to the formalism presented by Ramsey.<sup>41</sup> It has been shown that variations of  $\sigma_{\text{dia}}$  for light and heavy nuclei in a range of molecular environments are less than 5%.<sup>42</sup> The observed chemical shift range for heavy atoms is dominated by variations of  $\sigma_{\text{para}}$ .<sup>43</sup> For this reason, changes in  $\sigma_{\text{dia}}$  usually are neglected, and with the

assumption of Pople<sup>44</sup> and the average excitation energy (AEE) approximation<sup>45</sup> changes of  $\sigma$  can be roughly estimated with the following equation:

$$\sigma_{\text{para}} \approx - \frac{\langle r^{-3} \rangle}{\Delta E} \sum Q_{\text{AB}} \quad (1)$$

In eq 1  $r$  denotes the distance of the valence d electrons from the  $^{57}\text{Fe}$  nucleus,  $\Delta E$  is the average electronic excitation energy, and  $Q_{\text{AB}}$  is the bond order and charge density term. An increase in the  $^{57}\text{Fe}$  chemical shift can then be rationalized as being due to either a decrease in the d-orbital expansion (nephelauxetic effect) or in  $\Delta E$  that is often approximated by the HOMO–LUMO gap. Chemical shift trends of the measured complexes will be discussed on the basis of these considerations.

**Variation of Alkyl Ligands R in Type I Complexes CpFe(CO)<sub>2</sub>R.** Electronic ligand effects in CpFe(CO)<sub>2</sub>X (X = alkyl, aryl, hal, CN) complexes have been reported as early as 1967.<sup>46</sup> Linear relationships between the IR absorption frequency  $\nu(\text{CO})$  and the half-wave reduction potentials  $E_{1/2}$  as well as the Hammett substituent constant  $\sigma_1$  were found. An increase in the electron-acceptor capability of X leads to increased IR frequencies and decreased values for  $E_{1/2}$ . In 1968 King<sup>47</sup> reported a correlation between  $^1\text{H}$  chemical shifts (cyclopentadienyl signal) and IR stretching frequencies  $\nu(\text{CO})$  for the same complexes. Gansow et al.<sup>48</sup> confirmed these results and found further linear relationships between the  $^{13}\text{C}$  NMR shifts of the carbonyl and the IR stretching frequencies  $\nu(\text{CO})$  as well as the Taft parameter  $\sigma_1$ . All of these previous correlation studies were attributed to changes of the electronic nature of X. From earlier  $^{57}\text{Fe}$  NMR studies<sup>12,23</sup> it was known that the iron shift is extremely sensitive to electronic ligand effects, but also steric effects were clearly recognizable in substituted (diene)Fe(CO)<sub>3</sub> complexes.<sup>13</sup> In addition, it was shown by  $^{59}\text{Co}$  NMR of alkylcobaloximes<sup>4</sup> that steric ligand effects can be recorded directly at the Co center. We, therefore, expected that small changes in the ligand sphere, such as steric ligand effects, might also be discernible in the spectra of type I complexes.

A comparison of the  $^{57}\text{Fe}$  chemical shifts within the complex series I reveals a dependence on the steric effect of the alkyl ligands R in CpFe(CO)<sub>2</sub>R: complexes (1–7) with sterically more demanding ligands resonate at higher frequencies as shown in Figure 1. Lengthening and branching of the alkyl chain results in increased  $\delta(^{57}\text{Fe})$  values. The covered range of about 120 ppm confirms the high sensitivity of  $\delta(^{57}\text{Fe})$  to this steric alkyl group effect. The correlation of  $\delta(^{57}\text{Fe})$  with different steric ligand parameters ( $V$ ,<sup>49</sup>  $\zeta_{\text{f}}$ ,<sup>50</sup>  $\Omega_{\text{s}}$ ,<sup>51</sup>  $v$ ,<sup>52</sup>

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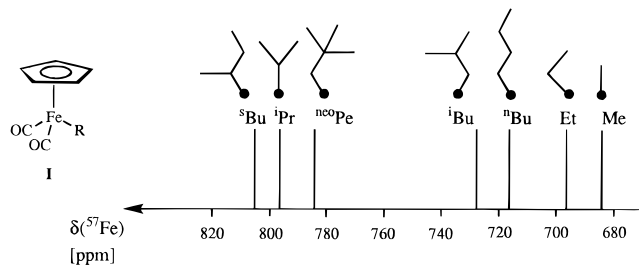
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**Figure 1.** Graphical representation of  $^{57}\text{Fe}$  chemical shifts in complexes of type I.

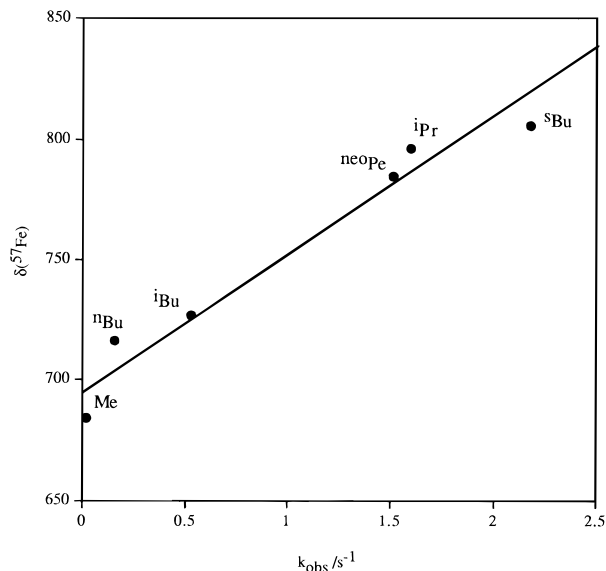
**Table 2.** Reaction Rates  $k_{\text{obs}}$  for the CO Insertion Reaction of Type I Complexes with  $\text{PPh}_3$  and  $^{57}\text{Fe}$  Chemical Shifts

R in $\text{CpFe}(\text{CO})_2\text{R}$	$k_{\text{obs}}/\text{s}^{-1}$	$\delta(^{57}\text{Fe})/\text{ppm}$
Me	$2.1 \times 10^{-2}$	684
$^n\text{Bu}$	$1.6 \times 10^{-1}$	716
$^i\text{Bu}$	$5.3 \times 10^{-1}$	727
neoPe	1.5	784
$^i\text{Pr}$	1.6	796
$^s\text{Bu}$	2.2	805

$E_s$ ,<sup>53</sup> and  $E_s'$ <sup>54</sup>) gave plots similar to those found in alkylcobaloximes<sup>4</sup> and alkylrhodoximes.<sup>8</sup> Thus,  $\delta(^{57}\text{Fe})$  responds very sensitively to steric changes in  $\text{CpFe}(\text{CO})_2\text{R}$  complexes (1–7) in contrast to  $\delta(\text{H})$ ,  $\delta(^{13}\text{C})$ , or  $\nu(\text{CO})$  which vary only within a small range and give no evidence for such an effect.

To check whether the above steric effect reflects the strength of the Fe–C  $\sigma$ -bond, the complexes of type I were reacted with triphenylphosphine in refluxing THF to obtain the corresponding  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COR}$  complex (type II, 17–22). The CO insertion reaction into the Fe–C bond was followed by the decrease of the highest IR CO band at about  $2000\text{ cm}^{-1}$ . The reaction conditions were rendered pseudo-first-order by adding triphenylphosphine in at least 10-fold excess. Our results, which are in agreement with earlier CO insertion studies,<sup>55</sup> are summarized in Table 2.

Indeed,  $\delta(^{57}\text{Fe})$  was found to correlate linearly with  $k_{\text{obs}}$  of the CO insertion reaction, as shown in Figure 2. High  $^{57}\text{Fe}$  shielding (i.e. a low-frequency resonance) corresponds to a slow CO insertion reaction and therefore a strong Fe–C bond (large  $\Delta H^\ddagger$ ).<sup>56</sup> Thus, the  $^{57}\text{Fe}$  chemical shift seems to offer a direct indication of the reactivity of the Fe–C  $\sigma$ -bond in these complexes. The changes of  $\delta(^{57}\text{Fe})$  can be explained by the  $\langle r^{-3} \rangle$  term in eq 1: a complex with bulky R ligands which undergoes a fast CO insertion reaction will have a weaker and, therefore, longer Fe–C bond resulting in a larger  $\langle r^{-3} \rangle$  term (nephelauxetic effect). However, if the weaker Fe–C bond is associated with a smaller HOMO/LUMO gap, the  $\Delta E$  term may also be responsible for the deshielding effect. Therefore,  $\delta(^{57}\text{Fe})$  increases, as observed in the experiment (Figure 2). To support the explanation of weaker and longer Fe–C bonds for sterically more demanding R ligands and because no X-ray crystallographic data for type I complexes are



**Figure 2.** Correlation between the CO insertion rate,  $k_{\text{obs}}$ , for the reaction  $\text{CpFe}(\text{CO})_2\text{R} + \text{PPh}_3 \rightarrow \text{CpFe}(\text{CO})(\text{PPh}_3)\text{COR}$  and  $\delta(^{57}\text{Fe})$  of type I complexes ( $r = 0.976$ ).

available, ab-initio calculations of the geometry<sup>57</sup> were carried out for  $\text{CpFe}(\text{CO})_2\text{R}$ , R = Me (1),  $^n\text{Bu}$  (3), and  $^i\text{Pr}$  (6). They confirmed our expectations and showed that the metal–alkyl  $\sigma$ -bond distance increases with the steric demand of R: Fe–Me =  $2.062\text{ \AA}$ ; Fe– $^n\text{Bu}$  =  $2.081\text{ \AA}$ ; Fe– $^i\text{Pr}$  =  $2.116\text{ \AA}$ .

**Variation of Ligands L in Type III Complexes  $\text{CpFe}(\text{CO})(\text{L})(\text{COMe})$ .** For the displacement of the solvent from  $[\text{CpFe}(\text{CO})(\text{COMe})(\text{solvent})]^+$  radicals by organic nitriles it has previously been reported<sup>58</sup> that the rate of reaction decreases as the size of the nitrile increases. A linear correlation was found between  $\log k$  and Tolman's cone angle  $\theta$  of the nitrile. In the electrochemically promoted carbonyl insertion reaction of  $\text{CpFe}(\text{CO})(\text{PR}_3)\text{Me}$ ,<sup>59,60</sup> different stereoelectronic effects of the  $\text{PR}_3$  ligand on the rates were reported for each reaction step. In the current study, a steric effect, which depends on the size of the ligand L, was found for the neutral type III complexes. Tolman's cone angle of the phosphorus ligand<sup>61</sup> correlates linearly with  $\delta(^{57}\text{Fe})$ , as shown in Figure 3. The shifts cover a range of 500 ppm. The fact that the point L = CO (8) fits the correlation very well, even though the electronic behavior of CO is different from that of  $\text{PR}_3$ , strongly supports the predominant steric influence on  $\delta(^{57}\text{Fe})$  in this series.

**Variation of Ligands R in Type II Complexes  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$ .** A strong electronic effect was found in  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$  complexes for the series R = H (9), Me (1), and I (16). The chemical shift  $\delta(^{57}\text{Fe})$  varies over more than 2000 ppm—the more electronegative ligands R causing decreased shielding. A similar effect has been reported by Benn<sup>28</sup> for  $\text{CpFe}(\text{PMe}_3)_2\text{R}$

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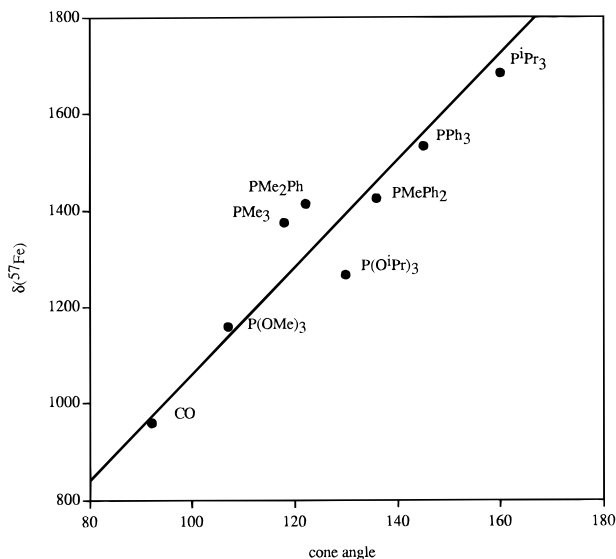
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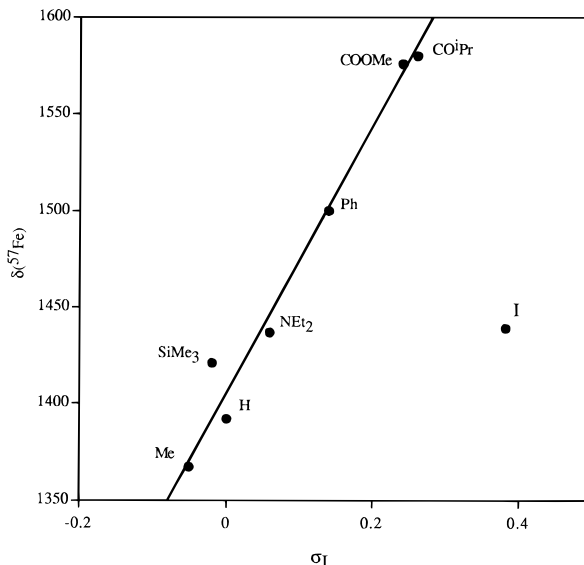


**Figure 3.** Correlation of  $\delta(^{57}\text{Fe})$  with Tolman's cone angle  $\theta^{61}$  of ligand L in type **III**  $\text{CpFe}(\text{CO})(\text{L})\text{COMe}$  complexes ( $r = 0.941$ ).

complexes and  $\delta(^{57}\text{Fe})$  was rationalized by the  $\langle r^{-3} \rangle$  dependence (eq 1).

The substitution of one CO by  $\text{PPh}_3$  to yield  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$  complexes ( $\text{R} = \text{alkyl}$ ), results in  $\delta(^{57}\text{Fe})$  values that are about 700 ppm higher than in series **I**. These findings were already made in type **III** complexes and explained by the steric requirement of the  $\text{PPh}_3$  ligand. Within series **II** ( $\text{R} = \text{alkyl}$ ; **10–15**),  $\delta(^{57}\text{Fe})$  again covers a range of about 120 ppm, but the sequence of the ligands R has changed when compared with type **I** complexes (**1–7**). The  $\delta(^{57}\text{Fe})$  values of the complexes with  $\text{R} = \text{acyl}$  (**17–22**) all lie within 25 ppm, probably because the ligands differ only at the  $\beta$ -position relative to the iron center. In all complexes of type **II** the coupling constants  $^1J(^{57}\text{Fe}, ^{31}\text{P})$  were found to be similar (54–61 Hz; Table 1) which indicates little variation in the Fe–P bond. Indeed, a search on the crystallographic data in the Cambridge Structural Database<sup>62</sup> showed that the Fe– $\text{PPh}_3$  bond in 21 different complexes with the general structure  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$  (type **II**,  $\text{R} = \text{alkyl, acyl}$ ) varies by only 0.01 Å.

Davies and Seeman<sup>63</sup> described the stereochemical situation in complexes of type **II** as pseudo-octahedral. Therefore, the bond angles  $\text{R–Fe–PPh}_3$  and  $\text{CO–Fe–PPh}_3$  lie around  $90^\circ$ . One phenyl ring of the  $\text{PPh}_3$  ligand forms a plane approximately parallel to the  $\text{R–Fe–CO}$  plane. The distance between these two planes is ca. 3–4 Å.<sup>63</sup> Large R ligands would lead to steric interactions between the R and  $\text{PPh}_3$  groups. Therefore, the observed ligand effects in type **II** ( $\text{R} = \text{alkyl, acyl}$ ) complexes seem to be mainly of steric origin. Furthermore, it could be shown by  $^1\text{H}$  nuclear Overhauser experiments for type **II** complexes with large acyl groups (e.g.  $\text{R} = \text{CO}^{\text{neo}}\text{Pe}$ ) that beside the  $\text{R}/\text{PPh}_3$  interaction (NOE: 5.6%) an interaction between the R and Cp groups also exists (NOE: 8.5%). This observation is an additional indication for the presence of steric interligand effects for type **II** complexes and could explain the



**Figure 4.** Correlation of  $\delta(^{57}\text{Fe})$  with the Taft parameter  $\sigma_I^{67}$  of the substituent Y in type **IV**  $(\text{C}_5\text{H}_4\text{Y})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$  complexes.  $r = 0.987$  without the data point for  $\text{Y} = \text{I}$ .

changed sequence of  $\delta(^{57}\text{Fe})$  values for type **II** versus type **I** complexes.

**Variation of Substituents Y in Type IV Complexes  $(\text{C}_5\text{H}_4\text{Y})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ .** The rationalization of the effects induced by the Cp ring in substituted cyclopentadienyl complexes is of considerable interest. The catalytic activity of homogeneous Ziegler–Natta catalysts is strongly influenced by cyclopentadienyl substituents.<sup>64</sup> For complexes of the type  $(\text{C}_5\text{H}_4\text{Y})\text{Fe}(\text{CO})(\text{L})\text{I}$ ,<sup>65</sup> infrared spectroscopy<sup>66</sup> and  $^1\text{H}$  NMR spectroscopy<sup>34,35</sup> document electronic and steric effects of Y. In our series of type **IV** complexes, the influence of Y on  $\delta(^{57}\text{Fe})$  was found to depend mainly on the electronic properties of Y, which are displayed via the Cp–Fe  $\pi$ -bond (Figure 4). Electron acceptor substituents,  $\text{Y} = \text{CO}^i\text{Pr}$  and  $\text{COOMe}$ , at the Cp ring induce larger  $^{57}\text{Fe}$  chemical shifts compared with the electron donor substituents,  $\text{Y} = \text{Me, H, and SiMe}_3$ , as expected. The iron shift covers a range of 200 ppm. Figure 4 shows the correlation of  $\delta(^{57}\text{Fe})$  with the electronic substituent parameter  $\sigma_I$  (Taft)<sup>67</sup> for type **IV** complexes. Correlations of  $\delta(^{57}\text{Fe})$  with other electronic substituent parameters were also linear but of lower significance. The data point for  $\text{Y} = \text{I}$  lies outside the linear correlation curve ( $r = 0.987$ ), probably owing to steric interactions between I and the bulky  $\text{PPh}_3$  ligand. To provide more information on that question, the crystal structure of  $(\text{C}_5\text{H}_4\text{I})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$  (**32**) was determined. Indeed, it shows (Figure 5) that the I atom adopts the *anti* conformation with respect to the P atom (torsion angle  $\text{I–C}(1)\text{–Fe–P}$ :  $-163.3(2)^\circ$ ). Similar *anti* conformations were also found in  $(\text{C}_5\text{H}_4\text{I})\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$  and in  $(\text{C}_5\text{H}_4\text{–CHPh}_2)\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$  (torsion angle  $\text{Y–C}(1)\text{–Fe–P}$ :  $-166.7$  and  $165.5^\circ$ , respectively). The  $\text{Y–C}(1)\text{–Fe–P}$  torsion angle is found to be smaller for the complex  $(\text{C}_5\text{H}_4^t\text{Bu})\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$  ( $120.9^\circ$ ).<sup>68</sup>

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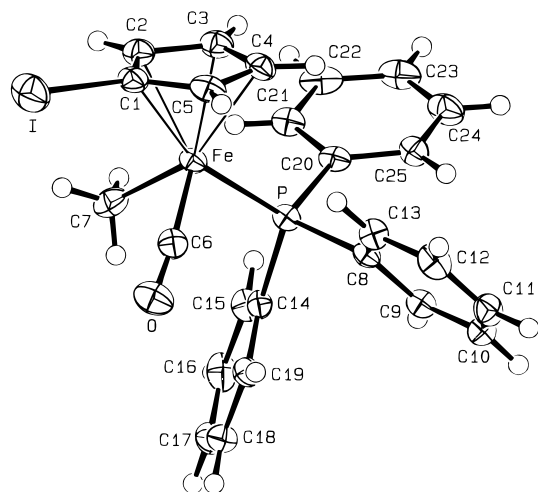
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**Figure 5.** Thermal ellipsoid plot of the structure of **32**.

**Table 3. One-Bond  $^{57}\text{Fe}$ ,  $^{13}\text{C}$  Coupling Constants of Type IV Complexes**

no.	compd	$^1J(^{57}\text{Fe}, ^{13}\text{C})/\text{Hz}$
<b>12</b>	$(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$	10.9
<b>29</b>	$(\text{C}_5\text{H}_4\text{Me})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$	11.0
<b>30</b>	$(\text{C}_5\text{H}_4\text{SiMe}_2)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$	11.2
<b>31</b>	$(\text{C}_5\text{H}_4\text{NEt}_2)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$	11.3
<b>32</b>	$(\text{C}_5\text{H}_4\text{I})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$	11.5
<b>34</b>	$(\text{C}_5\text{H}_4\text{COOMe})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$	10.3
<b>35</b>	$(\text{C}_5\text{H}_4\text{CO}^i\text{Pr})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$	12.0

The electronic substituent effects of Y on the other ligands at the iron center were also observed in type IV complexes:  $\nu(\text{CO})$  as well as  $\delta(^{31}\text{P})$  correlate well with the Hammett parameter  $\sigma_p$ .<sup>67</sup>

To observe the possible effects of the Y substituent on the Fe–C  $\sigma$ -bond, the coupling constants  $^1J(^{57}\text{Fe}, ^{13}\text{C})$  of type IV complexes were measured by the recently published method employing ( $^1\text{H}$ ,  $^{57}\text{Fe}$ ) inverse correlation with a binomial suppression of signals of the ( $^{57}\text{Fe}$ ,  $^{12}\text{C}$ ) isotopomer.<sup>69</sup> These results are shown in Table 3. In contrast to the large chemical shift variation, the  $^1J(^{57}\text{Fe}, ^{13}\text{C})$  coupling constants are rather insensitive to changes of Y, and their values lie in the range of  $11 \pm 1$  Hz. Therefore, it can be assumed that the Fe–C  $\sigma$ -bond in type IV complexes is not strongly affected by the Y substituent. For type I complexes  $^1J(^{57}\text{Fe}, ^{13}\text{C})$  coupling constants are significantly smaller ( $9 \pm 1$  Hz), which could be due to the missing phosphorus donor.<sup>70</sup> The reported coupling constants are about three times smaller than  $^1J(^{57}\text{Fe}, ^{13}\text{CO})$ .<sup>12</sup>

**Longitudinal Relaxation Times  $T_1$ .** Measurements of  $T_1$  relaxation times of  $^{57}\text{Fe}$  are difficult by direct detection, owing to the low receptivity of the nucleus. Only a limited amount of such data is available.<sup>71</sup> Using the double polarization transfer method with  $^{31}\text{P}$  detection<sup>72</sup> we have determined  $T_1$  values in the present series. These values are given in Table 1. Measurements in two different magnetic fields (9.4 and 14.1 T) enabled the determination of the contribution

of the field-dependent chemical shift anisotropy mechanism (CSA). In the case of cyclopentadienyliron complexes with the  $\text{PPh}_3$  ligand (types II and IV) CSA is the dominant relaxation mechanism. The relaxation times of these complexes lie in the ranges 3.4–5 s and 1.7–2.3 s in the magnetic fields of 9.4 and 14.1 T, respectively. Complexes with an acyl ligand (**17–19**, **21**, **22**) relax slightly more slowly than those with a methyl ligand and a substituted cyclopentadienyl ring (**29**, **31**, **32**, **35**), suggesting a larger CSA in the latter. In contrast to the  $^{57}\text{Fe}$  chemical shifts, the differences between relaxation times for type IV complexes are relatively small. Also, in type II complexes, the relaxation times are only slightly different for variable ligands. Drastic changes of longitudinal relaxation and its mechanism are introduced with substitution of the  $\text{PPh}_3$  ligand by  $\text{PMe}_3$  or  $\text{P}(\text{OMe})_3$ . In both cases (**25** and **23**)  $T_1$  increases by a factor of 4–5 at 14.1 T. The slower relaxation is expected to be due to shorter correlation times  $\tau_c$  as compared with the  $\text{PPh}_3$  complexes. In addition, the observed decrease of the CSA contribution (Table 1) indicates a reduced asymmetry of the ligand field.

## Conclusions

The systematic  $^{57}\text{Fe}$  NMR study of four series of cyclopentadienyliron complexes has shown that shielding of the iron nucleus is controlled in a subtle manner by ligand properties and that electronic and steric effects can be clearly distinguished.

The *electronic* ligand effects for ligands in the  $\alpha$ -position to iron, observed in type II complexes  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$ , R = H, Me, and I (**9**, **12**, **16**), were found to be strongest ( $\Delta\delta = 2000$  ppm). In type IV complexes,  $(\text{C}_5\text{H}_4\text{Y})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ , the *electronic* substituent effect of Y is 10 times smaller, because Y acts via two bonds, one being a  $\pi$ -bond. Still smaller, but consistent, *steric* effects were discovered when the ligand atom in the  $\alpha$ -position and its hybridization were held constant. In that case, if an alkyl ligand has sufficient space, as in  $\text{CpFe}(\text{CO})_2\text{R}$  (type I), the volume of R influences the shielding of the iron nucleus, presumably via the Fe–C  $\sigma$ -bond strength. This is supported by correlation of  $^{57}\text{Fe}$  shielding with the CO insertion rate. Even if steric changes in the  $\alpha$ -position to iron are very large, as in type III complexes,  $\text{CpFe}(\text{CO})(\text{L})\text{COMe}$ , where the cone angle ( $\theta$ ) of L correlates with  $\delta(^{57}\text{Fe})$ , the *steric* effect is still four times smaller than the *electronic*  $\alpha$ -effect. When steric changes were made in the  $\beta$ -position, as in type II complexes,  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$ , R = acyl, only a moderate effect on the iron shielding was observed.

One-bond  $^{57}\text{Fe}$ ,  $^{13}\text{C}$  coupling constants of the Fe–C  $\sigma$ -bond are not correlated with the chemical shift variations induced by ligand effects in the investigated complexes. The dominant  $T_1$  relaxation mechanism of the complexes with  $\text{PPh}_3$  ligands was found to be due to chemical shift anisotropy, and no other significant ligand or substituent effects are observable. However,  $T_1$  increases considerably in  $\text{P}(\text{OMe})_3$  and  $\text{PMe}_3$  complexes with a concomitant decrease of the field-dependent CSA contribution.

The great sensitivity of  $^{57}\text{Fe}$  NMR shielding to electronic and steric effects renders it a useful probe into the structure and reactivity of cyclopentadienyliron complexes.

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## Experimental Section

**General Methods.** Standard  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker ARX-300 spectrometer at 300.1 and 75.4 MHz referenced to residual undeuterated solvent with chemical shifts being reported as  $\delta/\text{ppm}$  from TMS.  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AM-400-WB spectrometer at 161.9 MHz externally referenced to 85%  $\text{H}_3\text{PO}_4$  ( $\Xi = 40.480747$  MHz). IR spectra were recorded on a Perkin-Elmer 298 IR spectrophotometer. All reactions and purifications were carried out under nitrogen using Schlenk-tube techniques.<sup>73</sup> All solvents were deoxygenated, dried, and distilled prior to use.

**$^{57}\text{Fe}$  NMR Measurements.** Indirect two-dimensional NMR spectra were recorded at 300 K on a modified Bruker AM-400-WB spectrometer ( $B_0 = 9.4$  T) with an Aspect 3000 computer. For the  $(^{31}\text{P}, ^{57}\text{Fe})\{^1\text{H}\}$  measurements, an additional, third channel consisting of a PTS-160 synthesizer, a Bruker pulse modulator, and a B-SV 3 BX heterodecoupler unit with a low-frequency amplifier was used. A 5-mm inverse triple-resonance probehead, low-frequency range tuneable between 9 and 41 MHz, was employed. In our experiments,  $90^\circ$  pulses were  $14 \mu\text{s}$  ( $^{31}\text{P}$ ) and  $32 \mu\text{s}$  ( $^{57}\text{Fe}$ ). For inverse correlation experiments, a standard HMQC sequence was used with magnitude calculation in F1. Sample concentrations of about 0.3 M and recording times of 4–8 h were required. Typical acquisition parameters were relaxation delays of 2 s, spectral widths in F2 of 250 Hz and in F1 of 10000 Hz, 1k data points in F2, 512 data points in F1, and addition of 24 scans for each of 512 increments. To check that the observed  $^{57}\text{Fe}$  signals were not folded a second experiment with a reduced F1 spectral width of 1000 Hz was recorded. Complexes of type **I** were recorded by direct  $^{57}\text{Fe}$  observation at 19.4 MHz on a Bruker AMX-600 spectrometer ( $B_0 = 14.1$  T) using a broadband probe head. Sample concentrations of about 4 M and recording times of 12–15 h were required. Typically 14 000 points were sampled for a spectral width of 8000 Hz. A pulse width of  $33 \mu\text{s}$  ( $90^\circ$ ) and a relaxation delay of 2.5 s were chosen. All spectra were recorded at 300 K in  $\text{C}_6\text{D}_6$  and 5 mm tubes at natural  $^{57}\text{Fe}$  abundance. The  $^{57}\text{Fe}$  chemical shifts are reported in ppm relative to neat  $\text{Fe}(\text{CO})_5$  as an external standard ( $\Xi = 3.237$  798 MHz). The reproducibility was found to be  $\pm 0.5$  ppm; coupling constants  $J(^{57}\text{Fe}, ^{31}\text{P})$  are  $\pm 0.5$  Hz. For inverse detection experiments on the modified Bruker AMX-600, the TBI-LR triple resonance inverse probehead ( $^1\text{H}$ ,  $^{31}\text{P}$ , BB (7–20.5 MHz)) for ( $^1\text{H}$ ,  $^{57}\text{Fe}$ ) and ( $^{31}\text{P}$ ,  $^{57}\text{Fe}$ ) experiments was employed. The  $90^\circ$  pulse angle was ca.  $11 \mu\text{s}$  for  $^1\text{H}$ ,  $25 \mu\text{s}$  for  $^{31}\text{P}$ , and  $30 \mu\text{s}$  for  $^{57}\text{Fe}$ . For decoupling of  $^{31}\text{P}$ , a  $90^\circ$  low-power pulse of  $225 \mu\text{s}$  was used in the ( $^1\text{H}$ ,  $^{57}\text{Fe}$ ) $\{^{31}\text{P}\}$  correlations.

Relaxation time measurements in all cases were performed on the Bruker AM-400 (9.4 T) and Bruker AMX-600 (14.1 T) spectrometers. Samples (ca. 0.5 M in  $\text{C}_6\text{D}_6$ ) sealed in the 5 mm sample tubes were carefully cleaned and degassed by several freeze–pump–thaw cycles. The double polarization transfer method  $^{31}\text{P}$ – $^{57}\text{Fe}$ – $^{31}\text{P}$  was employed, with series of the  $^{31}\text{P}$   $180^\circ$  pulses spaced by 5 ms during relaxation delay, without refocusing delay before acquisition and with continuous  $^1\text{H}$  decoupling.<sup>72</sup> A spectral width of 250 Hz, acquisition time of 2 s, repetition time of  $1.5$ – $2 T_1$  ( $^{31}\text{P}$ ), and a temperature of 300 K were used for all  $^{57}\text{Fe}$  measurements. The experimental time was ca. 12 h. Relaxation rates in two magnetic fields were calculated on the basis of the logarithm of the intensity in 16 time points using linear regression. The intensities of both doublet components were averaged.

For the measurement of  $^1J(^{57}\text{Fe}, ^{13}\text{C})$  coupling constants at natural isotope abundance, ( $^1\text{H}$ ,  $^{57}\text{Fe}$ ) $\{^{31}\text{P}\}$  HMQC inverse correlation with a (1 3 3 1) binomial excitation pulse and continuous WALTZ-16 decoupling of  $^{31}\text{P}$  was employed.<sup>69</sup>

Solutions of approximately 100 mg (0.2–0.5 mmol) of iron complex in  $\text{C}_6\text{D}_6$  solution in 5-mm sample tubes at  $300 \pm 0.1$  K were measured on a Bruker AMX-600 spectrometer. In all cases,  $^2J(^{57}\text{Fe}, ^1\text{H})$  of about 2 Hz was used for polarization transfer. Repetition times were at least  $1.5 T_1(^1\text{H})$ . Spectral widths of 100 Hz in F1 and 250 Hz in F2 were used, 1024 data points were collected in F2, and 64  $t_1$  increments with about 100 scans for each were acquired and zero-filled to 512 frequency points in F1. The experimental time was ca. 12 h.

**Syntheses.** The complexes of types **I**–**III** and the precursors of type **IV** complexes were synthesized by literature procedures:  $\text{CpFe}(\text{CO})_2\text{R}$  (type **I**, **1**–**8**);<sup>74,75</sup>  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$  (type **II**),  $\text{R} = \text{alkyl}$  (**10**–**15**),<sup>32</sup>  $\text{R} = \text{acyl}$  (**17**–**22**);<sup>33</sup>  $\text{CpFe}(\text{CO})(\text{L})\text{COMe}$  (type **III**, **19**, **23**–**28**);<sup>33</sup>  $(\text{C}_5\text{H}_4\text{Y})\text{Fe}(\text{CO})(\text{PPh}_3)\text{X}$ ,  $\text{X} = \text{halogen}$ ,  $\text{Y} = \text{H}$ ,  $\text{Me}$ ,  $\text{SiMe}_3$ ,  $\text{Ph}$ ,<sup>34,35,39,76</sup>  $\text{X} = \text{Br}$  and  $\text{Y} = \text{NET}_2$ ;<sup>77</sup>  $(\text{C}_5\text{H}_4\text{I})\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$ ,<sup>35,38,39</sup>  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COOMe})$ ;<sup>78–80</sup>  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$  (**9**).<sup>30</sup>

**Preparation of  $(\text{C}_5\text{H}_4\text{Y})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$ ,  $\text{Y} = \text{Me}$ ,  $\text{SiMe}_3$ ,  $\text{NET}_2$ , **I**, and  $\text{Ph}$  (**29**–**33**).** Typically 0.50 mmol of the complex  $(\text{C}_5\text{H}_4\text{Y})\text{Fe}(\text{CO})(\text{PPh}_3)\text{I}$ ,  $\text{Y} = \text{Me}$ ,  $\text{SiMe}_3$ ,  $\text{Ph}$ , and **I**, or  $(\text{C}_5\text{H}_4\text{NET}_2)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{Br})$  was dissolved in 15 mL of THF, and at room temperature 0.55 mmol of Grignard-reagent  $\text{MeMgI}$  (Fluka pract  $\sim 22\%$  in THF) was added dropwise. The color of the reaction mixture changed from green to red. Then the solvent was removed and the residue was chromatographed on silica gel with hexane/ $\text{Et}_2\text{O}$  (1:1).

**$(\text{C}_5\text{H}_4\text{Me})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$  (**29**):** red crystals (170 mg, 93%). IR (benzene): 1902 (s, CO).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 7.85–7.20 (*m*, 15H,  $\text{PPh}_3$ ); 4.27 (*bs*, 2H, Cp); 4.05, 3.93 (2 *bs*, 2H, Cp); 1.91 (*s*, 3H,  $\text{CH}_3$ ); 0.48 (*d*,  $^3J(\text{P},\text{H}) = 6.5$ , 3H,  $\text{Fe}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 223.5 (*d*,  $^2J(\text{C},\text{P}) = 30.5$ , CO); 137.8 (*d*,  $^1J(\text{C},\text{P}) = 38.9$ ,  $\text{PPh}_3$ ); 134–127 (*m*,  $\text{PPh}_3$ ); 99.4, 88.3, 85.4, 81.8, 79.1 (5 *s*, Cp); 12.6 (*s*,  $\text{CH}_3$ ); –17.5 (*d*,  $^2J(\text{C},\text{P}) = 21.3$ ,  $\text{Fe}-\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 85.6 (*s*).  $^{57}\text{Fe}$  NMR ( $\text{C}_6\text{D}_6$ ): 1367 ( $^1J(\text{Fe},\text{P}) = 56.4$ ).

**$(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$  (**30**):** deep red powder (150 mg, 90%). IR (benzene): 1902 (s, CO).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 7.50–6.80 (*m*, 15H,  $\text{PPh}_3$ ); 4.49, 4.35, 4.11, 3.68 (4 *bs*, 4H, Cp); 0.29 (*s*, 9H,  $\text{Si}(\text{CH}_3)_3$ ); 0.19 (*d*,  $^3J(\text{P},\text{H}) = 6.2$ , 3H,  $\text{Fe}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 223.8 (*d*,  $^2J(\text{C},\text{P}) = 33.2$ , CO); 137.6 (*d*,  $^1J(\text{C},\text{P}) = 39.3$ ,  $\text{PPh}_3$ ); 134.5–127.5 (*m*,  $\text{PPh}_3$ ); 102.8, 89.1, 86.4, 84.8, 81.4 (5 *s*, Cp); 0.0 (*s*,  $\text{Si}(\text{CH}_3)_3$ ); –21.1 (*d*,  $^2J(\text{C},\text{P}) = 22.0$ ,  $\text{Fe}-\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 85.7 (*s*).  $^{57}\text{Fe}$  NMR ( $\text{C}_6\text{D}_6$ ): 1421 ( $^1J(\text{Fe},\text{P}) = 54.7$ ).

**$(\text{C}_5\text{H}_4\text{NET}_2)\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$  (**31**):** red oil (41 mg, 52%). IR (benzene): 1892 (s, CO).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 7.64–6.92 (*m*, 15H,  $\text{PPh}_3$ ); 4.36, 3.95, 3.46, 2.93 (4 *m*, 4H, Cp); 2.73, 2.72 (*q*,  $^3J(\text{H},\text{H}) = 7.3$ , 4H,  $\text{CH}_2$ ); 0.79 (*t*,  $^3J(\text{H},\text{H}) = 7.1$ , 6H,  $\text{CH}_3$ ); 0.20 (*d*,  $^3J(\text{P},\text{H}) = 6.0$ , 3H,  $\text{Fe}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 223.2 (*d*,  $^2J(\text{C},\text{P}) = 29.8$ , CO); 138.0 (*d*,  $^1J(\text{C},\text{P}) = 36.6$ ,  $\text{PPh}_3$ ); 134–127 (*m*,  $\text{PPh}_3$ ); 78.7, 76.7, 67.4, 57.1, 57.0 (5 *s*, Cp); 44.6 (*s*,  $\text{CH}_2$ ); 12.8 (*s*,  $\text{CH}_3$ ); –16.5 (*d*,  $^2J(\text{C},\text{P}) = 20.2$ ,  $\text{Fe}-\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 87.1 (*s*).  $^{57}\text{Fe}$  NMR ( $\text{C}_6\text{D}_6$ ): 1437 ( $^1J(\text{Fe},\text{P}) = 56.6$ ).

**$(\text{C}_5\text{H}_4\text{I})\text{Fe}(\text{CO})(\text{PPh}_3)\text{Me}$  (**32**):** red oil (254 mg, 53%). IR (benzene): 1918 (s, CO).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 7.60–7.05 (*m*, 15H,  $\text{PPh}_3$ ); 4.56, 4.30, 3.89, 3.79 (4 *m*, 4H, Cp); 0.53 (*d*,  $^3J(\text{P},\text{H}) = 6.5$ , 3H,  $\text{Fe}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 221.2 (*d*,  $^2J(\text{C},\text{P}) = 31.6$ , CO); 135.3 (*d*,  $^1J(\text{C},\text{P}) = 39.8$ ,  $\text{PPh}_3$ ); 132–125 (*m*,  $\text{PPh}_3$ ); 92.6, 86.7, 85.2, 82.8, 81.4 (5 *s*, Cp); –15.7 (*d*,  $^2J(\text{C},\text{P}) = 20.6$ ,  $\text{Fe}-\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 83.7 (*s*).  $^{57}\text{Fe}$  NMR ( $\text{C}_6\text{D}_6$ ): 1439 ( $^1J(\text{Fe},\text{P}) = 56.5$ ).

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**(C<sub>5</sub>H<sub>4</sub>Ph)Fe(CO)(PPh<sub>3</sub>)Me (33):** deep red oil (113 mg, 60%). IR (benzene): 1911 (s, CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.85–7.15 (m, 15H, PPh<sub>3</sub>, 5H, Ph); 5.04, 4.81, 4.39, 4.32 (4 bs, 4H, Cp); 0.54 (d, <sup>3</sup>J(P,H) = 6.3, 3H, Fe–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>): 222.3 (d, <sup>2</sup>J(C,P) = 31.3, CO); 137.0 (d, <sup>1</sup>J(C,P) = 39.4, PPh<sub>3</sub>); 135–125 (m, PPh<sub>3</sub>, Ph); 87.5, 85.9, 84.1, 82.1, 77.9 (5 s, Cp); –18.8 (d, <sup>2</sup>J(C,P) = 20.8, Fe–CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 84.1 (s). <sup>57</sup>Fe NMR (CDCl<sub>3</sub>): 1500 (<sup>1</sup>J(Fe,P) = 55.8).

**Preparation of (C<sub>5</sub>H<sub>4</sub>COOMe)Fe(CO)(PPh<sub>3</sub>)Me (34).** A 248 mg (0.526 mmol) amount of CpFe(CO)(PPh<sub>3</sub>)(COOMe) was dissolved in 20 mL of THF. At –78 °C 0.33 mL (0.526 mmol) of *n*-BuLi (Fluka pract, 1.6 M in hexane) was added dropwise and the solution stirred for 10 min. To the deep violet solution 0.03 mL (0.526 mmol) of CH<sub>3</sub>I (Fluka purum) was added at once, and the color changed to orange-red. Chromatography over silica gel (1:1 hexane/Et<sub>2</sub>O) afforded 157 mg (0.324 mmol, 61%) of (C<sub>5</sub>H<sub>4</sub>COOMe)Fe(CO)(PPh<sub>3</sub>)Me. IR (benzene): 1917 (s, CO), 1717 (m, COOMe). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.70–7.15 (m, 15H, PPh<sub>3</sub>); 5.42, 5.25, 4.17, 4.04 (4 bs, 4H, Cp); 3.71 (s, 3H, OCH<sub>3</sub>), 0.65 (d, <sup>3</sup>J(P,H) = 6.0, 3H, Fe–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 221.7 (d, <sup>2</sup>J(C,P) = 32.4, CO); 167.0 (s, COOR); 136.5 (d, <sup>1</sup>J(C,P) = 40.7, PPh<sub>3</sub>); 134–127 (m, PPh<sub>3</sub>, Cp); 92.0, 89.0, 84.2 (3 s, Cp); 50.9 (s, OCH<sub>3</sub>); –19.8 (d, <sup>2</sup>J(C,P) = 21.1, Fe–CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 82.7 (s). <sup>57</sup>Fe NMR (C<sub>6</sub>D<sub>6</sub>): 1576 (<sup>1</sup>J(Fe,P) = 56.6).

**Preparation of (C<sub>5</sub>H<sub>4</sub>CO<sup>*i*</sup>Pr)Fe(CO)(PPh<sub>3</sub>)Me (35).** The same procedure as for **34** was used to synthesize (C<sub>5</sub>H<sub>4</sub>CO<sup>*i*</sup>Pr)Fe(CO)(PPh<sub>3</sub>)Me, but to 134 mg (0.278 mmol) of CpFe(CO)(PPh<sub>3</sub>)(CO<sup>*i*</sup>Pr) in 20 mL of THF was added 0.18 mL (0.290 mmol) of *n*-BuLi (Fluka pract, 1.6 M in hexane) dropwise at room temperature and the solution stirred for 10 min. Addition of 0.02 mL (0.321 mmol) of CH<sub>3</sub>I, filtration over silica gel, and crystallization with hexane yielded 58 mg (0.117 mmol, 42%) of (C<sub>5</sub>H<sub>4</sub>CO<sup>*i*</sup>Pr)Fe(CO)(PPh<sub>3</sub>)Me as an orange powder. IR (benzene): 1920 (s, CO), 1661 (m, CO-*i*Pr). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.75–7.10 (m, 15H, PPh<sub>3</sub>); 5.30, 5.10, 4.08, 4.02 (4 bs, 4H, Cp); 3.09 (sept, <sup>3</sup>J(H,H) = 6.8, 1H, CH), 1.38 (d, <sup>3</sup>J(H,H) = 6.3, 3H, CH<sub>3</sub>); 1.36 (d, <sup>3</sup>J(H,H) = 6.4, 3H, CH<sub>3</sub>); 0.53 (d, <sup>3</sup>J(P,H) = 5.9, 3H, Fe–CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 221.7 (d, <sup>2</sup>J(C,P) = 33.0, CO); 202.0 (s, CO-*i*Pr); 136.3 (d, <sup>1</sup>J(C,P) = 40.7, PPh<sub>3</sub>); 134–127 (m, PPh<sub>3</sub>); 93.1, 90.3, 85.1, 84.0, 82.7 (5 s, Cp); 36.8 (s, CH); 19.0 (s, CH<sub>3</sub>); 18.8 (s, CH<sub>3</sub>); –19.9 (d, <sup>2</sup>J(C,P) = 21.2, Fe–CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 83.0 (s). <sup>57</sup>Fe NMR (C<sub>6</sub>D<sub>6</sub>): 1580 (<sup>1</sup>J(Fe,P) = 55.9).

**Crystallographic Analysis of (CpI)Fe(CO)(PPh<sub>3</sub>)Me (32).** Crystals of C<sub>25</sub>H<sub>22</sub>FeIOP, obtained from hexane/diethyl ether, were used for a low-temperature X-ray structure determination. All measurements were made on a Rigaku AFC5R diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) and a 12 kW rotating anode generator. The intensities of three standard reflections were measured after every 150 reflections and remained stable throughout the data collection. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction, based on azimuthal scans of several reflections,<sup>81</sup> was applied. An attempt with an analytical absorption correction did not yield better results. The space group was determined from the systematic absences. Equivalent reflections were merged. Data collection and refinement parameters are given in Table 4.

The structure was solved by Patterson methods using SHELXS86,<sup>82</sup> which revealed the positions of the I and Fe atoms. All remaining non-hydrogen atoms were located in a Fourier expansion of the Patterson solution. The non-hydrogen atoms were refined anisotropically. All of the H atoms were fixed in geometrically calculated positions with a C–H distance of 0.95 Å. Individual isotropic temperature

Table 4. Crystallographic Data for **32**

empirical formula	C <sub>25</sub> H <sub>22</sub> FeIOP
fw	552.17
cryst color, habit	red, prism
cryst dimens (mm)	0.20 × 0.38 × 0.39
temp (K)	173(1)
cryst system	monoclinic
space group	P2 <sub>1</sub> /n (No. 14)
Z	4
reflcs for cell deternm	25
2 $\theta$ range for cell deternm (deg)	39–40
unit cell params	
<i>a</i> (Å)	7.787(3)
<i>b</i> (Å)	15.768(3)
<i>c</i> (Å)	17.960(4)
$\beta$ (deg)	101.58(3)
<i>V</i> (Å <sup>3</sup> )	2160.4(9)
<i>F</i> (000)	1096
<i>D</i> <sub>x</sub> (g cm <sup>-3</sup> )	1.697
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	2.215
scan type	$\omega/2\theta$
2 $\theta$ (max) (deg)	60
transm factors (min, max)	0.727, 1.000
tot. reflcs measd	6941 (+ <i>h</i> , + <i>k</i> , $\pm$ <i>l</i> )
sym indepdnt reflcs	6291
<i>R</i> <sub>int</sub>	0.032
reflcs used [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	4817
params refined	284
final <i>R</i>	0.0524
final <i>wR</i>	0.0748
weights	$w = [\sigma^2(F_o) + (0.015F_o)^2]^{-1}$
goodness of fit	2.618
final $\Delta_{\max}/\sigma$	0.004
$\Delta\rho$ (max, min) (e Å <sup>-3</sup> )	1.39, –1.55

factors were refined for all H atoms. Refinement of the structure was carried out on *F* using full-matrix least-squares procedures, which minimized the function  $\sum w(|F_o| - |F_c|)^2$ . The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $(\sin \theta)/\lambda$ , and various classes of indices showed no unusual trends. A correction for secondary extinction was not applied. There was poor agreement between the *F<sub>o</sub>* and *F<sub>c</sub>* values of 26 reflections as well as several large peaks of residual electron density near the Fe atom. Small irregularities in the shape of the crystal made accurate indexing of the crystal faces difficult, and therefore, it was necessary to use the  $\psi$ -scan method for absorption correction. It is unlikely that these discrepancies result from disorder in the structure, and the cause is most probably the inadequacy of the absorption correction.

Neutral atom scattering factors for non-hydrogen atoms were taken from Maslen, Fox, and O'Keefe,<sup>83</sup> and the scattering factors for H atoms were taken from Stewart, Davidson, and Simpson.<sup>84</sup> Anomalous dispersion effects were included in *F<sub>c</sub>*,<sup>85</sup> the values for *f'* and *f''* were those of Creagh and McAuley.<sup>86</sup> All calculations were performed using the TEXSAN crystallographic software package.<sup>87</sup>

**Reactivity Studies.** To a THF solution of  $7 \times 10^{-3}$  M CpFe(CO)<sub>2</sub>R typically at least 0.07 M PPh<sub>3</sub> was added. This mixture was heated under reflux, and in periodic time intervals the infrared spectra of small samples were recorded on a Perkin-Elmer 298 IR spectrophotometer. Solution cells

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of 0.1 mm path length with sodium chloride windows were used. The progress of the reaction was followed by observing the disappearance of the highest CO band at about  $2000\text{ cm}^{-1}$ . The recorded spectra were evaluated with *pseudo*-first-order kinetics by plotting  $\ln(A_t - A_\infty)$  against  $t$  ( $A_t$ , absorption at time  $t$ ;  $A_\infty$ , absorption after completion of the reaction).

**Acknowledgment.** The authors thank the Swiss National Science Foundation and the Dr. Helmut Legerlotz-Stiftung for financial support.

**Supporting Information Available:** Listings of fractional atomic coordinates and equivalent isotropic temperature factors, interatomic distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates and  $U$  values (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM950989B