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Kinetic Investigation of Phosphine Exchange in $CpFe(CO)(L)CH_3$ ($L = PPh_3, PPh_2Me$): Rate of Thermal Formation of the 16-Electron Species $CpFe(CO)CH_3$

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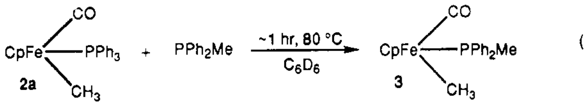
Introduction

We recently discovered that decomposition of methoxycarbyne complex **1** in the presence of the doubly-labeled "product" **2b**-d_3 gave rise to methyl exchange in the mononuclear products **2a** and **2b**, without any exchange in recovered **1**.[1] In the absence of the carbyne, methyl exchange occurred between **2a** and **2b**-d_3 but only after prlonged heating (Scheme I). It occurred to us that one explanation for these experiments was that **1** gives rise to some reactive species that is responsible for methyl exchange, while **2a** and **2b**-d_3 either do not give rise to that species or do so only upon prolonged heating. Since the products of **1** are $MeCpMn(CO)_3$ and $CpFe(CO)(PPh_3)CH_3$, an obvious candidate for the reactive species is the 16-electron intermediate $CpFe(CO)CH_3$, since trapping by PPh_3 would directly give the iron product **2a**. A necessary test of this hypothesis is the determination of the potential thermal rate of formation of $CpFe(CO)CH_3$ from **2a**, since its facile formation would preclude its candidacy as the methyl exchange intermediary. In this paper we describe kinetic experiments to test this hypothesis.

Results

Preliminary experiments suggested that phosphine substitution of $CpFe(CO)(PPh_3)CH_3$ (**2a**) by the more nucleophilic phosphine PPh_2Me to give $CpFe(CO)(PPh_2Me)CH_3$ (**3**) occurred at a convenient rate at 80 °C (eq 1). The rate of substitution was determined by ^1H NMR spectroscopy by monitoring the methyl resonance for both **2a** and **3**. Small amounts of $CpFe(PPh_2Me)_2CH_3$[2] were always detected at the beginning of the reactions before heating commenced, but the amount of this material did not change during any of the reactions. The cause of this reaction is unknown. Reactions were carried out under pseudo-first-order conditions (>5 equiv of PPh_2Me) and were followed for 3–4 half-lives. Linear first-order plots were obtained; kinetic data are collected in Table I, and representative plots are shown in Figure 1. Reactions were carried out at three different phosphine concentrations at 80 °C; no dependence of rate on phosphine concentration was detected. The same was true at 65 °C, where two phosphine concentrations were used. The Eyring plot (Figure 2), while conducted over the relatively limited range of 25 °C, nevertheless gave only a small deviation in the entropy, so the positive value of 13 ± 4 eu is sufficiently reliable from which to draw a conclusion.



(1)

Scheme I

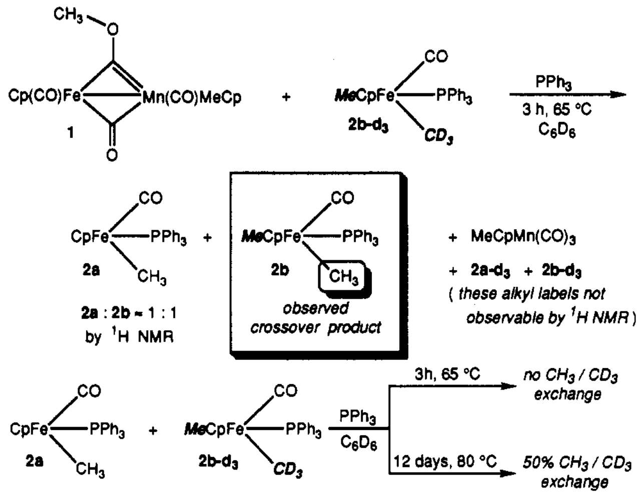
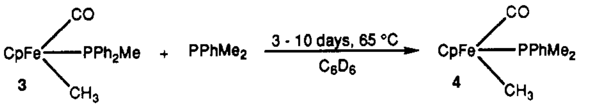


Table I. Rate Constants Measured in C_6D_6 for the Reactions of $CpFe(CO)(PPh_3)CH_3$ (**2a**) with PPh_2Me and $CpFe(CO)(PPh_2Me)CH_3$ (**3**) with $PPhMe_2$

T (°C)	$[PPh_2Me]$ (M)	$[PPhMe_2]$ (M)	10^5k_{obs} (s^{-1})
65	0.057		5.91 ± 0.16
65	0.52		6.08 ± 0.10
65			5.99 ± 0.08 (av)
80	0.091		35.3 ± 1.3
80	0.22		40.9 ± 0.7
80	0.59		36.8 ± 0.5
80			37.6 ± 2.4 (av)
90	0.08		157 ± 4
65		0.12	0.258 ± 0.002
65		0.71	0.738 ± 0.012
65		1.34	1.225 ± 0.006

Reaction of the PPh_2Me adduct **3** with the more nucleophilic dialkylphosphine[3] $PPhMe_2$ was also examined (eq 2). Since it was anticipated that an equilibrium might exist since the product stabilities might be more similar than **2a** and **3**, relatively large excesses (>13:1) of $PPhMe_2$ were used, but in fact complete conversion to product **4** was observed, giving linear first-order decomposition of **3** (Figure 3). In this case, the rate of reaction did depend on phosphine concentration, but the plot of observed rate constant vs $[PPhMe_2]$ gave a nonzero intercept (Figure 4), showing that a phosphine-independent pathway was still operative.



(2)

Discussion

A mechanism consistent with the kinetic results is shown in Scheme II. For PPh_3 adduct **2a**, the apparent lack of dependence of the rate of phosphine substitution on phosphine concentration requires the formation, in the rate-determining step, of an intermediate from **2a** that is rapidly trapped by PPh_2Me to give **3**. The absence of falloff in rate at low phosphine concentration is simply a consequence of the rapidity of this trapping, relative to reversion back to starting material by trapping with PPh_3. For PPh_2Me adduct **3**, the nonzero intercept in Figure 4 demonstrates the presence of a phospine-independent pathway that is presumably analogous to that seen for **2a**, while the presence of the

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[1] (a) Fong, R. H.; Hersh, W. H. *Organometallics* **1985**, *4*, 1468–1470. (b) Fong, R. H.; Lin, C.-H.; Idmoumaz, H.; Hersh, W. H. *Ibid.* **1993**, *12*, 503–516. (c) Fong, R. H.; Hersh, W. H. Manuscript in preparation.

[2] Lehmkuhl, H.; Mehler, G.; Benn, R.; Rufińska, A.; Schroth, G.; Krüger, C.; Raabe, E. *Chem. Ber.* **1987**, *120*, 1987–2000.

[3] (a) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1987**, *26*, 1826–1828. (b) Bush, R. C.; Angelici, R. J. *Ibid.* **1988**, *27*, 681–686. (c) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1–7.

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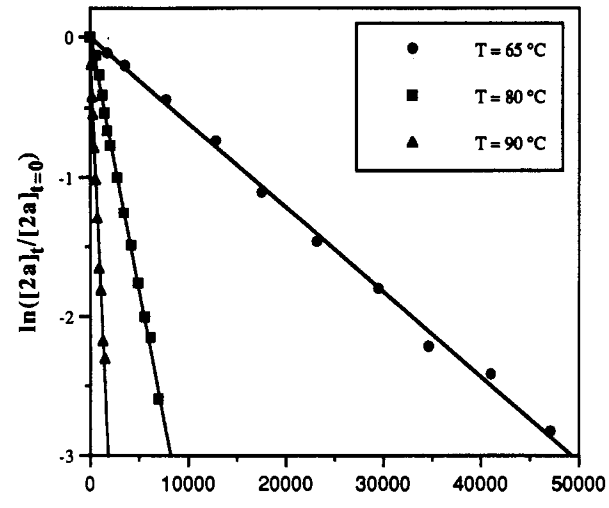


Figure 1. Typical first-order plots of the rate of phosphine substitution of **2a** by PPh_2Me. The lower temperature runs are for the highest concentrations of [PPh_2Me].

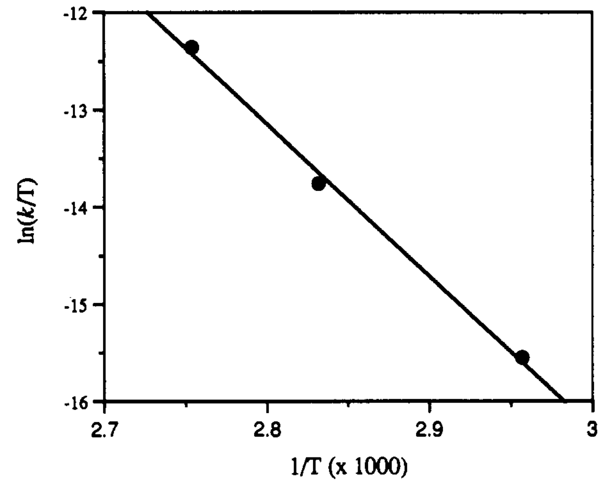


Figure 2. Eyring plot for reaction of **2a** with PPh_2Me. Derived parameters are $\Delta H^{\ddagger} = 30.9 \pm 1.4$ kcal/mol and $\Delta S^{\ddagger} = 13 \pm 4$ eu.

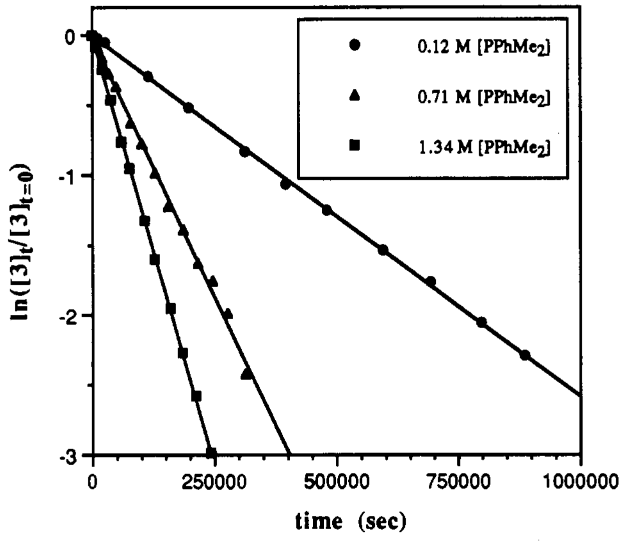


Figure 3. First-order plots of the rate of phosphine substitution of **3** by $PPhMe_2$ at 65 °C in C_6D_6.

bimolecular phosphine-dependent pathway arises due to the greater nucleophilicity of PPh_2Me compared to PPh_3.[3] The positive entropy derived from the Eyring plot for the reaction of **2a** is also consistent with the dissociative nature of the rate-determining step.[4] Comparison of the rates of dissociation for the PPh_3 and PPh_2Me ligands also supports the dissociative nature of this reaction, since the more strongly coordinating alkylphosphine ligand dissociates ~36× slower than PPh_3 at 65 °C. We conclude that the data provide sufficient kinetic evidence for the thermal formation of the formally unsaturated 16-electron intermediate $CpFe(CO)CH_3$.[5]

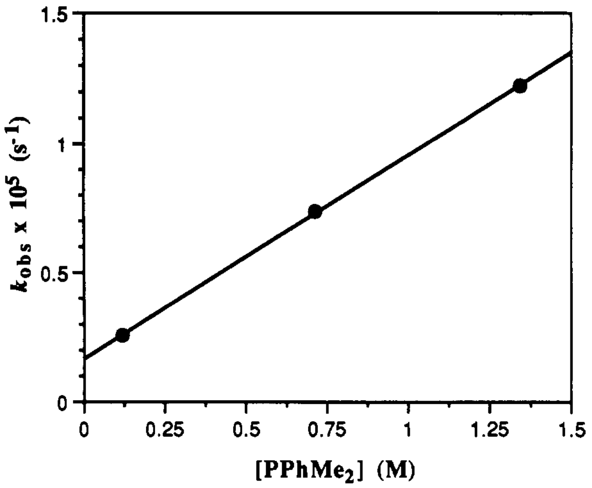
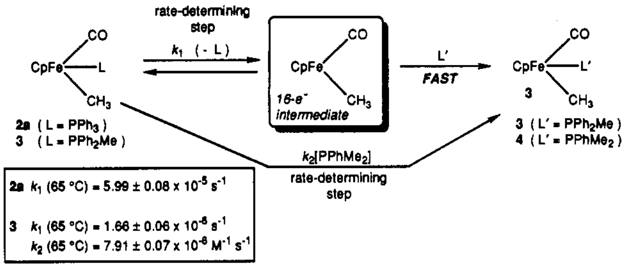


Figure 4. Plot of first-order rate constants for decomposition of **3** vs concentration of $PPhMe_2$ at 65 °C in C_6D_6.

Scheme II



There are very few examples in the literature of thermal formation of $CpFe(CO)CH_3$. For instance, heating $CpFe(CO)_2CH_3$ with PPh_3 mainly gives the acetyl complex $CpFe(CO)(PPh_3)(COCH_3)$ at ~69 °C, although at ~99 °C decarbonylation of this gives **2a** but without involvement of $CpFe(CO)CH_3$.[6] Heating **2a** at ~67 °C with $P(OR)_3$ (R = Me, *n*-butyl, Ph) gives $CpFe(CO)(P(OR)_3)CH_3$,[6] however, perhaps via dissociative phosphine loss to give $CpFe(CO)CH_3$. Another example of phosphine "substitution" is that of $CpFe(CO)(PPhMe_2)H$, which undergoes rapid reversible loss of $PPhMe_2$ on the NMR time scale at

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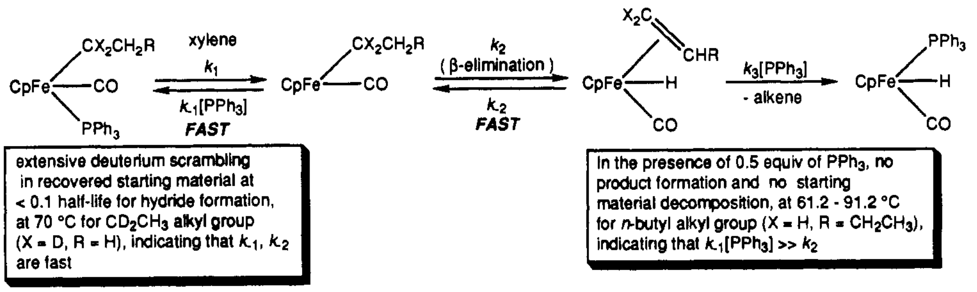
(4) Darensbourg, D. J. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: San Diego, CA, 1982; Vol. 21, pp 113–150.

(5) A reviewer suggested an alternative mechanism in which rate-determining methyl migration followed by fast attack of phosphine would give $CpFe(L)(L')C(O)CH_3$ as an intermediate, which could then undergo fast loss of phosphine and carbon monoxide deinsertion to effect phosphine exchange. This mechanism would be surprising since rate-determining methyl migration rather than phosphine dissociation would not be expected to give the observed positive entropy and the rate differences between **2a** and **3**. However, it can be excluded rigorously only if the acetyl is stable under the reaction conditions. A few examples of such diphosphine acyl complexes are known,[a,b] but while they do not form by thermal reaction of $CpFe(CO)(L)CH_3$,[c,d] their thermal stability has not been reported, although in one case the diphosphine acetyl complex was detected (but no yield reported) after refluxing $[Cp(PMe_3)_2Fe{=}C(OMe)CH_3][CpW(CO)_3]$ in benzene for 5 h.[e] (a) Brunner, H.; Vogt, H. *J. Organomet. Chem.* **1981**, *210*, 223–236. (b) Alt, H. G.; Eichner, M. E.; Jansen, B. M.; Thewalt, U. *Z. Naturforsch. B* **1982**, *37B*, 1109–1115. (c) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363–1403. (d) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77–88. (e) Grötsch, G.; Malisch, W. *Ibid.* **1984**, *262*, C38–C42.

(6) Su, S. R.; Wojcicki, A. *J. Organomet. Chem.* **1971**, *27*, 231–240.

Scheme III



extensive deuterium scrambling in recovered starting material at < 0.1 half-life for hydride formation, at 70 °C for CD_2CH_3 alkyl group (X = D, R = H), indicating that k_{-1}, k_{-2} are fast

In the presence of 0.5 equiv of PPh_3, no product formation and no starting material decomposition, at 61.2 - 91.2 °C for *n*-butyl alkyl group (X = H, R = CH_2CH_3), indicating that $k_{-1}[PPh_3] >> k_2$

temperatures as low as 40 °C,[7] so clearly the nature of the σ-bound ligand is relevant to the rate of phosphine dissociation.

The best evidence in the literature of phosphine dissociation and thermal formation of $CpFe(CO)CH_3$ comes from Reger's work on the thermal decomposition of several $CpFe(CO)(PPh_3)$(alkyl) derivatives.[8] These results are summarized in Scheme III. Thermal loss of PPh_3 gives the 16-electron intermediate shown which via subsequent (and reversible) β-elimination leads to deuterium scrambling in recovered starting material. Even at early reaction time, the scrambling is extensive, requiring that the reversible β-elimination occurs many times before PPh_3 displaces the ethylene to give the hydride product. In the presence of as little as 0.5 equiv of PPh_3, no reaction occurs, so presumably the β-elimination step is not reached. The rate-determining step of the reaction must be the final alkene displacement, however, so only a lower limit on k_1 in Scheme III, the rate constant analogous to those that we have examined, can be determined from Reger's work. The rate of decomposition of the starting alkyl was measured from 61.2 to 91.2 °C for the *n*-butyl derivative, for instance giving rate constants $k(61.2\ °C) = 4.53 \times 10^{-5}\ s^{-1}$ and $k(74.8\ °C) = 1.02 \times 10^{-4}\ s^{-1}$, which are in fact comparable to the rate constants measured for the phosphine substitution of **2a**. This would tend to suggest that the rate constant for formation of the unsaturated intermediate in Scheme III, k_1, is significantly larger than that for **2a**. One explanation for this might be the greater steric bulk of the *n*-butyl group compared to a methyl group, which would tend to increase the rate of ligand dissociation.[4,9] We are currently examining rates of reaction of $CpFe(CO)(PPh_3)Et$ in order to address this issue.[10] The only other kinetic study of which we are aware, due to Brunner,[11] provides further evidence of steric acceleration of phosphine dissociation: the rate of epimerization of diastereomerically pure $Cp'Fe(CO)(L)CH_3$ (L = (*S*)-$Ph_2PN(Me)CH(Me)Ph$) was 10–20 times faster for Cp′ = indenyl than for Cp′ = cyclopentadienyl. For the cyclopentadienyl case, the rate constant for phosphine dissociation from the major diastereomer was $6.3 \times 10^{-5}\ s^{-1}$ at 70.0 °C in C_6D_6, while, for the indenyl case, a large positive activation entropy (18 ± 1 eu, determined over a 10° range) was found. These values are similar to those described above, as was the conclusion that the rate-determining step is phosphine dissociation.

Photolysis of $CpFe(CO)_2CH_3$ leads to CO dissociation and putative $CpFe(CO)CH_3$, which is trapped by, for instance, PPh_3 to give **2a**.[12] However, the 16-electron intermediate $CpFe(CO)CH_3$ has not been observed in frozen inert-gas matrices,[12c,13] although it was apparently observed in a polyvinyl chloride film matrix at 12 K.[14] Warming to 40 K led to recombination with the free CO formed from the photolysis of $CpFe(CO)_2CH_3$, and the authors suggested that the failure to observe the unsaturated intermediate in the frozen gas matrix was due to rapid recombination even at 12 K due to the smaller "cage" compared to that in the PVC matrix. Clearly $CpFe(CO)CH_3$ is extremely reactive, so its intermediacy in thermal reactions is somewhat surprising. In benzene solution, of course, weak solvent coordination to yield $CpFe(CO)(\eta^2\text{-}C_6D_6)CH_3$ is reasonable,[15] although while photolysis of $CpFe(CO)_2CH_3$ in pentane in the presence of ethylene yields $CpFe(CO)(ethylene)CH_3$, this complex decomposes above −30 °C.[16] Thus, thermally generated $CpFe(CO)CH_3$ in benzene will be effectively coordinatively-unsaturated.

In conclusion, we have shown that phosphine dissociation from $CpFe(CO)(L)CH_3$ (L = PPh_3, PPh_2Me) occurs to give the reactive intermediate $CpFe(CO)CH_3$ in C_6D_6, which is trapped by L to return to starting material or by an external ligand to give the phosphine-exchange product. Rather than being a particularly slow reaction, or occurring exclusively by an associative S_N2 type of substitution mechanism, phosphine dissociation is surprisingly rapid, given the known high reactivity of the intermediate formed. That is, our expectation at the outset of this study was that phosphine dissociation would be slow compared to decomposition of methoxycarbyne **1** (Scheme I), but in fact the two rates are essentially (albeit coincidentally) the same.[1c] In conclusion, since methyl exchange is slow in the absence of **1** despite the formation of $CpFe(CO)CH_3$ on the same time scale as carbyne decomposition, the intermediacy of $CpFe(CO)CH_3$ as the catalyst for the fast methyl exchange reaction in Scheme I is ruled out.

Experimental Section

General Methods. All manipulations of air-sensitive compounds were carried out either in a Vacuum Atmospheres inert-atmosphere drybox under recirculating nitrogen or by using standard Schlenk techniques. ^1H NMR spectra were recorded on an IBM/Bruker WP-200SY spectrometer; chemical shifts are reported relative to hydrogen in C_6D_6 (δ 7.15). Benzene-d_6 was purified by vacuum-transfer from sodium benzophenone ketyl. Other synthetic details are the same as those described elsewhere.[1b]

^1H NMR Experiments. The iron starting materials and products have been previously reported.[1b,2,3c,6,12a,17] All kinetic runs were carried out as follows: In the glovebox, **2a** (or **3**) and Ph_3CH (internal ^1H NMR integration standard) were loaded into an NMR tube sealed to a 14/20

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(7) Shackleton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnston, L. J.; Baird, M. C. *Organometallics* **1990**, *9*, 2248–2253.

(8) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789–2794.

(9) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171–176.

(10) The rate constant for the first-order decomposition of $CpFe(CO)(PPh_3)Et$ to give $CpFe(CO)(PPh_3)H$ in C_6D_6 is $k(65\ °C) = (8.59 \pm 0.30) \times 10^{-6}\ s^{-1}$ in the presence of 0.007 M [PPh_3] (0.4 equiv of PPh_3), measured to 4.5 half-lives: Hersh, W. H. Unpublished results.

(11) Brunner, H.; Fisch, K.; Jones, P. G.; Salbeck, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1521–1523.

(12) (a) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177–1181. (b) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Ibid.* **1976**, *15*, 1910–1918. (c) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602–611.

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(14) Hooker, R. H.; Rest, A. J.; Whitwell, I. *J. Organomet. Chem.* **1984**, *266*, C27–C30.

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(16) Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1365–1374.

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ground glass joint, while liquid PPh_2Me (or $PPhMe_2$) was dissolved in a small amount of C_6D_6 and transferred and rinsed into the tube. Benzene-d_6 was added to a height of ~3.5 cm, a vacuum stopcock was fitted to the tube, and the tube was attached to a vacuum line. The tube was submitted to three freeze–pump–thaw cycles and sealed with a torch. Heating was carried out by inverting the tube in a thermostatted water bath; samples were quenched by immersing in an ice bath, and the tube was centrifuged prior to recording each NMR spectrum. The volume was calculated according to the equation $V = \pi(0.213)^2h$, where h is the height of the solvent measured immediately after removal from the hot bath. For the decomposition of **2a** to **3**, the $FeCH_3$ methyls were monitored (**2a**, δ 0.30, d, J_{PH} = 6.4 Hz; **3**, δ 0.105, d, J_{PH} = 6.7 Hz) since the Cp doublets are nearly coincident, while, for the decomposition of **3** to **4**, the Cp doublets were monitored (**3**, δ 4.105, d, J_{PH} = 1.2 Hz; **4**, δ 4.026, d, J_{PH} = 1.3 Hz).

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