Mechanism of Alkyl Migration from Oxygen to Metal in **Iron-Manganese Ethoxycarbyne Complexes.** Induction of Postcleavage Intermolecular Ethyl Exchange by Hydride Bridging of Mononuclear Iron Species

Hamid Idmoumaz,^{1a} Chien-Hsing Lin,^{1b} and William H. Hersh^{*,1a}

Department of Chemistry and Biochemistry, Queens College of the City University of New York, Flushing, New York 11367-1597, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Received May 11, 1995[∞]

The iron-manganese ethoxycarbyne $Cp(CO)Fe(\mu-COCH_2CH_3)(\mu-CO)Mn(CO)MeCp$ (2a) undergoes thermal decomposition at 65 $^{\circ}$ C to give MeCpMn(CO)₃ and, in the presence of PPh₂Me, CpFe(CO)(PPh₂Me)CH₂CH₃ (4a). The reaction is first order in carbyne and zero order in phosphine and exhibits a kinetic deuterium isotope effect $k_{\rm H}/k_{\rm D} = 2.0 \pm 0.1$. Crossover experiments between 2a and its bis MeCp, CD_2CD_3 analog (2b- d_5) or between **2a**- d_5 and **2b** result in scrambling of the alkyl label between products **4a** and **4a**- d_5 and their MeCp analogs 4b and 4b- d_5 . A crossover experiment between 2a and 2b- ^{13}C labeled specifically at the ethoxy methylene carbon gave complete ${}^{13}C$ exchange in the methylene carbons of 4a,b but no ¹³C exchange in the starting materials after 50% conversion and no 13 C scrambling into the methyl position of **4a**,**b**. Ethylene does not affect the rate of decomposition of **2b** or **2b** d_5 , does not affect ethyl scrambling, and is not incorporated into **4b** during the decomposition of **2b**- d_5 , ruling out ethylene rather than ethyl exchange. The course of the reaction between 2a and 2b- d_5 is not altered by the additives 2,6-di-*tert*-butyl-4-methoxyphenol, galvinoxyl, or thiophenol, ruling out involvement of radicals. "Control crossover" experiments between $2\mathbf{a} \cdot d_5$ and $4\mathbf{b}$ and between $2\mathbf{b} \cdot d_5$ and $4\mathbf{a}$ give no exchange. However, the iron hydride $RC_5H_4Fe(CO)(PPh_2Me)H$ (R = H, **5a**; R = Me, **5b**) forms by β -elimination from RCpFe(CO)CH₂CH₃ followed by PPh₂Me displacement of ethylene, and alkyl exchange occurs when **2b** and **5a** are combined under the reaction conditions but not when 4b and 5a are combined. A mechanism for ethyl exchange is described in which catalytic amounts of **5a**, **5b**, and deuterated analogs **5a**- d_1 and **5b**- d_1 intercept the 16-electron carbyne decomposition intermediates $CpFe(CO)CH_2CH_3$, $MeCpFe(CO)CH_2CH_3$, and their C_2D_5 analogs to give hydride-bridged species. Concomitant migration of the ethyl group and the PPh_2Me ligand between the two iron atoms in these bridged species followed by cleavage to regenerate the hydride and 16-electron intermediate completes the exchange event. Slower trapping of the 16-electron intermediates by PPh_2Me irreversibly removes them from the catalytic cycle, giving products $4a_{,b}$, $4a_{-d_5}$, and $4b_{-d_5}$.

Introduction

We have previously reported the syntheses of the first neutral heterodinuclear μ_2 -alkoxycarbyne complexes Cp- $(CO)Fe(\mu$ -COR)(μ -CO)Mn(CO)MeCp (1, R = CH₃; 2, R $= CH_2CH_3$) and described the unprecedented oxygento-iron migration reaction of the carbyne alkyl group.^{2,3} As shown in Scheme 1, the overall transformation involves not only alkyl migration but also metal-metal bond cleavage to give $MeCpMn(CO)_3$ and what could be the 16-electron fragment CpFe(CO)R (R = CH₃, CH₂-CH₃) which is then trapped by phosphine to give CpFe-(CO)(L)R $(L = PPh_3, R = CH_3; L = PPh_2Me, R =$ CH₂CH₃). Determination of whether migration reactions are intramolecular or intermolecular is a necessary step in any mechanistic study and is particularly urgent here due to the fact that cluster cleavage occurs. Preliminary work reported for the methoxycarbyne case revealed the presence of intermolecular methyl exchange reactions,² and the 16-electron $CpFe(CO)CH_3$ fragment⁴ seemed to be a reasonable candidate for mediation of the observed methyl scrambling. In order to test this hypothesis we sought to remove the CpFe- $(CO)CH_3$ by trapping at a faster rate with increased amounts of PPh₃, but such efforts fail because 1 additionally undergoes S_N2 dealkylation by PPh₃ to give the MePPh₃⁺ salt 3,³ a reaction that also occurs readily with a related iron-chromium methoxycarbyne.⁵ Clearly the dealkylation reaction needed to be slowed down in order to implement faster trapping by using higher phosphine concentrations or even more nucleophilic phosphines. Since $S_N 2$ reactions of *ethyl* electrophiles are known to be much slower than those of *methyl* electrophiles,⁶ we chose to examine the *ethoxy*carbyne 2. While the $S_N 2$ reaction was in fact eliminated even

^{*} Abstract published in Advance ACS Abstracts, August 1, 1995.

 ^{(1) (}a) Queens College. (b) University of California.
 (2) Fong, R. H.; Hersh, W. H. Organometallics 1985, 4, 1468-1470.
 (3) Fong, R. H.; Lin, C. H.; Idmoumaz, H.; Hersh, W. H. Organo-U. Organization and the second metallics 1993, 12, 503-516.

⁽⁴⁾ Hersh, W. H.; Hunte, F.; Siegel, S. Inorg. Chem. 1993, 32, 2968-2971.

⁽⁵⁾ Wang, B.; Hersh, W. H.; Rheingold, A. L. Organometallics 1993, 12, 1319-1330.

⁽⁶⁾ March, J. Advanced Organic Chemistry, 4th ed.; Wiley-Interscience: New York, 1992; pp 228, 339.





in the presence of the more nucleophilic PPh₂Me ligand, products form which are *still* due to *inter*molecular migration despite the presumed faster trapping of putative CpFe(CO)CH₂CH₃. In this paper we report details of these new crossover studies and show that scrambling of the ethyl label can occur *after* the initial migration from oxygen to metal via metal hydrides formed by β -hydride elimination from intermediate iron ethyl species.

Results

Kinetics of Thermal Decomposition. The major products of thermal decomposition of ethoxycarbynes 2a,b are shown in Scheme 1. Characterizations of starting materials and products have been described previously³ and so are only summarized here. In the absence of phosphines decomposition of 2a or 2b gives $MeCpMn(CO)_3$ in high yield but $CpFe(CO)_2CH_2CH_3$ or $MeCpFe(CO)_2CH_2CH_3$, respectively, in low yields. Alkyl cleavage also evidently occurs, with formation of ethane, ethylene, and $[CpFe(CO)_2]_2$; since CO is the limiting reagent, $[CpFe(CO)]_4$ forms⁷ as the major iron-containing product, along with an uncharacterized precipitate. In the presence of PPh₂Me the stoichiometrically formed products are MeCpMn(CO)₃ and CpFe(CO)(PPh₂Me)- CH_2CH_3 (4a) or $MeCpFe(CO)(PPh_2Me)CH_2CH_3$ (4b) from 2a or 2b, respectively. First-order decomposition of **2a** (Figure 1) was observed at 65 °C in C_6D_6 with virtually identical rate constants both in the absence and presence of PPh_2Me (Table 1, runs 1 and 2). Since the rate is completely independent of phosphine concentration, large excesses of PPh₂Me were not necessarily used in subsequent mechanistic runs. The bis MeCp analog 2b decomposes at a slightly faster rate (run 6), while the CD_2CD_3 analogs **2a**- d_5 and **2b**- d_5 each decompose more slowly. Kinetic deuterium isotope effects were calculated by computing the weighted averages⁸ of the rate constants for decomposition of each



Figure 1. First-order plots of decomposition of ethoxycarbynes **2a** (Table 1, run 1), **2a**- d_5 (run 5), **2b** (run 6), and **2b**- d_5 (run 3). For readability the plots have been adjusted to give zero intercepts, rather than using the value of the first point by plotting $\ln([carbyne]_t/[carbyne]_{t=0})$ as usual, since the first points did not all fall on the least-squares fit lines.





of the ethoxycarbyne analogs 2a, 2a- d_5 , 2b, and 2b- d_5 using all of the data in Table 1; results are collected in Table 2.

Carbyne Crossover Experiments. Two crossover experiments were carried out for the ethoxycarbynes as shown in Scheme 2, one between **2a** and **2b**- d_5 and one between **2a**- d_5 and **2b** (runs 3 and 4). Both gave essentially complete scrambling of the ethyl label. Analysis of these reactions was complicated by the fact that the ethyl CH₃ signals of the products **4a**,**b** overlap with each other and with the phosphine methyl, as does the downfield member of the two diasterectopic CH₂ hydrogens in **4a**. However, the separation of the upfield

⁽⁷⁾ Landon, S. J.; Rheingold, A. L. Inorg. Chim. Acta 1981, 47, 187-189.

⁽⁸⁾ Hamilton, W. C. Statistics in Physical Science; The Ronald Press Co.: New York, 1964; pp 43, 78.

Table 1.	Summary of Experimental Data: Rate Constants for Carbyne Decomposition and Carbyne and						
Product Crossover Results ^a							

run	[carbyne] (M)	[L] (M)	[additive](M)	$10^4 k \; ({ m s}^{-1})^a$	crossover ^b
1	[2a] = 0.042	$[PPh_2Me] = 0$		1.06 ± 0.04	- restance
2	[2a] = 0.065	$[PPh_2Me] = 0.675$		0.986 ± 0.027	
3	[2a] = 0.048	$[PPh_2Me] = 0.123$	$[2b-d_5] = 0.048$	1.10 ± 0.028	ves
4	$[2a - d_5] = 0.027$	$[PPh_2Me] = 0.081$	[2b] = 0.023	0.568 ± 0.040	ves
5	$[2a-d_5] = 0.027$	$[PPh_2Me] = 0.083$	[4b] = 0.026	0.517 ± 0.017	no (4a - h_5 not detected after 9.4 h)
6	[2b] = 0.047	$[PPh_2Me] = 0.093$		1.38 ± 0.03	· · · · · · · · · · · · · · · · · · ·
4	[2b] = 0.023	$[PPh_{2}Me] = 0.081$	$[2a-d_5] = 0.027$	1.27 ± 0.05	ves (see run 4 above)
7	[2b] = 0.046	$[PPh_2Me] = 0.100$	$[C_2H_4] = 0.16$	1.12 ± 0.10	5% yield 5b , 5% C ₂ H ₆ , 50% 4b , 76% MeCpMn(CO) ₃
8	[2b] = 0.016	$[PPh_2Me] = 0.034$	$[C_2H_4] = 0.03$	1.39 ± 0.06	10% yield 5b , 5% C ₂ H ₆ , 53% 4b , 94% MeCpMn(CO) ₃
9 ^c	[2b] = 0.019	$[PPh_2Me] = 0.063$	[5a] = 0.020	1.23 ± 0.11	yes; $5a:5b \approx 2:1$ (65% exchange) after 23% conversion of 2b and 1:1 (100% exchange) after 38% conversion of 2b; 36% yield $5a + 5b$, 41% $4a + 4b$ 30% C.H. 4% C.H.
10	$[\mathbf{2b}^{-13}C] = 0.030$	$[PPh_2Me] = 0.056$		1.67 ± 0.21	no exchange of ¹³ C from CH ₂ to CH ₃ of ethyl group in $4b$ - ¹³ C; 5b detected
11	$[\mathbf{2b}^{-13}C] = 0.022$	$[PPh_2Me] = 0.070$	[2a] = 0.024		no exchange of ¹³ C from CH ₂ of 2b - ¹³ C to CH ₂ of 2a after \sim 50% conversion (95 min); complete exchange of ¹³ C in CH ₂ of 4a - ¹³ C and 4b - ¹³ C
3	$[2\mathbf{b} \cdot d_5] = 0.048$	$[PPh_{9}Me] = 0.123$	[2a] = 0.048	0.882 ± 0.019	ves (see run 3 above)
12	$[2\mathbf{b} \cdot d_5] = 0.034$	$[PPh_{2}Me] = 0.095$	[4a] = 0.034	0.96 ± 0.04	no (4b - h_5 not detected after 6.2 h)
13	$[2\mathbf{b} \cdot d_5] = 0.026$	$[PPh_{9}Me] = 0.134$	$[C_2H_4] = 1.17$	0.86 ± 0.02	no (4b - h_5 not detected after 9.4 h)
14	$[2\mathbf{b} \cdot d_5] = 0.028$	$[PPh_2Me] = 0.079$	$[C_{2}H_{4}] = 0.19, [2a] = 0.027$	0.72 ± 0.06	ves (same as without C_2H_4)
15	$[2\mathbf{b} \cdot d_5] = 0.024$	$[PPh_2Me] = 0.076$	$[\text{phenol}]^d = 0.030, [2a] = 0.025$	0.73 ± 0.09	ves (same as without phenol)
16	$[2b-d_5] = 0.022$	$[PPh_2Me] = 0.067$	$[galv]^e = 0.011, [2a] = 0.022$	0.97 ± 0.07	ves (same as without galvinoxyl)
17	$[\mathbf{2b} \cdot d_5] = 0.022$	$[PPh_2Me] = 0.064$	[PhSH] = 0.008, [2a] = 0.022	0.83 ± 0.04	yes (same as without PhSH; 1:1 5a:5b detected)
18	$[\mathbf{2b} \cdot d_5] = 0.028$	$[PPh_2Me] = 0.087$	$[CCl_4] = 0.06, [\mathbf{2a}] = 0.028$	0.69 ± 0.08	yes (crossover of 4a and 4b same as without CCl ₄ ; no 5a or 5b detected; yields are low)
19		$[PPh_2Me] = 0.014$	$[\mathbf{4b}] = 0.031, [\mathbf{5a}] = 0.024$		no (4a not detected after 22.5 h; 5a:5b \approx 92.8)

^{*a*} All data collected in C_6D_6 solvent at 65 °C. ^{*b*} Crossover of alkyl label between **2a** and **2b**, except as noted. Ethyl exchange could not be quantified but by inspection was judged to be complete in all cases. ^{*c*} See Experimental Section for further details of this run. ^{*d*} Phenol = 2,6-di-*tert*-butyl-4-methoxyphenol. ^{*e*} galv = galvinoxyl.

Table 2.	Weighted	Average	Rate	Constants	for	
Ethoxycarbyne Decomposition ^a						

compd	$10^4 k \; ({ m s}^{-1})$	$k_{ m H}/k_{ m D}$
2a	1.05 ± 0.02	
$2a \cdot d_5$	0.52 ± 0.02	2.0 ± 0.1
2b	1.34 ± 0.02	
$\mathbf{2b}$ - d_5	0.87 ± 0.01	1.54 ± 0.03

^a Data taken from runs 1-3 (**2a**; see Reaction section of Experimental Section), 4-5 (**2a**- d_5), 4, 6-9 (**2b**), and 3, 12-18 (**2b**- d_5).

member of the diastereotopic CH_2 hydrogens in 4a,b is just great enough to carry out the analysis, despite its presence in each as a 16-line multiplet due to phosphorus and hydrogen coupling. However, since this signal overlapped that due to the ethane at δ 0.79 that formed in the reaction,³ the samples were routinely stripped of solvent and volatiles and run through a short chromatography column before analysis. Acetone- d_6 was found to give slightly better separation than deuterated benzene, toluene, CD₂Cl₂, CD₃NO₂, and C₆D₅NO₂, and PPh₂Me was found to give slightly better separation and cleaner reactions than PPhMe₂ or PPh₃; PMe₃ apparently gave dealkylation as shown in Scheme 1 for 1 and PPh₃ to in this case give (presumably) $[Cp(CO)Fe(\mu -$ CO)₂Mn(CO)MeCp][Me₄P]. At 500 MHz, the spectra could be analyzed directly (Figure 2a-d), while at 200 MHz the separation was marginal although on a qualitative basis the presence of ethyl scrambling was clear. Nevertheless, irradiation of the coincident CH_3 resonances of the products, and partial decoupling of the nearby remaining diastereotopic CH_2 proton, reduced the complex multiplet to a broad doublet for **4a** or **4b**, or a broad triplet for the 1:1 mixture, that could be simply and convincingly interpreted (Figure 2e-h).

Ethoxycarbyne Crossover Control Experiments. In order to look for ethyl exchange in the carbynes, a crossover reaction was run to partial completion and the carbyne composition analyzed by FAB mass spectrometry (Xe, m-nitrobenzyl alcohol matrix). No molecular ion peaks due to any carbynes were observed, perhaps due to decomposition in the presence of PPh_2Me . In order to avoid mass spectrometry, the experiment was conducted using **2b** labeled with ${}^{13}C$ (99% enrichment) in the CH_2 group of the ethoxycarbyne ligand (2b-¹³C), allowing the starting materials 2a and 2b-¹³C to be examined directly by ¹³C NMR spectroscopy for scrambling of the ${}^{13}CH_2CH_3$ group (run 11, Scheme 3). The CH_2 resonances for each of the cis and trans isomers of 2a,b are separated by about 0.2 ppm, and the DEPT-135 sequence was used to suppress the methylcyclopentadienyl methine signals since they have similar chemical shifts.³ As can be seen in Figure 3, no exchange of the ethyl between $2b^{-13}C$ and 2a occurred after the reaction was 50% complete. However, complete exchange in the products $4a^{-13}C$ and $4b^{-13}C$ is clearly shown by the similar heights of the ¹³C-labeled product



Figure 2. ¹H NMR spectra of representative final reaction mixtures showing the upfield FeC(H)HCH₃ multiplets of 4a,b, 4a- d_5 , and 4b- d_5 in acetone- d_6 . Spectra (a)-(d) were taken at 500 MHz, and (e)-(h) at 200 MHz with homonuclear decoupling of the C(H)HCH₃ hydrogens (irradiation at δ 1.114). The difference in chemical shift between the two sets of spectra is due to the high decoupler power required for (e)-(h), since the irradiated hydrogens do not have coincident chemical shifts. Key: (a) Crossover reaction of 2a- d_5 and 2b (run 4) showing a mixture of 4a and 4b; (b) "control" crossover of 2b- d_5 and 4a showing only 4a (run 12); (c) 4b; (d) 4a; (e) crossover reaction of 2a and 2b- d_5 in the presence of ethylene (run 14) showing mixture of 4a and 4b; (f) control reaction of 4b and 5a showing only 4b (run 19); (g) 4b; (h) 4a.

peaks (which are doublets due to coupling to phosphorus) and so confirms the results previously obtained by ¹H NMR (Figure 2a,e). No other peaks from **2a**, **2b**, **4a**, or 4b due to natural abundance ¹³C were visible. Lastly, the "control" crossover between ethoxycarbyne $2a-d_5$ and product 4b (run 5, Scheme 4), as well as that between 2b- d_5 and 4a (run 12, Figure 2b), gave no crossover at all. It is interesting to note that no ethane was detected in these reactions, indicating that this product arises from the decomposing carbyne (and so would be C_2D_6 here), although some ethylene was still seen. Since in these cases no crossover was observed between the products $4\mathbf{a}$ - d_5 and $4\mathbf{b}$, and between $4\mathbf{a}$ and **4b**- d_5 , it was unnecessary to carry out a separate crossover reaction between the ethyl products 4a and **4b**- d_5 (for instance) as a check on the source of exchange in the carbyne crossover experiment between (for instance) 2a and 2b- d_5 .

Due to the presence of ethane and ethylene in the product mixtures upon ethoxycarbyne decomposition, a



Figure 3. ¹³C NMR spectra of **2b**-¹³C, **2a**, and **4a**,**b** in C₆D₆ at 50 MHz showing the ethoxycarbyne methylene singlets near 83 ppm due to the cis and trans isomers³ and the product FeCH₂CH₃ doublets (due to phosphorus coupling) near -3 ppm: (a) DEPT-135 NMR (C₆D₆) of the crossover reaction of **2b**-¹³C and **2a** run to 50% completion (run 11) showing only unreacted **2b**-¹³C (with no formation of **2a**-¹³C) but complete exchange of **4a**-¹³C and **4b**-¹³C; (b) broadband decoupled spectrum of **2a**; (c) broad-band decoupled spectrum of **4b**.

Scheme 3. ¹³C Crossover Experiment: Products and Unreacted Starting Materials



series of experiments was conducted to probe for the presence of radical species or the involvement of β -e-limination reactions that might lead to crossover (Scheme 5). In all cases **2a** and **2b**- d_5 were used since they decompose at similar rates, compared to **2a**- d_5 and **2b** (Table 2). No changes in crossover or rate of decomposition were seen upon addition of 2,6-di-*tert*-butyl-4-methoxyphenol, galvinoxyl, or thiophenol (runs 15–17). For CCl₄ (run 18), decomposition (to unknown products) of the starting ethoxycarbynes commenced before heating and very low yields of **4a**,**b** were obtained, although crossover still occurred.

The β -elimination pathway, even more than the radical pathway, would provide an obvious intermolecular exchange mechanism. Given the complexity of the ¹H NMR signals, it was considered possible that *ethylene* exchange was occurring rather than *ethyl* exchange. Decomposition of **2b** in the presence of ethylene occurred at the same rate as in the absence of



ethylene (runs 7 and 8). More convincingly, reaction of 2b- d_5 in the presence of 45 equiv of ethylene (run 13) did not result in the formation of any 4b- h_4 or 4b- h_5 , and again the rate of reaction was unaffected. The crossover reaction between 2a and 2b- d_5 was also unaffected by ethylene (run 14). Lastly, decomposition of 2b- ^{13}C , where the ethyl group is selectively labeled at the CH₂ carbon, gave only 4b-1- ^{13}C , with no evidence from ¹H or ¹³C NMR of scrambling of the label from the CH₂ carbon into the methyl carbon (run 10, Scheme 5). The ¹³C crossover experiment described above (Scheme

3, Figure 3) confirms this result. All of these experiments clearly show that *reversible* ethylene exchange does not occur.

While β -elimination as a *stoichiometric* exchange pathway is precluded by the above results, the direct involvement of CpFe(CO)(PPh₂Me)H (5a), the presumed organometallic product of β -elimination from 2a in the presence of PPh₂Me, was examined next since the PPh₃ and PPhMe₂ analogs are known stable compounds.⁹⁻¹¹ A search in the hydride region of the ¹H NMR spectra of a number of reactions (runs 7, 8, 17) indeed revealed the presence of hydride doublets (due to phosphorus coupling) due to authentic 5a (-13.44 ppm) and/or (presumably) MeCp analog **5b** (-13.36 ppm; the hydride signal of $MeCpFe(CO)_2H$ is 0.12 ppm downfield of that of $CpFe(CO)_2H$,¹¹ comparable to the 0.08 ppm difference here). The only experiment in which the NMR was searched unsuccessfully for 5a,5b was run 18 involving hydride scavenger CCl₄,¹²⁻¹⁴ but the low product yields do not allow us to rule out sensitivity limitations as the cause. While the control crossover experiments between carbynes $2a \cdot d_5$ or $2b \cdot d_5$ and 4b or 4a had given no exchange, the substoichiometric formation of hydrides **5a,b** left open the possibility of a *catalytic* exchange process. The hydride crossover experiments shown in Scheme 6 therefore were carried out, and this time carbyne **2b** and hydride **5a** gave complete scrambling of both the ethyl and hydride labels on the Cp and MeCp products 4a,b and 5a,b (run 9). Since no exchange occurred between the products 4b and 5a (run 19), this hydride-induced ethyl exchange reaction provides a sufficient mechanism for carbyne crossover. A catalytic crossover mechanism consistent with these results is presented in the Discussion.

Discussion

Mechanism of Alkyl Migration. The decomposition of the ethoxycarbyne follows unimolecular kinetics. as evidenced by the linear first-order plots of decomposition. While it might be argued that NMR kinetics are not sufficiently precise to observe the curvature in a log plot that would be indicative of bimolecular kinetics, in fact similar rate constants have been observed in some runs where fairly different starting concentrations of the carbynes were used; for instance in run 2 [2a] is 1.5 times [2a] in run 1, in run 7 [2b] is 3 times [2b] in run 8, and in run 3 [**2b**- d_5] is 2 times [**2b**- d_5] in run 16. Moreover, bimolecular plots (i.e. 1/[2a] vs *t* rather than the first-order plot of $\ln [2a]$ vs t) give curved plots with a variety of rate "constants". Carbyne decomposition is zero-order in PPh_2Me , and no S_N2 dealkylation of the carbyne (to give $EtPPh_3^+$ salts) is observed. This result is particularly gratifying since it formed the basis for choosing to examine **2a** as described in the Introduction, but it is also somewhat surprising given the relative

⁽⁹⁾ Kalck, P.; Poilblanc, P. C. R. Acad. Sci., Ser. C 1972, 274, 66-69.

⁽¹⁰⁾ Reger, D. L.; Culbertson, E. C. J. Am. Chem. Soc. 1976, 98, 2789-2794.
(11) Shackleton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnston,

 ⁽¹¹⁾ Snackleton, T. A.; Mackle, S. C.; Fergusson, S. B.; Johnston,
 L. J.; Baird, M. C. Organometallics 1990, 9, 2248–2253.
 (12) Piper, T. S.; Wilkinson, G. J. Inorg. Nucl. Chem. 1956, 3, 104–

⁽¹³⁾ Figer, F. S., Wikinson, G. S. *Integ. Place: Chem.* 1000, 5, 104
(13) Bainbridge, A.; Craig, P. J.; Green, M. J. Chem. Soc. A 1968,

⁽¹³⁾ Bainoridge, A.; Craig, P. J.; Green, M. J. Chem. Soc. A 1908, 2715–2718.

⁽¹⁴⁾ Green, M. L. H.; Knowles, P. J. J. Chem. Soc., Perkin Trans. 1 1973, 989–991.

Scheme 6. Hydride Crossover Experiments



Scheme 7. A Proposed Mechanism of Ethoxycarbyne Decomposition



ease with which dealkylation of 1 by the less nucleophilic phosphine¹⁵⁻¹⁷ PPh₃ occurs.

A proposed mechanism for the unimolecular decomposition reaction is shown in Scheme 7. The relevant data on which to base speculation are that there is a kinetic deuterium isotope effect for the ethoxycarbyne decomposition $(k_{\rm H}/k_{\rm D} = 2.0 \pm 0.1 \text{ for } 2a \text{ and } 1.54 \pm 0.03$ for 2b), the methylcyclopentadienyl iron ethoxycarbynes decompose more rapidly than the cyclopentadienyl iron ethoxycarbynes $(k_{MeCp}/k_{Cp} = 1.5 \pm 0.2)$, and ethyl migration is somewhat faster than methyl migration.¹⁸ The deuterium isotope effect is a secondary kinetic isotope effect (SKIE) since C-D bond cleavage does not occur in this reaction and can be further classified as an α and/or β effect since there are deuterium atoms both α and β to the C-O bond that is cleaved. For both the α and β SKIE, observation of a normal deuterium isotope effect $(k_{\rm H}/k_{\rm D} > 1)$ is associated with rehybrid-

Scheme 8. "Nucleophilic" Migration Reactions

Migration with electron pair to electrophilic metal



ization at the cleavage site from sp³ to sp^{2.6,19} While interpretation of secondary isotope effects is still an active area of research,²⁰⁻²⁵ such a rehybridization would appear to be *inconsistent* with alkyl migration with its electron pair, a reaction that would be related formally to β -hydride elimination (Scheme 8).²⁶⁻²⁸ Despite this, Gable²⁵ has recently argued that alkyl migration in a rhenium diolate system *is* consistent with observation of a normal SKIE, and as shown in Scheme 8, the rhenium system is a remarkably good analog of ours. The rate-determining step was proposed to be migration of the methylene carbon from oxygen to metal, although since no S_N1 character was proposed, a normal β secondary isotope effect due to hyperconju-

⁽¹⁵⁾ Honeychuck, R. V.; Hersh, W. H. Inorg. Chem. 1987, 26, 1826–1828.

⁽¹⁶⁾ Bush, R. C.; Angelici, R. J. Inorg. Chem. **1988**, 27, 681–686. (17) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. Organometallics **1989**, 8, 1–7.

⁽¹⁸⁾ Hersh, W. H.; Fong, R. H. Manuscript in preparation.

 ⁽¹⁹⁾ Carey, F. A.; Sundberg, R. J. Advanced Organic Chemistry, Part
 A: Structure and Mechanisms, 3rd ed.; Plenum Press: New York, 1990;
 pp 218-220.

⁽²⁰⁾ Wolfe, S.; Kim, C. K. J. Am. Chem. Soc. 1991, 113, 8056-8061.
(21) Poirier, R. A.; Wang, Y. L.; Westaway, K. C. J. Am. Chem. Soc.

¹⁹⁹⁴, *116*, 2526–2533. (22) Hostetler, M. J.; Bergman, R. G. J. Am. Chem. Soc. **1992**, *114*, 7629–7636.

 ⁽²³⁾ Abuhasanayn, F.; Kroghjespersen, K.; Goldman, A. S. J. Am. Chem. Soc. 1993, 115, 8019-8023.

⁽²⁴⁾ Gajewski, J. J.; Brichford, N. L. J. Am. Chem. Soc. 1994, 116, 3165-3166.

⁽²⁵⁾ Gable, K. P.; Phan, T. N. J. Am. Chem. Soc. 1994, 116, 833-839.

⁽²⁶⁾ Thorn, D. L.; Hoffmann, R. J. Am. Chem. Soc. **1978**, 100, 2079–2090.

⁽²⁷⁾ Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. J. Am. Chem. Soc. 1985, 107, 7109-7116.

⁽²⁸⁾ Delbecq, F. Organometallics 1990, 9, 2223-2233.



Ethyl migration via nucleophilic Fe attack



gation⁶ was not considered. Hence only the two deuterium atoms in the α KIE were presumed to be involved, giving a reasonable SKIE of ~1.1 per deuterium atom. In **2a**, the SKIE assuming only an α SKIE of 1.4 per deuterium atom is high, but if comparable α and β effects were operative, the effect spread out over *five* deuterium atoms would be a more palatable 1.15 per atom. Unlike Gable's system, however, this would imply S_N1 character in the ethyl migration transition state.

If one accepts that the SKIE is indicative of S_N1 character in the migration, then the reactions in Scheme 8 that involve electron-pair migration to an electrophilic metal are not appropriate models for carbyne decomposition. Support for S_N1 character in the ethyl migration comes from the electrophilic character of the carbon bound to the carbyne oxygen, as seen for instance by the $S_N 2$ dealkylation of 1 to give 3 (Scheme 1), the X-ray crystal structure of 2a which shows the sp² hybridization of the carbyne oxygen atom³ which presumably polarizes the C-O bond toward electrophilic cleavage, and the even higher degree of dealkylation of a related iron-chromium methoxycarbyne.⁵ Rather than the β -hydride mode of alkyl migration, then, we instead picture the migration as shown in Scheme 9 proceeding via a nucleophilic attack of iron on the ethyl group. Molecular orbital calculations on isoelectronic [CpFe- $(CO)]_2(\mu$ -CO) $(\mu$ -L) compounds²⁹ do not appear to support or reject either of the two directions of electron flow represented by Schemes 8 and 9. The HOMO is metalbased although not energetically isolated, so a number of orbitals might serve to attack the alkyl group, while the LUMO is M–M σ^* antibonding in character and is located in the plane of the bridging ligands, and so could perhaps serve as an electrophilic site. The enhancement in rate for the MeCp ligand is in accord with the mechanism shown since the MeCp ligand is a better electron donor than the Cp ligand and would therefore make the iron more nucleophilic. The enhancement in rate for the ethoxycarbyne over the methoxycarbyne is in accord with this mechanism since to the extent that there is any S_N1 character to the reaction, positive charge buildup on the ethyl CH2 carbon would be easier than on the methyl group of the methoxycarbyne. Clearly such detailed conclusions drawn on the basis of the combined α and β SKIE are speculative, but two more general conclusions are warranted: ethyl migration occurs in the rate-determining step and the kinetic isotope effect is large relative to those that have been reported. We would also suggest a third conclusion: the SKIE merits scrutiny in simpler but better understood migration reactions.

In addition to providing supporting evidence of nucleophilic attack of iron on the ethyl group, the MeCp





effect provides suggestive evidence that the migration occurs directly to iron rather than manganese, although we have not measured rates for any CpMn analogs for comparison. The proposed electronically saturated intermediate (Scheme 7) formed via the electrophilic or nucleophilic pathways would consist of MeCpMn(CO)₃ side-bound to the iron, and it is reasonable to suggest that this species will rapidly decompose via cleavage of the Fe-Mn and μ -CO bonds to give the 16-electron intermediate CpFe(CO)Et. In the absence of an external trapping ligand, decomposition of CpFe(CO)Et apparently occurs via β -hydride elimination to give ethane and ethylene, while scavenging of CO from more extensive decomposition leads to the low yields of CpFe- $(CO)_2$ Et. Loss of the ethyl group yields $[CpFe(CO)_2]_2$ upon CO scavenging and the tetrameric cluster [CpFe-(CO)]₄ without any additional CO. In the presence of phosphines, the 16-electron species is trapped to give $CpFe(CO)(PPh_2Me)Et.$

We now consider an alternative saturated intermediate. Unbridging of the carbyne along with bridging of the Fe carbonyl ligand would give a terminal ethoxycarbyne complex with semibridging carbonyl ligands (Scheme 10). This mechanism has two attractive features. First, the structure of the intermediate is based on that of isoelectronic Co-Mn and Rh-Mn semibridged compounds such as Cp(PMe₃)Co(μ -CO)₂Mn(CO)MeCp, which further undergo ligand-induced Co-Mn cleavage with expulsion of MeCpMn(CO)₃ and formation of CpCo-(PMe₃)L as shown.³⁰⁻³² Second, we have previously noted that carbyne unbridging must be involved in cis/ trans isomerization of alkoxycarbynes,^{3,5} and so this mechanism allows an attractive albeit unrequired con-

⁽²⁹⁾ Bursten, B. E.; Cayton, R. H. J. Am. Chem. Soc. 1986, 108, 8241-8249.

⁽³⁰⁾ Leonhard, K.; Werner, H. Angew. Chem., Int. Ed. Engl. 1977, 16, 649-650.

⁽³¹⁾ Werner, H.; Juthani, B. J. Organomet. Chem. 1981, 209, 211-218.

⁽³²⁾ Werner, H. Pure Appl. Chem. 1982, 54, 177-188.

nection to that reaction channel. We note that carbyne migration to either metal is reasonable since the carbyne bridge is nearly symmetrical as seen from the X-ray crystal structure of **2a**,³ despite the formal double bond to manganese. While the analogy between the cleavage of the terminal ethoxycarbyne and the Co-Mn model appears close since both yield CpMn(CO)₃ and ligand adducts of the remainder of the heterodinuclear species, the Co-Mn reaction is bimolecular while the carbyne reaction is not. However, this difference could arise readily from the differing stabilities of these species. Since the rate-determining step apparently involves ethyl migration rather than carbyne unbridging or cluster cleavage, decomposition of the semibridged intermediate would necessarily involve rate-determining ethyl migration either to give the previously proposed saturated intermediate with the single carbonyl bridge or to give CpFe(CO)Et directly as shown with concomitant cluster cleavage. The key difference between this mechanism and that in Scheme 9 is simply that the migration occurs from a terminal rather than a bridging ethoxycarbyne. Related migrations for proposed terminal hydroxy, stannoxy, and alkoxycarbyne intermediates or the reverse migration from metal to oxygen to give a terminal siloxycarbyne intermediate have been proposed, 33-37 and so it is possible that, in this cluster reaction as in others,³⁸⁻⁴⁰ the "interesting" chemistry occurs at a single metal site.

Mechanism of Intermolecular Alkyl Exchange. While the crossover experiments between the doublylabeled carbynes shown in Scheme 2 resulted in intermolecular ethyl exchange in the mononuclear products, they do not address the question of when or how the exchange occurs; in principle, exchange can occur at a number of testable points in the mechanism shown in Scheme 7, and these are now considered.

Alkyl exchange can in principle occur before carbyne decomposition occurs. The standard control experiment, in which a crossover reaction was run to partial conversion and then the unreacted starting carbynes examined for alkyl exchange, was carried out and analyzed by ¹³C NMR on ¹³C-labeled material (Scheme 3, run 11), but no crossover in the starting materials was observed. In principle, alkyl exchange among the carbynes could occur concomitant with carbyne decomposition, so that the unreacted carbynes would not exhibit crossover. However, such a scheme would give bimolecular decomposition kinetics, but as described above in detail (for this very reason), only unimolecular kinetics were observed.

Alkyl exchange also in principle can occur after carbyne decomposition occurs, that is, among the mononuclear products. This was not tested explicitly by reaction of (for instance) 4a and $4b-d_5$, but since no exchange was observed in the "control" crossover reactions (Scheme 4) in which one ethyl product is generated in the presence of the other, no ethyl exchange can be occurring among the mononuclear iron ethyls 4a,b and their deuterated analogs. The control crossover result stands in sharp contrast to the complete methyl crossover observed with methoxycarbyne 1 and MeCpFe(CO)- $(PPh_3)CD_3$,^{2,18} and so an explanation is required for the different methoxy and ethoxy control crossover results. We have shown that the 16-electron intermediate CpFe- $(CO)CH_3$, presumed to form from 1 in the ratedetermining step, also forms from CpFe(CO)(PPh₃)CH₃ by phosphine dissociation and at a comparable rate.⁴ Since the methyl products, like their ethyl counterparts 4a,b, do not undergo alkyl exchange by themselves during the carbyne decomposition, CpFe(CO)CH₃ alone cannot be responsible for alkyl exchange, although it may well participate in methyl exchange with a carbyne decomposition product. The absence of *ethyl* exchange in the control crossover experiment may perhaps be explained most simply by the presumed lower concentration of CpFe(CO)CH₂CH₃, if the 16-electron intermediates are involved somehow in the control crossover. Faster trapping of this intermediate by the more nucleophilic phosphine PPh₂Me compared to trapping of $CpFe(CO)CH_3$ by PPh₃ would lower the concentration of CpFe(CO)CH₂CH₃, as would rapid β -hydride elimination (see below). In complementary fashion, PPh₂Me is less labile than PPh₃; for instance PPh₂Me dissociation from CpFe(CO)(PPh₂Me)CH₃ is 36 times slower at 65 °C than is PPh₃ dissociation from CpFe(CO)(PPh₃)- CH_{3} ,⁴ and we presume the ethyl analogs follow the same trend.

An alternative explanation for the different methyl and ethyl control crossover results arises by consideration of the relative ease of alkyl group bridging of two metal centers, which presumably must occur at some point in the crossover reaction. That is, while methyl bridges between two metal atoms are well-known,⁴¹⁻⁴⁴ *ethyl* bridges (which involve bridging by the CH_2 group⁴⁵)are only well-known between electron-deficient centers such as lithium and aluminum,46-50 and even for methyl-bridged compounds, most transition metal examples involve high-oxidation-state electron-deficient metals.^{41,43,44} The best-studied cases are the aluminum alkyls, where two types of experiment show that methyl bridging is favored over ethyl bridging but not by a large amount: the "trialkyl" aluminum species R₃Al exist predominantly (typically >96%) as the dimers $R_2Al(\mu$ - $R_{2}AlR_{2}$ in solution (R = Me, Et, Pr, n-Bu, n-octyl), but the equilibrium shifts toward the monomer with increasing size of the alkyl group,^{49,50} and in the mixed dimer Et₃Me₃Al₂ the methyl group is favored in the bridging site by a factor of 6.48 Rare examples of μ -alkyl (other than μ -methyl) complexes involving metal carbonyl compounds include one having an ethyl-bridged

⁽³³⁾ Nicholas, K. M. Organometallics 1982, 1, 1713-1715.

⁽³⁴⁾ Schubert, U.; Hörnig, H. J. Organomet. Chem. 1987, 336, 307-315

⁽³⁵⁾ Schubert, U. J. Organomet. Chem. 1988, 358, 215-228.

⁽³⁶⁾ Chatani, N.; Fukumoto, Y.; Murai, S. J. Am. Chem. Soc. 1993, 115, 11614-11615.

⁽³⁷⁾ Gibson, D. H.; Ye, M.; Sleadd, B. A.; Mehta, J. M.; Mbadike, O. P.; Richardson, J. F.; Mashuta, M. S. Organometallics 1995, 14, 1242-1255

⁽³⁸⁾ Bergman, R. G. Acc. Chem. Res. 1980, 13, 113-120.

⁽³⁹⁾ Fyhr, C.; Garland, M. Organometallics 1993, 12, 1753-1764. (40) Garland, M. Organometallics 1993, 12, 535-543.

⁽⁴¹⁾ Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. Chem. Rev. 1983, 83, 135-201. (42) Bursten, B. E.; Cayton, R. H. Organometallics 1986, 5, 1051-

^{1053.}

⁽⁴³⁾ Theopold, K. H. Acc. Chem. Res. 1990, 23, 263-270.
(44) Waymouth, R. W.; Potter, K. S.; Schaefer, W. P.; Grubbs, R. H. Organometallics 1990, 9, 2843-2846.

⁽⁴⁵⁾ Yamamoto, O. Bull. Chem. Soc. Jpn. 1964, 37, 1125-1128.
(46) Brown, T. L. Adv. Organomet. Chem. 1965, 3, 365-395.
(47) Oliver, J. P. Adv. Organomet. Chem. 1970, 8, 167-209.

⁽⁴⁸⁾ Yamamoto, O.; Hayamizu, K. J. Phys. Chem. 1968, 72, 822-

⁸²⁸ (49) Smith, M. B. J. Organomet. Chem. 1974, 70, 13-33.

⁽⁵⁰⁾ Oliver, J. P. Adv. Organomet. Chem. 1977, 16, 111-130.

Alkyl Migration in Fe-Mn Complexes

Os-Os bond⁵¹ and another having a *p*-methylbenzylbridged W-Re bond.⁵² Thus, even if carbyne decomposition yields some intermediate that initiates methyl bridging from product CpFe(CO)(PPh₃)CH₃ and consequent methyl exchange in the control crossover reaction, the analogous *ethyl* bridging from product **4** might not occur and so preclude exchange in the ethyl control crossover reaction. The fact that crossover nevertheless occurs between carbynes 2a and 2b-d5, and between 2a d_5 and **2b** paradoxically requires that there be an alkyl exchange pathway in the ethyl case that need not be present in the methyl case.

A radical exchange mechanism is one possibility that would be more likely for ethyl than methyl radicals.^{53,54} However, the similarity in rates, and high reproducibility for the ethoxycarbyne kinetics in particular.⁵⁵ argue against the involvement of radicals in the ratedetermining step. A number of additives (Scheme 5) were found to have no effect on either the rate or crossover reaction for the ethoxycarbynes, as well. Two of the additives, 2,6-di-tert-butyl-4-methoxyphenol and galvinoxyl, are used to initiate and/or quench radical reactions by forming and intercepting radical chain carriers.^{11,53,56,57} Thiophenol was tried on the basis of its stabilization of CpFe(CO)₂H,¹¹ which was suggested to be due to trapping of adventitious 1-electron oxidizing reagents. Lastly, CCl₄ was tried since it too can trap organometallic radicals $^{58-60}$ as well as hydrides by donation of a chlorine atom, but as noted, it caused decomposition of the starting carbynes; only very low yields of product, which nevertheless exhibited crossover, were obtained.

With establishment that radicals are unlikely to be involved, the obvious pathway that could be available to the ethoxycarbyne but not the methoxycarbyne would involve β -elimination. Of particular interest is a result due to Reger¹⁰ shown in Scheme 11. Thermal loss of PPh₃ gives the 16-electron intermediate shown which 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 PPh₃ displaces the ethylene to give the hydride product. In the presence of PPh₃, no reaction occurs, so presumably the β -elimination step is not reached. A number of reactions established that reversible β -elimination was not occurring for the ethoxycarbyne. Free ethylene had no effect on the reaction and was not incorporated into the product (Scheme 5, runs 7, 8, 13, 14), and most convincingly use of ethoxycarbyne specifically ¹³C-labeled at the methylene of the ethyl group gave rise to no scrambling of

(54) Hudson, A.; Lappert, M. F.; Lednor, P. W.; MacQuitty, J. J.; Nicholson, B. K. J. Chem. Soc., Dalton Trans. **1981**, 2159–2163. (55) The ethoxycarbynes follow what we call "bicoastal kinetics"; that

is, the same rate constants were obtained in Los Angeles and New York and by different workers using different equipment.

(60) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. J. Am. Chem. Soc. **1983**, 105, 6018-6021.

Scheme 11



this label into the methyl position in the mononuclear products (Scheme 5, runs 10, 11). Since trapping of photochemically-generated CpFe(CO)CH₂CH₃ by PPh₃ is known to be faster than β -elimination,⁶¹ it is not surprising that even if this 16-electron intermediate forms, it will be trapped by PPh₂Me faster than entry into the reversible ethylene manifold. But since ethylene is in fact a reaction product, displacement of ethylene by PPh₂Me must simply be faster than olefin insertion to give back the 16-electron intermediate, and the expected hydride would be a stable compound.^{10,11} Small amounts were indeed found in the ethoxycarbyne decomposition reactions and prompted the crossover reaction between 2b and 5a (Scheme 6, run 9). In contrast to the control crossover, complete exchange of hydride and ethyl groups occurred between the iron centers of the Cp hydride 5a and the MeCp carbyne decomposition product 4b. This result could also occur by direct scrambling between the mononuclear alkyl and hydride products, but the control experiment between 4b and 5a shown in Scheme 6 (run 19) eliminated that mechanism and demonstrated the necessity of the carbyne for exchange.

The mechanism shown in Scheme 12 is proposed to take advantage of the presence of this hydride in order to generate the crossover results. The key facts that any ethyl exchange scheme must account for are that there is no reversible β -elimination, the ethyl group is exchanged intact without scrambling of the two carbons, and there is no exchange once the iron alkyl products are formed. This last point arises from the control crossover (Scheme 4), where the "other product" that is already present does not exchange with the carbynederived product. Thus, not only do the products not undergo exchange among themselves, the decomposing carbyne yields no products that mediate exchange among the existing products. As shown in Scheme 12, we propose that the 16-electron intermediate CpFe(CO)-CH₂CH₃ formed in the rate-determining step from carbyne **2a** can (1) be trapped by PPh_2Me to give product

⁽⁵¹⁾ Cree-Uchiyama, M.; Shapley, J. R.; St. George, G. M. J. Am. Chem. Soc. **1986**, *108*, 1316–1317. (52) Jeffery, J. C.; Orpen, A. G.; Stone, F. G. A.; Went, M. J. J. Chem.

Soc., Dalton Trans. 1986, 173-186.

⁽⁵³⁾ Labinger, J. A.; Osborn, J. A.; Coville, N. J. Inorg. Chem. 1980, 19, 3236-3243.

⁽⁶¹⁾ Kazlauskas, R. J.; Wrighton, M. S. Organometallics 1982, 1, 602 - 611





4a, (2) undergo β -elimination followed by substitution of ethylene with PPh_2Me to give hydride **5a**, or (3) undergo ethyl exchange via trapping by the saturated hydride 5b (or $5b-d_1$). The first outcome, trapping to give 4a, ends the involvement of the ethyl group; loss of phosphine to re-enter the exchange cycle does not occur, as shown by the control crossover where "preformed" **4b** does not exchange with product $4a \cdot d_5$. The second outcome, β -elimination to give the ethylene hydride complex and from it 5a, has precedent in the PPh_3 analog of $4a^{10}$ as seen above (Scheme 11). However, since no deuterium scrambling as well as no ¹³C scrambling has been seen, ethylene insertion to give back an iron ethyl must not occur, so formation of the ethylene hydride must be followed immediately by phosphine displacement of ethylene. The relative amount of hydrides 5a,b detected is quite small, however, so this pathway is a minor one. The third outcome leads to exchange as shown. If one starts at the point of entry into the catalytic cycle starting with **2a** going on to 16electron intermediate CpFe(CO)CH₂CH₃, then trapping of this intermediate by **5b**- d_1 generated from **2b**- d_5 is proposed to give rise to an electronically saturated hydride-bridged dinuclear complex. While ethyl-bridged species are rare as described above, hydride bridging of metal-metal bonds obviously is not, and related mechanisms involving μ -hydrides have been proposed for a number of bimolecular reductive elimination reactions.⁶²⁻⁶⁶ In addition, ethyl migration between

⁽⁶²⁾ Norton, J. R. Acc. Chem. Res. 1979, 12, 139-145.

⁽⁶³⁾ Janowicz, A. H.; Bergman, R. G. J. Am. Chem. Soc. 1981, 103, 2488-2489.

⁽⁶⁴⁾ Jones, W. D.; Huggins, J. M.; Bergman, R. G. J. Am. Chem. Soc. 1981, 103, 4415-4423.

⁽⁶⁵⁾ Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. J. Am. Chem. Soc. **1982**, 104, 619-621.

⁽⁶⁶⁾ Barborak, J. C.; Cann, K. Organometallics 1982, 1, 1726-1728.

Alkyl Migration in Fe-Mn Complexes

transition metal centers bridged by another atom has also been proposed⁶⁷ and in at least two cases observed by dynamic NMR.^{51,68} Here we propose that phosphine migration occurs concomitant with ethyl migration, and complete equilibration would make it equally likely that decomposition of this species occurs to give back the starting materials as well as the crossover hydride **5a**- d_1 and the 16-electron crossover intermediate $MeCpFe(CO)CH_2CH_3$. Trapping of this intermediate by phosphine would give the crossover product 4b, which would then be out of the catalytic exchange cycle. Hydride **5a**- d_1 would remain in the cycle, however, and could trap MeCpFe(CO)CD₂CD₃ generated from carbyne **2b**- d_5 to give the hydride-bridged intermediate required to effect ethyl- d_5 exchange. Following equilibration and cleavage, CpFe(CO)CD₂CD₃ (and ultimately crossover product $4a \cdot d_5$ along with hydride $5b \cdot d_1$ would be generated. The catalytic cycle would then have come full-circle.

One feature of this mechanism is that any of the four hydrides **5a** or **5a**- d_1 and **5b** or **5b**- d_1 can carry the chain, since the bridging hydride or deuteride is never incorporated into the ethyl products. Hydride **5a** can form directly from **2a** as can **5b**- d_1 from **2b**- d_5 , and the hydride crossover products would form in the cycle, **5b** from **5a** and **5a**- d_1 from **5b**- d_1 . Hydride crossover likely also occurs without the carbynes, since it is known that CpFe(CO)₂D and MeCpFe(CO)₂H rapidly exchange,¹¹ and we observed complete equilibration of the Cp and MeCp hydrides well before the carbyne was consumed in the reaction of **2b** and **5a**. The isotopic identity of the bridging group as hydride or deuteride, as well as the number of reaction pathways for H/D exchange, is not proposed to have any effect on ethyl exchange.

The main problem with the ethyl exchange mechanism is the proposal that hydride 5b (for instance) must trap the 16-electron intermediate $CpFe(CO)CH_2CH_3$ to give ethyl exchange at a rate comparable to that of trapping by PPh_2Me to give 4a. That is, in considering the three reaction channels available to the 16-electron intermediate CpFe(CO)CH₂CH₃, we noted that the β -elimination pathway is relatively slow, but in order for complete ethyl exchange to occur, entry into the catalytic cycle must be faster than removal from the cycle by trapping by PPh₂Me. This must be the case since the alkyl products 4a or $4a \cdot d_5$ and 4b or $4b \cdot d_5$ cannot re-enter the catalytic cycle on the basis of the control crossover experiments between (for instance) 2a and 4b- d_5 . The crossover experiments all occur in the presence of excess PPh₂Me, and so while it appears remarkable that this phosphine does not prevent formation of an ethyl exchange species by hydride bridging by 5, at present we have no simpler explanation.

Conclusion

We have discovered the first example of a novel alkoxycarbyne " β -elimination" reaction, in which an alkyl group migrates from oxygen to iron. The observed secondary kinetic isotope effect shows that ethyl migra-

tion occurs in the rate-determining step and suggests an "electrophilic" migration mechanism by which a metal electron pair attacks the alkyl group. While we have been unable to prove that this reaction is intramolecular. the facts that the reaction is unimolecular and does not involve radicals eliminate any simple candidates for an intermolecular alkyl exchange mechanism. We have, on the other hand, demonstrated that exchange can occur after alkyl migration and metal-metal bond cleavage. While the "control crossover" experiment shows that exchange does not occur between the carbyne and the *final* ethyl products, the hydride crossover experiment shows that exchange nevertheless can be mediated by the observed β -elimination product CpFe- $(CO)(PPh_2Me)H$. This isolable hydride is proposed to trap the unsaturated 16-electron species CpFe(CO)CH₂-CH₃ and catalytically give ethyl exchange via a hydridebridged intermediate. While we are uncomfortable with the counterintuitive proposal that MeCpFe(CO)(PPh₂-Me)H must trap the 16-electron species $CpFe(CO)CH_2$ - CH_3 competitively with PPh_2Me , as long as free ethyl radicals are not involved then any exchange mechanism will involve steps that at some point must pit an organometallic against PPh₂Me. Future work on these compounds must address the surprising requirement that the organometallic hydride in this case is at least as effective a kinetic trap as the donor phosphine.

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. NMR spectra were recorded on Bruker WP-200, AM-360, and AM-500 and IBM/ Bruker WP-200SY spectrometers; ¹H chemical shifts are reported relative to residual protons at δ 7.15 in C₆D₆ and δ 2.04 in acetone- d_6 , ¹³C relative to C₆D₆ at 128.0 ppm, and ³¹P relative to external H₃PO₄ at 0 ppm. Infrared spectra were obtained on a Perkin-Elmer 237 spectrometer or Mattson 4020 Galaxy FT-IR with 0.1 mm NaCl solution cells. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were obtained on an AEI-MS902 (EI) and an AEI-MS9 with FAB gun using xenon, at 5 kV in a matrix of NOBA (m-nitrobenzyl alcohol). Photolyses were carried out with a medium-pressure 450 W mercury Hanovia lamp.

All solvents were treated under nitrogen. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Hexane was purified by washing successively with 5%nitric acid in sulfuric acid, water, sodium bicarbonate solution, and water and then dried over calcium chloride and distilled from *n*-butyllithium in hexane. Acetone- d_6 was dried over molecular sieves and vacuum transferred prior to use, and benzene- d_6 was purified by vacuum transfer from sodium benzophenone ketyl. Compounds 2a,b were prepared as we have previously described.³ Triphenylphosphine was recrystallized from ethanol, Ph₃CH was recrystallized from hexane, and PPh₂Me (Pressure Chemical, Strem), galvinoxyl (Aldrich), and ethylene (Aldrich) were used as received. Iodomethane d_3 (Aldrich), iodoethane- d_5 (Aldrich), iodoethane- $1^{-13}C$ (Cambridge Isotope Laboratories), thiophenol, and TMS were vacuum transferred from CaH₂, and CCl₄ was vacuum transferred from P₂O₅.

 $Cp(CO)Fe(\mu$ - $COCD_2CD_3)(\mu$ -CO)Mn(CO)MeCp (2a- d_5). A solution of 229.9 mg (1.427 mmol) of CD_3CD_2I in 3 mL of benzene was added to a solution of 368.6 mg (1.434 mmol) of CF_3SO_3Ag in 2 mL of benzene, and the mixture was heated at 55 °C in a stopcock-sealed vessel for 12 h. The filtered solution was then added to 552.9 mg (1.417 mmol) of $[Cp(CO)Fe(\mu$ -

⁽⁶⁷⁾ Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. J. Am. Chem. Soc. **1984**, 106, 7451– 7461.

⁽⁶⁸⁾ Okeya, S.; Meanwell, N. J.; Taylor, B. F.; Isobe, K.; Vazquez de Miguel, A.; Maitlis, P. M. J. Chem. Soc., Dalton Trans. **1984**, 1453– 1460.

 $CO)_2Mn(CO)MeCp]^-Na^+$ in 25 mL of THF. After treatment as described for the protio compound,³ 150 mg of a 1:1 mixture of the desired product and $[CpFe(CO)_2]_2$ was obtained from the benzene extraction. This was then subject to preparative TLC (Aldrich 20 \times 20 cm silica plates, 250 μ m thickness) in two portions. A 65 mg fraction was eluted a total of 10 times with 1:1 benzene/hexanes, each time allowing the plate to dry before rerunning, giving $[CpFe(CO)_2]_2$ as the higher R_f band and $2a \cdot d_5$ as the lower R_f band. The lower band yielded 27 mg of a mixture that on the basis of ¹H NMR consisted of 9 mol % $[CpFe(CO)_2]_2$ and 91 mol % 2a-d₅. The remaining 85 mg of the 1:1 mixture was eluted a total of three times with 1:4 ether/hexanes, again allowing the plate to dry before rerunning, giving $[CpFe(CO)_2]_2$ as the lower R_f band and 2a d_5 as the higher R_f band. This latter band yielded 33 mg of a mixture that on the basis of ¹H NMR consisted of 7.4 mol % $[CpFe(CO)_2]_2$ and 92.6 mol % **2a**- d_5 . No signals appeared at ~ 4.7 ppm in the ¹H NMR spectrum (C₆D₆), indicating the absence of any CH₂ ethyl hydrogen atoms.

MeCp(CO)Fe(μ -CO)(μ -COCD₂CD₃)Mn(CO)MeCp (2bd₅). This compound was conveniently prepared as previously described for 2b,³ using CD₃CD₂SO₃CF₃, prepared as described above for 2a-d₅, and [MeCp(CO)Fe(μ -CO)₂Mn(CO)MeCp]⁻Na⁺, giving material suitable for use without any further purification; a 2.5% residual CH₂ peak from the ethoxy group was visible by ¹H NMR spectroscopy.

MeCp(CO)Fe(μ -CO)(μ -CO¹³CH₂CH₃)**Mn(CO)MeCp (2b**-¹³C). This compound was prepared as described above for **2b** d_5 , using CH₃¹³CH₂SO₃CF₃ prepared from iodoethane-1-¹³C and silver triflate: ¹H NMR (C₆D₆): δ 4.73 (dq, J_{CH} = 149 Hz, J_{HH} = 7.2 Hz, ¹³CH₂CH₃), 4.37–3.89 (m, MeCp), 1.91, 1.86, 1.84, 1.77 (s, cis, cis, trans, trans *Me*Cp, ~2:2:1:1), 1.725 (s, *Me*Cp of [MeCpFe(CO)₂]₂ impurity, 24% by weight), 1.265 (dt, ² J_{CH} = 4.4 Hz, J_{HH} = 7.2 Hz, ¹³CH₂CH₃); ¹³C NMR (C₆D₆) 83.17 (cis-¹³CH₂CH₃), 82.59 (trans-¹³CH₂CH₃) ppm, cis:trans \approx 3:2.

CpFe(CO)(PPh₂Me)C₂H₅ (4a). To a solution³ of 1.29 g (6.43 mmol) of CpFe(CO)₂-Na⁺ in 25 mL of THF was added 1.15 g (7.39 mmol) of CH₃CH₂I (purified by vacuum transfer from CaH_2). The mixture was stirred for 50 min and then concentrated in vacuo until it took on a gel-like consistency. Hexane was added to dissolve the product, the yellow solution was filtered through Celite, and the solvent was removed in vacuo to give 0.90 g (72.5% yield) of CpFe(CO)₂C₂H₅ as a yellow oil. A 0.775 g (3.76 mmol) sample of this material and 0.731 g (3.66 mmol) of PPh₂Me were dissolved in 20 mL of hexane and photolyzed for 3 h at room temperature under a slow nitrogen purge (1-2 bubbles/s of nitrogen from a syringe needle). The solvent was removed under vacuum and the product chromatographed on a silica column by elution with 1:1 pentane/chloroform. A red-orange band was collected which following solvent removal yielded an oil found by ¹H and ^{31}P NMR to contain ${\sim}40$ mol % of the phosphine along with the desired product; no chromatographic method was found that allowed these two compounds to be separated. The oil was washed briefly with 1 mL of CH₃I in 3 mL of THF, and the white precipitate of PPh₂Me₂⁺I⁻ was filtered on Celite. Following solvent removal, 250 mg (18% yield) of product was obtained as an orange powder: IR (THF) 1888 (s) cm⁻¹; ¹H NMR (C₆D₆) δ 7.42–7.38 (m, 2H), 7.31–7.28 (m, 2H), 7.05– 6.98 (m, 6H, Ph), 4.136 (d, J = 1.0 Hz, 5H, Cp), 1.59 - 1.52 (m, J)CHCH₃), 1.518 (t, J = 7.5 Hz, CH₂CH₃), 1.511 (d, J = 8.0 Hz, PCH_3 , 7H for δ 1.59–1.51), 0.79–0.71 (m, 1H, CHCH₃); ¹H NMR (acetone- d_6 , 500 MHz) δ 7.58–7.55 (m, 2H), 7.47–7.41 (m, 4H), 7.38-7.34 (m, 4H, Ph), 4.356 (d, J = 1.0 Hz, 5H, Cp),1.879 (d, J = 8.3 Hz, 3H, PCH₃), 1.33-1.27 (m, 1H, CHCH₃), 1.110 (dt, $J_{PH} = 2$ Hz, $J_{HH} = 7.4$ Hz, 3H, CH_2CH_3), 0.40–0.33 (m, 1H, CHCH₃); ¹³C NMR (C₆D₆) 222.47 (d, $J_{CP} = 32.86$ Hz, FeCO), 140.61, 139.79, 139.61, 138.90, 132.20, 132.00, 131.83, 131.65 (140.6-138.9, ipso carbons of Ph; 132.2-131.6, o, *m*-carbons of Ph; *p*-carbons obscured by solvent; chemical shifts and J_{CP} of the (presumed) doublets cannot be assigned), 84.05 (s, CpFe), 23.33 (d, $J_{CP} = 4.0$ Hz, CH_2CH_3), 16.90 (d, $J_{CP} =$

28.4 Hz, PCH_3), -3.48 (d, $J_{CP} = 19.7$ Hz, CH_2CH_3 , assignment confirmed by DEPT-135 NMR) ppm; ³¹P NMR (C₆D₆) 67.88 ppm. Anal. Calcd for C₂₁H₂₃OPFe: C, 66.69; H, 6.13. Found: C, 65.94; H, 6.15.

MeCpFe(CO)(PPh₂Me)C₂H₅ (4b). A mixture of PPh₂Me (1.128 g, 5.63 mmol) and $MeCpFe(CO)_2C_2H_5$ (1.247 g, 5.66 mmol; prepared as described above for $CpFe(CO)_2Et$, in 88% yield as a yellow oil) in 50 mL of hexane was photolyzed as described above for 4a. The solvent was removed under vacuum and the dark oily product chromatographed on a silica column by elution with benzene to give a yellow, a deep orange, and last a green band. Solvent removal from the deep orange fraction yielded 1.61 g of a deep orange viscous oily residue (4b and PPh_2Me) which was treated with 1.5 mL of CH_3I in 5 mL of THF. The exothermic reaction was accompanied by a great deal of bubbling and gave a green solution with a white solid presumed to be $PPh_2Me_2^+I^-$. Filtration followed by solvent removal gave a green oily residue that was rechromatographed on silica with benzene. The second fraction (deep orange) was collected and the solvent removed, giving a deep orange viscous oil. The ¹H NMR spectrum in acetone- d_6 showed that the product was slightly contaminated (5%) by weight) by $MeCpFe(CO)_2C_2H_5$ (the signals overlap in C_6D_6 , but in acetone- d_6 the MeCp signals of MeCpFe(CO)₂C₂H₅ at δ 4.75, 4.69 (m, 4H) are well separated from those of 4b). The product was left under vacuum for 2 days in an only partially successful attempt to remove the MeCpFe(CO)₂C₂H₅, giving \sim 98% pure 4b in 19% yield: IR (THF) 1890 (s) cm⁻¹; ¹H NMR $(C_6D_6) \delta 7.43 - 7.39 (m, 2H), 7.34 - 7.32 (m, 2H), 7.06 - 7.01 (m, 2H), 7.06 - 7.00 (m, 2H), 7.0$ 6H, Ph), 4.12 (m, 1H), 4.00 (m, 1H), 3.87 (m, 1H), 3.85 (m, 1H, MeCp), 1.80 (s, 3H, MeCp), 1.53 (d, J = 8.9 Hz, and overlapping m, 6H, PMe and CH_2CH_3 , 1.46-1.42 (m, 1H, CHCH₃), 0.85–0.78 (m, 1H, CHCH₃); ¹H NMR (acetone-d₆, 500 MHz) & 7.60-7.57 (m, 2H), 7.46-7.43 (m, 4H), 7.37-7.35 (m, 4H, Ph), 4.28, 4.22, 4.04, 4.03 (s, 1H each, MeCp), 1.885 (d, J = 8.65 Hz, 3H, PMe), 1.876 (s, 3H, MeCp), 1.15 (m, CHCH₃), 0.46-0.41 (m, CHCH₃); ¹³C NMR (C₆D₆) 222.71 (d, $J_{CP} = 31.4$ Hz, FeCO), 140.98, 140.16, 139.31, 138.62 (ipso carbons of Ph; chemical shifts and J_{CP} of the (presumed) doublets cannot be assigned), 131.80 (d, $J_{CP} = 19.6$ Hz), 129.20 (d, $J_{CP} = 4.3$ Hz; o, m, or p-carbons of Ph; remainder of Ph obscured by solvent) 97.42 (s, ipso carbon of MeCp), 86.45 (s), 85.71 (s), 82.93 (s), 80.70 (s, MeCp), 23.29 (s, CH_3CH_2), 17.11 (d, $J_{CP} = 29.1$ Hz, PCH_3 , 13.07 (s, MeCp), -2.19 (d, $J_{CP} = 20.2$ Hz, CH_2CH_3 , confirmed by DEPT-135 NMR) ppm; ^{31}P NMR (C_6D_6) 67.59 ppm. Anal. Calcd for $C_{22}H_{25}OPFe$: C, 67.36; H, 6.42. Found: C, 65.94; H, 6.26.

CpFe(CO)(PPh₂Me)H (5a). In a manner analogous to that reported for the PPhMe₂ analog,^{9,69} a solution of CpFe-(CO)₂I (0.714 g, 2.35 mmol) in 10 mL of ether was added dropwise at room temperature to a suspension of lithium aluminum hydride (1.00 g, 26.35 mmol) in 10 mL of ether. After 15 min, a solution of PPh₂Me (0.464 g, 2.32 mmol) in 2 mL of ether was added dropwise at -20 °C. The mixture was allowed to warm to room temperature after 20 min and then was hydrolyzed with degassed distilled water. The organic layer was dried (MgSO₄) and filtered, and the solvent was removed under vacuum at -5 °C, giving 0.513 g of an oily yellowish-green residue. Analysis by ¹H NMR (C₆D₆) showed that the desired product was contaminated by free phosphine. Addition of CH₃I in hexane as carried out for the purification of **4a**,**b** led only to product decomposition. A portion of the residue (184 mg) was subjected to preparative TLC using a mixture of benzene/hexane (3/1) as the eluting solvent, giving 5a (115 mg) as a yellow oil. Analysis by ¹H NMR indicated the oil to consist only of **5a** and free PPh₂Me in a 1.655:1 molar ratio or 74.3% by weight 5a (overall yield 29% based on CpFe(CO)₂I): ¹H NMR (C₆D₆) δ 7.57–7.32, 7.04 (m, 10 H, Ph), 4.21 (s, 5H, Cp), 1.63 (d, ${}^{2}J_{PH} = 8.65$ Hz, 3H, Me), -13.44 (d,

⁽⁶⁹⁾ Davison, A.; McCleverty, J. A.; Wilkinson, G. J. Chem. Soc. **1963**, 1133-1138.

 ${}^{2}J_{PH} = 77.0$ Hz, 1H, FeH). Anal. Calcd for 74.32% C₁₉H₁₉-OPFe and 25.68% C₁₃H₁₃P: C, 68.46; H, 5.74. Found: C, 66.36; H, 5.58.

¹H NMR Reactions. General Method. In the glovebox. reactants were loaded into an NMR tube that had been sealed to a 14/20 ground glass joint. TMS was added (as an internal NMR integration standard) via microliter syringe, and C₆D₆ was added as the solvent used to transfer the weighed liquid PPh₂Me into the NMR tube. The tube was fitted with a vacuum stopcock, attached to a vacuum line, frozen, and evacuated. The tube was submitted to two freeze-pumpthaw cycles. For the ethylene experiments, a known volume and pressure of ethylene was added via vacuum transfer. The tube was then sealed with a torch. The sample was heated (inverted) in a thermostated constant-temperature water bath. The volume (in mL) used to calculate the concentrations was determined according to the formula $V = \pi (0.213)^2 h$, where h is the height in cm of the solution measured immediately after removing the sample from the water bath. The NMR tube was cooled in water immediately after removing from the bath and centrifuged prior to recording each NMR spectrum. All data are collected in Table 1.

Reactions of 2a, 2a- d_5 , **2b, 2b**- d_5 , **2b**- ^{13}C , **4a,b, and 5a.** Kinetic runs of the decomposition of the ethoxycarbynes were analyzed by monitoring the disappearance of (1) the combined *Me*Cp singlets of the cis and trans isomers at δ 1.86 and 1.80 of **2a** (runs 1 and 2), (2) the CH₂ signal at δ 4.71 of **2a** (run 3, 500 MHz), the trans *Cp*Fe singlet at δ 4.49 of **2a**- d_5 (runs 4 and 5), and (3) the cis-MeCp singlet at δ 1.91 of **2b** and **2b**- d_5 (runs 3, 4, 7-10, 12-18), each relative to the TMS resonance. Rate constants for decomposition of 2a in the presence of 2b- ^{13}C or **2b**- d_5 could not be determined at 200 MHz (runs 11, 14-18) due to the absence of any suitably resolved peaks at this field strength. After the crossover reactions were complete, the NMR tubes were broken open in the glovebox, the solvent was removed under vacuum (in order to remove the ethane formed), and the mixture was chromatographed on a pipet column in benzene. The fast moving orange band (containing the mononuclear alkyls 4 contaminated by PPh₂-Me) was collected, the solvent was again removed, and the sample was dissolved in acetone- d_6 for ¹H NMR analysis. The only reactions analyzed for 5a,b (by examination of the hydride region of the ¹H NMR spectrum) were those conducted near the chronological end of this work; results are noted in Table 1. Chromatography of run 9 (2b and 5a) gave a clean mixture of 4a,b, 5a,b, and PPh₂Me from which the ¹H NMR spectrum (C_6D_6) of **5b** could be extracted: δ 4.03 (m, 2H, MeCp), 3.99 $(m, 2H, MeCp), 1.80 (s, 3H, MeCp), 1.65 (d, J_{PH} = 8.6 Hz, 3H)$ PPh_2Me), -13.36 (d, $J_{PH} = 77.0$ Hz, FeH).

Acknowledgment. Financial support for this work from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and NSF Grant No. CHE-9096105 is gratefully acknowledged.

OM950342R