Stereospecific Synthesis of $(\mu_3\text{-COCH}_3)(\mu_2\text{-C(H)CH}_3)(\text{Cp})(\text{MeCp})\text{Fe}_2\text{Mn(CO)}_5$, the First Carbyne–Ethylidene Cluster, and Intramolecular Hydrogen Migration To Give $(\mu_2\text{-C(H)OCH}_3)(\mu_3\text{-CCH}_3)(\text{Cp})(\text{MeCp})\text{Fe}_2\text{Mn(CO)}_5$, the First Carbene–Ethylidyne Cluster

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Summary: Addition of diazoethane to the (μ_3-COCH$_3$)-Fe$_2$Mn cluster **1** stereospecifically yields μ_3-methoxycarbyne, μ_2-ethylidene cluster **2**, which undergoes slow decomposition to yield the diastereomeric cluster **3** via ethylidene "rotation", μ-σ,π methoxyvinyl complex **4** via carbyne–ethylidene coupling, and μ_2-methoxycarbene, μ_3-ethylidyne cluster **5** via intramolecular hydrogen migration from the ethylidene to the carbyne ligand. In the presence of a CO atmosphere, the isomerization of **2** to **3** is slowed, while the isomerization to **5** is completely inhibited.

We recently reported the rational synthesis of the first carbyne–methylene "difunctional" cluster, $(\mu_3\text{-COCH}_3)(\mu_2\text{-CH}_2)(\text{Cp})(\text{MeCp})\text{Fe}_2\text{Mn(CO)}_5$, and the PPh$_3$-induced intramolecular coupling reaction of the carbyne and methylene functionalities to give the methoxyvinyl compound $\text{Cp(CO)Fe}(\mu\text{-C(OCH}_3\text{)=CH}_2)(\mu\text{-CO})\text{Fe(CO)}_2\text{PPh}_3$.[1] Since this system appeared to provide a rare opportunity to examine the stereochemistry of cluster-mediated carbon–carbon bond formation,[2] we decided to prepare an alkyl-labeled analogue. We report here the remarkable stereospecific synthesis of a carbyne–ethylidene cluster, as well as carbyne–ethylidene coupling to give a single methoxyvinyl compound. We also describe the unexpected consequences of this simple structural change, including room-temperature ethylidene "rotation", intramolecular hydrogen migration from the ethylidene carbon to the carbyne carbon to give the isomeric carbene–ethylidyne cluster, and differential CO inhibition of these isomerization reactions.

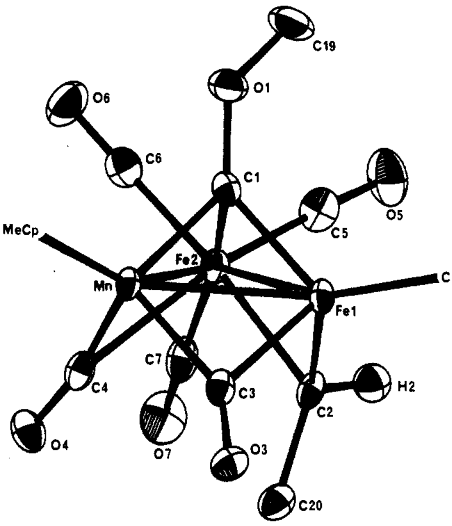

Figure 1. ORTEP drawing of **2**. Selected bond distances (Å) and angles (deg): Mn–Fe(1), 2.554 (1); Mn–Fe(2), 2.670 (1); Fe(1)–Fe(2), 2.503 (1); C(1)–Mn, 1.911 (3); C(1)–Fe(1), 1.898 (3); C(1)–Fe(2), 1.973 (3); C(1)–O(1), 1.351 (3); C(1)–O(1)–C(19), 118.54 (21); C(2)–Fe(1), 1.942 (3); C(2)–Fe(2), 2.097 (3); C(2)–H(2), 0.950 (43); C(2)–C(20), 1.515 (4); Fe(1)–C(2)–Fe(2), 78.48 (10); H(2)–C(2)–C(20), 111.0 (26); C(3)–Fe(1), 2.001 (3); C(3)–Mn, 1.895 (3); Fe(1)–C(3)–O(3), 133.19 (21); Mn–C(3)–O(3), 144.61 (22); C(4)–Mn, 1.803 (3); C(4)–Fe(2), 2.504 (3); Mn–C(4)–O(4), 161.52 (23).

Reaction of diazoethane with trinuclear carbyne cluster **1**[1] gave rise to the desired difunctional clusters **2** and **3** as well as clusters subsequently identified as **4** and **5**, in a 21:1:0.2:0.4 ratio (Scheme I). Crystallization of this initial product mixture from methylene chloride/hexane at −40 °C allowed the isolation of pure **2** in 62% yield. Initial characterization[3] of the carbynes was made on the basis of the low-field methine quartets in the ^{1}H NMR at δ 9.45 and 9.09 for **2** and **3**, respectively, characteristic of μ-alkylidenes.[1,4] The ^{13}C NMR spectra exhibited peaks at 348.4 and 356.5, 275.2 and 271.6, 244.8 and 243.5, and 182.1 and 187.2 ppm, for **2** and **3**, respectively, due to the μ_3-COCH$_3$, μ-CO, MnCO, and μ_2-C(H)CH$_3$ carbons.[4] The bands near 275 ppm in particular are typical of a carbonyl bridging an Fe–Mn bond[1,5] and those near 245 ppm of a "nearly terminal" Mn carbonyl;[1] since no band typical of a CpFeCO near 230 ppm was present,[6] ethylidene bridging of the iron atoms in both clusters was indicated. This structure was confirmed by means of a single-crystal X-ray diffraction study of **2** (Figure 1);[3] the overall geometry is similar to that previously seen for the simple methylene analogue,[1] and the ethylidene methyl is syn to the metal triangle.

Cluster **2** decomposes within 8–10 days at room temperature to give **3**, **4** (~1%), and **5** (~25%); **3** independ-

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[1] Fong, R. H.; Hersh, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 2843–2845.

[2] Ligand coupling that involves sp^2 or sp^3 centers, with the further requirement that the stereocenter not be eliminated (a–h), is much less common than coupling that involves sp centers or (via hydrogen migration) results in conversion to one (i–p): (a) Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roue, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 862–864. (b) Dickson, R. S.; Fallon, G. D.; Nesbit, R. J.; Pain, G. N. *J. Organomet. Chem.* **1982**, *236*, C61–C64. (c) Mackenzie, P. B.; Ott, K. C.; Grubbs, R. H. *Pure Appl. Chem.* **1984**, *56*, 59–61. (d) Laws, W. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 116–117. (e) Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508–510. (f) Saez, I. M.; Meanwell, N. J.; Nutton, A.; Isobe, K.; Vazquez de Miguel, A.; Bruce, D. W.; Okeya, S.; Andrews, D. G.; Ashton, P. R.; Johnstone, I. R.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1565–1575. (g) Saez, I. M.; Meanwell, N. J.; Taylor, B. F.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1987**, 361–363. (h) Dickson, R. S.; Fallon, G. D.; Jenkins, S. M.; Nesbit, R. J. *Organometallics* **1987**, *6*, 1240–1246. (i) Clauss, A. P.; Shapley, J. R.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 7387–7388. (j) Vollhardt, K. P. C.; Walborsky, E. C. *Ibid.* **1983**, *105*, 5507–5509. (k) Park, J. T.; Shapley, J. R. *Ibid.* **1983**, *105*, 6182–6184. (l) Nuel, D.; Dahan, F.; Mathieu, R. *Ibid.* **1985**, *107*, 1658–1664. (m) Didier, N.; Dahan, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436–1439. (n) Chi, Y.; Shapley, J. R. *Ibid.* **1985**, *4*, 1900–1901. (o) Ros, J.; Commenges, G.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1087–1094. (p) Nuel, D.; Dahan, F.; Mathieu, R. *Organometallics* **1986**, *5*, 1278–1279.

[3] Data for new compounds and details of the X-ray diffraction studies of **2** and **5** may be found in the supplementary material.

[4] For NMR data on iron and manganese μ_2-ethylidene, μ_2-carbene, μ_3-ethylidyne, and μ_3-carbyne compounds, see: (a) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417–1426. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918. (c) Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaün, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 1357–1362. (d) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023–2032. (e) Wong, W.-K.; Chiu, K. W.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1557–1563. (f) Lourdichi, M.; Mathieu, R. *Organometallics* **1986**, *5*, 2067–2071. (g) Hodali, H. A.; Shriver, D. F. *Inorg. Chem.* **1979**, *18*, 1236–1241. (h) Aitchison, A. A.; Farrugia, L. J. *Organometallics* **1986**, *5*, 1103–1112.

[5] Fong, R. H.; Hersh, W. H. *Organometallics* **1985**, *4*, 1468–1470.

[6] This result was confirmed by using ^{13}CO-enriched **1** in the synthesis of **2** and **3**.

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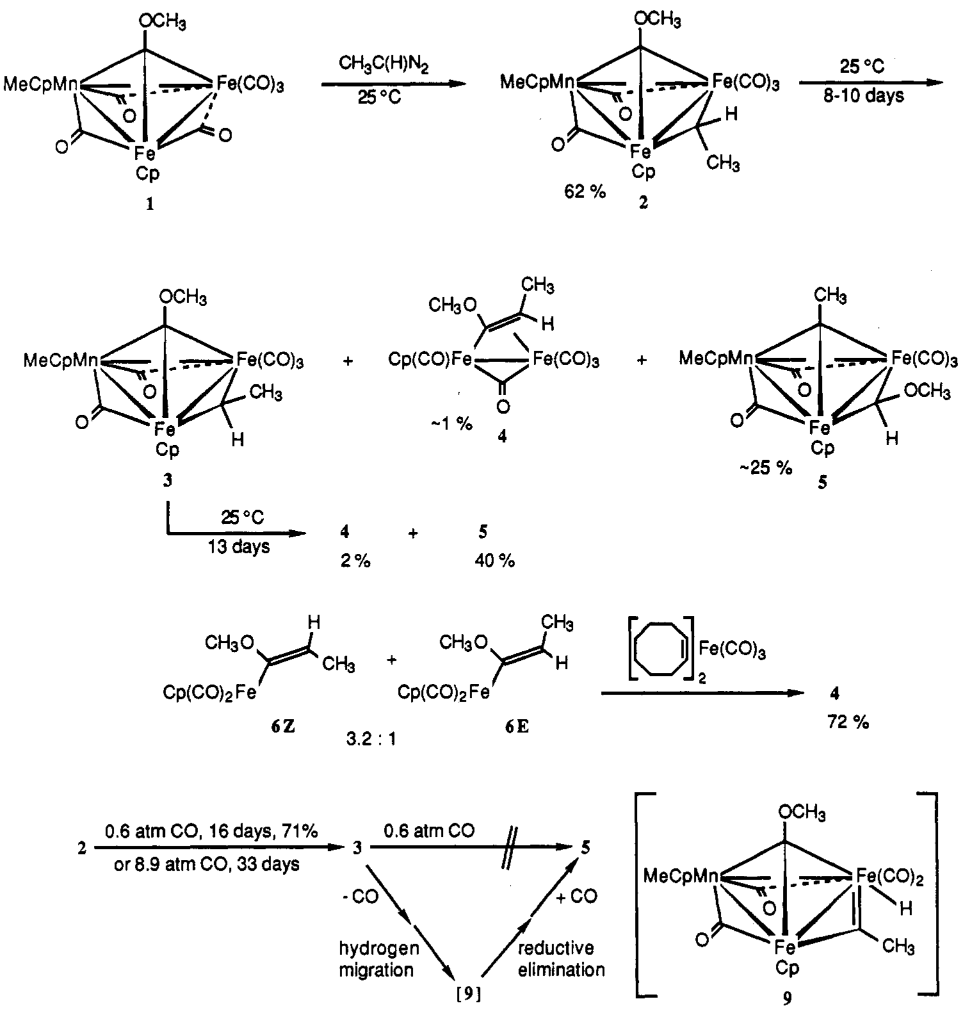
Scheme I



ently decomposes to **4** (2%) and **5** (40%) in 13 days, so its concentration does not build up to an appreciable extent during the decomposition of **2**.[7] Only a single isomer of the μ-vinyl compound **4**—formed via carbyne–ethylidene coupling[1]—is observed, and it also can be prepared by an independent synthesis from the mononuclear methoxyvinyl compounds **6Z** and **6E** as shown in Scheme I.[1,3] The obvious problem is that since we have been unable to generate the opposite double-bond isomer of **4**, we cannot determine if it is stable under the reaction conditions.[8] The major product of thermal isomerization of **2** and **3**[7] was identified by ^{1}H NMR[4] as the isomeric carbene-ethylidyne cluster **5**, on the basis of the observation of *singlets* at δ 9.42 for the methine hydrogen and 3.37 for the ethylidyne methyl hydrogens (Scheme I).[3] The ^{13}C NMR[4] exhibited peaks at 338.3 (μ-CCH_3), 272.1 (Fe(μ-CO)Mn), 243.1 (MnCO), and 228.4 (μ_2-C(H)OCH$_3$, $^1J_{CH}$ = 155 Hz, $^3J_{CH}$ = 5.2 Hz) that once again suggested the μ_2 ligand to be bridging the iron atoms. The structure was again confirmed by X-ray crystallography,[3] which in this case revealed a methoxycarbene moiety with the hydrogen syn to the metal triangle, rather than anti as in **2** (Figure 2).

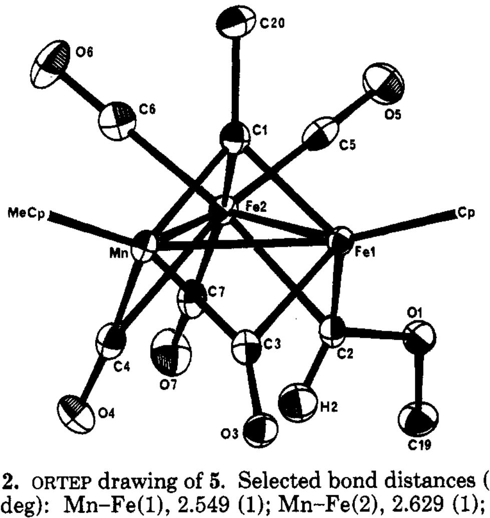


Figure 2. ORTEP drawing of **5**. Selected bond distances (Å) and angles (deg): Mn–Fe(1), 2.549 (1); Mn–Fe(2), 2.629 (1); Fe(1)–Fe(2), 2.518 (1); C(1)–Mn, 1.926 (3); C(1)–Fe(1), 1.901 (3); C(1)–Fe(2), 1.955 (3); C(1)–C(20), 1.501 (4); C(2)–Fe(1), 1.916 (3); C(2)–Fe(2), 2.129 (3); C(2)–H(2), 1.007 (41); C(2)–O(1), 1.385 (3); Fe(1)–C(2)–Fe(2), 76.80 (10); H(2)–C(2)–O(1), 107.7 (23); C(2)–O(1)–C(19), 115.97 (21); C(3)–Fe(1), 1.999 (3); C(3)–Mn, 1.884 (3); Fe(1)–C(3)–O(3), 133.44 (21); Mn–C(3)–O(3), 144.59 (21); C(4)–Mn, 1.800 (3); C(4)–Fe(2), 2.477 (3); Mn–C(4)–O(4), 161.76 (23).

The most important mechanistic question to resolve is whether or not the apparent hydrogen migration reaction that yields **5** from **3** (and/or **2**)[7] is intramolecular. Reaction of a mixture of **2** and its deuteriated MeCp$_2$ analogue (μ_3-COCH$_3$)(μ_2-C(D)CH$_3$)(MeCp)$_2$Fe$_2$Mn(CO)$_5$ (**7**-d_1) gave after 5 days at 31 °C only **5** and its d_1 MeCp$_2$ analogue **8**-d_1, with less than 5% crossover in the methine hydrogen.[9]

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[7] While it cannot be ruled out with certainty, there is no evidence that **2** *directly* yields either **4** or **5**.

[8] The double bond geometry of **4** was determined by conversion to a PPh$_3$ adduct, the X-ray crystal structure of which revealed the *E* configuration; Fong, R. H., unpublished results.

The hydrogen migration from the *ethylidene* to the *carbyne* carbon is therefore intramolecular. A reasonable mechanism would involve loss of CO from **3**, migration of the ethylidene hydrogen that is syn to the metal triangle in **3** to give an intermediate such as **9** (Scheme I), and reductive elimination followed by recoordination of CO to give **5**. In fact, evidence for the first part of this proposal is provided by the observation that the isomerization of **3** to **5** *is completely inhibited by 0.6 atm of CO*. More remarkable, however, is the observation that CO *also slows the isomerization of 2 to 3*. Thus, while complete decomposition of **2** takes 8–10 days in the absence of CO, isomerization to **3** takes 16 days under 0.6 atm of CO[10] and 33 days under 8.9 atm of CO.[11] Monitoring in situ by ^{1}H and ^{13}C NMR (using ^{13}CO in the latter case) provided no evidence for the presence of intermediates in these reactions, precluding involvement of species such as 50-electron open clusters formed via *association* of CO[12] and suggesting that the inhibition is indeed due to reversible *dissociation* of CO from **2** and **3**.[13] A related observation for a tungsten–osmium bridged benzylidene cluster, in which the irreversible "rotation" was completely halted by CO, led to the suggestion that the rotation could involve hydrogen migration, as in **9**.[14] Since the isomerization of **2** to **3** is not halted, however, this precludes involvement of **9** as a *common* intermediate in our isomerization reactions, and also suggests that *two* unsaturated clusters formed via CO loss are involved, one leading to ethylidene "rotation" and the other to hydrogen migration. Alternatives to **9** for the conversion of **2** to **3** could include methoxycarbyne migration to the opposite cluster face (but not methyl migration[5] to another carbonyl since no ^{13}C incorporation into the carbyne carbon of **3** is seen upon isomerization of ^{13}CO-enriched **2**) and bridging/terminal interconversion of the ethylidene; even though this latter mechanism for rotation does not formally require CO loss, one might speculate that in this case a more reactive unsaturated cluster could be required for such a process to occur.[15] A final implication of the CO-mediated isomerization of **2** to **3** is that **3** is the thermodynamically more stable isomer, which therefore requires that the stereospecific formation of **2** from **1** is due to a kinetic preference for **2**.

In conclusion, we have observed a remarkable cluster-mediated intramolecular carbon-to-carbon hydrogen migration. While we are not aware of any comparable rearrangements in difunctional clusters, examples that involve rearrangements of individual ligands on clusters may be related.[16] Unfortunately, the stereochemical aspect of this study remains unresolved due to the apparent lack of thermodynamic stability of one of the two possible methoxyvinyl isomers. Further work on this mechanistic problem and that of the ethylidene "rotation" is in progress.

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Supplementary Material Available: Spectroscopic data for new compounds and tables of crystallographic data for **2** and **5** and details of the solutions (23 pages); tables of structure factors for **2** and **5** (23 pages). Ordering information is given on any current masthead page.

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[9] In this experiment, **7** was 95% deuteriated. A separate reaction of **2** and **7**-d_7, where the ethylidene methine hydrogen was only 70% labeled but the ethylidyne and carbyne methyls were 99+% deuteriated, indicated that less than 5% crossover of the two methyl fragments had occurred as well. The relevant signals in **5** and **8** were well-separated in the ^{1}H NMR at 500 MHz.

[10] Under these conditions, 96% conversion of **2** gave **3** in 71% yield; $MeCpMn(CO)_3$ (22%) and $Cp_2Fe_2(CO)_4$ (17%) were the only other identifiable products. This experiment allows the only practical means of generating reasonably pure **3**, since chromatography on silica gel regenerates **2** (giving a 1:2.7 mixture of **2**:**3**), while chromatography of pure **2** gives a 4.6:1 mixture of **2**:**3**.

[11] These three reactions were carried out at room temperature in sealed tubes with triphenylmethane added as an internal integration standard and were monitored by ^{1}H NMR at regular intervals. Despite the absence of precise temperature control, they yielded linear first-order plots for the disappearance of **2** (k(**2**)) and, in the presence of CO so that **3** does not go on to give **5**, the appearance of **3** (k(**3**)): $P_{CO} = 0$ atm, $k(\mathbf{2}) = (4.0 \pm 0.2) \times 10^{-6}\ s^{-1}$; $P_{CO} = 0.6$ atm, $k(\mathbf{2}) = (2.8 \pm 0.2) \times 10^{-6}\ s^{-1}$, $k(\mathbf{3}) = (2.3 \pm 0.2) \times 10^{-6}\ s^{-1}$; $P_{CO} = 8.9$ atm, $k(\mathbf{2}) = (1.13 \pm 0.04) \times 10^{-6}\ s^{-1}$, $k(\mathbf{3}) = (9.2 \pm 0.8) \times 10^{-7}\ s^{-1}$.

[12] See for instance: (a) Huttner, G.; Schneider, J.; Müller, H.-D.; Mohr, G.; von Seyerl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76-77. (b) Richter, F.; Vahrenkamp, H. *Organometallics* **1982**, *1*, 756–757. (c) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Ibid.* **1983**, *2*, 1194–1202. (d) Adams, R. D.; Yang, L.-W. *J. Am. Chem. Soc.* **1983**, *105*, 235–240. (e) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169–208.

[13] Two reviewers suggested that this influence of CO on the rate of isomerization of **2** to **3** is small and *not* necessarily evidence of a dissociative mechanism, and that the rate inhibition could be accounted for by an associative reaction of CO with **2** that reduces its concentration. In the latter case, formation of an intermediate due to CO association can slow the appearance of **3** only if its concentration builds up in solution to observable levels (which it does not), but nevertheless if this were to happen, increasing the CO pressure would be expected to increase rather than decrease the rate of disappearance of **2**. Formation of a long-lived intermediate is also inconsistent with the similarity in k(**2**) and k(**3**). The *magnitude* of the degree of CO inhibition, rather than being small, is in fact comparable to that seen in some cluster substitution reactions that on the basis of kinetic evidence have been shown to proceed via initial CO dissociation.[13a–d] Here the rate data[11] is consistent with reversible loss of CO from **2** followed by ethylidene "rotation" and subsequent trapping by CO to give **3** according to eq 1. Thus, a reciprocal plot (k_{-1}, $k_2 \gg k_1$)

$$\mathbf{2} \underset{k_{-1}\,(+CO)}{\overset{k_1\,(-CO)}{\rightleftharpoons}} [I] \xrightarrow{k_2} \xrightarrow{+CO} \mathbf{3} \qquad (1)$$

of k_1^{-1} vs. P_{CO} is linear and gives $k_1 = (3.5 \pm 0.4) \times 10^{-6}\ s^{-1}$ and $k_{-1}/k_2 = 32 \pm 5\ M^{-1}$ where [CO] = 0.0075 M in benzene at 25 °C and 1 atm of CO and extrapolation of [CO] on the basis of Henry's law is assumed:[13e] (a) Poë, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860–1866. (b) DeWit, D. G.; Fawcett, J. P.; Poë, A. *Ibid.* **1976**, 528–533. (c) Ma'mun, A.-H.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6248–6254. (d) Fox, J. R.; Gladfelter, W. L.; Wood, T. G.; Smegal, J. A.; Foreman, T. K.; Geoffroy, G. L.; Tavanaiepour, I.; Day, V. W.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 3214–3223. (e) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1–9.

[14] Chi, Y.; Shapley, J. R.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1987**, *6*, 301–307.

[15] Processes involving bridging/terminal alkylidene interconversion have been proposed in a number of systems, but rotation of the alkylidene when it is terminal is not required (nor has it been proposed) in order to account for the observed isomerizations: (a) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861–862. (b) Laws, W. J.; Puddephatt, R. J. *Ibid.* **1983**, 1020–1021. (c) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464–475. (d) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1985**, *4*, 793–794. (e) Williams, G. D.; Lieszkovszky, M.-C.; Mirkin, C. A.; Geoffroy, G. L. *Ibid.* **1986**, *5*, 2228–2233.

[16] (a) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 219–222. (b) Cree-Uchiyama; Shapley, J. R.; St. George, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 1316–1317. (c) Doherty, N. M.; Fildes, M. J.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1355–1357. (c) Byrne, P. G.; Garcia, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *Ibid.* **1987**, 53–55. (d) Delgado, E.; Hein, J.; Jeffery, J. C.; Ratermann, A. L.; Stone, F. G. A.; Farrugia, L. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1191–1199.