3806 *J. Am. Chem. Soc.* **1993,** *115,* 3806-3807

# Formation of Vinylcarbene and Heterocyclic Carbene Complexes from the Reaction of the Carbene Anion $[Cp(CO)_2Mn{=}C(OEt)CH_2]^-$ with Aldehydes

Chae S. Yi and Gregory L. Geoffroy*

*Department of Chemistry*
*The Pennsylvania State University*
*University Park, Pennsylvania 16802*

Corbet A. White and Arnold L. Rheingold

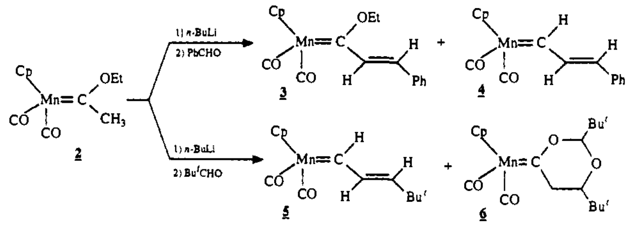
*Department of Chemistry*
*The University of Delaware*
*Newark, Delaware 19716*

*Received January 19, 1993*

Carbene complexes that have been deprotonated at the $\beta$-carbon ("carbene anions", $[L_nM{=}C(OR)CR_2]^-$) are well-established reagents for the elaboration of carbene complexes via their nucleophilic addition to electrophilic substrates.[1] For example, they undergo alkylation to yield carbene complexes having a modified carbene substituent, react with epoxides to form heterocyclic carbene complexes, and add to enol ethers, aldehydes, and ketones to form, after elimination of $OR^-$ or $OH^-$, vinylcarbene complexes. Herein we describe two new transformations of carbene anions which involve the reaction of $[Cp(CO)_2Mn{=}C(OEt)CH_2]^-$ (**1**) with PhCHO and $Bu^tCHO$ to form heterocyclic carbene complexes and vinylcarbene complexes in which the ethoxide substituent has been replaced with a hydride simultaneously with formation of the vinyl substituent.

Our initial objective was to prepare alkoxy-substituted vinylcarbene complexes of the form $Cp(CO)_2Mn{=}C(OEt)CR{=}CR_2$ to use as precursors for the preparation of vinylcarbyne complexes $[Cp(CO)_2Mn{\equiv}C{-}CR{=}CR_2]^+$ via $BCl_3$-induced abstraction of the alkoxy substituent.[2] Earlier work[1d,3] suggested that the desired vinylcarbene complexes would result from reaction of the carbene anion **1** with aldehydes. However, when **1** was generated *in situ* from the reaction of *n*-BuLi (1 equiv) with $Cp(CO)_2Mn{=}C(OEt)CH_3$ (**2**) and then allowed to react with benzaldehyde, the surprising result was a 1:4 mixture of the desired complex $Cp(CO)_2Mn{=}C(OEt)CH{=}CHPh$ (**3**) and the unexpected product $Cp(CO)_2Mn{=}CHCH{=}CHPh$ (**4**) in which the ethoxy group has been replaced by a hydride, Scheme I. Another surprising transformation is the formation of the cyclic carbene complex **6** upon reaction of carbene anion **1** with the aliphatic aldehyde $Bu^tCHO$.[4] This species forms in a 1:2 ratio with the protiovinylcarbene complex **5**, but none of the expected ethoxyvinylcarbene complex was produced. Complexes analogous to **5** and **6** also formed upon reaction of carbene anion **1** with $CH_3CHO$. Complexes **3–6** were separated by column chromatography on alumina (2:1 pentane/$Et_2O$) and were isolated as spectroscopically characterized microcrystalline solids.[5] $^1H$ NMR data showed an (*E*) configuration of the vinyl substituents in **3–5** and that a single diastereomer of **6** was formed, although the relative stereochemistry of the chiral centers cannot yet be assigned. Complex **3** was also fully defined by an X-ray diffraction study (see Figure 1 of the supplementary material).[6]

**Scheme I**



The formations of **4–6** are unprecedented in reactions of carbene anions with aldehydes, and it is thus important to understand their mechanism of formation. Key questions concern the source of the hydrogen on $C_\alpha$ in **4** and **5** and the fate of the aldehyde oxygen in their formation. First, it was observed that 2 equiv of aldehyde were necessary to reach complete reaction in all cases. It was further observed that treatment of $Cp(CO)_2Mn{=}C(OEt)CD_3$ (>95% $D_3$)[7] with *n*-BuLi (1 equiv) followed by PhCHO gave formation of **3**-$d_1$ and **4**-$d_1$, with the latter having no deuterium incorporation at $C_\alpha$ (by $^1H$ NMR). Similarly, treatment of **1** with PhCDO (99.5% D, MSD) gave a 3:1 mixture of $Cp(CO)_2Mn{=}CDCH{=}CDPh$ (**4**-$d_2$) and $Cp(CO)_2Mn{=}C(OEt)CH{=}CDPh$ (**3**-$d_1$). These results indicate that the hydrogen on $C_\alpha$ derives from the aldehyde substrate and not from 1,2-hydride migration from the $\beta$-$CH_3$ hydrogens of $Cp(CO)_2Mn{=}C(OEt)CH_3$. It was also shown that the salt left after extraction of the organometallic products from the reaction of **1** with PhCHO contained lithium benzoate,[8] implying that the second equivalent of PhCHO needed to drive the reaction to completion forms $PhCO_2^-$ via abstraction of the oxygen atom from the first equivalent of PhCHO in a Cannizaro-type reaction.

The above results suggest the mechanistic paths outlined in Scheme II. Addition of **2** to the electrophilic aldehyde carbon would give **7**, which upon loss of LiOH would form **3**, as has been observed in previous carbene anion reactions.[1d,3] Complexes **4–6** must form via addition of a second equivalent of aldehyde to **7**

---

[1] For leading references, see: (a) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, 1989; Vol. 1, p 209. (b) Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press, New York, 1976; Chapter 3. (c) Aoki, S.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985. (d) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503. (e) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (f) Aumann, R. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer: Berlin, 1987; p 69. (g) Dötz, K. H. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer: Berlin, 1987; p 85.

[2] Fisher, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

[3] (a) Casey, C. P. *Chemtech* **1979**, 378. (b) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1974**, *77*, 345. (c) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947.

[4] For a related organic reaction, see: Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932.

[5] **3**: $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$ 7.48 (d, $J$ = 15.4 Hz, C*H*=CHPh), 7.34–7.00 (m, Ph), 6.82 (d, $J$ = 15.4 Hz, =C*H*Ph), 4.78 (q, $J$ = 7.1 Hz, $OCH_2$), 4.46 (s, Cp), 1.25 (t, $J$ = 7.1 Hz, $OCH_2CH_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz) $\delta$ 281.5 (Mn=*C*), 233.5 (*C*O), 140.3 (*C*H=CHPh), 136.9–127 (Ph), 122.6 (=*C*HPh), 87.3 (Cp), 72.7 (O*C*$H_2$), 15.0 ($OCH_2CH_3$); IR (hexane) $\nu_{CO}$ = 1956 (s), 1896 (s) $cm^{-1}$; MS(EI) $m/z$ = 336 ($M^+$). Anal. Calcd for $C_{18}H_{17}O_3Mn$: C, 64.29; H, 5.10. Found: C, 64.01; H, 5.01. **4**: $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$ 15.27 (d, $J$ = 12.8 Hz, Mn=C*H*), 8.70 (dd, $J$ = 14.7, 12.8 Hz, C*H*=CHPh), 7.38–7.00 (m Ph), 6.42 (d, $J$ = 14.7 Hz, =C*H*Ph), 4.57 (s, Cp); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz) $\delta$ 319.5 (Mn=*C*H), 231.0 (br s, *C*O), 142.2 (*C*H=CHPh), 136.6 (ipso Ph), 135.1 (CH=*C*HPh), 128–127 (Ph), 90.7 (Cp); IR (hexane) $\nu_{CO}$ = 1979 (s), 1919 (s) $cm^{-1}$; MS (EI) $m/z$ = 292 ($M^+$). Anal. Calcd for $C_{16}H_{13}O_2Mn$: C, 65.76; H, 4.46. Found: C, 65.74; H, 4.65. **5**: $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$ 15.43 (d, $J$ = 12.5 Hz, Mn=C*H*), 8.03 (dd, $J$ = 14.7, 12.5 Hz, Mn=CHC*H*=), 5.73 (d, $J$ = 14.7 Hz, C*H*$Bu^t$), 4.52 (s, Cp), 0.94 (s, $Bu^t$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz) $\delta$ 326.5 (Mn=*C*H), 232.7 (CO), 149.9 (Mn=CH*C*H=), 146.6 (=*C*H$Bu^t$), 90.3 (Cp), 33.4 (*C*$Me_3$), 28.8 (C*Me*$_3$); MS(EI) $m/z$ = 272 ($M^+$); IR (hexane) $\nu_{CO}$ = 1981, 1920 $cm^{-1}$. **6**: $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$ 4.52 (s, Cp), 4.25 (dd, $J$ = 18.4, 7.9 Hz, Mn=CC*H*H), 3.08 (dd, $J$ = 18.4, 5.9 Hz, Mn=CCH*H*), 2.92 (dd, $J$ = 7.8, 5.9 Hz, $CH_2$C*H*$Bu^t$), 0.95 (s, $Bu^t$), 0.74 (s, $Bu^t$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz) $\delta$ 330.5 (Mn=*C*), 233.8 (*C*O), 233.0 (*C*O), 108.7 (O*C*H($Bu^t$)O), 86.8 (Cp), 80.6 ($CH_2$*C*H$Bu^t$), 52.1 (Mn=C*C*$H_2$), 35.6 and 34.2 (*C*$Me_3$), 24.4 and 24.2 (C*Me*$_3$); MS(EI) $m/z$ = 374 ($M^+$); IR (hexane): $\nu_{CO}$ = 1960, 1895 $cm^{-1}$. Anal. Calcd for $C_{19}H_{27}O_4Mn$: C, 60.96; H, 7.27. Found: C, 60.55; H, 7.47.

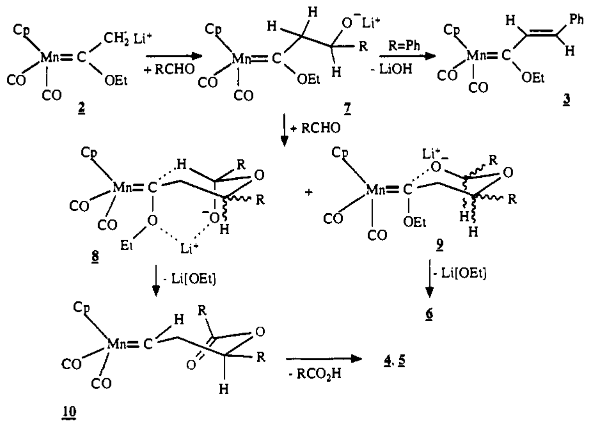
[6] Crystal data for **3**: $C_{18}H_{17}MnO_3$, deep red, triclinic, $P\bar{1}$, $a$ = 7.755(2), $b$ = 10.482(3), and $c$ = 11.393(4) Å, $\alpha$ = 63.12(3), $\beta$ = 88.40(3), $\gamma$ = 74.27(2)°, $Z$ = 2, $d_x$ = 1.413 g $cm^{-3}$, $\mu$(Mo K$\alpha$) = 8.55 $cm^{-1}$, $T$ = 299 K, 2808 independent observed data ($2\theta_{max}$ = 52°). $R(F)$ = 0.032, $R_w(F)$ = 0.046.

[7] Kreiter, C. G. *Angew Chem., Int. Ed. Engl.* **1968**, *7*, 390.

[8] Neutralization of this salt with HCl(aq) and extraction into $CH_2Cl_2$ gave a 72% yield of $PhCO_2H$.

0002-7863/93/1515-3806$04.00/0

**Scheme II**



to form an intermediate that can yield the observed products via the chairlike six-membered transition states **8** and **9**, which differ in the orientation of the substituents derived from the second aldehyde. The anionic oxy group on the end of the chain in **9** can directly displace ethoxide to give the heterocyclic carbene complex **6**. Likewise, hydride transfer to the carbene carbon can occur from **8** with concomitant loss of the ethoxide ion to give **10**, which in turn would form the observed protiovinylcarbene complexes **4** and **5** via 1,2-elimination of benzoic acid. As noted above, the ethoxycarbene complex **3** only formed with the aromatic aldehyde PhCHO, which may reflect the reduced nucleophilicity of the oxy anion of intermediate **7** when R = aryl compared to R = alkyl. Similarly, the absence of cyclic carbene products analogous to **6** from the reaction with PhCHO may in part be a consequence of the reduced nucleophilicity of the oxy anion of **9**, making displacement of the ethoxy group less likely.

Careful control of the reaction conditions led to the selective formation of the above products. For example, the use of NaOMe as base to deprotonate **2** to form carbene anion **1** in the reaction with PhCHO gave exclusive formation of **4**. NaOMe is only sparingly soluble in the THF solvent used, and thus at any point in the reaction the concentration of **2** (and **7**) would be low relative to the PhCHO concentration, conditions which would favor addition of a second equivalent of aldehyde to **7** and thus the formation of **4**. Similarly, the use of 2 equiv of *n*-BuLi in this reaction gave near quantitative formation of **3** (92%). Under these conditions, the concentration of **7** should be high relative to the aldehyde concentration, and thus the formation of **3** would be favored over **4**. Also, the use of KH or NaOMe as base in the $\mathrm{Bu^tCHO}$ reaction gave a near quantitative yield of **6**. We suggest this may reflect a greater tendency of $\mathrm{Na^+}$ and $\mathrm{K^+}$ to coordinate only to the oxy anion as in **9**, which would lead to **6**, whereas $\mathrm{Li^+}$ is known to chelate two or more oxygen atoms to form structurally rigid intermediates,[9] favoring **8** over **9** and, from those, **5** over **6**.

Of the two new transformations described above, the formation of the protio-substituted vinylcarbene complexes **4** and **5** via hydride transfer of an aldehydic hydrogen to the carbene carbon is the most unusual, but this reaction is related to the Cannizaro reaction, which also involves the disproportionation of aldehydes.[10] Compared to the well-developed chemistry of alkoxy-substituted vinylcarbene complexes, the chemistry of unsubstituted vinylcarbene complexes have been much less explored, in part because of the relative difficulty in preparing such species.[11] The method described above appears to provide a facile route to such compounds and should permit a more extensive investigation of their chemistry.

**Acknowledgment.** We gratefully acknowledge the U.S. Department of Energy, Office of Basic Energy Sciences for support of this research.

**Supplementary Material Available:** Tables of atomic positional parameters, selected bond lengths and angles, X-ray crystallographic data, and Figure 1, an ORTEP drawing of 3 (4 pages). Ordering information is given on any current masthead page.

---

(9) (a) Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 1. (b) Heathcock, C. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 111. (c) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (d) Li, Y.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3684. (e) Meyers, A. I.; Miller, D. B.; White, F. H. *J. Am. Chem. Soc.* **1988**, *110*, 4778 (f) Ritter, R. H.; Cohen, T. *J. Am. Chem. Soc.* **1986**, *108*, 3718. (g) Hoffmann, R. W.; Bewersdorf, M.; Ditrich, K.; Krüger, M.; Stürmer, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1176. (h) House, H. O.; Crumrine, D. S.; Teranish, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310.

(10) (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985. (b) Geissman, T. A. *Org. React.* **1944**, *2*, 94. (c) Hauser, C. R.; Hamrick, P. J., Jr.; Stewart, A. T. *J. Org. Chem.* **1956**, *21*, 260.

(11) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Gagné, M. R.; Grubbs, R. H. *Organometallics* **1992**, *11*, 3933. (c) Casey, C. P.; Nagashima, H. *J. Am. Chem. Soc.* **1989**, *111*, 2352. (d) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610.