3824 *J. Am. Chem. Soc.* **1993,** *115,* 3824–3825

A New Form of Coordinated Carbon: An Unsupported C_3 Chain Spanning Two Different Transition Metals

Weiqing Weng, James A. Ramsden, Atta M. Arif, and
J. A. Gladysz*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received February 2, 1993

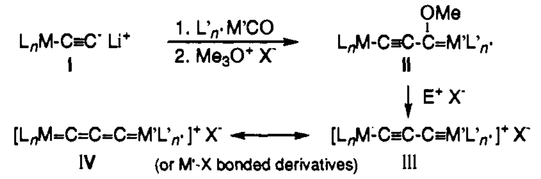
Diverse forms of elemental carbon (C_x) have been incorporated into stable transition-metal complexes. Representative examples include single carbon atoms entombed in polymetallic clusters, C_{60} and related allotropes bound as π-ligands, and unsupported C_1 and C_2 chains spanning two metals.[1-5] In addition to their intrinsic appeal as basic research objectives, such compounds have promising materials and catalytic properties.[6,7]

Recently, several complexes have been prepared that contain unsupported C_4 chains linking two transition metals.[5] However, complexes with C_3 or higher *odd-membered* chains are unknown. We sought to develop methodology that would allow this class of compounds to be accessed. In particular, we have shown that transition-metal ethynyl complexes, $L_nMC{\equiv}CH$, can react with strong organolithium bases to give C_2 derivatives $L_nMC{\equiv}C^- Li^+$ (**I**). These can be functionalized by electrophiles in high yields.[4c,8] Hence, we planned to append a third carbon by elaboration to bimetallic Fischer carbene complexes containing C_3OMe units (**II**), as shown in Scheme I. Methoxy groups have been previously abstracted from many Fischer carbene complexes, giving either cationic or neutral carbyne complexes.[9] In the case of **II**, this would yield the C_3 adduct **III**, to which the fully cumulated resonance form **IV** might make a structural contribution.

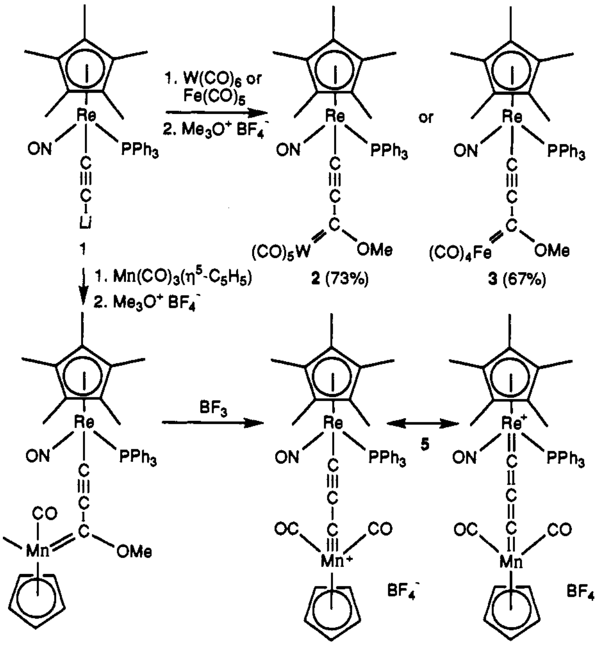
Thus, the rhenium/lithium C_2 species $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CLi)$ (**1**) was generated as reported earlier[8] and treated with the carbonyl complexes $W(CO)_6$, $Fe(CO)_5$, and $Mn(CO)_3(\eta^5\text{-}C_5H_5)$. Subsequent additions of $Me_3O^+BF_4^-$ gave the bimetallic alkynyl Fischer carbene complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}C{-}C(OMe){=})M(CO)_x(\eta^5\text{-}C_5H_5)_y$ ($M/x/y$ = **2**, W/5/0; **3**, Fe/4/0; **4**, Mn/2/1) in 67–73% yields, as summarized in Scheme II.

Complexes **2**–**4** were characterized by microanalysis and IR, NMR (^1H, ^{13}C, ^{31}P), and mass spectroscopy.[10] Their structures followed readily from these data, which included mass spectral parent ions. The IR $\nu_{C\equiv C}$ (**2**/**3**/**4** 2061/2041/1968 cm^{-1}, m-s) and ν_{CO} absorptions were assigned by comparisons with other Fischer carbene complexes, including $C{\equiv}C$ derivatives.[11] The ^{13}C NMR spectra showed downfield CM [ppm, C_6D_6: 253.2 (d, J_{CP} = 3 Hz, J_{CW} = 93 Hz), 256.6 (s), 283.9 (s)] and ReCC resonances [C_α/C_β 204.9 (d, J_{CP} = 12 Hz)/157.5 (s, J_{CW} = 10 Hz), 204.0 (d, J_{CP} = 13 Hz)/152.0 (s), 166.8 (d, J_{CP} = 14 Hz)/146.2 (s)]. However, the ReC_α chemical shifts and IR ν_{NO} values (1674-1648 cm^{-1}, s) were intermediate between those of alkynyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CR)$ [98-86 ppm (d, J_{CP} = 16–18 Hz); 1629–1637 cm^{-1}) and vinylidene complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)({=}C{=}CRR')]^+BF_4^-$ [329 ppm (d, J_{CP} = 10–11 Hz); 1681–1698 cm^{-1}].[8] These and other data suggested contributions by zwitterionic $^+Re{=}C{=}C{=}C(OMe){-}M^-$ resonance forms.

Scheme I. Bimetallic C_3 Complexes. Synthetic Strategy



Scheme II. Syntheses of C_3OMe and C_3 Complexes



Thus the crystal structure of **2** was determined (Figure 1).[10] The ReC bond length (1.973(7) Å) was between those of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C{=}CH(1\text{-naphthyl})]^+PF_6^-$ (2.066(7), 1.84(2) Å),[12] which provide models for the limiting $Re\text{-}C{\equiv}C\text{-}C(OMe){=}W$ and $^+Re{=}C{=}C{=}C(OMe){-}W^-$ resonance forms. Also, the C–C(OMe) bond in **2** (1.38(1) Å) was shorter than the $C{-}CH_3$ bond in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (1.48(1) Å) and the R–C(OR′) bonds in tungsten carbene complexes (RC-

---

[1] Lead 1992 references to carbide cluster compounds: (a) Chisholm, M. H.; Hammond, C. E.; Johnston, V. J.; Streib, W. E.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 7056. (b) Akita, M.; Sugimoto, S.; Tanaka, M.; Moro-oka, Y. *Ibid.* **1992**, *114*, 7581. (c) Adams, C. J.; Bruce, M. I.; Liddell, M. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1314.

[2] Lead references to C_{60} complexes: (a) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 5455. (b) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Ibid.* **1991**, *113*, 9408.

[3] Lead references to $L_nMCM'L'_{n'}$ complexes: (a) Beck, W.; Knauer, W.; Robl, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 318. (b) Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324.

[4] Lead references to $L_nMCCM'L'_{n'}$ complexes: (a) Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316. (b) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *Ibid.* **1991**, *113*, 8466. (c) Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. A. *Ibid.* **1992**, *114*, 5890.

[5] $L_nMCCCCM'L'_{n'}$ complexes: (a) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992. (b) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (c) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411. (d) Crescenzi, R.; Sterzo, C. L. *Organometallics* **1992**, *11*, 4301.

[6] (a) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165. (b) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293.

[7] Izumi, Y.; Chihara, T.; Yamazaki, H.; Iwasawa, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1395.

[8] Ramsden, J. A.; Weng, W.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3635.

[9] Fischer, H. In *Carbyne Complexes*; Fischer, H., Hoffmann, P., Kreiβl, F. R., Schrock, R. R., Schubert, U., Weiss, K., Eds.; VCH: New York, 1988; Chapter 1.

[10] Data are given in the supplementary material. The BF_4 anions in **5**$\cdot(CH_2Cl_2)_{0.5}$ were slightly disordered, and 19 of the 103 independent non-hydrogen atoms were refined isotropically.

[11] (a) $(RC{\equiv}CC(OR'){=})W(CO)_5$: Köhler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1976**, *113*, 11. Fischer, E. O.; Freiβl, F. R. *Ibid.* **1972**, *35*, C47. (b) $(RC{\equiv}CC(OR'){=})Fe(CO)_4$: Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3414.

[12] Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096.

0002-7863/93/1515-3824$04.00/0

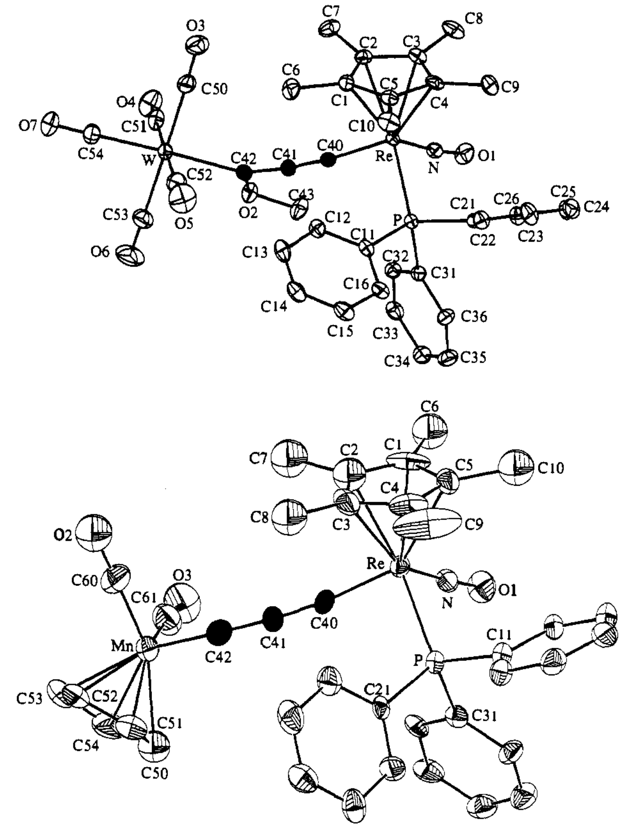


Figure 1. Structures of **2** (top) and the cation of a CH_2Cl_2 hemisolvate of **5** (bottom). Selected bond lengths (Å) and angles (deg): **2**, Re-C40 1.973(7), C40–C41 1.23(1), C41–C42 1.38(1), C42–02 1.353(9), C42–W 2.200(8), Re–P 2.398(2), Re–C40–C41 172.3(7), C40–C41–C42 174.5(8), C41–C42–O2 116.5(7), C41–C42–W 128.1(6); **5**·$(CH_2Cl_2)_{0.5}$ (two independent cations), Re–C40 1.92(1)/1.93(1), C40–C41 1.26(2)/1.28(2), C41–C42 1.32(2)/1.28(2), C42-Mn 1.75(2)/1.75(2), Re–P 2.413(4)/2.410(4), Re–C40–C41 173(1)/175(1), C40–C41–C42 175(2)/170(2), C41–C42–Mn 178(1)/178(2).

(OR′)=)W(CO)$_5$ (1.48–1.52 Å).[13] These trends indicate that the zwitterionic resonance form is a significant but not dominant[14] structural contributor.

Despite abundant literature precedent,[9] repeated attempts to remove the methoxy group from **2** were unsuccessful. However, BF_3 gas has been previously shown to convert manganese carbene complexes (RC(OR′)=)Mn(CO)$_2$(η^5-C_5H_5) to cationic carbyne complexes [(RC≡)Mn(CO)$_2$(η^5-C_5H_5)]$^+BF_4^-$.[15] Accordingly, reaction of **4** and BF_3 gave the target C_3 complex [(η^5-C_5H_5)Re(NO)(PPh$_3$)(CCC)Mn(CO)$_2$(η^5-C_5H_5)]$^+BF_4^-$ (**5**) in 95% yield after workup (Scheme II).

Complex **5** was characterized analogously to **2**–**4**.[10] The FAB mass spectrum gave a strong ion for the cation, and the ^{13}C NMR spectrum showed ReC, C*C*C, and CMn resonances at 194.9 (d, J_{CP} = 12.3 Hz), 169.9, and 286.4 ppm. The IR ν_{NO} absorption (1701 (s) cm^{-1}) was in the region noted above for $^+$Re=C=C complexes, and bands at 2037 (s), 1987 (s), and 1889 (vs) were assigned as ν_{CO}, ν_{CO}, and $\nu_{C\equiv C}$ or ν_{CCC}, respectively. The CMn ^{13}C NMR peak was closer to those of manganese propadienylidene complexes (R$_2$C=C=C=)Mn(CO)$_2$(η^5-C_5H_5) (305–331 ppm)[16] than to those of carbyne complexes [(RC≡)Mn(CO)$_2$(η^5-C_5H_5)]$^+$X$^-$ (356–357 ppm).[17] These and other data suggested a dominant structural contribution by the fully cumulated $^+$Re=C=C=C=Mn resonance form **5b** (Scheme II).

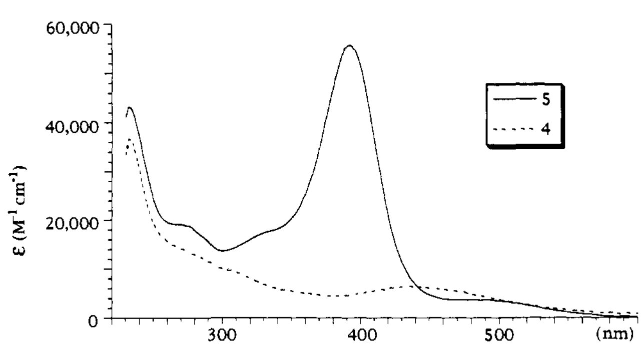


Figure 2. UV/visible spectra of **4** and **5** (CH_2Cl_2, ambient temperature, 3.0–3.9 × 10^{-5} M).

Thus, the crystal structure of **5** was determined (Figure 1).[10] Two independent cations with similar metrical parameters were found in the unit cell. The six MCC and CCC bond angles ranged from 170(2)° to 178(2)° for an essentially linear ReCCCMn linkage. The four CC bonds ranged from 1.26(2) to 1.32(2) Å, indicative of predominant double bond character.[18] The ReC bonds (1.92–1.93(1) Å) were shorter than that in **2**, and the MnC bonds (1.75(2) Å) were closer to that in a propadienylidene complex (R$_2$C=C=C=)Mn(CO)$_2$(η^5-C_5H_5) (1.806(6) Å)[19] than to that in a vinyl-substituted carbyne complex [(R$_2$C=CHC≡)Mn(CO)$_2$(η^5-C_5H_5)]$^+BF_4^-$ (1.665(5) Å).[20] Hence, **5b** best represents the structure of the C_3 complex.

The physical and chemical properties of **5** are under investigation. For example, the UV/visible spectrum (Figure 2) shows an extremely strong absorption at 392 nm and a weaker one at 484 nm (ε 56 000, 3700 M^{-1} cm^{-1}). Complexes **2**–**4** also give visible absorptions, as illustrated for **4** (446 nm, ε 9700 M^{-1} cm^{-1}). We speculate that some of these arise from charge transfer from rhenium to the other metal center. Extensions of our methodology to other novel forms of coordinated carbon, and additional properties of **2**–**5**, will be reported in the near future.[21,22]

Supplementary Material Available: Characterization of **2**–**5**; tables of crystallographic data and structural parameters for **2** and **5** (16 pages); listing of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

---

(13) (a) Daran, J.-C.; Jeannin, Y. *Acta Crystallogr.* **1980**, *B36*, 1392. (b) Toledano, C. A.; Parlier, A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 576. (c) Alvarez, C.; Pacreau, A.; Parlier, A.; Rudler, H.; Daran, J.-C. *Organometallics* **1987**, *6*, 1057. (d) Macomber, D. W.; Hung, M.-H.; Verma, A. G.; Rogers, R. D. *Ibid.* **1988**, *7*, 2072. (e) Cordes, A. W.; Graham, J. B.; Lu, J.; Ferede, R.; Allison, N. T. *Acta Crystallogr.* **1989**, *C45*, 1623. (f) Breimair, J.; Weidmann, T.; Wagner, B.; Beck, W. *Chem. Ber.* **1991**, *124*, 2431.

(14) The CW bond length in **2** (2.200(8) Å) is closer to those in carbene complexes (RC(OR′)=)W(CO)$_5$ (2.09–2.22 Å)[13] than to those in anionic alkyl complexes [RW(CO)$_5$]$^-$ (2.31–2.34 Å): Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045. Darensbourg, D. J.; Bauch, C. G.; Rheingold, A. L. *Ibid.* **1987**, *26*, 977.

(15) (a) Fischer, E. O.; Chen, J.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231. (b) Handwerker, B. M.; Garrett, K. E.; Nagle, K. L.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1562.

(16) (a) Berke, H. *Chem. Ber.* **1980**, *113*, 1370. (b) Kolobava, N. E.; Ivanov, L. L.; Zhvanko, O. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, *478*, 2646.

(17) (a) Fischer, E. O.; Meineke, E. W.; Kreißl, F. R. *Chem. Ber.* **1977**, *110*, 140. (b) Fischer, E. O.; Postonov, V. N.; Kreißl, F. R. *J. Organomet. Chem.* **1982**, *231*, C73.

(18) The C=C bond lengths in allene and butatriene are 1.31–1.28 Å: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 21.

(19) Berke, H.; Huttner, G.; Seyerl, J. V. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36*, 1277.

(20) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *262*, 39.

(21) Weng, W.; Arif, A.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.*, in press.

(22) We thank the DOE for support of this research.