

The hydrosilane-based reductions are remarkable in light of practicability [extremely mild conditions (0 °C to room temperature) and easy handling of commercially readily available hydrosilanes] and provide an alternative efficient approach to aldols of both threo and erythro configurations.

Registry No. 1a, 99114-14-4; 1b, 99114-15-5; 1c, 99114-16-6; 1d, 99114-17-7; 1e, 99114-18-8; 1f, 99114-19-9; 1g, 32742-19-1; 1h, 99114-20-2; 1i, 99114-21-3; 1j, 99114-22-4; 1k, 88635-97-6; 1l, 64854-05-3; 1m, 99114-34-8; 2a, 99114-37-1; 2b, 99114-39-3; 2c, 99114-24-6; 2d, 99114-26-8; 2l, 92282-67-2; 3a, 99114-38-2; 3b, 99114-23-5; 2e, 99114-27-9; 2f, 99114-29-1; 2g, 99210-93-2; 3c, 99114-25-7; 3e, 99114-28-0; 3f, 99114-30-4; 3g, 99210-95-4; 3h, 99114-31-5; 3i, 99114-32-6; 3i (silyl ether), 99114-40-6; 3j, 99114-33-7; 3k, 99210-94-3; 3l, 63647-69-8; *threo-4*, 84412-89-5; *threo-4* (amide), 99114-35-9; *erythro-4*, 84412-87-3; *erythro-4* (amide), 99114-36-0.

(23) The reduction of α -substituted β -amino ketones with NaBH_4 or LiAlH_4 gives poor stereoselectivities in general: Tramontini, M. *Synthesis* 1982, 605.

(24) Stereochemical assignment of α -methyl- β -hydroxycarbonyl compounds by ^1H or ^{13}C NMR spectroscopy: Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Porrung, M. C.; Sohn, J. E.; Lampe, J. J. *Org. Chem.* 1980, 45, 1066. Heathcock, C. H.; Pirrung, M. C.; Sohn, J. E. *Ibid.* 1979, 44, 4294.

New Carbon-Carbon Bond-Forming Reaction of Carbon Monoxide: Remarkable Trialkylation of a Carbonyl Ligand in a Molybdenum Pentadienyl Complex

Michael S. Kralik, John P. Hutchinson, and Richard D. Ernst*

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

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Carbon monoxide may be converted to a wide range of chemically more useful materials by means of a variety of very important processes. Among these can be included the water-gas shift reaction, hydroformylation, methanol synthesis, methanation, and the Fischer-Tropsch reaction, as well as the large number of applications for metal carbonyls in organic synthesis.^{1c,2} Crucial to these processes is the ability of the carbonyl or carbonyl-containing ligands (e.g., acyl) to undergo facile insertion and coupling reactions. We now wish to report a spontaneous and novel coupling reaction which occurs on the attempted preparation of $(2,4\text{-C}_7\text{H}_{11})\text{Mo}(\text{CO})_3\text{CH}_3$ (C_7H_{11} = dimethylpentadienyl). This reaction is unusual with regard to its facility, as well as the fact that three coupling steps are involved, which lead to trialkylation of a carbonyl group, thereby converting it to an O-bound alkoxide ligand,

(1) (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 259-288. (b) Anderson, R. B. "The Fischer-Tropsch Synthesis"; Academic Press: Orlando, 1984. (c) Sneed, R. P. A. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, p 19.

(2) Wender, I.; Pino, P. "Organic Synthesis with Metal Carbonyls"; Wiley: New York, 1968, 1977; Vol. 1, 2.

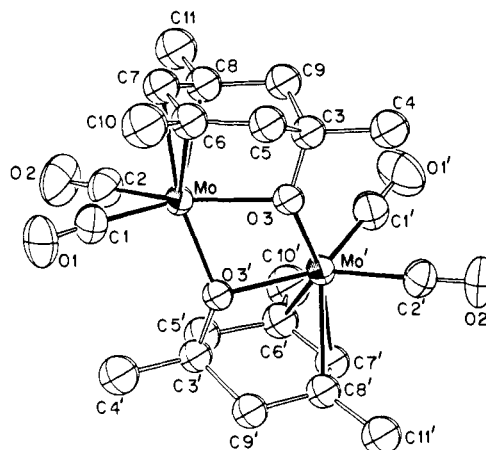
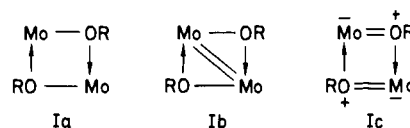


Figure 1. Perspective view of the $(2,4\text{-C}_7\text{H}_{11})\text{Mo}(\text{CO})_3\text{CH}_3$ dimer. While no crystallographic symmetry is present, the primed atoms are approximately related to the unprimed atoms by an inversion operation.

during which conversion of the pentadienyl group to an η^3 -cyclohexenyl ligand takes place. Besides revealing the nature of the coupling reaction, this report suggests that pentadienyl ligands may impart quite unique and potentially useful reaction chemistry to their metal complexes.

Treatment of $(\text{diglyme})\text{Mo}(\text{CO})_3$ ³ in THF with 1 equiv of $\text{K}(2,4\text{-C}_7\text{H}_{11})$ apparently leads to the formation of the $(2,4\text{-C}_7\text{H}_{11})\text{Mo}(\text{CO})_3$ anion.⁴ Addition of 1 equiv of CH_3I at -78 °C leads to a further reaction, producing a dark solution. Subsequent extraction with hexane, followed by low-temperature crystallization, leads to pure, crystalline material in reasonable isolated yield (48%). The product has been characterized by NMR spectroscopy, IR and mass spectroscopy, elemental analysis, and single-crystal X-ray diffraction.⁵ The ^1H NMR spectrum of this compound is similar to that which would be expected for a compound such as $(2,4\text{-C}_7\text{H}_{11})\text{Mo}(\text{CO})_3\text{CH}_3$ (1), in that four resonances were present for the pentadienyl fragment (CH_3 , CH , endo and exo CH_2) and a fifth resonance was observed for the additional methyl group. This pattern excluded the possibility of coupling of an alkyl or acyl group to a single end of the pentadienyl fragment as has been found for butadiene ligands.⁶ However, the endo and exo CH_2 resonances were unusually close together, appearing as an AA' pair at ca. 1.64 ppm. In addition, the ^{13}C NMR spectrum contained one extra quaternary carbon atom resonance. The actual nature of the product was elucidated by single-crystal X-ray diffraction (Figure 1).^{5c} A dimeric complex has resulted, in which, besides being coordinated by two carbonyl ligands, each molybdenum atom is coordinated by two oxygen atoms and an allyl fragment, which have been constructed from the pentadienyl ligand, the third carbonyl group, and the methyl group. Since a partial resonance hybrid such as 1a would only



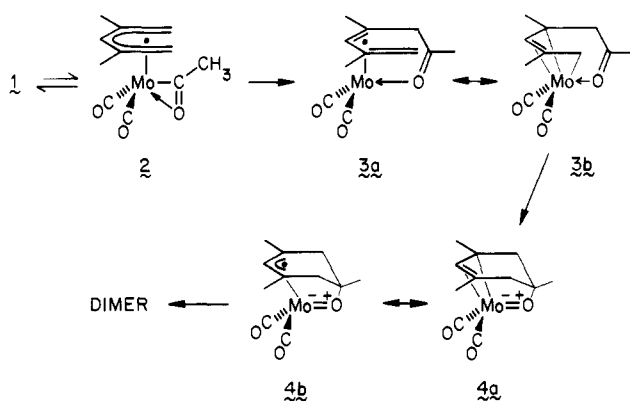
(3) Werner, R. P. M.; Coffield, T. H. *Chem. Ind. (London)* 1960, 936.

(4) (a) The complex may be isolated following toluene extraction. Good NMR data have been obtained and IR data are similar to those in related anions.^{4b-d} (b) Behrens, U.; Edelmann, F. *J. Organomet. Chem.* 1984, 263, 179. (c) Ceccon, A.; Gambaro, A.; Venzo, A. *J. Chem. Soc., Chem. Commun.* 1985, 540. (d) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* 1979, 101, 3535.

(5) (a) Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{Mo}$: C, 45.53; H, 4.86. Found: C, 45.37; H, 5.09. (b) ^1H NMR: δ 2.43 (s, 1H), 1.91 (s, 6H), 1.64 (AA' multiplet, 4H), 1.18 (s, 3H). (c) The crystals are monoclinic (space group $P2_1/n$) with $Z = 4$ dimeric units and $a = 16.782$ (5) Å, $b = 8.461$ (2) Å, $c = 17.523$ (2) Å, $\beta = 110.99$ (2)°. Data were collected out to 50° in 2θ leading to 2942 unique, observed ($I > 2.5\sigma(I)$) reflections. Anisotropic refinement led to agreement indices of $R = 0.038$ and $R_w = 0.046$.

(6) Bannister, W. D.; Green, M.; Haszeldine, R. N. *Proc. Chem. Soc., London* 1964, 370.

Scheme I



lead to a 16-electron configuration, it would seem likely that other interactions could be present. In this regard, one can note that the separation between molybdenum atoms is 3.215 (1) Å, comparable to the value of 3.235 (1) Å observed in $[(C_5H_5)Mo(CO)_3]_2$ ⁷ but much longer than the value of 2.448 (1) Å in $[(C_5H_5)Mo(CO)_2]_2$.⁸ The Mo-O-Mo angles are rather large compared to the O-Mo-O angles (102.0 (2)° vs. 71.6 (1)°), leading to an extremely short O...O separation of 2.421 Å, which suggests little metal-metal bonding (cf., 1b). However, the sums of the three bond angles about the oxygen atoms average 116.3°, close to that expected for sp² hybridization. It would therefore seem likely that 18-electron configurations are reached through π interactions with the oxygen atoms (1c).

Particularly remarkable about this complex, however, is the multistep coupling process that has taken place, during which one carbonyl ligand is converted to an alkoxy.⁹ To our knowledge this represents a very new mode of reactivity for a transition-metal carbonyl complex. While it was recognized that subsequent coordination of additional ligands to an actual $Mo(2,4-C_7H_{11})(CO)_3(CH_3)$ complex might bring about a coupling reaction, it was a surprise to find that such events would take place spontaneously and particularly that the acyl group would couple to *both* ends of the pentadienyl group. A possible mechanism for this process is set out in Scheme I. While most steps have precedent,^{6,10} the final coupling process (3 → 4a) is unusual. By utilizing an alternative representation for metal-butadiene bonding (3b), however, one can regard this as an intramolecular alkylation of a coordinated ketone.¹¹ That a similar cyclization process is not commonly (if ever) observed for related allyl and butadiene compounds might reflect the greater strain in the expected smaller ring products. It may also be noted that the overall reaction bears some similarity to the hydrogenation of CO in the methanol synthesis except that the former reaction is stoichiometric and involves the transfer of alkyl groups, rather than hydrogen atoms, to the carbonyl carbon atoms. In addition, there is some resemblance to the formation of metal-enediolates in various metal carbonyl reactions.¹²

It appears that the coupling chemistry of transition-metal-pentadienyl compounds will prove to be very versatile. Almost certainly the rather unique aspects will lead to useful applications,¹³

(7) (a) Wilson, F. C.; Shoemaker, D. P. *J. Chem. Phys.* **1957**, *27*, 809. (b) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.
(8) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535.

(9) (a) The conversion of an alkoxy to a carbonyl ligand has been observed.^{9b} (b) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546.

(10) Williams, G. M.; Rudisill, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 3357.

(11) Lindsell, W. E. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, **1982**; Vol. 1, p 192.

(12) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393. (c) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706. (d) Planalp, R. P.; Anderson, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774.

and one can note in particular that the combination of five-membered and single-membered fragments into six-membered rings is an uncommon synthetic strategy. We have, in addition, observed a number of coupling reactions involving other unsaturated organic molecules with metal-pentadienyl compounds,¹⁴ and we are pursuing in greater detail this chemistry and its potential applications.

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Supplementary Material Available: Listing of the positional parameters for the non-hydrogen atoms of the molybdenum compound, a table of bond distances and angles, and a structure factor table (14 pages). Ordering information is given on any current masthead page.

(13) (a) In other applications, pentadienylsilanes^{13b} and anions^{13c} have been employed for pentadienylations, while pentadienylnickel compounds undergo limited coupling reactions.^{13d} Cyclohexadienylmetal compounds have a number of useful applications.^{13e,f} (b) Seyferth, D.; Pornet, J.; Weinstein, R. M. *Organometallics* **1982**, *1*, 1651. (c) Gerard, F.; Miginiac, P. *Bull. Soc. Chim. Fr.* **1974**, 1924, 2527. (d) Hegedus, L. S.; Varapath, S. *Organometallics* **1982**, *1*, 259. (e) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463 and references therein. (f) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

(14) Ernst, R. D.; Kralik, M. S.; Melendez, E., unpublished results.

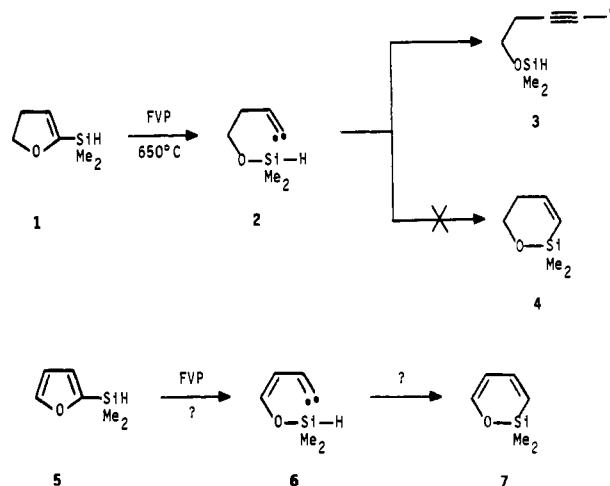
Silapyran and Silacyclobutene Formation in the Gas-Phase Pyrolysis of 2-(Dimethylsilyl)furan

Thomas J. Barton* and Brian L. Groh

Department of Chemistry, Iowa State University
Ames, Iowa 50011

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Recently we have reported¹ that flash vacuum pyrolysis of α -silyl enol ethers provides a route to vinylidenes via reductive elimination of an alkoxy silane. We have also reported² a single attempt to utilize this reaction with a cyclic enol ether 1 as a method of ring expansion, but the resulting vinylidene 2 exclusively preferred to collapse to acetylene 3 rather than undergo Si-H insertion to yield 4. However, it was hoped that greater rigidity



(1) Barton, T. J.; Groh, B. L. *J. Org. Chem.* **1985**, *50*, 158.

(2) Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 7221.