

diphenylacetylene, or isobutylene did not significantly affect either the room-temperature ^1H or $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** or the thermolysis reaction to form the C–C cleaved product **2**.

Although the intriguing potential intermediate $\text{L}_4\text{Ru}=\text{O}$ could be involved in some of these transformations, we believe it is more likely that the reactions are initiated by attack of electrophile at the nucleophilic oxygen of the metallacycle, followed by elimination of olefin (a process analogous to that observed in electrophile-catalyzed dehydration of tertiary alcohols).¹⁴ Additional mechanistic studies on these unusual C–O and C–C cleavage reactions are in progress to test this hypothesis, as is further exploration of the chemistry of metallacycle **3**.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Supplementary Material Available: Spectroscopic and analytical data for complexes **3–5** and **7–10** (3 pages). Ordering information is given on any current masthead page.

(14) March, J. *Advanced Organic Chemistry*; John Wiley and Sons: New York, 1985.

Syntheses of a σ,π -Bidentate Bicyclo[3.2.1]octene Complex of Manganese via Carbene–Dienyl Coupling and of a Novel η^2 -Arene Species

Chenjie Wang, Mark G. Lang, and John B. Sheridan*

Department of Chemistry
Rutgers, The State University of New Jersey
Newark, New Jersey 07102

Arnold L. Rheingold

Department of Chemistry, University of Delaware
Newark, Delaware 19716

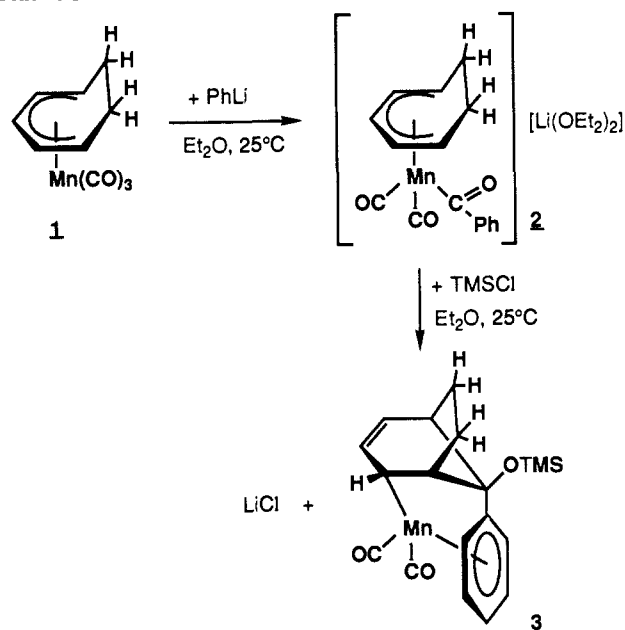
Received November 3, 1989

The syntheses, reactions, and study of transition-metal carbene complexes containing olefin and/or polyene ligands have attracted much interest in recent years,¹ particularly in their relevance to olefin metathesis catalysis,² cyclopropanation reactions,³ and the Ziegler–Natta polymerization of olefins.⁴ In contrast, the synthesis of dienyl or trienyl complexes containing carbene ligands has not been reported, due in part to a lack of suitable acylmetallate precursors.

In our laboratory we are attempting to develop new synthetic strategies that involve intramolecular acyl- and/or carbene-polyene coupling in dienyl-acyl and dienyl-carbene complexes. It is hoped that this approach will prove of synthetic use in both the stereoselective functionalization of polyenes and the construction of bicyclic rings.

Herein we describe the formation of a novel bidentate bicyclic ligand that apparently results from a coupling between a carbene ligand and the C(1) and C(5) carbons of a cycloheptadienyl ring. The product is a bicyclo[3.2.1]oct-2-ene complex (**3**) in which the

Scheme I



organic moiety is both σ -bound to the metal and π -bound through an arene substituent at C(8). More interestingly, the reaction of this new complex with triphenylphosphine results in the formation of an $(\eta^3\text{-allyl})\text{Mn}(\text{CO})_2(\text{PPh}_3)$ derivative which contains a highly distorted transition-metal– η^2 -arene interaction. This latter crystallographically characterized complex shows the arene ligand as principally η^1 -bonded to the metal with a Mn–C distance of 2.445 (10) Å.

Reaction of $[\text{Mn}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$ (**1**)⁵ with 1 equiv of PhLi in diethyl ether gives the highly air and moisture sensitive orange crystalline salt $[\text{Mn}(\text{CO})_2(\text{C}(\text{O})\text{Ph})(\eta^5\text{-C}_7\text{H}_9)] [\text{Li}(\text{Et}_2\text{O})_2]$ (**2**) (Scheme I), which has been spectroscopically characterized.⁶ Reaction of **2** with TMSCl [$\text{TMS} = \text{Si}(\text{CH}_3)_3$] in diethyl ether at room temperature does not give the expected carbene complex but the new orange species (**3**) (Scheme I).

Complex **3** can be isolated in 84% yield (based on **1**) as a moderately stable orange solid and was fully characterized by elemental analysis and ^1H , ^{13}C , ^1H – ^1H (2D COSY), and ^1H – ^{13}C (2D COSY) NMR and IR spectroscopy.⁶ It appears to derive from the coupling of a “transient” carbene ligand with the terminal dienyl carbon atoms of the C_7 ring concomitant with migration of the metal to the phenyl group of the original acyl ligand. The formation of an η^6 -arene complex was confirmed by the absence of any aromatic protons in the ^1H NMR spectrum of **3** and the presence of signals between δ 4.90 and 6.20 typical of π -bound arenes.^{1c} As shown in Scheme I, the metal remains σ -bonded to the original C_7 ring at C(4), making the new ligand a σ,π -bidentate bicyclo[3.2.1]oct-2-ene⁷ moiety.

The coupling of dienes with “transient” carbene ligands on iron has been reported by Chen and co-workers,¹ and in the reaction of $[(\eta^4\text{-cycloocta-1,5-diene})(\text{CO})_2\text{FeC}(\text{O})\text{Ph}]^-$ with TMSCl , complete migration of iron to the phenyl group was observed without any residual σ -bonding to the original eight-membered ring.^{1c} The formation of **3** differs in that it gives a bidentate ligand and most likely proceeds via sequential alkyl-carbene and alkyl-olefin migratory insertions, assuming the dienyl ligand is represented as a diene-alkyl species. A similar mechanism is proposed in ref 1c for the formation of the iron complex mentioned above.

(5) Haque, F.; Miller, J.; Pauson, P. L.; Tripathi, J. B. *J. Chem. Soc., Dalton Trans.* 1971, 743.

(6) Analytical and spectroscopic data are included in the supplementary material.

(7) Complexes of this ligand have previously been made from strained-ring iron carbene complexes. (a) Bly, R. S.; Silverman, G. S.; Bly, R. K. *J. Am. Chem. Soc.* 1988, 110, 7730. (b) Bly, R. S.; Silverman, G. S. *Organometallics* 1984, 3, 1765.

(1) (a) Chen, J.; Lei, G.; Jin, Z.; Hu, L.; Wei, G. *Organometallics* 1988, 7, 1652 and references therein. (b) Chen, J.; Yin, J.; Lei, G.; Wang, Y.; Lin, G. *J. Chem. Soc., Dalton Trans.* 1989, 635. (c) Chen, J.; Yin, J.; Fan, Z.; Xu, W. *J. Chem. Soc., Dalton Trans.* 1988, 2803 and references therein. (d) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* 1986, 108, 2173 and references therein. (e) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* 1984, 106, 3754.

(2) Katz, T. J. *Adv. Organomet. Chem.* 1977, 16, 283.

(3) Moser, W. R. *J. Am. Chem. Soc.* 1969, 91, 1141.

(4) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* 1978, 604.

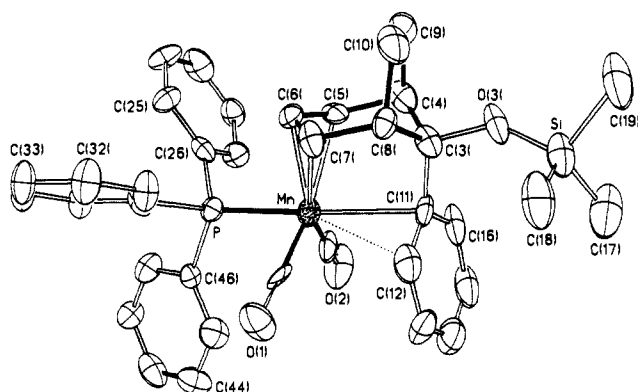
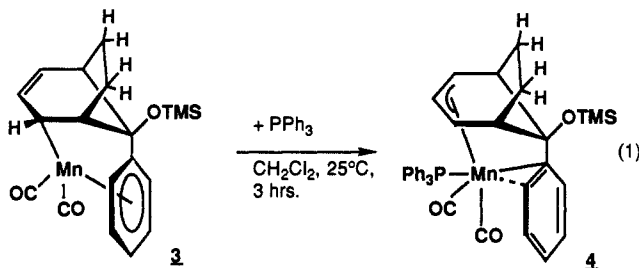


Figure 1. Molecular structure and labeling scheme for **4**. Distances (Å): Mn-P, 2.266 (3); Mn-C(5), 2.265 (11); Mn-C(6), 2.081 (11); Mn-C(7), 2.214 (11); Mn-C(11), 2.445 (10); Mn-C(12), 2.567 (10). Angles (deg): C(1)-Mn-C(2), 105.5 (5); C(1)-Mn-P, 85.5 (4); C(2)-Mn-P, 83.8 (4); P-Mn-C(11), 167.3 (3); C(1)-Mn-C(11), 104.4 (5); C(2)-Mn-C(11), 85.9 (4); C(5)-C(6)-C(7), 118.2 (9).

Complex **3** is an unusual analogue of other arene-alkyl manganese complexes prepared by both the Brookhart⁸ and Sweigart⁹ groups, in which the former showed that alkyl migration to the endo face of the arene could be induced by addition of PPh₃.⁸ We have therefore reacted **3** with PPh₃ in an attempt to promote coupling of the metal σ -bonded carbon C(4) and the phenyl substituent. However, a more unusual reaction forming a highly distorted η^2 -arene complex occurred. Thus, addition of 1-2 equiv of PPh₃ to **3** in CH₂Cl₂ results in the formation of **4** containing an (η^3 -allyl)Mn(CO)₂(PPh₃) fragment η^2 -bonded to the phenyl ring, eq 1.



Complex **4** was isolated in 40% yield (based on **3**) as analytically pure deep red microcrystals. Its structure was confirmed by ¹H, ¹³C, and ³¹P NMR and IR spectroscopy,⁶ as well as by an X-ray diffraction study.¹⁰ An ORTEP drawing of **4** is shown in Figure 1 and shows a pseudooctahedral structure about manganese with the phosphine and η^2 -phenyl ligand trans to one another. The Mn-C(11) distance of 2.445 (10) Å is clearly a bond, albeit weak, and the long Mn-C(12) distance of 2.567 (10) Å suggests that both C(11) and C(12) are involved in a highly distorted η^2 -arene-metal interaction. The Mn...C(16) distance is 3.250 (11) Å. The distortion in the η^2 -ligand is such that it appears almost η^1 -bonded to manganese; however, a twist of the phenyl ring about the C(3)-C(11) axis and a tilt of the bicyclic ligand brings C(12) close to the metal.¹¹

(8) (a) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 1730. (b) Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745.

(9) Halpin, W. A.; Williams, J. C., Jr.; Hanna, T.; Sweigart, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 376.

(10) Crystal data for **4**: C₃₇H₃₈MnO₂PSi, monoclinic, P2₁/c, *a* = 10.153 (4) Å, *b* = 9.741 (3) Å, *c* = 33.346 (11) Å, β = 96.24 (3)°, *V* = 3278.5 (24) Å³, *Z* = 4, *D* (calcd) = 1.306 g cm⁻³, μ (Mo K α) = 5.03 cm⁻¹, *T* = 293 K. Of 3769 data collected (Nicolet R3m diffractometer, 4° ≤ 2 θ ≤ 42° with no higher angle data omitted), 3424 were independent and 1989 with *F*_o ≥ 5 σ (*F*_o) were observed. Solution was by direct methods, and refinement included anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were idealized, and the phenyl rings in PPh₃ were constrained to rigid hexagons. *R*_p = 8.08%, *R*_w = 8.08%, *S* = 1.976, and $\Delta\rho$ = 1.58 e/Å³. Computations used SHELXTL software.

(11) A referee has noted that this tilt results in an asymmetry in the η^3 -allyl bonding such that C(7) is 0.051 Å closer to Mn than C(5).

Complex **4** is stable as a solid, but in solution, a small amount of **3** and free PPh₃ are also observed, indicating a delicate balance between η^2 - and η^6 -arene ligation. Noteworthy is that the NMR data for **4** suggest no arene bonding to Mn (e.g., no ³¹P coupling to the arene carbons and only four arene ¹³C NMR resonances), which may be due to a rapid complexation/decomplexation of the arene double bond in solution. Surprisingly, addition of excess PPh₃ to **3** does not form a Mn(CO)₂(PPh₃)₂ derivative with complete arene dissociation, presumably due to steric factors, and may explain the stability of the novel structure **4**.

The formation of **3** demonstrates a potentially viable approach to the construction of bicyclic ring systems via the intramolecular coupling of two unsaturated ligands at a metal center. In addition, the reaction of **3** with PPh₃ indicates that facile decomplexation of the organic moiety should be possible via treatment with added ligands followed by protonation of the remaining M-C σ -bond. Further studies on **3** and **4** involving the functionalization of the bicyclo[3.2.1]oct-2-ene ring and other diene-yl-carbene complexes are in progress.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Rutgers Research Council for financial support.

Supplementary Material Available: Tables of X-ray characterization data for **4** including listings of fractional coordinates, bond lengths, bond angles, thermal parameters, and hydrogen atom coordinates, spectroscopic and analytical data for **2-4**, and 1D and 2D NMR spectra for **3** (12 pages); listing of observed and calculated structure factors for **4** (12 pages). Ordering information is given on any current masthead page.

Uranium(VI) Organoimido Complexes

Carol J. Burns,^{1a} Wayne H. Smith,^{1b} John C. Huffman,^{1c} and Alfred P. Sattelberger*,^{1a}

*Inorganic and Structural Chemistry Group (INC-4) and
Nuclear Materials Process Technology Group (NMT-2)
Los Alamos National Laboratory
Los Alamos, New Mexico 87545
Molecular Structure Center, Indiana University
Bloomington, Indiana 47405*

Received June 29, 1989

Complexes containing multiply bonded alkylidene, alkylidyne, imido, nitrido, and oxo ligands, and selected combinations thereof, are part of the tapestry of tungsten(VI) chemistry. There are numerous examples of such complexes, many of which were discovered within the past decade, and the interest in these high-energy systems stems, in large measure, from their ability to effect transformations of unsaturated organic and inorganic substrates.² The multiply bonded oxo group is well-known in discrete high-valent complexes of the next group 6 element, uranium, but nearly always in the form of the linear uranyl ion, UO₂²⁺.³ Aside from uranyl complexes, the only reported molecular coordination compounds of U(VI) are UF₆, UCl₆, and the binary alkoxides, U(OR)₆.^{3,4} Uranium(VI) compounds containing

(1) (a) Inorganic and Structural Chemistry Group (INC-4), Mail Stop C346. (b) Nuclear Materials Process Technology Group (NMT-2), Mail Stop E501. (c) Molecular Structure Center, Indiana University.

(2) Nugent, W. A.; Mayer, J. A. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988 and references therein.

(3) (a) Weigel, F. In *The Chemistry of the Actinide Elements*; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; Chapter 5 and references therein. (b) Burns, C. J.; Sattelberger, A. P. *Inorg. Chem.* **1988**, *27*, 3692. (c) Paine, R. T.; Ryan, R. R.; Asprey, L. B. *Inorg. Chem.* **1975**, *14*, 1113. (d) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1989.

(4) Bacher, W.; Jacob, E. In *Handbook on the Physics and Chemistry of the Actinides*; Freeman, A. J., Keller, C., Eds.; Elsevier North-Holland: Amsterdam, 1985; Volume 3, Chapter 7 and references therein.