$C_5H_5)]$ ($n \leq 3$);[21] again cleavage of the metal-metal system must occur.

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Registry No. 1, 96109-94-3; 2, 96109-95-4; 3, 13007-90-4; 4, 96109-96-5; 9, 96109-97-6; $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, 12091-64-4; $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$, 12091-65-5; $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, 12107-35-6; $Na[W(CO)_3(\eta\text{-}C_5H_5)]$, 12107-36-7; $[NiCl_2(PPh_3)_2]$, 14264-16-5.

Supplementary Material Available: Listings of positional and thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes for 2 (21 pages). Ordering information is given on any current masthead page.

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Uranium-Carbon Multiple-Bond Chemistry. 5.[1] Carbon-Oxygen Bond Cleavage in a Uranium Phosphonium Enolate Manganese Complex

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Summary: Upon heating, the carbon-oxygen bond in $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$ can be cleaved to form $Cp(OC)_2MnC{\equiv}CPMe_2Ph$, **3**. Crystals of **3** belong to space group $P2_1/c$, with unit cell parameters of a = 10.611 (2) Å, b = 18.603 (3) Å, c = 8.193 (2) Å, β = 102.55 (2)°, Z = 4, and V = 1578.7 (6) Å^3. The structure of **3** shows it to be a phosphonium acetylide.

We have proposed[1,2] that coordinated carbon monoxide can be activated by reaction with the uranium-carbon multiple bond in $Cp_3U{=}CHPMePhR$[3-5] (**1a**, R = Me; **1b**, R = Ph), where Cp = $\eta\text{-}C_5H_5$, Me = CH_3, and Ph = C_6H_5. An example[2] of this is a carbonyl coupling which results in allyl formation during the reaction of 1 with $[CpFe(CO)_2]_2$. We postulated[2] that the initial step of this process is the insertion of a terminal carbonyl into the uranium-carbon multiple bond. In the previous paper of this series[1] such an insertion was documented in a reaction of $CpMn(CO)_3$ with **1a** which produces $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$, **2**. We argued that the organouranium compound had activated the carbon-oxygen bond by decreasing its bond order through the strong tendency of U(IV) to accept electrons from oxygen. In this communication we report that the carbon-oxygen bond in **2** can be *cleaved* under fairly mild conditions to form a complex, $Cp(OC)_2MnCCPMe_2Ph$, **3**, containing a zwitterionic phosphonium acetylide ligand. The overall reaction is the *formation of a new carbon-carbon triple bond accompanied by the deoxygenation of a terminal carbonyl.*

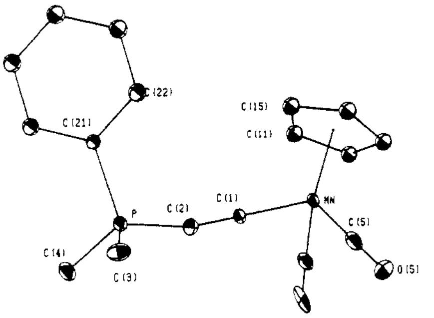
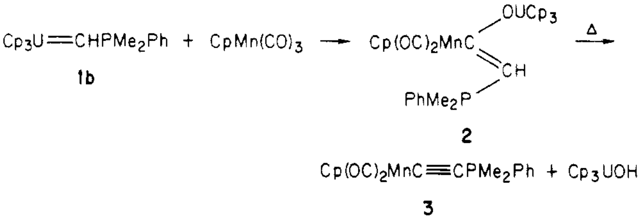


Figure 1. An ORTEP drawing of $Cp(OC)_2MnCCPMe_2Ph$, 3. Some important bond distances (Å) and angles (deg): Mn-C(1) = 1.895 (5), Mn-C(5) = 1.744 (7), Mn-C(6) = 1.742 (6), C(1)-C(2) = 1.221 (7), P-C(2) = 1.683 (6); Mn-C(1)-C(2) = 179.6 (4), P-C(2)-C(1) = 166.6 (5).

As previously described[1] an equimolar mixture of **1b** and $CpMn(CO)_3$ in THF produced **2**. After evaporation of the THF, the remaining red-brown solid was dissolved in toluene, refluxed for 1 h, and filtered. Upon addition of an equal volume of heptane and cooling to room temperature, translucent yellow crystals of **3** formed in 55% yield.[6]



$$\underset{\textbf{1b}}{Cp_3U{=}CHPMe_2Ph} + CpMn(CO)_3 \longrightarrow \underset{\textbf{2}}{Cp(OC)_2MnC(OUCp_3){=}CH(PMe_2Ph)} \xrightarrow{\Delta} \underset{\textbf{3}}{Cp(OC)_2MnC{\equiv}CPMe_2Ph} + Cp_3UOH$$

The structure of **3**, belongs to the monoclinic space group $P2_1/c$, with unit cell parameters of a = 10.611 (2) Å, b = 18.603 (3) Å, c = 8.193 (2) Å, β = 102.55 (2)°, Z = 4, and V = 1578.7 (6) Å^3, was determined by X-ray diffraction.[7] An ORTEP drawing is shown in Figure 1; a summary of crystal and data collection parameters and listings of bond distances and angles, positional and thermal parameters, and the observed and calculated structure factors can be found as supplementary material.

The molecular structure of **3** reveals a zwitterionic phosphonium acetylide ligand coordinated to $Cp(OC)_2Mn$. The $MnC{\equiv}CP^+R_3$ unit is rare, the only other structure determination being $Br(OC)_4MnC{\equiv}CPPh_3$,[8,9] **4**. A Re analogue of **4**,[9] $(OC)_5WC{\equiv}CPPh_3$,[10] and $(CH_3C_5H_4)(OC)_2MnC{\equiv}CPMe_3$,[11] **5**, have also been synthesized. As expected for an acetylide, the Mn-C(1)-C(2) angle, 179.6

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[1] Part 4 of this series: Cramer, R. E.; Higa, K. T.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 7245-7247.

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[6] NMR (C_6D_6, chemical shifts in ppm from Me_4Si): CH_3P 1.90 (6 H, d, J_{PCH} = 14.0 Hz); Cp 4.43 (5 H, s); Ph 7.60 (1 H, m), 7.93 (2 H, m), 8.08 (2 H, m). IR (Nujol mull, 1800-2000 cm^{-1}): 1972 vs, 1887 vs, 1852 vs. Two of these IR bands will arise from CO stretches and the third from the C≡C stretch. The assignment of a particular vibration to a specific frequency is not certain.[9,11]

[7] A single crystal was mounted in a glass capillary and sealed under nitrogen. X-ray data was collected by using a Syntex $P\bar{1}$ diffractometer and processed as previously described.[21] The structure was solved with SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976, using Patterson methods to locate the uranium, followed by refinements and Fourier maps to locate the remaining atoms. The Cp and Ph groups were refined as rigid bodies with H atoms included, using the standard parameters included in SHELX-76.

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0276-7333/85/2304-1140$01.50/0

(4)°, is nearly linear; however, C(1)–C(2)–P is slightly bent, 166.6 (5)°. The P–C(2) bond, 1.683 (6) Å, is shorter than a P–C single bond and appears typical of resonance-stabilized phosphoylides.[12] The C(1)–C(2) distance, 1.221 (7) Å, is not significantly different from other metal–acetylide complexes where this distance ranges between 1.20 and 1.22 Å.[13,14] Similar features are also observed[8] for 4. The Mn–C(1) bond length, 1.895 (5) Å, is longer than Mn–C double-bond distances of 1.68 (2) Å and 1.79 (2) Å in $Cp(OC)_2Mn{=}C{=}CHPh$[15] and $Cp(OC)_2Mn{=}C{=}C{=}CMe_2$,[16] respectively, but is shorter than the single-bond distance of 2.185 (11) Å determined for $(OC)_5MnCH_3$[17] by electron diffraction. It is also significantly shorter than 1.99 (1) Å observed[8] for the Mn–C bond in 4. In 4 the phosphonium acetylide ligand is trans to carbonyl ligands, which are good π acceptors, while in 3 it is trans to a Cp ligand which competes poorly for metal π electrons. Consequently back-bonding into the acetylide ligand should be greater in 3 accounting for the shorter metal–carbon bond. Similarly, the Mn–carbonyl distances in 3 are also shorter than those in 4, by about 0.10 Å. This is not an isolated phenomenon, and Mn–C bond lengths to ligands *trans* to carbonyls are typically 0.06–0.12 Å longer than the analogous distances in ligands trans to weak π acceptors.[18,19] The decrease in both the Mn–acetylide and Mn–carbonyl distances in 3 compared to 4 indicates that the phosphonium acetylide ligand is a good π acceptor. Thus, the Mn C bond in 3 probably should be ascribed partial double-bond character.

The conversion of 2 to 3 formally involves the elimination of Cp_3UOH, via the cleavage of the oxygen–carbon bond and the abstraction of a proton from the beta carbon atom.[20] Precedence for the reaction can be found in the very recently reported[11] reaction of a closely related silyl vinyl ether complex.

$$(CH_3C_5H_4)(OC)_2MnC(OSiMe_3)CHPMe_3 \rightarrow (CH_3C_5H_4)(OC)_2MnC{\equiv}CPMe_3 + Me_3SiOH$$

In both reactions C–O bond cleavage has been promoted by the attachment of an oxophilic group which presumably weakens the carbon–oxygen bond and activates it. The present case demonstrates that the attachment of an oxophilic metal ion, such as uranium, to an oxygen can also induce C–O bond cleavage. The ability of the uranium–carbon multiple bond to either deoxygenate or induce coupling[2] of coordinated carbon monoxide indicates the potential use of organouranium complexes as synthetic reagents and may have relevance to catalytic CO reduction processes.

Acknowledgment. The support of this work by the National Science Foundation, Grant CHE82-10244 (J.W.G. and R.E.C.), and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Table I, crystal, data collection, and reduction parameters, Table II, bond distances and angles for $Cp(OC)_2MnCCPMe_2Ph$, Table III, positional and thermal parameters for anisotropically refined atoms of $Cp(OC)_2MnCCPMe_2Ph$, Table IV, positional and thermal parameters for isotropically refined atoms of $Cp(OC)_2MnCCPMe_2Ph$, and Table V, observed and calculated structure factors for $Cp(OC)_2MnCCPMe_2Ph$ (11 pages). Ordering information is given on any current masthead page.

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(20) While Cp_3UOH has not yet been unambigously identified as a reaction product, a green-brown solid precipitates during the reaction. NMR spectra obtained during reactions run in THF-d_8 contain a peak at about −2.5 ppm. After filtration and drying under vacuum, the molecular ion observed in EI mass spectrum of this material is at *m/e* 882, which corresponds to the anhydride $(Cp_3U)_2O$. While Cp_3UOH has been mentioned in the secondary literature,[22] its characterization and properties have not been reported in the primary literature or in the habilitation thesis[23] where its synthesis is described. In deoxygenated water $Cp_3U(H_2O)_n{}^+$ is stable, however, in basic solution the system appears to be complicated by reactions of OH^- at the cyclopentadienide. In aqueous basic solutions of Cp_3UCl an incompletely characterized bright green precipitate, which is postulated to be an oxyhydroxide, forms.[24] Very recently an NMR resonance obtained during a controlled oxidation of Cp_3UR conducted in saturated C_6D_6 solutions at 27 °C has been tentatively assigned to $(Cp_3U)_2O$, −3.16 ppm. Upon addition of small amounts of water a new peak, tentatively assigned to Cp_3UOH, appears at −3.40 ppm.[25]

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Synthesis of 1,3-Metallatitanacyclobutanes of Group 4[†]

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Summary: The reaction of the 1,3-di-Grignard reagent $Cp_2Ti(CH_2MgBr)_2$ (**2**) with the metallocene dichlorides Cp_2MCl_2 (M = Ti, Zr, Hf) gave the 1,3-metallatitanacyclobutanes $Cp_2\overline{MCH_2TiCp_2CH_2}$ (M = Ti, **1a**; M = Zr, **1b**; M = Hf, **1c**, respectively).

Titanacyclobutanes continue to receive a high level of attention including their synthesis,[1] bonding aspects,[2] and

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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