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Synthesis of Heterobimetallic Allene Complexes

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The first dinuclear complex containing a four-electron μ-η^2,η^2-allene ligand was synthesized from the reaction of allene with $[Cp(CO)_2Mo]_2$ (Cp = η^5-C_5H_5) and was reported in 1977.[1] Thereafter, a number of complexes of this type were prepared,[2] notably by photolysis of dinuclear complexes with a bridging cyclopropylidene ligand.[2b,c] Several dinuclear and trinuclear metal complexes containing allenyl ligands in various bonding modes have been prepared by initially using a propargyl ligand as a template.[3] Despite these and other reports,[4] methods that lead to formation of a heterodinuclear μ-η^2,η^2-allene complex are still lacking.[5] In exploring the chemistry of a tungsten β-(chlorocarbonyl)allylic complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$ (**1a**),[6] we prepared several dinuclear complexes by replacing the Cl atom with another metal group and found photolysis of such complexes provided a systematic approach to the dinuclear μ-η^2,η^2-allene complexes. Herein, we report several complexes synthesized via this approach and their characterization.

The reaction of $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$ (**1a**)[6] with $Cp(CO)_3W^-$ in THF resulted in the formation of a homonuclear complex $Cp(CO)_2W[\mu\text{-}\eta^3,\eta^1\text{-}CH_2C(CO)CH_2]W(CO)_3Cp$ (**2a**). Heteronuclear analogues $Cp(CO)_2M(\mu\text{-}\eta^3,\eta^1\text{-}CH_2C(CO)CH_2)M'$ (**2b**, M = Mo, M′ = $W(CO)_3Cp$; **2c**, M = W, M′ = $Fe(CO)_2Cp$; **2d**, M = W, M′ = $Re(CO)_5$) were prepared similarly. However, attempts to prepare similar complexes using the $Cp(CO)_3Mo^-$ anion were unsuccessful. We believe that metal anions with weak nucleophilicity[7] may not be applicable for the preparation of **2** employing this synthetic strategy. On the basis of the EAN rule, the two metal centers in **2** bridged by a μ-η^3,η^1-β-carbonylallylic ligand should have no M–M bond. Complexes **2** were characterized through a combination of microanalytical data and IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.[8] For example, in the ^{1}H NMR spectrum of **2a** at room temperature, the two inequivalent Cp groups displayed a sharp resonance and a broad resonance and the allylic *syn* and *anti* protons appeared as two broad resonances at δ 2.76 and 1.38, respectively. These broad resonances are due to the fluxional behavior of the *endo* and *exo* configurations of the allylic group. At 240 K, the two broad resonances at δ 2.76 and 1.38 of **2a** were resolved into two sets of allylic protons at δ 2.78, 1.16 and 2.68, 1.58,[8] assignable to those of the *endo* and *exo* isomers, respectively.

Photolysis of complexes **2a–c** with UV irradiation in benzene resulted in the loss of two CO ligands and afforded the dinuclear allene complexes $Cp(CO)_2M(\mu\text{-}\eta^2,\eta^2\text{-}CH_2{=}C{=}CH_2)M''$ (**4a**, M = W, M″ = $W(CO)_2Cp$; **4b**, M = Mo, M″ = $W(CO)_2Cp$; **4c**, M = W, M″ = $Fe(CO)Cp$); see Scheme I. Complexes **4** were characterized by spectroscopic methods. In addition, the molecular structure of **4c** was determined by an X-ray diffraction analysis.[9] In each unit cell, there are two independent molecules which are an enantiomeric pair and differ only slightly in their bond lengths and angles. Figure 1 shows one of the molecules. As expected, the C_3 unit is nonlinear with a C–C–C bond angle of 140(4)°. The three-carbon allene unit sits above the W–Fe axis in a criss-cross arrangement. This geometry allows interaction of one π-bond of the allene with the W center and of the second π-bond of the allene with the Fe center. With such a structure, the heteronuclear system should display two sets of inequivalent geminal protons, i.e. proximal and distal with respect to the M–M′ bond. Indeed, in the ^{1}H NMR spectra of heteronuclear allene complexes, four allene protons displayed four multiplet resonances (δ 4.50, 3.02, 2.66, 2.40 for **4c** and δ 4.22, 3.69, 2.67, 2.45 for **4b**). In contrast, in the homonuclear system,[1] there is a C_2 axis passing through the center carbon of the allene ligand and the midpoint of the M–M vector. Therefore, in the ^{1}H NMR spectrum of **4a**, a deceptively simple triplet pattern for the methylene protons was observed.

In the photolytic decarbonylation reactions of **2a** and **2b**, an intermediate formulated as $Cp(CO)_2M(\mu\text{-}\eta^3,\eta^1\text{-}CH_2CCH_2)\text{-}W(CO)_3Cp$ (**3a**, M = W; **3b**, M = Mo) was observed. Presumably, the two metal centers in **3** are bridged by a η^3,η^1-allylic ligand as shown in the Scheme I.[10] Complexes **3a** and **3b** were observed but not isolated.[8] Interestingly, for rhenium complex **2d**, only one decarbonylation was attained and the complex $Cp(CO)_2W(\mu\text{-}\eta^3,\eta^1\text{-}CH_2CCH_2)Re(CO)_5$ (**3d**) was isolated in 45% yield. In the ^{1}H NMR spectrum of **3d**, the resonances of the allylic protons at δ 3.09, 1.67 are typical for *syn*/*anti* resonances of an allylic system. The mass spectrum of **3d** displayed parent peaks as well as fragmentations due to loss of CO.[7] W–Re metal–metal bonds have been observed in several complexes.[11] Reasons for no further decarbonylation of **3d** are not clear.

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(8) Preparations and spectroscopic data of these complexes are given in the supplementary material.

(9) Yellow crystals of **4c** were grown by slow diffusion of *n*-hexane into a dichloromethane solution of **4c** at 4 °C. Crystal data: space group $P2_12_12_1$, a = 7.606(2) Å, b = 12.333(6) Å, c = 31.072(7) Å, Z = 4. X-ray data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. A total of 2205 reflections were collected with use of the ω–2θ scanning technique between 2.0 and 49.9° in 2θ. A total of 1553 reflections with $I > 2\sigma(I)$ were used in the full-matrix least-squares refinement. The structure was solved by using heavy-atom methods with the NRCC computing package. The final values of the agreement indices were R = 0.062, R_w = 0.060, and GOF = 2.20.

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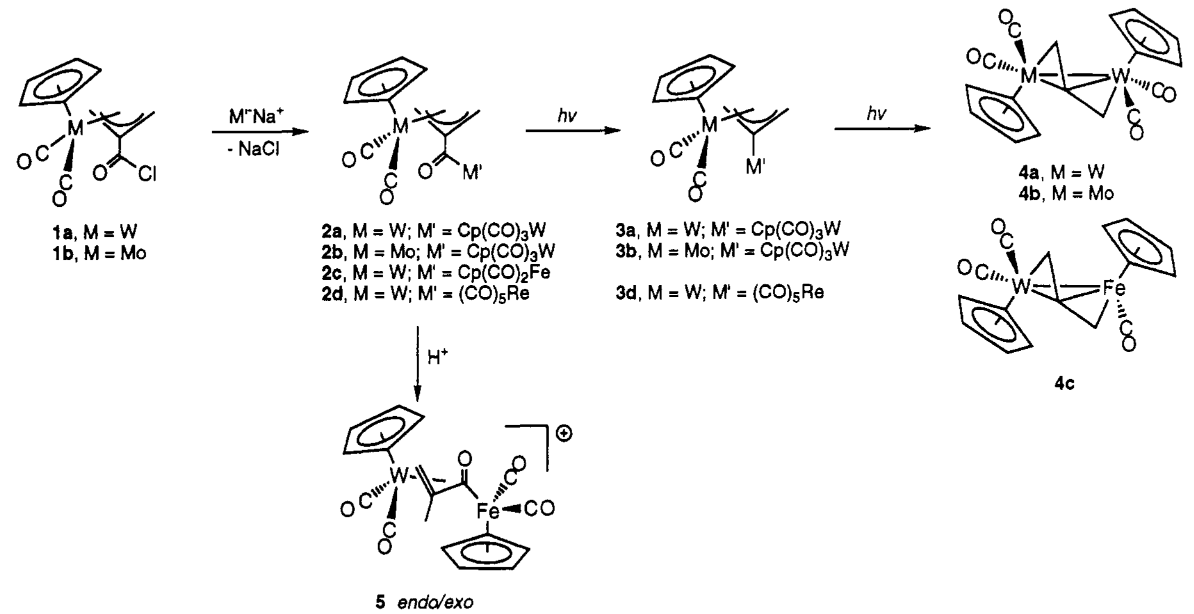
Scheme I



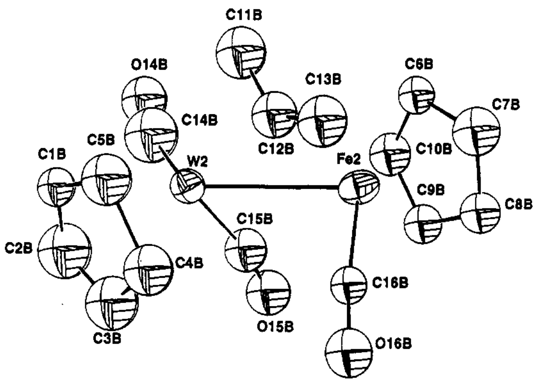


Figure 1. ORTEP drawing of Cp(CO)$_2$W(μ-η^2,η^2-CH$_2$=C=CH$_2$)Fe(CO)Cp (**4c**) with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Fe–C(12B), 1.91(4); Fe–C(13B), 2.08(5); W–C(11B), 2.34(4); W–C(12B), 2.07(4); C(12B)–C(13B), 1.34(6); C(11B)–C(12B), 1.45(6); C(11B)–C(12B)–C(13B), 140(4).

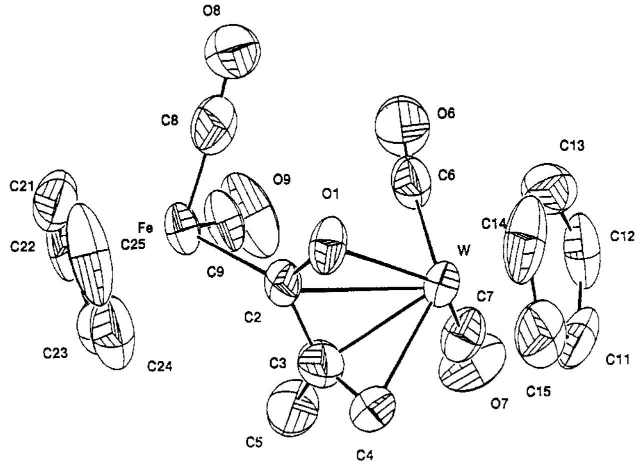


Figure 2. ORTEP drawing of Cp(CO)$_2$W(μ-η^4,η^1-CH$_2$=C(CH$_3$)-CH=O)Fe(CO)$_2$Cp (**5**) with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Fe–C(2), 1.946(1); W–O(1), 2.141(7); W–C(2), 2.49(1); W–C(3), 2.28(1); W–C(4), 2.24(1); C(2)–O(1), 1.32(1); C(2)–C(3), 1.43(2); C(3)–C(4), 1.42(2); C(3)–C(5), 1.49(2); C(2)–C(3)–C(4), 115(1); O(1)–C(2)–C(3), 110.7(9); C(4)–C(3)–C(5), 121(1).

Treatment of **2c** with HBF$_4$ resulted in the formation of a cationic enone complex [Cp(CO)$_2$W(μ-η^4,η^1-CH$_2$=C(CH$_3$)CO)-Fe(CO)$_2$Cp]BF$_4$ (**5**).[8] Complex **5** in solution gave a mixture of *endo*/*exo* isomers with a ratio of 6.4:1. The structure of **5** was also confirmed by X-ray diffraction analysis.[12] As shown in Figure 2, the enone group adopts an s-cis configuration and is in an *endo* conformation with respect to the Cp group.[13] The η^4-coordination of the enone group is revealed by the one W–O and three W–C bonding distances. A slightly longer W–C(2) separation of 2.49(1) Å as compared to the other W–C separations (2.24(1) and 2.28(1) Å) may be attributed to the steric effect of the iron moiety and to a relatively short W–O(3) distance of 2.141(7) Å. For a cationic molybdenum butadiene complex,[14] four isomers (*endo*/*exo* and *cis*/*trans*) have been observed at low temperature. In our case, the s-trans configuration was not observed probably due to the steric bulk of the metal moiety.

Using β-(chlorocarbonyl)allylic metal complexes as starting materials, we have demonstrated the preparation of a heteronuclear complex with a β-(carbonyl)allylic bridging ligand. Photolysis of this product led efficiently to the heteronuclear μ-η^2,η^2-allene complex. Reactivity of allene complexes with heteronuclear metal centers is currently under investigation.

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Supplementary Material Available: A textual presentation of the syntheses and spectroscopic data for **2a**, **2b**, **2c**, **2d**, **3b**, **4b**, **4c**, and **5** and tables of X-ray crystallographic data, positional parameters, anisotropic thermal parameters, and selected bond distances and angles for **4c** and **5** (11 pages). Ordering information is given on any current masthead page.

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