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Communications

Photoinduced Coupling of CO and Vinylidene Ligands—Formation of Cyclobutane-1,3-diones

Mokhles M. Abd-Elzaher,[†] Bernhard Weibert, and Helmut Fischer*

Fachbereich Chemie, Universität Konstanz, Fach M727, 78457 Konstanz, Germany

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Summary: Photolysis of pentacarbonyl vinylidene complexes of chromium and tungsten affords cyclobutane-1,3-dione derivatives, whereas thermolysis yields binuclear vinylidene nonacarbonyl complexes. In contrast to vinylidene complexes, photolysis of the diphenylallenylidene chromium complex gives, without incorporation of CO, the dimer of the allenylidene ligand, tetraphenylhexapentaene.

The photolysis of heteroatom-stabilized carbene complexes of chromium and molybdenum (Fischer carbene complexes) in the presence of various substrates[1] such as imines, olefins, aldehydes, amines, alcohols, CO, and isocyanides provides a convenient route to, for instance, β-lactams,[2] imidazolines, azapenams, dioxocyclams,[3] cyclobutanones,[4] butenolides,[5] β-lactones,[6] 2-aminobutyrolactones,[7] amino acid derivatives,[8] α-hydroxy acid derivatives,[9] and various other products.[10] These reactions are assumed to be initiated by a photolytically induced coupling of a CO ligand with the carbene ligand to generate metal-coordinated ketenes. These are then trapped by the substrate.[1] Despite several attempts,[11] it has not been possible to isolate or spectroscopically detect the presumed ketene complexes. However, there is considerable indirect evidence for the formation of short-lived metal-coordinated ketenes.[12]

In contrast to the photochemically induced coupling, the thermal intramolecular coupling of a CO and a CPh_2 ligand to form diphenylketene has been observed in the coordinatively unsaturated carbene complexes "$(CO)_4M{=}CPh_2$" (M = Cr, W).[13] The intermolecular carbonylations of a carbene ligand to form a ketene ligand at manganese and iron centers[14] and of the very electrophilic phenylcarbene complex $[(CO)_5W{=}C(C_6H_4R\text{-}p)H]$ (R = H, Me)[15] have likewise been reported.

Recently, the controlled, reversible conversion of a ketene ligand to carbene and CO ligands on a iridium center has been observed[16] and then studied by theoretical means.[17] Furthermore, the rapid exchange of the

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* To whom correspondence should be addressed. Fax: +49-7531-883136. E-mail: helmut.fischer@uni-konstanz.de.

[†] Present address: Inorganic Chemistry Department, National Research Centre, P.O. 12622 Dokki, Cairo, Egypt.

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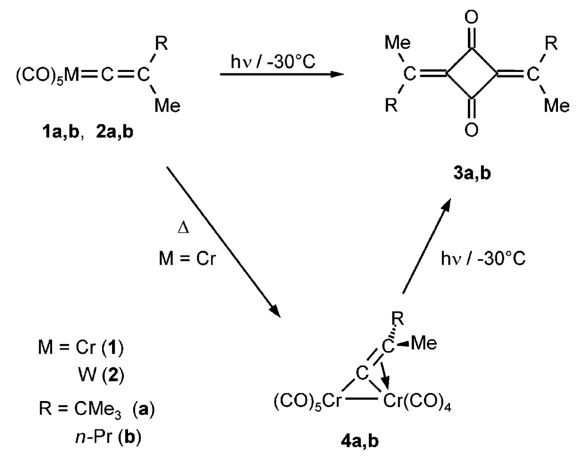
Scheme 1



carbonyl of the ketene ligand with CO ligands in manganese complexes of the type $[(\eta^5\text{-}C_5H_4R)(CO)_2Mn(\eta^2\text{-}R'(Ph)C{=}C{=}O)]$ may also involve a carbene carbonyl complex intermediate.[18]

The coupling of CO ligands with a metal-coordinated higher homologue of carbene ligands such as vinylidene or allenylidene ligands, however, has not been observed until now. We now report on the first photochemically induced coupling of a CO and a "C=C(Me)R" ligand at chromium and tungsten and on the formation of cyclobutane-1,3-diones.

The chromium vinylidene complexes **1a**,**b**, obtained as described previously[19] by the sequential reaction of $[Cr(CO)_6]$ with KC_8, the corresponding alkynyllithium compound, and trimethyloxonium tetrafluoroborate, are thermally unstable and decompose in solution at room temperature to form binuclear vinylidene-bridged nonacarbonyl chromium complexes (see Scheme 1, complexes **4a**,**b**).[19] In contrast, photolysis of **1a**,**b** in pentane–dichloromethane (1:1) at −30 °C for about 1 h[20] affords reaction mixtures, from which the cyclobutane-1,3-diones **3a**,**b** are isolated in 62 and 58% yield in addition to hexacarbonyl chromium (Scheme 1).

The ^1H and ^{13}C NMR spectra of **3a**,**b** show only one signal each for the C(sp^2)-bound methyl groups, indicating the presence of a single isomer. Only two resonances are observed for the four ring carbon atoms in the ^{13}C NMR spectra. Therefore, the methyl groups are trans oriented. These conclusions are supported by the X-ray structural analysis of **3a** (Figure 1).[21] The C=C and C=O distances and the distances within the four-membered ring are similar to those reported for related cyclobutane-1,3-diones.[23]

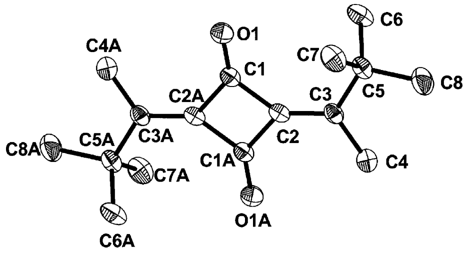
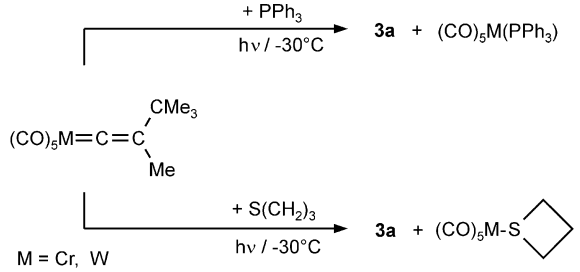


Figure 1. Molecular structure of cyclobutanedione **3a** in the crystal state (hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): C1–C2 = 1.505(2), O1–C1 = 1.2211(16), C3–C2 = 1.365(2), C3–C4 = 1.500(2), C3–C5 = 1.534(2); C1–C2–C1A = 88.6(1), C2–C1–C2A = 91.4(1), O1–C1–C2 = 133.6(1), C1–C2–C3 = 132.0(1). C2–C3–C4 = 118.0(1), C2–C3–C5 = 123.2(1).

Scheme 2



The cyclobutane-1,3-diones are the products of coupling of CO with the vinylidene ligand followed by dimerization of the resulting propadienone. The coupling must be photolytically induced, since on thermolysis of **1a**,**b** cyclobutane-1,3-diones are not formed. The yields considerably drop when the chromium complexes **1a**,**b** are replaced by the tungsten complexes **2a**,**b**. From the photolysis of **2a**,**b**, the cyclobutane-1,3-diones **3a**,**b** are obtained in only 27 and 19% yields, respectively.

The metal–carbonyl fragment can be trapped by nucleophiles. When the photolysis of **1a** or **2a** is carried out in the presence of triphenylphosphine or thiethane, the pentacarbonyl complexes $[(CO)_5ML]$ (M = Cr, W; L = PPh_3, $S(CH_2)_3$) are isolated from the reaction mixture in addition to **3a** (Scheme 2). The time required for complete conversion of **1a** and **2a** decreases from 1 h to about 25 to 30 min, suggesting that the coupling is reversible. However, the yield of **3a** likewise drops to 20–27%.

Presumably the coupling of CO and the vinylidene ligand to give a propadienone proceeds by an intramolecular pathway. Whether the formation of the cyclobutane-1,3-diones by "dimerization" of propadienones involves free propadienones or proceeds in a metal-centered fashion is at present unknown. A metal-centered mechanism seems more likely, since the cyclobutane-1,3-dione **3a** is also formed when the photolysis of **1a** is carried out in the presence of olefins or carbonyl compounds such as 2-methylpropene, ethyl vinyl ether, or acetone. Products derived from cycloaddition of the olefin or of acetone to propadienone could not be detected. Nevertheless, the intermediacy of free propadienones cannot completely be excluded.

Thermolysis of **1a** at room temperature affords the binuclear complex **4a** in high yield. Irradiation of **4a** in

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(21) Crystal data for **3a**: $C_8H_{12}O$, $M_r = 124.18$, monoclinic, $P2_1/n$, $a = 6.829(2)$ Å, $b = 10.524(3)$ Å, $c = 10.179(3)$ Å, $\beta = 96.11(2)°$, $V = 727.4(4)$ Å^3, $T = 188(2)$ K, $Z = 4$, $D = 1.134$ g/cm^3, 3618 reflections collected, 1586 unique reflections ($R_{\text{int}} = 0.0869$), which were used in the calculations. The final R1 and wR2 values (all data) were 0.0632 and 0.1129, respectively. The structure was solved by direct methods using the SHELXTL-97 program package.[22] The positions of the hydrogen atoms were found and refined isotropically. All other atoms were refined anisotropically.

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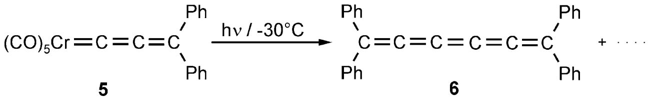
Scheme 3



pentane−dichloromethane at −30 °C again yields the cyclobutane-1,3-dione **3a**. The formation of **3a** from **4a** is faster (20−30 min versus 1 h) than from **1a**. Whether **4a** is an intermediate in the formation of **3a** from **1a** is at present unknown.

In contrast to vinylidene complexes, photolysis of the diphenylallenylidene chromium complex **5** does not give rise to the formation of any CO−allenylidene coupling product. Instead, irradiation of **5** in pentane−dichloromethane at −30 °C affords tetraphenylhexapentaene (**6**) in 83% yield,[20] formed by dimerization of the allenylidene ligand without incorporation of CO (Scheme 3).

Presumably loss of a CO ligand from **5** is much faster than CO/allenylidene coupling. Loss of CO from **5** would yield a coordinatively unsaturated complex that then could react with another complex **5** to form **6**. A similar mechanism has been proposed by Casey and Anderson to account for the observation that on thermolysis of the carbene complex (2-oxacyclopentylidene)pentacarbonylchromium mainly the dimer of the carbene ligand is formed and no cyclobutanone.[24]

The photoinduced dimerization of an allenylidene ligand has not been observed before, although the *thermal* dimerization of the di-*tert*-butylallenylidene ligand in $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C{=}C(t\text{-}Bu)_2]$ at 100 °C to form tetra-*tert*-butylhexapentaene has been reported.[25]

As has already been observed with vinylidene complexes, the thermal and the photolytic reactions of **5** differ. At room temperature complex **5** in pentane−dichloromethane slowly decomposes within about 2 days to give hexacarbonyl chromium. The formation of **6** cannot be detected. Addition of thiethane accelerates the decomposition process, and $[(CO)_5Cr\{S(CH_2)_3\}]$ is isolated from the reaction mixture instead of hexacarbonyl chromium. Again, hexapentaene **6** is not formed.

In carbonyl complex chemistry photolysis is often used instead of heating to initiate substitution reactions under mild conditions.[26] Our observations show that, when chromium and tungsten metallacumulenes are employed, thermally and photolytically initiated reactions can differ considerably. Instead of substitution reactions the photolysis induces coupling processes in pentacarbonyl vinylidene and allenylidene complexes (CO/vinylidene and allenylidene/allenylidene coupling).

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Supporting Information Available: Text describing the synthesis and characterization of the new compounds and details of the experimental procedures and figures and tables giving crystallographic data for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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