Supporting Information

for

Photo-induced coupling of CO and vinylidene ligands –

formation of cyclobutane-1,3-diones

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3. Experimental

3.1. General

All operations were carried out under nitrogen by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium-benzophenone ketyl (THF, diethyl ether) or CaH_2 (pentane, dichloromethane) and were freshly distilled prior to use. The silica gel used for chromatography (J. T. Baker, silica gel for flash chromatography) was nitrogen saturated. The yields refer to analytically pure compounds and were not optimized.

The vinylidene complexes **1a**[1] and **2a**[2] and the allenylidene complex **5**[3] were synthesized as previously described. Complexes **1b** and **2b** wee synthesized analogously. [Me$_3$O]BF$_4$ were prepared according to the literature procedures.[4] Metal hexacarbonyls (Aldrich), 3,3-dimethylbut1-yne (Aldrich), pent-1-yne (Fluka), diphenyl diazene (Aldrich), and trimethylene sulfide were commercial products and were used without further purification.

IR: FT-IR spectrophotometer (FTS70), Bio-Rad. All IR measurements were carried out at 298 K. ^{1}H-NMR, ^{13}C-NMR: Bruker AC 250. Unless specifically mentioned, NMR spectra were recorded in CDCl$_3$ at room temperature. Chemical shifts are reported in ppm relative to internal TMS. MS: Finnigan MAT 312 (EI). Elemental analysis: CHN-Analyser (CHN-O-RAPID) Heraeus. Photolysis reactions were carried out in a duran glass apparatus using a mercury high pressure lamp (TQ 150, Fa. Heraeus).

General procedure for photolysis of the vinylidene complexes 1a,b and 2a,b

About 5 mmol of the vinylidene complex was dissolved in 300 ml of pentane/dichloromethane (1:1) and photolyzed at –30°C for about 1 h in a Duran-glass apparatur (cut-off wavelength: 300 nm). The reaction was followed by IR spectroscopy. The photolysis was stopped when the vinylidene complex could not be detected any more. The solution was allowed to warmed to room temp. and the volume of the solution was reduced to about 10 ml. The solution was

chromatography at –30°C on silica. First, with pentane [M(CO)$_6$] was eluted. Subsequent elution with pentane/dichloromethane (ratio vide supra) gave the a yellow band containing the cyclobutane-1,3-dione.

2,4-Bis(1,2,2-trimethylpropylidene)-cyclobutane-1,3-dione (3a)

Photolysis of [(CO)$_5$Cr=C=C(t-Bu)Me] (**1a**) and elution of the yellow band with pentane/dichloromethane (9:1) gave 1.73 mmol of **3a** (62 % based on **1a**). Photolysis of [(CO)$_5$W=C=C(t-Bu)Me] (**2a**) and chromatography gave 0.75 mmol of **3a** (27 % based on **2a**). The microcrystalline powder obtained by recrystalization from pentane/dichloromethane (9:1) contained small amounts of dichloromethane. Mp: 175°C. IR (pentane): ν(CO) 1693 m, ν(C=C) 1590 m cm^{-1}. ^{1}H-NMR: δ 2.41 (s, 6H, Me), 1.30 (s, 18H, *t*-Bu). ^{13}C-NMR: δ 188.9 (C=O), 175.3 (C=*C*CH$_3$), 150.4 (*C*=CCH$_3$), 38.8 (*C*(CH$_3$)$_3$), 28.5 (C(*C*H$_3$)$_3$)), 17.7 (=C*C*H$_3$). MS (m/z, %): 248 (21.7) [M$^+$], 233 (19.4) [M$^+$- Me], 205 (15.7) [M$^+$ - Me - CO], 190 (16.4) [M$^+$ - Me – CO - Me]. Anal. Calcd. for C$_{16}$H$_{24}$O$_2$ (248.37) + 0.1 CH$_2$Cl$_2$: C, 75.21; H, 9.42. Found: C, 75.22; H. 9.58. Elemental analysis: C$_{16}$H$_{24}$O$_2$ (248.37) C, 77.36; H, 9.75;

2,4-Bis(1-methylbutylidene)cyclobutane-1,3-dione (3b)

Photolysis of [(CO)$_5$Cr=C=C(Pr)Me] (**1b**) and elution of the yellow band with pentane/dichloromethane (8:2) gave 1.73 mmol of **3b** (58 % based on **1b**). Photolysis of [(CO)$_5$W=C=C(Pr)Me] (**2b**) chromatography gave 0.48 mmol of **3b** (19 % based on **2b**). Mp: 182°C. IR (pentane): ν(CO) 1687 m, ν(C=C) 1585 m cm^{-1}. ^{1}H-NMR: δ 2.63 (t, *J* = 7.5 Hz, 4H, CH$_2$), 2.25 (s, 6H, =CCH$_3$), 1.59 (sext, *J* = 7.5 Hz, 4H, CH$_2$), 0.96 (t, *J* = 7.4 Hz, 6H, CH$_3$). ^{13}C-NMR: δ 190.4 (C=O), 163.5 (=*C*CH$_3$), 150.9 (*C*=CCH$_3$), 36.9 (=C*C*H$_3$), 21.4 (=C*C*H$_2$), 19.5 (*C*H$_2$CH$_3$), 13.8 (CH$_2$*C*H$_3$). MS (m/z, %): 220 (81.0) [M$^+$], 177 (50.4) [M$^+$ - CH$_2$CH$_2$CH$_3$], 134

(80.6) [M^+ - 2Pr]. Anal. Calcd. for $C_{14}H_{20}O_2$ (220.3): C, 76.31; H, 9.16. Found: C, 75.63; H, 9.24.

Photolysis of 1a in the presence of PPh$_3$

The photolysis of **1a** in the presence of 2.5 equivalents of PPh$_3$ was carried out as decribed above. Chromatography at –30°C on silica first with pentane gave [Cr(CO)$_6$] and then with pentane/dichloromethane (9:1) the cyclobutadione. Finally, with dichloromethane a second yellow band containing [CO)$_5$Cr(PPh$_3$)] was eluted. The complex was identified by comparison of its spectra with published data.[5]

Photolysis of 2a in the presence of PPh$_3$

The photolysis of **2a** in the presence of 2.5 equivalents of PPh$_3$ was carried out analogously. The reaction was followed by IR spectroscopy. Photolysis was stopped when the vinylidene complexes could not be detected any more. The solution was removed in vacuo. The cyclobutandione and [W(CO)$_6$] were extracted twice with 10 ml of pentane each and then twice with 15 ml of pentane/dichloromethane (1:1). The remaining [CO)$_5$W(PPh$_3$)] was still contaminated with small amounts of [W(CO)$_6$]. The complex was identified by comparison of its spectra with those published.[5]

Photolysis of 1a and 2a in the presence of trimethylene sulfide

The photolysis of **1a** in the presence of 2.5 eq. of trimethylene sulfide was carried out as described above. Chromatography at –30°C on silica first with pentane gave [Cr(CO)$_6$] and then with pentane/dichloromethane (9:1) the cyclobutadione **3a**. Finally, with pentane/dichloromethane (7:3) a second yellow band containing the complex **5** was eluted. Yield: 1.35 mmol (27 % based on **1a**). The complex was fully characterized and additionally identified by comparison of its spectroscopic data with those published earlier.[6] Mp: 29 - 30°C. IR (pentane): ν(CO) 1938 s, 1946 vs, 2069 m cm^{-1}. ^{1}H-NMR: δ 3.40 (t, J = 8.0 Hz, 4H, CH$_2$),

2.94 (quint, J = 8.0 Hz, 2H, CH$_2$). ^{13}C-NMR: δ 221.5 (*trans*-CO), 214.8 (*cis*-CO), 35.9 (2CH$_2$), 25.9 (CH$_2$). MS (m/z, %): 266 (4.2) [M$^+$], 238 (3.9) [M$^+$ - CO], 210 (4.5) [M$^+$ - 2CO], 182 (4.6) [M$^+$ - 3CO], 154 (7.7) [M$^+$ - 4CO], 126 (19.9) [M$^+$ - 5CO], 98 (15.3) [M$^+$ - 5CO - 2CH2], 84 (29.8) [M$^+$ - 5CO - 3CH$_2$]. Anal. Calc. for C$_8$H$_6$O$_5$CrS (266.19): C, 36.10; H, 2.27. Found C, 35.84; H 2.31.

Photolysis of **2a**, chromatography and separation of [(CO)$_5$W{S(CH$_2$)$_3$}] from the reaction products were carried analogously. The complex was identified by comparison of its spectra with published data.[6]

Photolysis of pentacarbonyl(diphenylallenylidene)chromium

A solution of 2.72 g (7.1 mmol) of pentacarbonyl(diphenylallenylidene)chromium (**5**) in 300 ml of pentane/dichloromethane (1:1) was photolyzed at –30°C for 4 h. The color of the solution gruadually changed from blue to green. The reaction was followed by IR spectroscopy. After 4 h the irradiation was stopped and the volume of the solution reduced to ca. 10 ml. Chromatography at –30°C on silica gave 5 fractions: the first one (slightly yellow, elution with pentane) contained [Cr(CO)$_6$], the second one (blue, elution with pentane/dichloromethane (20:1)) contained starting allenylidene complex, the third and the forth ones (different degree of green, elution with pentane/dichloromethane (10:1) and (8:2)) yielded mixtures of the allenylidene complex and tetraphenylhexapentaene (**6**). Finally, the fifth band (red-brown, elution with pentane/dichloromethane (3:2)) contained pure **6**. The compound **6** was identified by comparison of its spectra with published data.[7]

Yield: 1.13g (83 % based on **5**). Mp: 204°C (ref. f: 202-207°C). IR: ν(cumulene) 2154 m, 2125 s, 2054 m, ν(C=C) 1599 m cm^{-1}. ^{1}H-NMR: δ 7.82-6.63 (m, 20H, Ph). MS (m/z, %): 380 (0.91)

$[M^+]$, 303 (0.8) $[M^+ - Ph]$, 226 (1.1) $[M^+ - 2Ph]$, 214 (0.9) $[M^+ - 2Ph - C]$, 202 (1.3) $[M^+ - 2Ph - 2C]$.

*X-Ray structural analyses of **3a***

Single crystals suitable for X-ray structural analyses were obtained from pentane/dichloromethane (9:1). The measurements were performed at 188(2) K with a crystal mounted on a glass fiber on a Siemens P4 diffractometer (graphite monochromator, Mo-Kα radiation, $\lambda = 0.71073$ Å). For crystal data and refinement details see the Table 1. The structure was solved by direct methods using the SHELXTL-97 program package.[8] The positions of the hydrogen atoms were found and refined isotropically. All other atoms were refined anisotropically.

References

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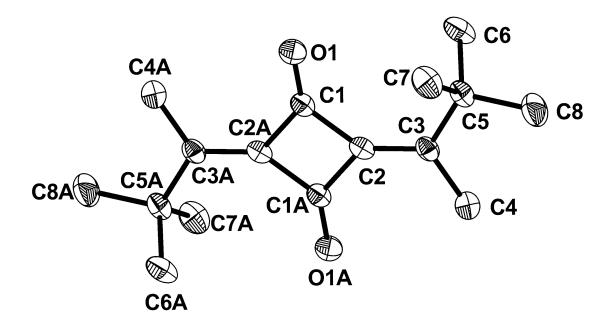
Structure of compound $(CO)_2[C=C(t\text{-Bu})Me]_2$ (**3a**)

Table 1. Crystal data and structure refinement for compound **3a**.

Empirical formula	$C_8H_{12}O$
Formula weight	124.18
Temperature	188(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 6.829(2) Å α = 90 deg.
	b = 10.524(3) Å β = 96.11(2) deg.
	c = 10.179(3) Å γ = 90 deg.
Volume	727.4(4) Å^3
Z, Calculated density	4, 1.134 Mg/m^3
Absorption coefficient	0.073 mm^{-1}
F(000)	272
Crystal size, colour, habit	0.4 x 0.35 x 0.3 mm, yellow, block
Theta range for data collection	2.79 to 26.99 deg.
Limiting indices	-8<=h<=8, -13<=k<=13, -13<=l<=13
Reflections collected / unique	3618 / 1586 [R(int) = 0.0869]
Completeness to theta = 26.99	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1586 / 0 / 130
Goodness-of-fit on F^2	1.021
Final R indices [I>2σ(I)]	R1 = 0.0451, wR2 = 0.1044
R indices (all data)	R1 = 0.0632, wR2 = 0.1129
Largest diff. peak and hole	0.308 and -0.161 e· Å^{-3}

Table 2. Bond lengths [Å] and angles [deg] for compound **3a**.

_____

O(1)-C(1)	1.2211(16)
C(3)-C(2)	1.365(2)
C(3)-C(4)	1.500(2)
C(3)-C(5)	1.534(2)
C(2)-C(1)	1.505(2)
C(2)-C(1)#1	1.5105(18)
C(1)-C(2)#1	1.5105(18)
C(4)-H(4C)	0.979(19)
C(4)-H(4B)	1.00(2)
C(4)-H(4A)	1.01(2)
C(5)-C(7)	1.541(2)
C(5)-C(8)	1.542(2)
C(5)-C(6)	1.545(2)
C(6)-H(6A)	1.001(18)
C(6)-H(6B)	0.99(2)
C(6)-H(6C)	0.99(2)
C(7)-H(7C)	0.99(2)
C(7)-H(7B)	1.00(2)
C(7)-H(7A)	1.00(2)
C(8)-H(8A)	0.99(2)
C(8)-H(8B)	1.01(2)
C(8)-H(8C)	1.01(3)

C(2)-C(3)-C(4)	117.96(13)
C(2)-C(3)-C(5)	123.20(12)
C(4)-C(3)-C(5)	118.82(13)
C(3)-C(2)-C(1)	132.00(12)
C(3)-C(2)-C(1)#1	139.42(13)
C(1)-C(2)-C(1)#1	88.56(10)
O(1)-C(1)-C(2)	133.60(13)
O(1)-C(1)-C(2)#1	134.96(14)
C(2)-C(1)-C(2)#1	91.44(10)
C(3)-C(4)-H(4C)	111.2(10)
C(3)-C(4)-H(4B)	113.9(12)
H(4C)-C(4)-H(4B)	108.7(18)
C(3)-C(4)-H(4A)	108.7(11)
H(4C)-C(4)-H(4A)	108.2(17)
H(4B)-C(4)-H(4A)	105.8(15)
C(3)-C(5)-C(7)	109.81(13)
C(3)-C(5)-C(8)	112.36(12)
C(7)-C(5)-C(8)	107.88(13)
C(3)-C(5)-C(6)	108.34(11)
C(7)-C(5)-C(6)	110.21(13)
C(8)-C(5)-C(6)	108.21(14)
C(5)-C(6)-H(6A)	108.7(11)
C(5)-C(6)-H(6B)	110.5(13)
H(6A)-C(6)-H(6B)	111.2(14)

C(5)-C(6)-H(6C)	108.2(12)
H(6A)-C(6)-H(6C)	111.7(17)
H(6B)-C(6)-H(6C)	106.4(16)
C(5)-C(7)-H(7C)	109.3(10)
C(5)-C(7)-H(7B)	113.5(10)
H(7C)-C(7)-H(7B)	109.8(17)
C(5)-C(7)-H(7A)	110.2(12)
H(7C)-C(7)-H(7A)	104.0(16)
H(7B)-C(7)-H(7A)	109.6(15)
C(5)-C(8)-H(8A)	110.7(11)
C(5)-C(8)-H(8B)	108.3(12)
H(8A)-C(8)-H(8B)	113.8(19)
C(5)-C(8)-H(8C)	110.1(15)
H(8A)-C(8)-H(8C)	106.8(16)
H(8B)-C(8)-H(8C)	107.0(18)

Table 3. Torsion angles [deg] for compound **3a**.

_____

C(4)-C(3)-C(2)-C(1)	0.4(2)
C(5)-C(3)-C(2)-C(1)	178.57(13)
C(4)-C(3)-C(2)-C(1)#1	-177.35(16)
C(5)-C(3)-C(2)-C(1)#1	0.8(3)
C(3)-C(2)-C(1)-O(1)	2.0(3)
C(1)#1-C(2)-C(1)-O(1)	-179.5(2)
C(3)-C(2)-C(1)-C(2)#1	-178.52(18)
C(1)#1-C(2)-C(1)-C(2)#1	0.0
C(2)-C(3)-C(5)-C(7)	55.00(17)
C(4)-C(3)-C(5)-C(7)	-126.82(15)
C(2)-C(3)-C(5)-C(8)	175.07(13)
C(4)-C(3)-C(5)-C(8)	-6.74(19)
C(2)-C(3)-C(5)-C(6)	-65.42(17)
C(4)-C(3)-C(5)-C(6)	112.76(15)

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C7 C 0.3515(3) 1.20938(18) 0.72628(15) 0.0386(4) Uani 1 1 d . . .
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C8 C 0.5151(3) 1.3271(2) 0.55563(19) 0.0422(4) Uani 1 1 d . . .
H7B H 0.234(3) 1.162(2) 0.7527(16) 0.045(5) Uiso 1 1 d . . .
H4C H 0.535(3) 1.115(2) 0.4072(16) 0.050(5) Uiso 1 1 d . . .
H4B H 0.352(3) 1.055(2) 0.3160(17) 0.056(6) Uiso 1 1 d . . .
H4A H 0.385(3) 1.206(2) 0.3174(17) 0.052(5) Uiso 1 1 d . . .
H7A H 0.385(3) 1.282(2) 0.7889(17) 0.057(6) Uiso 1 1 d . . .
H8A H 0.506(3) 1.358(2) 0.4638(19) 0.047(5) Uiso 1 1 d . . .
H8B H 0.543(3) 1.396(3) 0.6239(19) 0.064(6) Uiso 1 1 d . . .
H8C H 0.630(3) 1.266(3) 0.567(2) 0.078(7) Uiso 1 1 d . . .
H6A H 0.141(2) 1.387(2) 0.4717(17) 0.049(5) Uiso 1 1 d . . .
H6B H 0.028(3) 1.315(2) 0.5864(16) 0.051(5) Uiso 1 1 d . . .
H6C H 0.182(3) 1.425(2) 0.6296(18) 0.057(6) Uiso 1 1 d . . .

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O1 0.0425(6) 0.0315(6) 0.0374(6) -0.0116(5) 0.0135(4) -0.0058(5)
C3 0.0263(6) 0.0179(7) 0.0278(6) 0.0040(5) -0.0014(5) 0.0019(6)
```

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C2 0.0285(6) 0.0192(7) 0.0258(6) -0.0021(5) 0.0006(5) 0.0017(6)
C1 0.0268(6) 0.0203(7) 0.0278(6) -0.0004(6) 0.0010(5) 0.0009(6)
C4 0.0349(8) 0.0285(9) 0.0388(8) 0.0014(7) 0.0086(6) -0.0029(7)
C5 0.0305(7) 0.0212(7) 0.0324(7) -0.0011(6) -0.0015(5) -0.0032(6)
C6 0.0416(9) 0.0226(8) 0.0457(9) -0.0049(7) -0.0033(7) 0.0042(7)
C7 0.0460(9) 0.0347(10) 0.0327(8) -0.0014(7) -0.0060(7) -0.0042(8)
C8 0.0401(9) 0.0349(10) 0.0509(10) -0.0045(8) 0.0019(7) -0.0126(8)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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C3 C2 1.365(2) . ?
C3 C4 1.500(2) . ?
C3 C5 1.534(2) . ?
C2 C1 1.505(2) . ?
C2 C1 1.5105(18) 3_576 ?
C1 C2 1.5105(18) 3_576 ?
C4 H4C 0.979(19) . ?
C4 H4B 1.00(2) . ?
C4 H4A 1.01(2) . ?
C5 C7 1.541(2) . ?
C5 C8 1.542(2) . ?
C5 C6 1.545(2) . ?
C6 H6A 1.001(18) . ?
C6 H6B 0.99(2) . ?
C6 H6C 0.99(2) . ?
C7 H7C 0.99(2) . ?
C7 H7B 1.00(2) . ?
C7 H7A 1.00(2) . ?
C8 H8A 0.99(2) . ?
C8 H8B 1.01(2) . ?
C8 H8C 1.01(3) . ?

loop_
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C2 C3 C4 117.96(13) . . ?
C2 C3 C5 123.20(12) . . ?
C4 C3 C5 118.82(13) . . ?
C3 C2 C1 132.00(12) . . ?
C3 C2 C1 139.42(13) . 3_576 ?
C1 C2 C1 88.56(10) . 3_576 ?
O1 C1 C2 133.60(13) . . ?
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O1 C1 C2 134.96(14) . 3_576 ?
C2 C1 C2 91.44(10) . 3_576 ?
C3 C4 H4C 111.2(10) . . ?
C3 C4 H4B 113.9(12) . . ?
H4C C4 H4B 108.7(18) . . ?
C3 C4 H4A 108.7(11) . . ?
H4C C4 H4A 108.2(17) . . ?
H4B C4 H4A 105.8(15) . . ?
C3 C5 C7 109.81(13) . . ?
C3 C5 C8 112.36(12) . . ?
C7 C5 C8 107.88(13) . . ?
C3 C5 C6 108.34(11) . . ?
C7 C5 C6 110.21(13) . . ?
C8 C5 C6 108.21(14) . . ?
C5 C6 H6A 108.7(11) . . ?
C5 C6 H6B 110.5(13) . . ?
H6A C6 H6B 111.2(14) . . ?
C5 C6 H6C 108.2(12) . . ?
H6A C6 H6C 111.7(17) . . ?
H6B C6 H6C 106.4(16) . . ?
C5 C7 H7C 109.3(10) . . ?
C5 C7 H7B 113.5(10) . . ?
H7C C7 H7B 109.8(17) . . ?
C5 C7 H7A 110.2(12) . . ?
H7C C7 H7A 104.0(16) . . ?
H7B C7 H7A 109.6(15) . . ?
C5 C8 H8A 110.7(11) . . ?
C5 C8 H8B 108.3(12) . . ?
H8A C8 H8B 113.8(19) . . ?
C5 C8 H8C 110.1(15) . . ?
H8A C8 H8C 106.8(16) . . ?
H8B C8 H8C 107.0(18) . . ?

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C4 C3 C2 C1 0.4(2) . . . . ?
C5 C3 C2 C1 178.57(13) . . . . ?
C4 C3 C2 C1 -177.35(16) . . . 3_576 ?
C5 C3 C2 C1 0.8(3) . . . 3_576 ?
C3 C2 C1 O1 2.0(3) . . . . ?
C1 C2 C1 O1 -179.5(2) 3_576 . . . ?
C3 C2 C1 C2 -178.52(18) . . . 3_576 ?
C1 C2 C1 C2 0.0 3_576 . . 3_576 ?
C2 C3 C5 C7 55.00(17) . . . . ?
C4 C3 C5 C7 -126.82(15) . . . . ?
C2 C3 C5 C8 175.07(13) . . . . ?
C4 C3 C5 C8 -6.74(19) . . . . ?
C2 C3 C5 C6 -65.42(17) . . . . ?
C4 C3 C5 C6 112.76(15) . . . . ?

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