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Dicarbonyltris(η^2-*trans*-cyclooctene)ruthenium: Synthesis and Molecular Structure of the First Stable $M(CO)_2(olefin)_3$ Type Compound

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Summary: Photolysis of $Ru(CO)_5$ or $Ru_3(CO)_{12}$ in the presence of *trans*-cyclooctene (*t*-COE) gives $Ru(CO)_{5-x}(t\text{-COE})_x$ (x = 1–3). The bis- and tris(olefin) derivatives are obtained as a mixture of two isomers, symmetry D_3 and C_2. The structure of $Ru(CO)_2(t\text{-COE})_3$ (D_3 isomer) has been determined by X-ray diffraction.

Carbonyl–olefin complexes of the iron triad transition metals constitute an important area of investigation from both the synthetic[1a] and theoretical[1b] points of view. Although $M(CO)_3(olefin)_2$-type molecules have been synthesized,[2] structurally characterized,[3] and shown to be active catalyst precursors for olefin isomerization,[2a,4] the isolation of stable $M(CO)_2(olefin)_3$ compounds so far remained elusive.[5] In view of the known stability enhancement that *trans*-cyclooctene (*t*-COE) imparts on the metal–olefin bonding,[6] it was decided to investigate its reaction with ruthenium carbonyls [$Ru(CO)_5$ and $Ru_3(CO)_{12}$] under photochemical activation. Here we report the synthesis and structure of the first stable $M(CO)_2(olefin)_3$ molecule (M = Ru; olefin = *t*-COE).

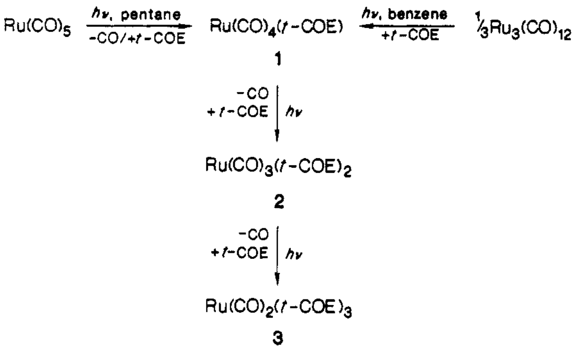
Photolysis of $Ru(CO)_5$ in the presence of *trans*-cyclooctene in pentane results in consecutive substitution of CO by the olefinic ligand and gives rise to (η^2-*t*-COE)$Ru(CO)_4$ (**1**), (η^2-*t*-COE)$_2Ru(CO)_3$ (**2**), and (η^2-*t*-COE)$_3Ru(CO)_2$ (**3**), depending on the wavelength and duration of irradiation (Scheme I).[7] With long-wavelength irradiation ($\lambda > 370$ nm) **1** is the exclusive product.

Alternatively, $Ru_3(CO)_{12}$ can be photolyzed in the presence of excess *t*-COE in benzene. Extended irradiation in a quartz immersion vessel gives an easily separable mixture of **2** and **3**.[8] Both of these two complexes are air and thermally stable solids, whereas **1** is isolated as an oily material that is somewhat labile in solution.

The CO stretching vibrational patterns of the complexes[7,8] are consistent with trigonal-bipyramidal geometry and equatorial positions of the olefinic ligands.

Because of the chiral nature of *t*-COE two isomers of **2** and **3** can be expected. Indeed, complex **2** was isolated as a mixture of **2A** (C_s symmetry) and **2B** (C_2 symmetry) which are virtually indistinguishable by infrared spectroscopy. Assignments of the ^{13}C NMR resonances[8] is based on the different CO patterns in the low-temperature spectrum (three lines with 1:1:1 intensity ratio for **2A** and two lines with 1:2 intensity ratio for **2B**). Likewise, the two isomers of **3** (**3A**, D_3 symmetry; **3B**, C_2 symmetry) are distinguished by ^{13}C NMR spectroscopy, in this case on the basis of the different number of lines in the organic region (one set of *t*-COE signals for **3A** and two sets of *t*-COE signals with 1:2 intensity ratio for **3B**). The two isomers, **3A** and **3B**, are separated by repetitive crystallization, **3A** being the predominant and more stable product.

Scheme I



Noteworthy is the observation that the ^{13}C NMR coordination shift [$\Delta\delta = \delta$ (*t*-COE) − δ (complex)] of the olefinic carbon atoms does not parallel the observed stabilities of the complexes but decreases in the order **1** > **2** > **3** (**1** $\Delta\delta$ = 78.1 ppm; **2A**, $\Delta\delta$ = 77.2 ppm; **2B**, $\Delta\delta$ = 74.5 ppm; **3A**, $\Delta\delta$ = 69.0 ppm; **3B**, $\Delta\delta$ = 72.2/71.1 ppm). This may be interpreted as a result of increasing demand for

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[†] Kohlenforschung.

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(5) Recently, labile $M(CO)_2(C_2H_4)_3$-type compounds have been observed and characterized. (a) Wuu, Y.-M.; Bentsen, J. G.; Brinkley, C. G.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 530 (M = Fe, Ru). (b) Kiel, G.-Y.; Takats, J.; Grevels, F.-W. *J. Am. Chem. Soc.* **1987**, *109*, 2227 (M = Os). (c) Gagné, M.; Takats, J., unpublished observations (M = Ru).

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(7) The following conditions refer to the most convenient preparation from $Ru(CO)_5$: **1**, $\lambda > 370$ nm, 1 h; **2**, $\lambda > 280$ nm, 1.5 h; **3** $\lambda > 180$ nm, 0.5 h. **1**: pale yellow oil; yield 90%; IR (pentane) ν_{CO} 2098 (m), 2017 (s), 1991 (s), 1988 (sh) cm^{-1}; ^{13}C NMR (CD_2Cl_2, −40 °C) δ 55.8 (CH), 41.9/36.8/28.6 (CH_2), 200.3 [CO; at −100 °C, δ 201.1 and 198.8 1:1].

(8) $Ru_3(CO)_{12}$ (1.00 g, 1.56 mmol) and *t*-COE (3 mL) in benzene (300 mL) were irradiated (Philips HPK 125 W, quartz immersion well) under Ar for 5 h. Concentration to 75 mL precipitated a white solid that was filtered off, washed with methanol, and dried under vacuum (0.96 g of **3A**, 42%; crystals of **3A** suitable for X-ray crystallography were obtained by recrystallization from toluene). The mother liquor was evaporated to dryness and extracted with methanol. The remaining residue was recrystallized from toluene to give **3B** (0.17 g, 7%). The methanol extract, upon concentration and cooling, gave several fractions of **2A**/**2B** with varying isomer ratios (total yield 0.35 g, 18%). **2A**/**2B**: off-white solid; IR (hexane) ν_{CO} 2070 (m), 1993 (s, br), 1985 (vs) cm^{-1}; ^{13}C NMR (toluene-d_8, 0 °C, data for **2A**/**2B** isomers) δ 56.7/59.4 (CH), 41.4/41.7 (CH_2), 37.0/37.2 (CH_2), 29.3 (CH_2), CO signals at −60 °C, 206.8, 199.2, 198.0 (1:1:1)/207.2, 198.6 (1:2). Anal. Calcd for $C_{19}H_{28}O_3Ru$: C, 56.28; H, 6.96; Ru, 24.92. Found: C, 56.93; H, 6.88; Ru, 24.36. **3A**: white crystals; mp 105 °C dec; IR (hexane) ν_{CO} 1945 (vs) cm^{-1}; ^{13}C NMR (toluene-d_8, 20 °C) δ 65.0(CH), 40.8/37.9/29.7(CH_2), 196.6(CO). Anal. Calcd for $C_{26}H_{42}O_2Ru$: C, 64.03; H, 8.68; Ru, 20.72. Found: C, 64.20; H, 8.72; Ru, 20.88. **3B**: white crystals; mp 100 °C dec; IR (hexane) ν_{CO} 1945 (vs) cm^{-1}: ^{13}C NMR (toluene-d_8, −20 °C, data for the two sets of *t*-COE signals in 2/1 intensity ratio) δ 61.7/62.2 (CH), 40.3/39.5 (CH_2), 37.5/37.6 (CH_2), 29.4 (CH_2), 197.5 (CO).

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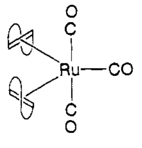
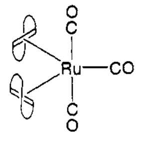
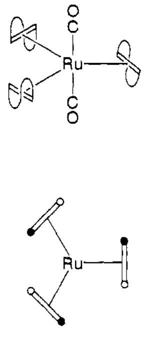


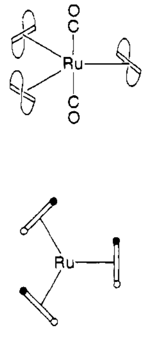
2A (C_s)



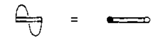
2B (C_2)



3A (D_3)



3B (C_2)



= = trans-cyclooctene

d(metal) → π^*(olefin) back-donation which, contrary to d(metal) → π^*(eq-CO) back-donation, is restricted to interaction with metal d orbitals in the equatorial plane.

The dynamic behavior of **2** and **3** is still under investigation. Preliminary results indicate that, in the case of **2**, CO scrambling and olefin rotation are not coupled, and the latter process appears to possess the lower energy barrier. Olefin rotation is not observable with **3A** for symmetry reasons but seems to freeze out in the case of **3B** at temperature below −60 °C.

To confirm unequivocally the geometry and to establish benchmark metrical parameters for this first stable M(CO)$_2$(olefin)$_3$-type complex, the structure of **3A** was determined by single-crystal X-ray crystallography[9] (Figure 1). The figure clearly shows the trigonal-bipyramidal geometry, trans disposition of the two carbonyl groups, olefinic ligands lying in the equatorial plane, and each properly oriented to allow for D_3 molecular symmetry (the molecule possesses rigorous, crystallographically imposed C_2 symmetry). The deviation of the three *t*-COE ligands from the equatorial plane is very small. The sum of the internal and external C–Ru–C angles is 360.3°, very close to the expected 360°. Thus this part of the molecule resembles greatly the established[10] and predicted[11] geometry for M(olefin)$_3$ (M = Ni, Pt) type complexes. The Ru–C(olefin) bond lengths (2.253, 2.250, and 2.244 Å) are comparable but marginally larger than similar distances in Ru(CO)$_3$(η^2-methyl acrylate)$_2$[12a] (2.223–2.245 Å) and in Ru(CO)$_4$(η^2-dimethyl fumarate)[12b] (2.197 and 2.199 Å).

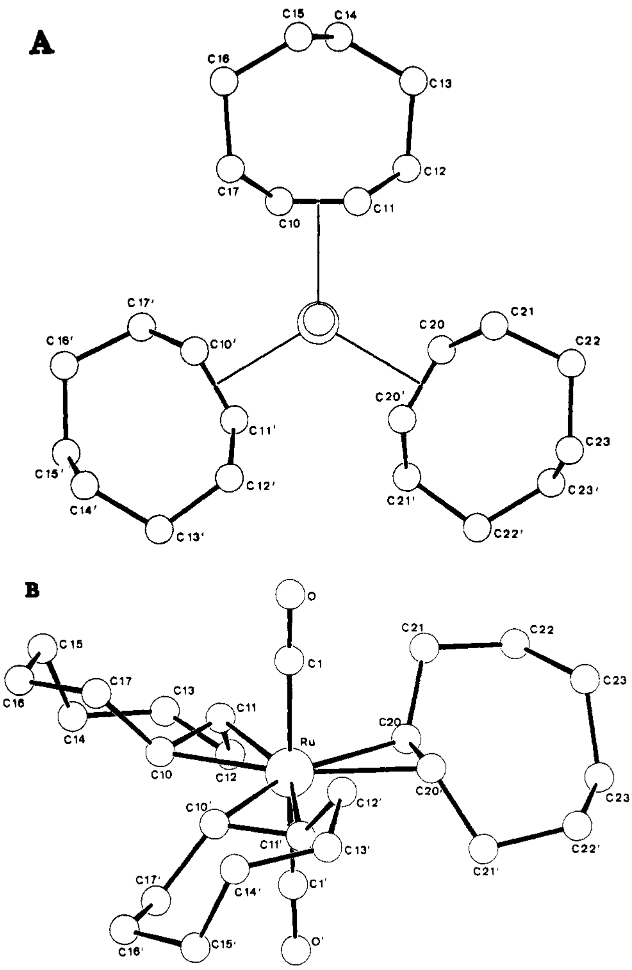


Figure 1. Molecular structure of **3A**: (A) view along O–C–Ru–C–O axis; (B) side view. Some relevant bond distances (Å): Ru–C1 = 1.930 (2), Ru–C10 = 2.253 (2), Ru–C11 = 2.250 (2), Ru–C20 = 2.244 (2), C10–C11 = 1.399 (2), C20–C20′ = 1.395 (2). Some relevant bond angles (deg): C1–Ru–C1′ = 178.6 (1), C10–Ru–C11 = 36.2 (1), C10–Ru–C10′ = 83.1 (1), C11–Ru–C20 = 84.3 (1), C20–Ru–C20′ = 36.2(1). (Primed atoms related to unmarked atoms by the twofold symmetry axis.)

The ready isolation of complex **3** and the dramatically improved stability compared to other simple olefin derivatives of mononuclear ruthenium carbonyls provide further evidence for the special place that *trans*-cyclooctene occupies in the chemistry of transition-metal olefin complexes. Full details on compounds **1–3**, the analogous osmium derivatives, and related Os(CO)$_{5-x}$(*cis*-cyclooctene)$_x$ (x = 1, 2) will be provided in a full report.

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Registry No. **1**, 110174-58-8; **2**, 110191-28-1; **3**, 110191-29-2; Ru(CO)$_5$, 16406-48-7; Ru$_3$(CO)$_{12}$, 15243-33-1.

Supplementary Material Available: Summary of the crystal data, final positional and thermal parameters, and bond distances and angles (9 pages); a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[9] Unintentionally, the X-ray analysis was performed at both laboratories. The results are virtually indistinguishable. Both sets of data have been submitted as supplementary material. For expediency only the relevant data from Mülheim appear explicity in the text. Crystal data of **3A**: monoclinic space group *C*2/*c* (No. 15); crystal size 0.18 × 0.43 × 0.29 mm; Z = 4; d_{calcd} = 1.30 g cm^{-3}; μ(Mo Kα) = 6.33 cm^{-1}; λ = 0.71069 Å; scan mode $\omega/2\theta$. Cell data were derived by least-squares procedure on θ values of 75 reflections: a = 19.927 (2), b = 11.7150 (5), c = 14.4924 (8) Å; β = 132.554 (4)°; V = 2492.2 Å^3. Total number of reflections: 5618 ($\pm h,\pm k,+l$) collected on an automated diffractometer (Enraf-Nonius CAD4); $(\sin\theta)/\lambda_{\max}$ 0.646; 2815 unique reflections of which 2588 were observed [$I \geq 2\sigma(I)$]; final R value, R = 0.018 [R_w = 0.026, $w = 1/\sigma^2(F_o)$]; GOF = 1.53.

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