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Preparation, chemistry, and structure of new ruthenium complexes

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Dedicated to the memory of Daniel F. Chodosh, a remarkable man, a good friend and an imaginative chemist.

Abstract

Several new monomeric Ru iodide complexes, coordinated to the η^5-cylopentadienol ligand, were prepared from the dimer complex (η^5-$C_4Ph_4COHOCC_4Ph_4$-η^5)(μ-H)$(CO)_4Ru_2$, and the monomer complex (η^4-C_4Ph_4CO)$(CO)_3Ru$. Their mode of formation and chemistry were studied, and their structures were determined by X-ray diffraction analyses. In addition, two structurally interesting dimeric complexes were unexpectedly formed, and were also structurally characterized. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Iodide; Crystallography; Synthesis; Chemistry

The organo–ruthenium complex **1** [1a], central to several other related complexes, was found to exhibit interesting, diverse, and useful types of catalytic chemistry, reported by us in several publications [1b–f], as well as by others [2]. In essence, complex **1** exhibits the type of chemistry which is associated with its two fragments **2** and **3**, resulting from the thermal dissociation of the dimer **1**. While **2** (18-electron complex) is stable in solution and could be readily observed by IR and ^{1}H-NMR, the formation of the unstable **3** (16-electron complex) was postulated on the basis of the resulting catalytic chemistry of **1**. The simple synthesis of **1** [1a], its stability, and its simple non-stringent handling conditions, make it an attractive and practical catalyst.

In the present work we have studied stoichiometric reactions of **1** with methyl iodide. In addition to unraveling the resulting new structures (X-ray crystallography), the chemistry involved was anticipated to elicit new concepts for planning catalytic reactions.

1. Chemistry

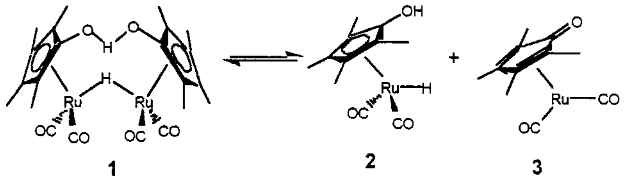
Complex **1** was reacted under nitrogen in benzene, and also in THF, with methyl iodide. The progress of the reactions was conveniently monitored by IR spectroscopy and TLC. The reaction products were separated by column chromatography, then crystallized and characterized by X-ray crystallography.

Monomeric products **4** and **5** were obtained as outlined in Scheme 1. The dimer **6** was formed in a trace quantity.

The major products **4** and **5** were readily separated by column chromatography (silica) due to the substantial difference in their polarity. The physical and spectral properties of the above three complexes are presented in Table 1. Complexes **4**–**6** were subjected to X-ray diffraction analyses, and their ORTEP diagrams are presented in Figs. 1–3.

Mechanistically **4** and **5** are considered to originate from **2** and **3**. We are proposing a scheme for the reaction of methyl iodide with **1**, involving its dissociated species **2** and **3** (Scheme 2).

The transformation of **2** to **5** was supported experimentally. A solution of **2** in benzene was prepared by



Each cyclopentadienyl ring carries 4 phenyl rings.

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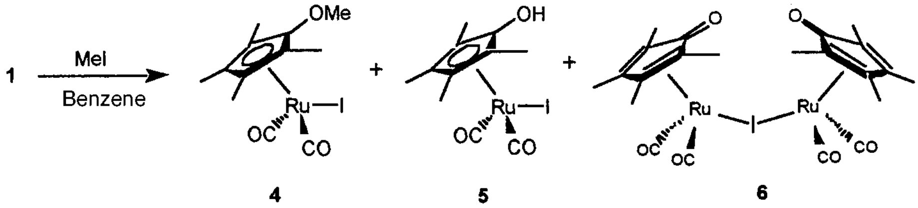


Scheme 1.

Table 1
Physical and spectral data

No.	M.p. (°C)	IR [a] (cm^{-1})	^1H-NMR [b] δ (ppm)	MS
4	195–196	2038, 1989	3.50 (s, 3H), 6.9–7.5 (m, 20H)	683 [M^+], 627 [M^+-2CO], 556 [M^+-I]
5	185 dec.	2038, 1989	1.25 (br, 1H, OH), 6.9–7.5 (m, 20H)	669 [M^+], 613 [M^+-2CO], 542 [M^+-I]
6		2059, 2025, 1982 [c]		
7	171–172	2038, 1990	1.50 (m, 4H), 3.2 (s, 3H), 3.71 (t, 2.5 Hz, 2H), 3.78 (t, 4.95 Hz, 2H), 6.95–7.51 (m, 20H)	755 [M^+], 699 [M^+-2CO], 629 [M^+-I]
8	217 dec.	1950	3.56 (s, 6H), 6.92–7.71 (m, 40H)	1311 [MH^+], 1255 [M^+-2CO], 1128 [$M^+-2CO-I$]

[a] IR spectra were recorded in dichloromethane.

[b] NMR spectra were recorded in $CDCl_3$/TMS.

[c] IR spectrum was recorded in KBr.

subjecting complex **1** to hydrogen pressure [1a]. Addition of MeI to this solution gave **5**, in a fast reaction, as a sole product. Thus **2** is the precursor of **5**, and therefore **3** must be the precursor complex of **4** in the reaction Scheme 1. Furthermore, reacting **3a** with methyl iodide gave **4** as a sole product, most probably via **3**. These results support the contention that the chemical behavior of dimer **1** in the above, as well as in other catalytic reactions is that of its dissociated monomeric constituents **2** and **3**. It is noteworthy that complex **5** was selectively obtained also by reacting the dimer **1** in benzene–toluene with iodine (see Section 3).

Mechanistically, **4** is obtained via the oxidative addition of MeI to the coordinately unsaturated 16-electron complex **3**. Complex **5** may be obtained via oxidative addition of MeI to the Ru atom of **2**, followed by reductive elimination of CH_4. However **2** is already a coordinately saturated 18-electron complex. The essential vacation of a coordination site may occur via $\eta^5 \rightarrow \eta^3$ rearrangement of the cyclopentadienyl system.

The propensity of **2** to readily hydrogenate a C–I bond may provide the basis for a catalytic cycle, provided that **5** could be hydrogenated back to **2** in situ. In two separate experiments, **5** was subjected to hydrogen pressure, 500 psi at 130°C in benzene, in the absence and in the presence of potassium carbonate. No trace of **2** could be detected (IR) in the resulting hydrogenation reaction mixtures. Nevertheless, on the assumption that **2** may still exist in a small equilibrium concentration in the hydrogenation reaction mixture, and in view of the observed fast transformation of **2** to **5**, 1-iodobutane was subjected to H_2 pressure (500 psi) in the presence of a catalytic amount of **5** in benzene at 125°C. The change of substrate concentration was followed by GC (internal standard). No reduction took place in the absence of carbonate. Very slow reduction did take place in the presence of carbonate after 24 h (63% conversion; 34 turnovers).

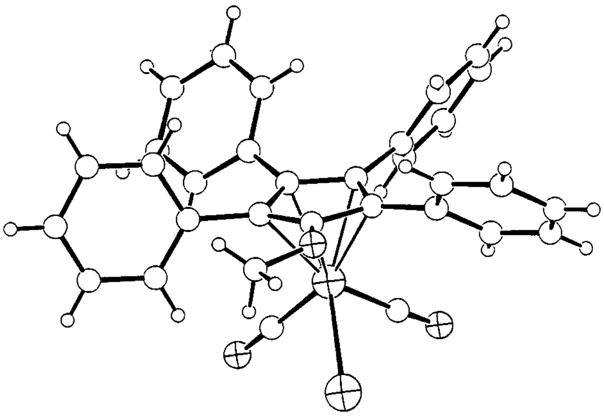


Fig. 1. Molecular structure, and selected crystallographic data for **4**. Bond lengths in Å: Ru1–I 2.693(1); Ru1–C2 1.882(5); Ru1–C4 1.899(6); C2–O3 1.127(6); C4–O5 1.116(6); C6–O11 1.329(6); Ring C–C (av.) 1.444 ± 0.021.

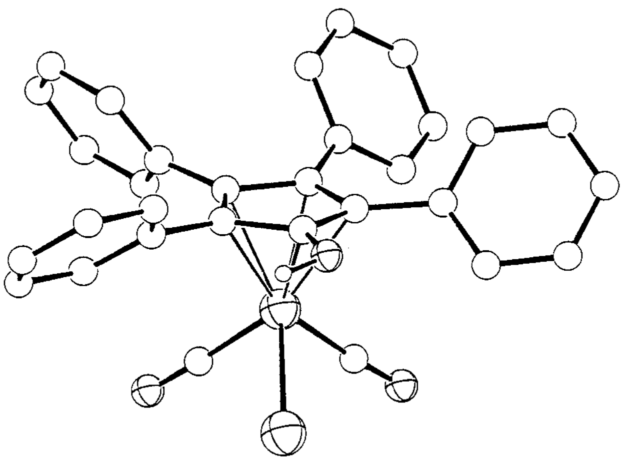


Fig. 2. Selected crystallographic data for **5**. Bond lengths in Å: Ru1–I 2.691(1); Ru1–C2 1.885(6); Ru1–C4 1.878(7); C2–O3 1.145(6); C4–O5 1.122(6); C6–O11 1.346(5); Ring C–C (av.) 1.437 ± 0.015.

The reluctance of **5** to undergo oxidative addition of H_2 may be attributed to the reduced electron density on the metal atom due to the Ru–halogen bond, or to its inability to undergo $\eta^5 \rightarrow \eta^3$ bond rearrangement. The reduced electron density was evident by the relatively high IR stretching frequencies of the CO groups bound to the metal (vide supra).

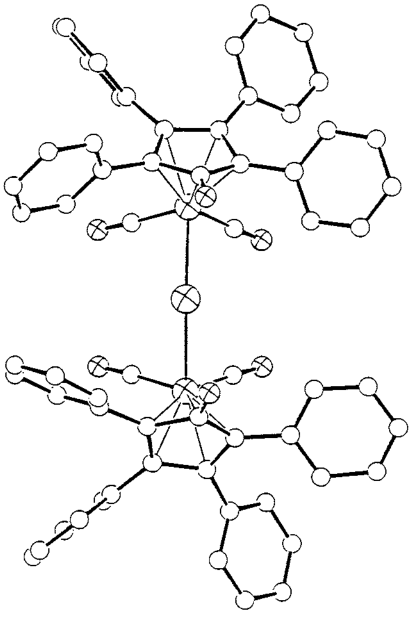
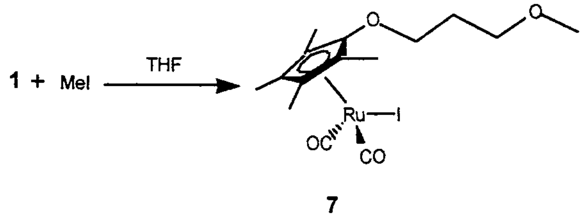
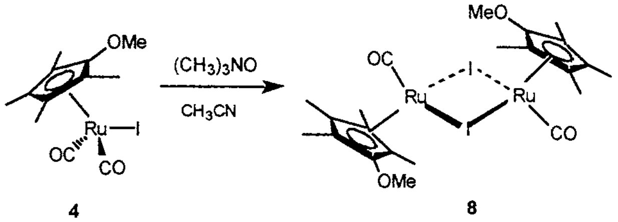


Fig. 3. Molecular structure, and selected crystallographic data for **6**. (Asterisked and nonasterisked labels relate to the two parts of this structure across the iodine bridge.) Bond lengths in Å: Ru1–I 2.727(1); Ru1*–I 2.714(1); Ru1–C2 1.897(8); Ru1*–C2* 1.891(8); Ru1–C4 1.889(6); Ru1*–C4* 1.907(6); C2–O3 1.149(10); C2*–O3* 1.143(10); C4–O5 1.133(8); C4*–O5* 1.119(8); C6–O11 1.235(7); C6*–O11* 1.255(6); C6–C7 1.480(9); C6*–C7* 1.448(7); C7–C8 1.439(7); C7*–C8* 1.451(7); C8–C9 1.449(8); C8*–C9* 1.448(8); C9–C10 1.443(9); C9*–C10* 1.422(7); C6–C10 1.480(7); C6*–C10* 1.464(8). Ru···Ru* 4.848.

Complex **7** (Fig. 4) was obtained from the reaction of **1** with MeI in THF, rather than benzene. Formally, the resulting structure implies iodo methylation cleavage of THF, with the resulting methoxy-4-iodobutane reacting with **1** to give **7**, depicted below. It is not clear whether the THF ring cleavage is catalyzed to any extent by the ruthenium complexes present in the reaction solution.



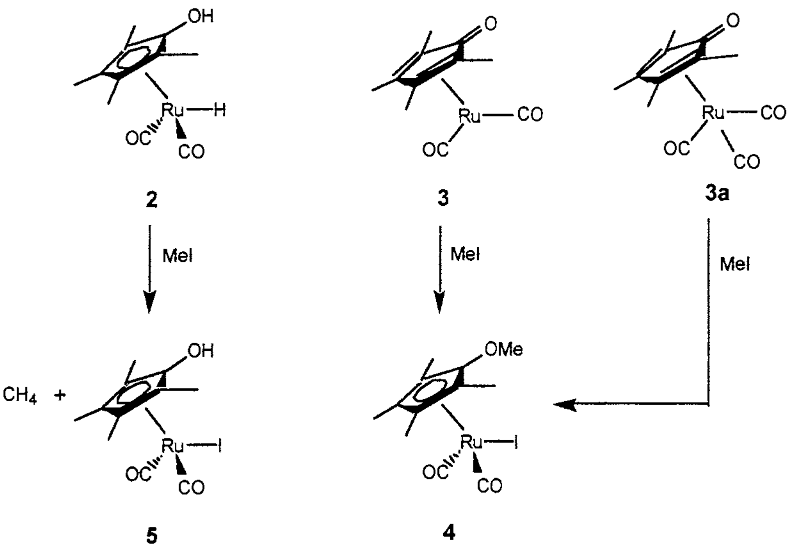
Attempts to exchange a CO ligand with CH_3CN by several hours reflux of **4** in acetonitrile failed. Resorting to trimethylamine oxide [3] (Shvo reagent) in acetonitrile led instead to the instantaneous formation of dimer **8**, the iodine being a better ligand than acetonitrile. This complex has a point symmetry, and is stable. The IR spectrum of **8** exhibits a single CO stretching band. Its X-ray structure is presented in Fig. 5.



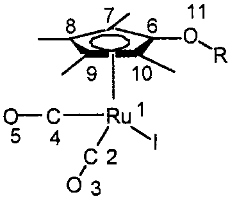
In conclusion, complexes **4** and **5** can now be obtained selectively with good yields in separate reactions. Thus, complex **4** can be generated from (η^4-C_4Ph_4CO)$(CO)_3$Ru (**3a**) with methyl iodide, while **5** is obtained by the action of iodine on (η^5-$C_4Ph_4COHOCC_4Ph_4$-η^5)(μ-H)$(CO)_4Ru_2$ (**1**). It stands to reason that other O-alkylated complexes, isostructural with **4**, can be prepared in a similar manner. These may serve as synthons for cationic Ru complexes after iodine abstraction, and may possibly function as polymerization and metathesis catalysts. The thermal dissociation of **8** is of interest, since it will generate a reactive Ru(d^6)–16-electron complex.

2. Structures

The numbering of important atoms in the five structures that were analyzed by X-ray diffraction is presented for convenience in the following scheme, where R = H, or alkyl group (for **6**, R is nonexistent). It should be noted that Ph groups (omitted) are bound to positions 7, 8, 9, and 10 of the ring.



Scheme 2.



The structural parameters as well as the IR spectra of complexes **4**, **5** and **7** are very similar. In accordance with a dicarbonyl structure, their IR spectra, which are identical, exhibit two carbonyl stretching bands. The rather high frequency (2038 cm^{-1}) implies weakly bound Ru–CO groups.

The hapticity of the ring in these complexes is assumed to be five. No clear bond alternation within the Cp rings could be discerned, and the rings are essentially planar. The average Ru distances to the four ring C atoms C7–C10 in **4** and **5** are 2.231 and 2.248 Å, respectively. The corresponding Ru–C6 distances are 2.359(5) and 2.312(5) Å. The Ru–C6 bond elongation may be attributed to minor non-planarity of the 5-membered ring. Dihedral angles of 6.5 and 2.9° are formed by the plane inscribing C6 and its two flanking C atoms with the C7–C10 plane in **4** and **5**. The deviation of C6 from the C7–C10 plane in **4** and **5** is 0.093(5) and 0.041(5) Å, respectively, and is away from the Ru atom. Such η^5-coordination results in Ru(II)–18-electron complexes.

The combined electron counting of the dimer **6** is 35, with a mean oxidation state of 1/2. The Ru atoms are equidistant from the bridging iodine atom, with a Ru–I–Ru angle of 126°. The Ru···Ru* distance of 4.848 Å indicates no bonding between the two metal atoms. The average Ru–I distance is 0.027 Å longer than the covalently bound I atom in **4** (i.e. by 27σ), thus accounting for its bridging of the neighboring Ru atom. In agreement with a Cp ring being a better σ donor than cyclopentadienone, a shift of the IR CO stretching bands to higher wave numbers in **6** compared to **4** was observed (Table 1). The average C6–O11 bond in **6** is 0.084 Å shorter than in **4**, reflecting on a substantial carbonyl π-bonding. The two ring carbonyls deviate markedly from the C7–C10 plane by 14.0° (0.222(5) Å) and 17.0° (0.256(5) Å) for C–6, the direction being away from the Ru atom. The structural data indicate no bond alternation in the ring 1,3-diene system. This has also been previously observed with the X-ray structure of (η^4-C_4Ph_4CO)$(CO)_3$Ru (**3a**) [1h], and attributed to back donation from the occupied metal d-orbitals to the LUMO of the diene. However, the two bonds flanking the carbonyl group (1.480(7) and 1.480(9) Å) are clearly longer than the average distance C7–C8–C9–C10 (1.443 Å). Furthermore, the average Ru distances to the four ring C atoms, C7–C10, in the

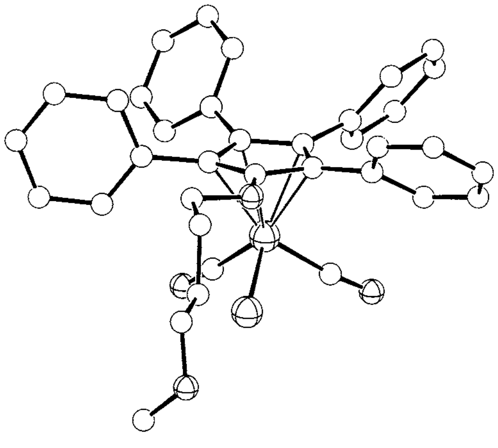


Fig. 4. Selected crystallographic data for **7**. Bond lengths in Å: Ru1–I 2.698(1); Ru1–C2 1.847(13); Ru1–C4 1.873(16); C2–O3 1.125(14); C4–O5 1.149(16); C6–O11 1.341(12); Ring C–C (av.) 1.444 ± 0.020.

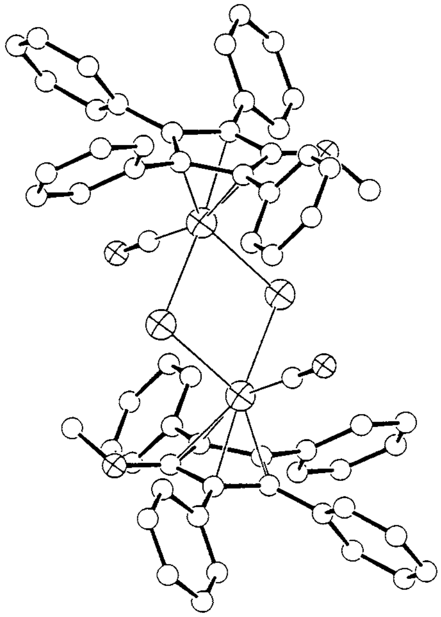


Fig. 5. Molecular structure and selected crystallographic data for **8**. Bond lengths in Å: Ru1–I 2.7271(5); Ru1–I* 2.7338(4); Ru1–C2 1.869(4); C2–O3 1.144(5); C6–O11 1.333(4); Ring C–C (av.) 1.450 ± 0.020.

two rings are 2.228 and 2.217 Å, while the distances Ru–C6 are 2.480(5) and 2.473(5) Å. These data clearly support an η^4-coordination of the 1,3-diene of the cyclopentadienone ring. The mode of formation of **6** is not clear.

To the best of our knowledge (October 1998 version of the Cambridge Crystallographic Database), no Ru complex, bridged by a single iodine atom only, has been reported in the literature. The structural fragment Ru–I–Ru has been established in dimer complexes having, in addition, a Ru–Ru bond (2.759–2.794 Å) and bridging chelating ligands [4].

As with complexes **4**, **5**, and **7**, no clear bond alternation within the Cp ring could be discerned in **8**. η^5-Coordination is supported by the essentially planar Cp ring, and hence **8** is a Ru(II)–18 e complex.

The two Ru–I bond lengths in **8** differ by only 0.007 Å, which amounts to 0.4%, and are therefore, essentially equivalent. However, the average Ru–I bond length is 0.037 Å ($>35\sigma$) longer than the covalent Ru–I bond in **4**, consistent with a bridging iodine atom via $p\pi$–$d\pi$ interaction. The Ru–CO bond in **8** is 0.021 Å (4σ) shorter relative to the average Ru–CO bond distance in **4**. This substantial shortening also induced a significant shift of the CO IR stretching band to lower frequency (1950cm^{-1}; Table 1). Taken together, iodine bridging of the two monomeric units must be strong, thus also accounting for the stability of **8** in refluxing acetonitrile.

Several doubly iodine bridged Ru dimer complexes are recorded in the literature, but none with Cp ligands [5]. However, only two such complexes with the iodine atoms as the only bridging atoms (Ru–Ru bond), were reported. The Ru–I bond lengths of 2.766, 2.761 Å are somewhat longer than those measured for **8**.

3. Experimental

3.1. (η^5-2,3,4,5-Tetraphenyl-1-methoxycyclopentadienyl)(iodo)dicarbonyl Ru(II) (4) and (η^5-2,3,4,5-tetraphenylcyclopentadien-1-ol)(iodo)dicarbonyl Ru(II) (5)

Dimer **1** (500 mg; 0.46 mmol) and methyl iodide (660 mg; 4.6 mmol) were dissolved in benzene (46 ml). The solution was refluxed for 5 h until the disappearance of the CO IR stretching band of **1**. The solvent was removed in vacuum, and the residue chromatographed on silica starting with methylene chloride (15%), petroleum ether (85%). Complex **4** emerged with methylene 20:80 chloride–petroleum ether, and complex **5** with methylene chloride. With ethyl acetate as eluent, a minute quantity of **6** was obtained as red crystals. The X-ray structures of **4**, **5** and **6** are presented in Figs. 1–3.

3.2. (η^5-2,3,4,5-Tetraphenylcyclopentadien-1-ol)(iodo)-dicarbonyl Ru(II) (5)

3.2.1. Method A

A solution of η^5-(2,3,4,5-tetraphenylcyclopentadienol)hydridocarbonyl Ru(II) (**2**) in benzene was prepared by hydrogenating **1** (100 mg; 0.09 mmol) in benzene (15 ml) in a stainless steel glass lined autoclave at 500 psi of hydrogen at 120°C for 4 h (IR: 2018, 1959 cm^{-1}). The solution was cooled and methyl iodide (0.5 ml; 8 mmol) was added. After 1 h reflux under nitrogen, the reaction solution showed IR bands at 2038 and 1989 cm^{-1}, and a single TLC spot identical with that of **5**. Evaporation of the solvent, and MS of the solid confirmed its molecular weight (Table 1).

3.2.2. Method B

Iodine (234 mg; 0.9 mmol) was added to a solution of **1** (100 mg; 0.09 mmol) in dry benzene (10 ml), and the mixture kept under nitrogen at room temperature (r.t.) for 2 h. The resulting solution was washed with a saturated sodium thiosulfate solution, then dried over $MgSO_4$. After solvent removal, the residue was chromatographed on silica. The pure product **5**, which was collected with methylene chloride (82 mg; 66%), had an IR spectrum and TLC identical to the product obtained by method A above.

3.3. (η^5-2,3,4,5-Tetraphenyl-1-methoxycyclopentadienyl)(iodo)dicarbonyl Ru(II) (**4**)

A solution of η^4-(C_4Ph_4CO)$(CO)_3$Ru (**3a**) (100 mg; 0.18 mmol) and methyl iodide (250 mg; 1.8 mmol) in toluene (10 ml) was refluxed under nitrogen for 3 h. The IR spectrum of the reaction mixture indicated the disappearance of all starting complex. After evaporation under vacuum, the residue was chromatographed on silica. With a solvent mixture of dichloromethane (70%) and petroleum ether (30%) a solid **4** (77 mg; 64%) was obtained, which had a TLC and IR spectrum identical to the product obtained in Section 3.1.

3.4. (η^5-2,3,4,5-Tetraphenyl-1-(4-methoxybutoxy)-cyclopentadienyl)(iodo)dicarbonyl Ru(II) (**7**)

A glass lined stainless steel autoclave was charged with **1** (108.4 mg; 0.1 mmol), THF (10 ml) and methyl iodide (142 mg; 1.0 mmol). The mixture was purged with nitrogen, and the closed reactor was heated at an oil bath temp of 140°C for 4 h. The reaction solution was cooled, the solvent removed in vacuum, and the residue dissolved in methylene chloride, and chromatographed on silica with methylene chloride. The product **7** was obtained by elution of the column with Et–Ac. It was crystallized from benzene, followed by methylene chloride–cyclohexane.

3.5. [(η^5-2,3,4,5-Tetraphenyl-1-methoxycyclopentadienyl)(carbonyl)]$_2$Ru$_2$(μ-I)$_2$ (**8**)

Trimethylamine oxide (27 mg; 0.36 mmol) was added to a solution of **4** (482 mg; 0.7 mmol) in acetonitrile (25 ml) under nitrogen. The heterogeneous mixture was stirred at r.t. for 4 min, after which it became homogeneous, acquiring a purple color. The solution was washed with water (2 × 10 ml), and the solvent evaporated in vacuum. Dark crystals of **8** were obtained from the evaporation residue, using methylene chloride–petroleum ether as crystallization solvent. The X-ray structure of **8** is presented in Fig. 5.

3.6. Crystal structures analyses

3.6.1. Crystal structure analyses of compounds **4**–**8**

The X-ray diffraction measurements were carried out on either a CAD4 (**7**, ω–2θ scan mode) or a KappaCCD (**4**–**6** and **8**, 1° ϕ-scans) Nonius diffractometer equipped with a graphite monochromator, using Mo–K_α ($\lambda = 0.7107$ Å) radiation. The intensity data were empirically corrected for absorption. The structures were solved by Patterson and direct methods (SHELXS-86 [6] or DIRDIF-96 [7]) and refined by full-matrix least-squares based on F^2) (SHELXL-97) [8]). Non-hydrogen atoms were treated anisotropically (except for those in the disordered fragments or solvates of some of the structures). The hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles, methyls being treated as rigid groups.

3.6.2. Crystal and experimental data

Compound **4**: $C_{32}H_{23}IO_3Ru \cdot CH_2Cl_2$, formula weight 768.4, monoclinic, space group $P2_1/n$, $T = 298$ K, $a = 12.074(1)$, $b = 17.791(1)$, $c = 14.528(1)$ Å, $\beta = 96.76(1)°$, $V = 3099.0$ Å^3, $Z = 4$, $D_{calc} = 1.647$ g cm^{-3}, $F(000) = 1512$, μ(Mo–K_α) = 17.1 cm^{-1}, crystal size ca. 0.20 × 0.15 × 0.08 mm, $2\theta_{max} = 56.6°$, 182 detector frames, 7653 unique reflections, $R_1 = 0.053$ for 3490 observations with $F_o > 4\sigma(F_o)$ and $R_1 = 0.125$ ($wR_2 = 0.150$) for all unique data, $|\Delta\rho| \leq 1.00$ e Å^{-3}. The CH_2Cl_2 solvate was found to be partially disordered.

Compound **5**: $C_{31}H_{21}IO_3Ru$, formula weight 669.5, monoclinic, space group $P2_1/n$, $T = 298$ K, $a = 12.132(1)$, $b = 10.260(1)$, $c = 21.278(1)$ Å, $\beta = 96.91(1)°$, $V = 2629.3$ Å^3, $Z = 4$, $D_{calc} = 1.691$ g cm^{-3}, $F(000) = 1312$, μ(Mo–K_α) = 18.0 cm^{-1}, crystal size ca. 0.20 × 0.10 × 0.07 mm, $2\theta_{max} = 56.6°$, 179 detector frames, 6517 unique reflections, $R_1 = 0.041$ for 1965 observations with $F_o > 4\sigma(F_o)$ and $R_1 = 0.193$ ($wR_2 = 0.089$) for all unique data, $|\Delta\rho| \leq 0.55$ e Å^{-3}, the hydroxyl proton was located on a difference-Fourier map.

Compound **6**: $(C_{31}H_{20}O_3Ru)_2I \cdot H_2O$, formula weight 1228.1, triclinic, space group $P\bar{1}$, $T = 298$ K, $a = 13.353(1)$, $b = 13.693(1)$, $c = 16.585(1)$ Å, $\alpha = 81.45(1)$, $\beta = 78.09(1)$, $\gamma = 78.94(1)°$, $V = 2893.2$ Å^3, $Z = 2$, $D_{calc} = 1.410$ g cm^{-3}, $F(000) = 1222$, μ(Mo–K_α) = 11.0 cm^{-1}, crystal size ca. 0.25 × 0.20 × 0.15 mm, $2\theta_{max} = 56.7°$, 348 detector frames, 14 334 unique reflections, $R_1 = 0.054$ for 9338 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.094$ ($wR_2 = 0.186$) for all unique data, $|\Delta\rho| \leq 1.01$ e Å^{-3}.

This compound crystallized as a hydrate; the analyzed crystal appeared to contain also additional solvent species (possibly water or EtOAc), which could not be identified in the crystallographic refinement. The contribution of the unrecognizable solvent (occupying about 490 Å^3 — i.e. 17% of the unit cell volume), was subtracted from the diffraction pattern by the 'Bypass' procedure [9]. The H_2O molecule was found also to be partially disordered. In the crystal it bridges between adjacent molecules of the ruthenium complex by hydrogen bonding to one carbonyl site of each species and creating a chained arrangement.

Compound **7**: $C_{36}H_{31}IO_4Ru$, formula weight 755.6, monoclinic, space group $P2_1/c$, $T = 298$ K, $a = 14.702(7)$, $b = 20.355(4)$, $c = 21.869(3)$ Å, $\beta = 93.02(2)°$, $V = 6535$ (3) Å^3, $Z = 8$, $D_{calc} = 1.536$ g cm^{-3}, $F(000) = 3008$, μ(Mo–K_α) = 14.6 cm^{-1}, crystal size ca. 0.40 × 0.30 × 0.20 mm, $2\theta_{max} = 46°$, 8503 unique reflections with positive intensities, $R_1 = 0.084$ for 6926 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.099$ ($wR_2 = 0.258$) for all unique data, $|\Delta\rho| \leq 1.66$ e Å^{-3}.

The asymmetric unit in this structure consists of two molecules of the organometallic complex, one reasonably well ordered and the other partly disordered. The latter involves different orientations of the –$(CO)_2I$ tripod at different sites in the crystal, a disorder which could be modeled in part by an interchange between the positions of the I and one of the CO ligands with relative occupancies of 64 and 36% of these ligands at the two sites. Conformation of the aliphatic residue in both molecules was found to be disordered as well (as a result of which most atoms here were assigned an isotropic U), and the two terminal atoms in the second species could not be located. The two molecules of the asymmetric unit differ also in the relative orientations of the aryl groups.

Compound **8**: $C_{31}H_{23}IO_2Ru$. CH_2Cl_2, formula weight 740.4, triclinic, space group $P\bar{1}$, $T = 117$ K, $a = 10.189(1)$, $b = 11.991(1)$, $c = 12.127(1)$ Å, $\alpha = 94.16(1)$, $\beta = 103.05(1)$, $\gamma = 91.71(1)°$, $V = 1437.9$ Å^3, $Z = 2$, $D_{calc} = 1.710$ g cm^{-3}, $F(000) = 728$, $\mu(\text{Mo–K}_\alpha) = 18.3$ cm^{-1}, crystal size ca. $0.35 \times 0.25 \times 0.05$ mm, $2\theta_{max} = 60.0°$, 183 detector frames, 7057 unique reflections, $R_1 = 0.042$ for 6199 observations with $F_o > 4\sigma(F_o)$, $R_1 = 0.048$ ($wR_2 = 0.145$) for all unique data, $|\Delta\rho| \leq 1.00$ e Å^{-3}, near the molecular framework of the Ru-complex (higher residual peaks (< 3.35 e Å^{-3}) and troughs (−2.17 e Å^{-3}) were observed near the partly disordered dichloromethane solvate).

The molecular structure represents a dimer, two iodine ligands being coordinated simultaneously to two inversion related Ru centers.

4. Supplementary material

The crystallographic data were deposited in the Cambridge Crystallographic Database, with the following deposition numbers: CSD-115323–CSD-115327 for compounds **4**–**8**, respectively.

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