Monatshefte für Chemie 130, 1301–1310 (1999)

Monatshefte für Chemie
Chemical Monthly

Synthesis of Ruthenium Cyclopentadienone Complexes *via* Oxidation of Hydroxyruthenocenes

Walter Simanko[1], **Roland Schmid**[1], **Karl Kirchner**[1,*], and **Kurt Mereiter**[2,*]

[1] Institute of Inorganic Chemistry, Vienna University of Technology, A-1060 Vienna, Austria
[2] Institute of Mineralogy, Crystallography, and Structural Chemistry, Vienna University of Technology, A-1060 Vienna, Austria

Summary. Oxidation of [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-PPh_3)]CF_3SO_3 (**1a**) and [Ru(η^5-$C_5H_4PPh_3$)(η^5-C_5H_4OH)]PF_6 (**1b**) with Br_2 (1 equiv.) affords the cyclopentadienone complexes [Ru(η^5-C_5H_5)(η^4-C_5H_3-O-2-PPh_3)Br]CF_3SO_3 (**2a**) and [Ru(η^5-$C_5H_4PPh_3$)(η^4-C_5H_4O)Br]PF_6 (**2b**) in 79 and 82% yield. When **2a** is treated with Ag^+ in CH_3CN, the dicationic complex [Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_3)(CH_3CN)](CF_3SO_3)$_2$ (**3**) is obtained, whereas with **2b** the *tris*-acetonitrile complex [Ru(η^5-$C_5H_4PPh_3$)(CH_3CN)$_3$](PF_6)$_2$ (**4**) is formed. X-Ray structures of **1a**, **2a**, and **2b** are reported.

Keywords. Ruthenium; Cyclopentadienone; Oxidation; Ylide complexes.

Synthese von Ruthenium-Cyclopentadienon-Komplexen durch Oxidation von Hydroxyruthenocenen

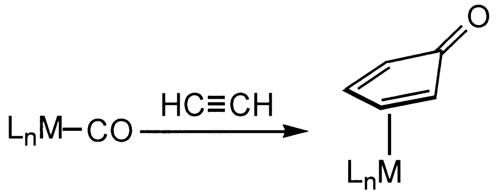
Zusammenfassung. Die Oxidation von [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-PPh_3)]CF_3SO_3 (**1a**) und [Ru(η^5-$C_5H_4PPh_3$)(η^5-C_5H_4OH)]PF_6 (**1b**) mit Br_2 (1 äquiv.) liefert die Cyclopentadienon-Komplexe [Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_3)Br]CF_3SO_3 (**2a**) und [Ru(η^5-$C_5H_4PPh_3$)(η^4-C_5H_4O)Br]PF_6 (**2b**) in 79 und 82% Ausbeute. Wird **2a** mit Ag^+ in CH_3CN umgesetzt, so erhält man den dikationischen Komplex [Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_3)(CH_3CN)](CF_3SO_3)$_2$ (**3**). Im Gegensatz dazu erhält man mit **2b** den *Tris*-acetonitril-Komplex [Ru(η^5-$C_5H_4PPh_3$)(CH_3CN)$_3$](PF_6)$_2$ (**4**). Die Röntgenstrukturen von **1a**, **2a** und **2b** wurden bestimmt.

Introduction

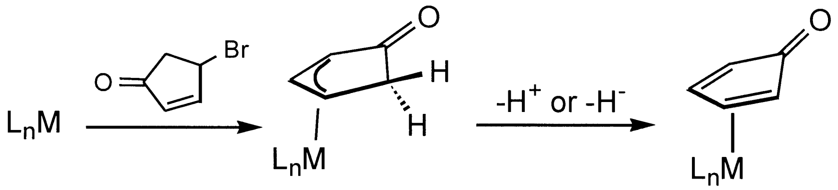
Cyclopentadienone (C_5H_4O) in the free state is a highly unstable molecule subject to rapid dimerization but can be stabilized upon coordination to transition metals. Thus, complexes containing this ligand have to be synthesized by carrying out reactions on suitable precursor complexes. For instance, it has been shown that transition metal carbonyl complexes are able to react with acetylenes to give cyclopentadienone complexes (Scheme 1). In fact, the first reported example of a

---

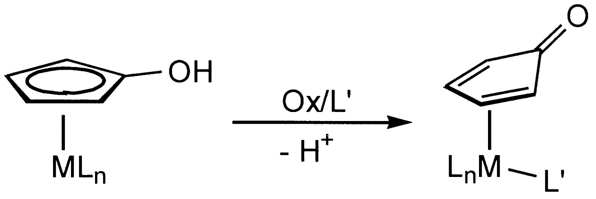
* Corresponding author



Scheme 1



Scheme 2



Scheme 3

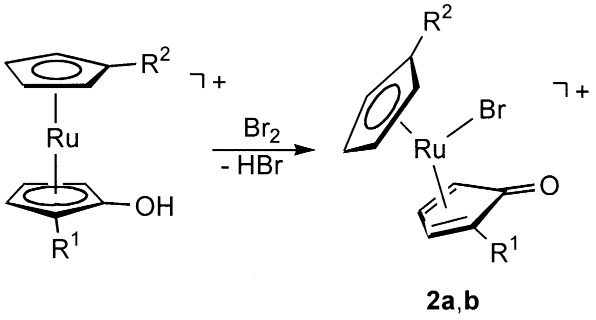
cyclopentadienone complex, Fe(η^4-C_5H_4O)$(CO)_3$, has been obtained by treating $Fe(CO)_5$, with excess HC≡CH at elevated pressure (max 20 bar) [1].

Another approach is the oxidative addition of 4-bromo-2-cyclopenten-1-one to a low-valent transition metal complex. The intermediate is typically an η^3-cyclopentenoyl complex which on deprotonation or hydride abstraction gives a cyclopentadienone complex (Scheme 2). This sequence has been successfully applied to the synthesis of complexes of the types [Ru(η^5-C_5R_5)(η^4-C_5H_4O)]Br (R = H, Me) [2] and $[Mo(L_3)(\eta^4\text{-}C_5H_4O)(CO)_2]^+$ (L_3 = *Cp*, *Tp*) [3].

Here we report that cyclopentadienone complexes may also be obtained by oxidation of complexes containing an η^5-hydroxycyclopentadienyl ligand in the presence of a potential donor *L'* as shown in Scheme 3. This will be demonstrated by reacting the hydroxyruthenocenes [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-PPh_3)]PF_6 and [Ru(η^5-$C_5H_4PPh_3$)(η^5-C_5H_4OH)]CF_3SO_3 with Br_2. X-Ray structures of representative complexes are given.

Results and Discussion

When a nitromethane solution of $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PPh_3)]^+$ (**1a**) and $[Ru[\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]^+$ (**1b**) is treated with Br_2 (1 equiv.), the cyclopentadienone complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}PPh_3)Br]^+$ (**2a**) and $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^4\text{-}C_5H_4O)Br]^+$ (**2b**) are obtained in 79 and 82% isolated yield, respectively (Scheme 4). Complexes **2a** and **2b** are air stable both in the solid

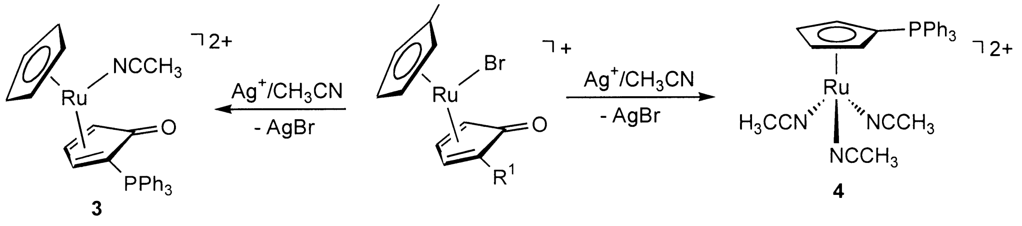


1a: $R^1 = PPh_3$, $R^2 = H$
1b: $R^1 = H$, $R^2 = PPh_3$

Scheme 4

state and in solution. Characterization was afforded by a combination of elemental analysis, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMr spectroscopy. In addition, the structure of both complexes has been determined by X-ray crystallography (*vide infra*). The ^1H NMR spectrum of **2a** consists of five signals: a multiplet pattern from $\delta = 7.95$–7.70 ppm (15H), three multiplets centered at $\delta = 6.49$ (1H), 5.69 (1H), and 4.75 ppm (1H), and a singlet at $\delta = 5.39$ ppm (5H). Due to the coupling with ^{31}P of the phosphine moiety the ^{13}C NMR resonances of the cyclopentadienone ring are split into doublets, excluding the resonance of the ketonic carbonyl carbon atom giving rise to a characteristic singlet at $\delta = 180.8$ ppm. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **2b** exhibit a pattern diagnostic for a mono-substituted C_5H_5 ring and a parent C_5H_4O ligand. The α and β protons of η^4-C_5H_4O give rise to two apparent triplets centered at $\delta = 4.08$ and 5.81 ppm, respectively, as expected for an AA′XX′ spin system. The α and β protons of η^4-$C_5H_4PPh_3$ give rise to two multiplets centered at $\delta = 6.07$ and 6.17 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the characteristic resonance of the ketonic carbonyl carbon atom of the C_5H_4O ligand is found at $\delta = 179.3$ ppm.

Treatment of **2a** with Ag^+ (1 equiv.) in CH_3CN as the solvent affords the dicationic complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}PPh_3)(CH_3CN)]^{2+}$ (**3**) in essentially quantitative yield as monitored by ^1H NMR spectroscopy (Scheme 5). The NMR



2a: $R^1 = PPh_3$, $R^2 = H$
2b: $R^1 = H$, $R^2 = PPh_3$

Scheme 5

spectra of **3** are similar to those of **2a** and are not discussed here. Unexpectedly, attempts to obtain the analogous complex $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^4\text{-}C_5H_4O)(CH_3CN)]^{2+}$ by following the procedure above with **2b** failed and, instead, the *tris*-acetonitrile complex $[Ru(\eta^5\text{-}C_5H_4PPh_3)(CH_3CN)_3]^{2+}$ (**4**) was obtained in 93% yield (Scheme 5). The fate of the C_5H_4O ring remains obscure and has not been further investigated. Complex **4** is readily identified by means of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The H_β and H_α protons of the $C_5H_4PPh_3$ ligand give rise to two doublets of doublets centered at $\delta = 5.14$ ($J_{HH} = 3.4$ Hz, $J_{HH} = 1.6$ Hz, 2H) and $\delta = 5.09$ ppm ($J_{HH} = 3.4$ Hz, $J_{HH} = 1.6$ Hz, 2H), respectively. The coordinated acetonitrile ligands exhibit a singlet resonance at $\delta = 2.48$ ppm (9H). In the $^{13}C\{^1H\}$ NMR spectrum characteristic resonances for the C_5 moiety of the $C_5H_4PPh_3$ are observed at $\delta = 82.9$ (d, $J_{PC} = 13.4$ Hz), 73.9 (d, $J_{PC} = 8.3$ Hz), and 54.7 ppm (d, $J_{PC} = 101.7$ Hz) assignable to the C_β, C_α, and *ipso* carbon atoms, respectively.

Crystal structure of **1a**

A structural view of the $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PPh_3)]^+$ cation and one $CF_3SO_3^-$ anion is shown in Fig. 1 with selected bond distances reported in the caption. The five-membered rings are nearly parallel to one another, the angle between the planes being 2.3°. The two C_5 rings adopt an approximately eclipsed conformation. Due to inductive effects of the phosphorus the Ru-C mean bond length to the $C_5H_3OH\text{-}2\text{-}PPh_3$ moiety is longer (2.190(4) Å) than to the C_5H_5 ring (2.176(5) Å). The C(1)–O(1) and P–C(2) bond distances are 1.351(4) and 1.775(3) Å, respectively. Both substituents are distinctly bent away from the least-squares plane though the C_5 ring atoms and away from Ru: O(1) by 0.197(5) Å and P by 0.081(5) Å. The hydroxy group is linked to the $CF_3SO_3^-$ anion *via* a comparatively short hydrogen bond $O(1)\cdots O(2) = 2.705$ Å. The specific orientation of the OH-group relative to

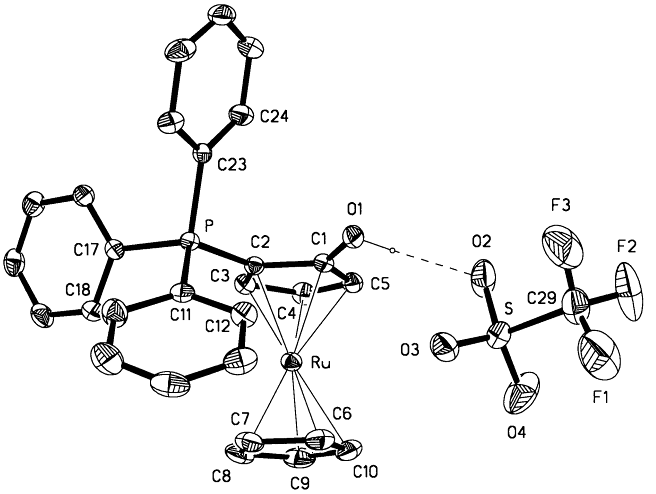


Fig. 1. Structural view of $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PPh_3)]CF_3SO_3$ (**1a**) showing 20% probability thermal ellipsoids; selected bond lengths (Å): Ru-C(1–5)$_{av}$ 2.190(4), Ru-C(6–10)$_{av}$ 2.176(4), C(1)-O(1) 1.351(4), P-C(2) 1.775(3), P-C(11) 1.803(3), P-C(17) 1.799(3), P-C(23) 1.795(3)

the C_5 ring introduces a distinct asymmetry in the bond angles C(2)–C(1)–O(1) = 122.4(3)° and C(5)–C(1)–O(1) = 128.8(3)° attributable to repulsion involving the OH hydrogen. These geometric features are in good agreement with $[Ru(\eta^5\text{-}C_5H_4\text{-}PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$, a related compound exhibiting an O–H···F hydrogen bond of 2.75 Å [4].

Crystal structures of **2a** *and* **2a′**

The $CF_3SO_3^-$ **2a** and PF_6^- (**2a′**) salts of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}PPh_3)Br]^+$ crystallize in relatively small needle-like crystals of similar lattice dimensions (Table 1) and in both cases in the acentric orthorhombic space group $Pna2_1$. They

Table 1. Crystallographic data for **1a**, **2a**, **2a′**, and **2b**

	1a	**2a**	**2a′**	**2b**
Formula	$C_{28}H_{24}F_3O_4PRuS$	$C_{29}H_{23}BrF_3O_4PRuS$	$C_{29}H_{23}BrF_6OP_2Ru$	$C_{29}H_{23}BrF_3O_4PRuS$
F_w	657.58	736.48	732.38	736.48
Crystal size mm	0.30×0.30×0.60	0.06×0.06×0.60	0.05×0.05×0.30	0.55×0.15×0.11
Space group	Pbca (No. 61)	$Pna2_1$ (No. 33)	$Pna2_1$ (No. 33)	$P2_1/c$(No. 14)
a/Å	16.773(6)	12.929(4)	12.223(5)	15.900(3)
b/Å	16.809(7)	25.427(8)	25.963(8)	10.598(3)
c/Å	19.978(8)	9.052(3)	8.835(3)	16.969(4)
β/°				96.00(1)
V/A^3	5633(4)	2976(1)	2804(1)	2844(1)
Z	8	4	4	4
$\rho_{calc}/g\cdot cm^{-3}$	1.551	1.644	1.735	1.720
T/K	295(2)	223(2)	298(2)	295(2)
μ/mm^{-1} (MoK_α)	0.741	2.045	2.160	2.140
Absorption correction	multi scan	multi scan	none	none
F(000)	2656	1464	1448	1464
Transmission Fractor (min/max)	0.66/0.86	0.72/0.80		
θ_{max}/deg	25	25	18	25
Index ranges	$-19 \leq h \leq 17$ $-19 \leq k \leq 19$ $-23 \leq l \leq 23$	$-9 \leq h \leq 15$ $-30 \leq k \leq 30$ $-10 \leq l \leq 10$	$-10 \leq h \leq 0$ $-22 \leq k \leq 0$ $-7 \leq l \leq 0$	$-17 \leq h \leq 17$ $0 \leq k \leq 12$ $0 \leq l \leq 20$
No. of rflns. measd.	27644	15486	1164	5142
No. of unique rflns.	4894	5073	1056	4975
No. of rflns $l > 2\sigma(l)$	3831	4416	863	3718
No. of parameters	353	364	171	363
R_1 ($l > 2\sigma(l)$)	0.035	0.045	0.043	0.036
R_1 (all data)	0.054	0.057	0.064	0.061
wR_2 (all data)	0.085	0.104	0.099	0.082
Diff. *Fourier* peaks min/max $eÅ^{-3}$	−0.29/0.47	−0.55/0.70	−0.33/0.47	−0.54/0.58

$R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR_2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2}$

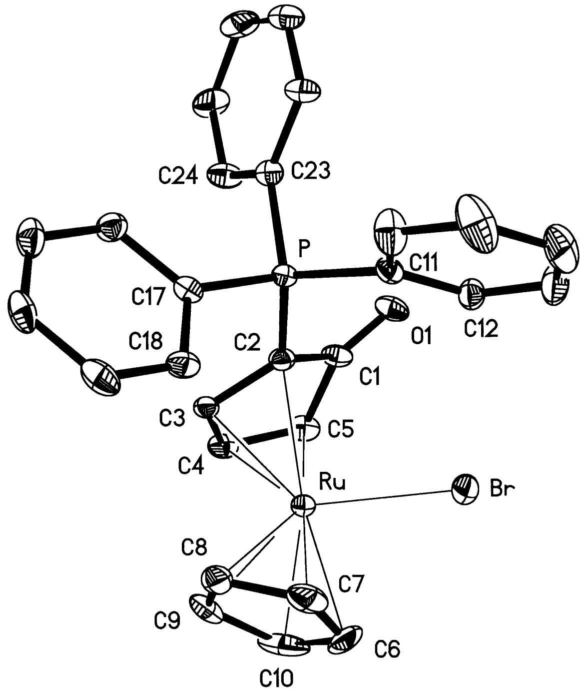


Fig. 2. Structural view of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_3O\text{-}2\text{-}PPh_3)Br]CF_3SO_3$ (**2a**) showing 20% probability thermal ellipsoids ($CF_3SO_3^-$ omitted for clarity); selected bond lengths (Å): Ru-C(2) 2.263(7), Ru-C(3) 2.142(7), Ru-C(4), 2.172(8), Ru-C(5) 2.265(8), Ru-C(6) 2.209(8), Ru-C(7) 2.200 (9), Ru-C(8) 2.164(8), Ru-C(9) 2.170(8), Ru-C(10) 2.200(9), Ru-Br 2.529(1), C(1)-O(1) 1.197(9), C(2)-P 1.763(7), C(2)-C(3) 1.43(1), C(3)-C(4) 1.43(1), C(4)-C(5) 1.40(1)

turned out to be isostructural, indicating that the crystal lattice is quite tolerant with respect to the anion incorporated into the host structure of the dominating Ru complexes. This finding is corroborated by the observation that crystals of **2a** were able to take up tetrahedral $AlBr_4^-$ anions furnished accidentally during repeated crystallization experiments in replacement of about 30% of the $CF_3SO_3^-$ groups (see Experimental section). A structural view of the Ru complex in **2a** is presented in Fig. 2 with selected bond distances reported in the caption. The two C_5 ring adopt an approximately staggered conformation. The cyclopentadienone ligand adopts an *endo* orientation with the PPh_3 substituent 0.37 Å out of plane of the butadiene unit and bent away from the metal. The metal-bonded cyclopentadienone shows the well known bending at C(2)/C(5) with an interplanar angle of 21.6(5)° between the butadiene part (C(2) through C(4)) and the carbonyl functionality (defined by the plane through O(1), C(1), C(2), and C(5)). In the parent compound $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]Br$ this angle is 20.6° [5]. The butadiene moiety is inclined to the $\eta\text{-}C_5\text{-}H_5$ ring at an angle of 36.7(5)°. The P-C(2) distance is 1.763(7) Å and the C(1)–O(1) distance is 1.197(9) Å. The Ru-C bond lengths to the cyclopentadienone are on average 2.153 Å for C(3)/C(4) and 2.264 Å for C(2)/C(5). These distances are longer by 0.012 and 0.035 Å than in compound **2b** with an unsubstituted cyclopentadienone ligand. The lengthening of the Ru–C bonds in **2a** is thus attributable to the inductive effect of the PPh_3 ligand.

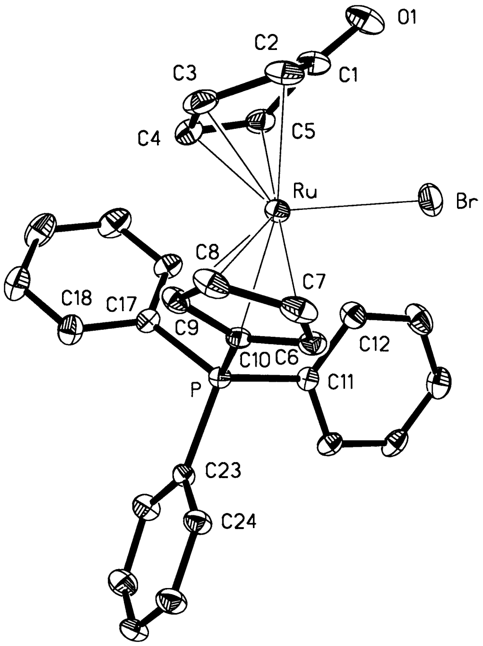


Fig. 3. Structural view of $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^4\text{-}C_5H_4O)Br]PF_6$ (**2b**) showing 20% probability thermal ellipsoids (PF_6^- omitted for clarity); selected bond lengths (Å): Ru-C(2) 2.228(4), Ru-C(3), 2.139(4), Ru-C(4) 2.144(4), Ru-C(5) 2.229(4), Ru-C(6) 2.223(4), Ru-C(7) 2.228(4), Ru-C(8) 2.209(4), Ru-C(9) 2.185(4), Ru-C(10) 2.222(4), Ru-Br 2.543(1), C(1)-O(1) 1.199(5), C(10)-P 1.782(4), C(2)-C(3) 1.402 (7), C(3)-C(4) 1.412(7), C(4)-C(5) 1.394(6)

Crystal structure of **2b**

A structural view of **2b** is shown in Fig. 3. Selected bond distances are reported in the caption. The major features of the $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]Br$ core of this complex are very similar to those of **2a**. The bending angle of the *exo*-oriented C_5H_4O ligand of 25.4(2)° is larger than in **2a**, whereas the inclination angle between the butadiene moiety and the cyclopentadienyl ring is somewhat smaller (34.5(2)°). These differences may be due to the absence of the electron withdrawing PPh_3 substituent at the cyclopentadienone ligand which also could cause the shortening of the bond lengths Ru-C(3)/C(4) = 2.142 Å and Ru-C(2)/C(5) = 2.229 Å in **2b**. The repulsion controlled distance Br–O(1), however, remains essentially unchanged (3.263 Å in **2a**, 3.252 Å in **2b**). The PPh_3-substituted cyclopentadienyl ring in **2b** shows, as expected, a lengthening of the Ru–C bonds (mean value 2.214 Å) in comparison to the unsubstituted ring in **2**a. The remaining bond distances Ru–Br = 2.453(6) Å, C(1)–O(1) = 1.199(5) Å, and C(10)-P = 1.782(4) Å in **2b** are in reasonable agreement with those in **2a** and related cyclopentadienone compounds.

Experimental

General

All manipulations were performed under an inert atmosphere of argon using *Schlenk* techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [6]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-PPh_3)]CF_3SO_3 (**1a**), [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-PPh_3)]PF_6 (**1a′**), and [Ru(η^5-$C_5H_4PPh_3$)(η^5-C_5H_4OH)]PF_6 (**1b**) were prepared according to the literature [4]. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Ac-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced internal *TMS* and external H_3PO_4 (85%). FT-IR spectra were recorded on a Mattson RS 2 spectrometer. Microanalysis were performed by Microanalytical Laboratories, University of Vienna, and agreed favourably with the calculated values.

[Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_3)Br]CF_3SO_3 (**2a**; $C_{29}H_{23}BrF_3O_4PRuS$)

A solution of **1a** (764 mg, 1.16 mmol) in CH_3NO_2 (2 cm^3) was treated with Br_2 (60 mm^3, 1.16 mmol), and the mixture was stirred for 1 h at room temperature. Upon addition of Et_2O a pink precipitate was formed which was collected on a glass frit, washed with Et_2O, and air dried. The crude product was redissolved in CH_3NO_2, and solid materials were removed by filtration. Addition of Et_2O resulted in the precipitation of **2a** as a pink powder.

Yield: 677 mg (79%); NMR (δ, CD_3NO_2, 20°C): 7.95–7.70 (m, 15H), 6.49 (m, 1H), 5.96 (m, 1H), 5.39 (s, 5H), 4.75 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20°C): 180.8 (C=O), 136.6 (d, J_{PC} = 3.0 Hz), 135.9 (d, J_{PC} = 10.9 Hz), 131.3 (d, J_{PC} = 12.9 Hz), 119.3 (d, J_{PC} = 91.5 Hz), 89.2 (C_5H_5), 87.1 (d, J_{PC} = 9.7 Hz), 83.6 (d, J_{PC} = 11.3 Hz), 81.9 (d, J_{PC} = 11.9 Hz), 61.9 (d, J_{PC} = 87.5 Hz) ppm; IR (KBr): $\nu = 1690\ cm^{-1}$ ($\nu_{C=O}$).

[Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_3)Br]PF_6 (**2a′**)

2a′ was prepared analogously to **2a** with **1a′** as the starting material.

[Ru(η^5-$C_5H_4PPh_3$)(η^4-C_5H_4O)Br]PF_6 (**2b**; $C_{28}H_{23}BrF_6OP_2Ru$)

This complex was prepared analogously to **2a** with **1b** (267 mg, 0.409 mmol) as the starting material.

Yield: 365 mg (82%); ^1H NMR (δ, CD_3NO_2, 20°C): 8.10–7.75 (m, 15H), 6.17 (dd, J = 4.05 Hz, J = 2.17 Hz, 2H), 6.07 (dd, J = 4.05 Hz, J = 2.17 Hz, 2H), 5.81 (vt, J_{HH} = 2.48 Hz, 2H), 4.08 (vt, J_{HH} = 2.48 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20°C): 179.3 (C=O), 137.7 (d, J_{PC} = 3.4 Hz), 136.1 (d, J_{PC} = 11.0 Hz), 132.0 (d, J_{PC} = 13.4 Hz), 117.7 (d, J_{PC} = 92.6 Hz), 101.0, 90.3 (d, J_{PC} = 8.5 Hz), 85.7, 80.8 (d, J_{PC} = 97.0), 73.7 ppm.

[Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_3)(CH_3CN)](CF_3SO_3)$_2$ (**3**; $C_{32}H_{26}F_6NO_7PRuS_2$)

$AgCF_3SO_3$ (83 mg, 0.324 mmol) was added to a flask containing **2a** (200 mg, 0.270 mmol) dissolved in CH_3CN (3 cm^3). After the reaction mixture was stirred for 1 h, AgBr was removed by filtration, and the crude product was precipitated with Et_2O as an orange solid. In order to remove AgBr completely, the complex was redissolved in CH_3NO_2 (3 cm^3). Solid materials were removed by filtration, and an analytically pure product was obtained upon precipitation with Et_2O.

Yield: 160 mg (70%); ^1H NMR (δ, CD_3NO_2, 20°C): 8.00–7.80 (m, 15H), 6.34 (m, 1H), 6.48 (m, 1H), 5.66 (s, 5H), 5.26 (m, 1H), 2.44 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20°C): 180.5 (d, J_{PC} = 6.4 Hz, C=O), 137.2 (d, J_{PC} = 2.9 Hz), 135.8 (d, J_{PC} = 11.1 Hz), 131.8 (d, J_{PC} = 12.9 Hz), 124.9 (CN), 118.0 (d, J_{PC} = 92.3 Hz), 92.6 (d, J_{PC} = 9.5 Hz), 90.9 (C_5H_5), 88.8 (d, J_{PC} = 10.2 Hz), 83.8 (d, J_{PC} = 9.9 Hz), 66.9 (d, J_{PC} = 86.6 Hz), 5.6 (CH_3) ppm; IR (KBr): 2326, 2299 (m, ν_{CN}), 1703 (s, $\nu_{C=O}$) cm^{-1}.

Attempts to prepare [Ru(η^5-$C_5H_4PPh_3$)(η^4-C_5H_4O)(CH_3CN)](PF_6)$_2$; formation of [Ru(η^5-$C_5H_4PPh_3$)(CH_3CN)$_3$](PF_6)$_2$ (**4**; $C_{29}H_{28}F_{12}N_3O_2P_3Ru$)

A solution of **2b** (175 mg, 0.239 mmol) in CH_3CN (10 cm^3) was treated with $AgPF_6$ (118 mg, 0.467 mmol), and the mixture was stirred for 1 h. The volume of the solution was then reduced to about 3 cm^3. Addition of Et_2O resulted in the formation of a yellow precipitate which was collected on a glass frit, washed with Et_2O, and dried under vacuum.

Yield: 187 mg (93%); ^{1}H NMR (δ, acetone-d$_6$, 20°C): 8.05–7.75 (m, 15H), 5.14 (dd, J_{HH} = 3.4 Hz, J_{HH} = 1.6 Hz, 2H), 5.09 (dd, J_{HH} = 3.4 Hz, J_{HH} = 1.6 Hz, 2H), 2.48 (s, 9H) ppm; ^{13}C{^{1}H} NMR (δ, acetone-d$_6$, 20°C): 137.0 (d, J_{PC} = 2.8 Hz), 135.9 (d, J_{PC} = 11.1 Hz), 131.9 (d, J_{PC} = 13.0 Hz), 128.7, 119.8 (d, J_{PC} = 92.5 Hz), 82.9 (d, J_{PC} = 13.4 Hz), 73.9 (d, J_{PC} = 8.3 Hz), 54.7 (d, J_{PC} = 101.7 Hz), 4.4 ppm; ^{31}P{^{1}H} NMR(δ, acetone-d$_6$, 20°C): 25.9 ppm

X-ray structure determinations of [Ru(η^5-C_5H_5)(η^5-C_5H_3OH-2-PPh_3)]CF_3SO_3 (**1a**), *[Ru(η^5-C_5H_5)(η^4-C_5H_3O-2-PPh_3)Br]CF_3SO_3* (**2a**), *[Ru(η^5-*C_5H_5*)(η^4-C_5H_3O-2-PPh_3)Br]PF_6* (**2a′**), *and [Ru(η^5-$C_5H_4PPh_3$)(η^4-C_5H_4O)Br]PF_6* (**2b**)

Crystal data and experimental details are given in Table 1. X-Ray data for **1a** and **2a** were collected on a Siemens Smart CCD area detector diffractometer (graphite monochromated MoK_α) radiation, λ = 0.71073 Å, a nominal crystal-to-detector distance of 4.45 cm, 0.3°ω-scan frames). For **2a′** and **2b**, X-ray data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated MoK_α radiation and the θ–2θ scan technique. Corrections for *Lorentz* and polarization effects, for crystal decay, and for absorption (**1a**, **2a**) were applied. All structures were solved by direct methods using the program SHELX97 [7]. Structure refinement on F^2 was carried out with the program SHELXL97 [8]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Compounds **2a** and **2a′** were found to be isostructural despite the significant shape difference of the CF_3SO_3 and PF_6 anions. In the investigated crystal of **2a** an $AlBr_4^-$ tetrahedron replacing about 30% of the $CF_3SO_3^-$ anions was clearly detected by X-ray diffraction and taken into account in the structure refinement but not in the chemical formula and derived quantities given in Table 1. This $AlBr_4^-$ anion was obviously introduced by a reaction with an aluminum foil used during repeated crystallization experiments that were necessary to obtain a crystal suitable for X-ray diffraction. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 118491, 118492, 118493, and 11494. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Financial support by the *Jubiläumsfonds der Oesterreichischen Nationalbank* is gratefully acknowledged (Project No. 6474).

References

[1] Repp W, Vetter H (1953) Justus Liebigs Ann Chem **582**: 133; Green MLH, Pratt L, Wilkinson G (1960) J Chem Soc 989

[2] Mauthner K, Mereiter K, Schmid R, Kirchner K (1994) Organometallics **13**: 5054; Kirchner K, Mereiter K, Umfahrer A, Schmid R (1994) Organometallics **13**: 1886

[3] Liebeskind LS, Bombrun A (1991) J Am Chem Soc **113**: 8736; Mauthner K, Slugovc C, Mereiter K, Schmid R, Kirchner K (1996) Organometallics **15**: 181

[4] Kirchner K, Mereiter K, Mauthner K, Schmid R (1994) Inorg Chim Acta **217**: 203
[5] Smith TP, Kwan KS, Taube H, Bino A, Cohen S (1984) Inorg Chem **23**: 1943
[6] Perrin DD, Armarego WLF (1988) Purification of Laboratory Chemicals, 3rd edn. Pergamon, New York
[7] Sheldrick GM (1997) SHELXS-97: Program for the solution of crystal structures. University of Göttingen, Germany
[8] Sheldrick GM (1997) SHELX-97. Program for crystal structure refinement. University of Göttingen, Germany

Received April 14, 1999. Accepted May 3, 1999