Cp*Ru Alkoxides with σ-Bridging Phenoxo Groups. X-ray Structure of [Cp*Ru(μ-OMe)(μ-OC_6H_3-2,4-(*t*-Bu)$_2$)]

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Summary: $[Cp^*RuOMe]_2$ (**1**) *reacts with phenols by successive exchange of one and two OMe groups for the phenolato group, forming mixed μ-methoxy−μ-phenolato complexes (**5**) and bis(μ-phenolato) dimeric complexes (**6**) successively. The latter, by an intramolecular rearrangement, convert into Cp*Ru(η*^{5}*-oxocyclohexadienyl) complexes (**7**). With phenol and 2-methyl-5-isopropylphenol (carvacrol) the stepwise reactions were followed by NMR spectroscopy. Using 2,4-di-tert-butylphenol, both the mono(phenolato) (**5c**) and bis(phenolato) (**6c**) complexes have been isolated. The latter complex is obtained best from Cp*Ru(proline) (**8**) and **1**. Complex **5c** was characterized by an X-ray structure. The molecular geometry is very similar to the one found for **1**.*

If $[Cp^*Ru(\mu\text{-OMe})]_2$ (**1**) is treated with an alcohol more acidic than MeOH, the exchange equilibrium (Scheme 1) generally places OR groups of the latter in the bridge position of the complex.[1] Phenols, which are more acidic than aliphatic alcohols, however, apart from the σ-bridging function analogous to aliphatic alcohols, can complex to a Cp*Ru moiety as π-ligands, either η^6-phenol or η^5-oxocyclohexadienyl, depending on the availability of protons. Reactions of **1** with a variety of different phenols have led invariably to π-phenol or oxocyclohexadienyl sandwich complexes as the only isolable products.[2] This was found not only for phenol itself, which reacted with **1** to yield Cp*Ru(η^5-C_6H_5O)·$2HOC_6H_5$, a complex with a planar oxocyclohexadienyl ligand firmly hydrogen-bonded to two molecules of phenol, but also with potentially chelating phenols such as salicylaldehyde or *o*-hydroxyacetophenone. Even pentafluorophenol gave exclusively the π-complex Cp*Ru(η^5-C_6F_5O).[3] Similarly, Tilley and co-workers reacted $[Cp^*Ru(\mu\text{-Cl})]_4$ with 2,6-di-*tert*-butylphenolate and isolated Cp*Ru(η^5-2,6-di-*tert*-butyl-1-oxocyclohexadienyl) in high yield.[4] From these experiments it appeared that phenols have a high preference to act as π-ligands toward the Cp*Ru moiety and that bridged σ-intermediates are not easily obtained.

Later work showed that the polarity of the solvent plays an important role in the reaction course and that σ-complexes show increased stability in less polar solvents. Since most of the earlier experiments were performed in acetone or diethyl ether, we have reinvestigated the reaction between **1** and phenols in benzene-d_6 by means of NMR spectroscopy, which allowed the detection of σ-intermediates. In addition to phenol (**2**), alkyl-substituted phenols, i.e., 5-isopropyl-2-methylphenol (carvacrol; **3**) and 2,4-di-*tert*-butylphenol (**4**), were investigated with the aim of sterically slowing the σ → π rearrangement.

Results

When **1** was mixed with phenol in a 3:1 Cp*Ru:phenol molar ratio, the ^{1}H NMR spectrum showed, apart from **1**, signals at δ 4.85 (bridging OMe) and 1.43 (Cp*) (Table 1) due to the mixed σ-bridged complex Cp*Ru(μ-OMe)(μ-OPh)RuCp* (**5a**), as well as weak signals due to the symmetrical complex **6a**. After addition of phenol up to the ratio Cp*Ru:Ph = 1:2, the signals of **1** disappeared and the NMR spectrum indicated a mixture of Cp*Ru(μ-$OPh)_2$RuCp* (**6a**) and Cp*Ru(η^5-C_6H_5O) (**7a**). When the mixture stood for 1 day further at ambient temperature, the rearrangement to **7a** was complete. The method is thus convenient for the generation of pure **7a**.

An analogous experiment was performed with the alkyl-substituted phenol carvacrol (**3**). A mixture of **1** and **3** with Cp*Ru:**3** stoichiometry slightly below 1:1 gave after 1 h at ambient temperature an NMR spectrum of almost pure $[Cp^*Ru(\mu\text{-carvacrol})]_2$ (**6b**) with some 10% of the mixed complex **5b** also present. Compound **6b** in turn rearranged with a half-life of about 2 days to the π-complex Cp*Ru(η^5-5-*i*-Pr-2-Me-C_6H_3O) (**7b**). After the rearrangement was complete, i.e., after no signals due to **6b** were left, the NMR spectrum still contained a small methyl signal at δ 2.52, which, by comparison with spectra obtained with less carvacrol (Table 1), can be confidently assigned to **5b**. This observation shows that only the doubly phenol-bridged complexes **6** undergo rearrangement to the π-complex and that the mixed σ-complexes **5** are stable in the absence of excess phenol.

Investigation of the exchange equilibrium between **1** and 2,4-di-*tert*-butylphenol in benzene-d_6 showed, 1 h after mixing, the mono(σ-2,4-di-*tert*-butylphenol) complex **5c** as the major component even in the presence of an excess of phenol. The equilibrium is shifted toward the bis(σ-2,4-di-*tert*-butylphenol) complex **6c** over the course of 24 h. Rearrangement of **6c** to **7c** requires about 2 weeks at ambient temperature in benzene solution to go to completion. An alternative preparative route leading to pure **6c** was found in the reaction of the proline complex **8**[5] with 2,4-di-*tert*-butylphenol (Scheme 2). Interestingly, the reaction of $[Cp^*RuCl]_4$ with lithium 2,4-di-*tert*-butylphenolate, as in the case

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(1) Hoernig, A.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 255.

(2) Koelle, U.; Wang, M. H.; Raabe, G. *Organometallics* **1991**, *10*, 257.

(3) Koelle, U.; Hoernig, A.; Englert, U. *Organometallics* **1994**, *13*, 4064.

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(5) Koelle, U.; Bücken, K.; Englert, U. *Organometallics* **1996**, *15*, 1376.

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Scheme 1

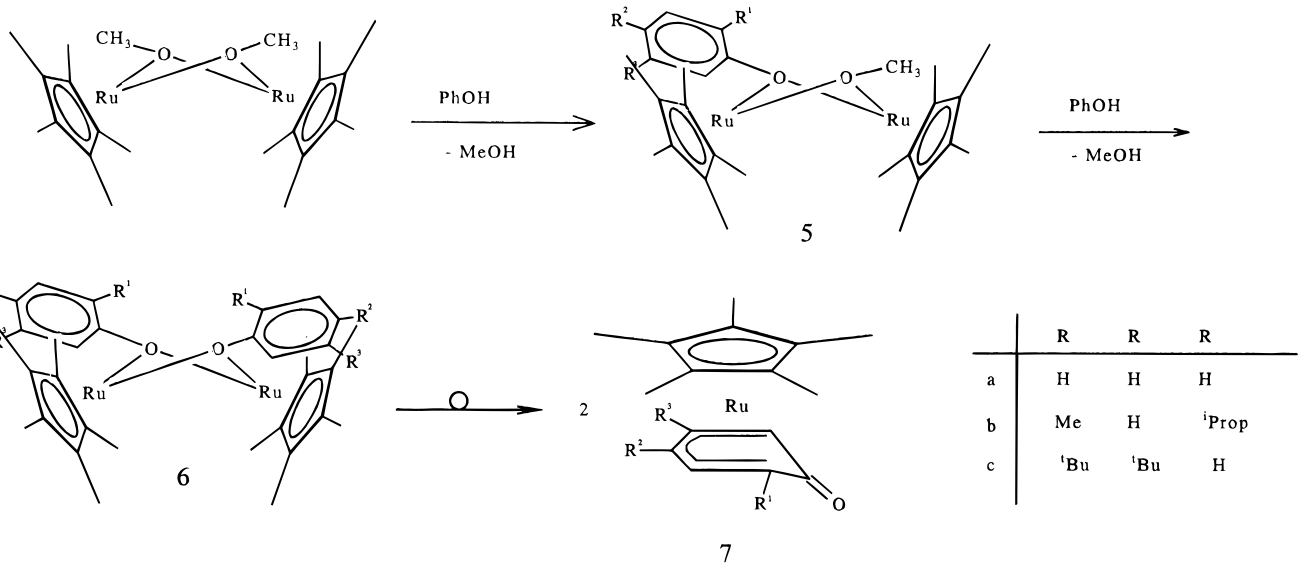
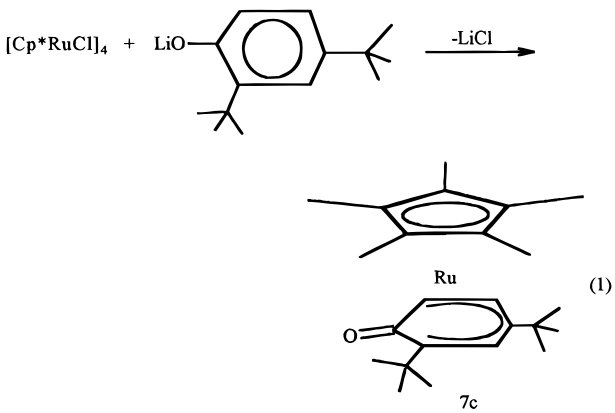


Table 1. ^{1}H NMR Resonances of Complexes 1, 5, 6, and 7 (δ; Benzene-d_6)

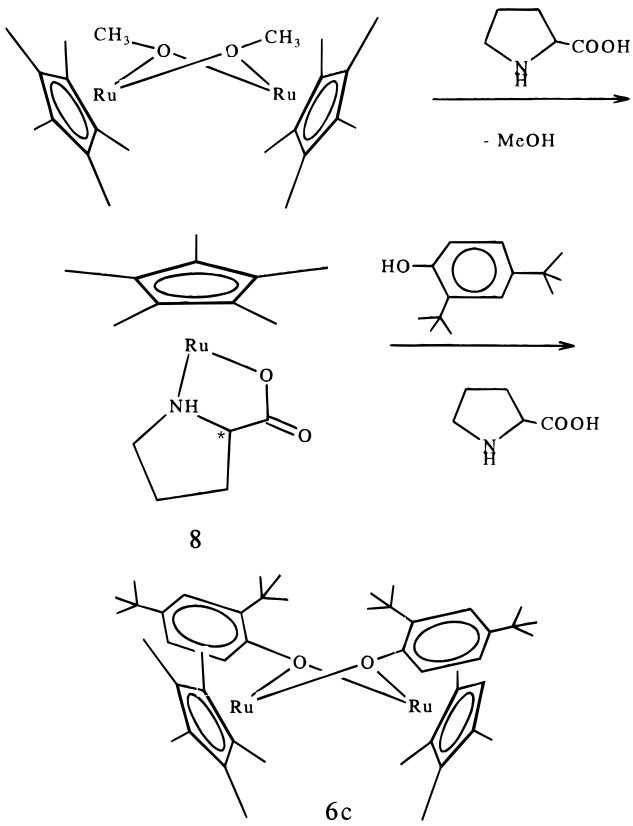
	Cp*	OMe	Me	*t*-Bu/i-Pr	arom H
1	1.62	4.82			
5a	1.43	4.85			6.7−7.5
5b	1.42	4.87	2.52	1.57 (d)	6.7−7.7
5c	1.46	4.90		1.45, 1.51	8.03, 7.5
6a	1.22				6.6−7.6
6b	1.20		2.51	1.48 (d)	6.7−7.5
6c	1.25			1.64.1.47	8.29, 7.47, 7.51
7a	1.48				4.06 (*p*), 4.35 (*m*), 4.97 (*o*)
7b	1.52		1.85	0.91 (d), 0.89	4.28 (*p*), 4.60 (*m*), 4.78 (*o*)
7c	1.56			0.98, 1.49	4.40 (*m*), 4.65 (*o*), 5.35 (*o*)

the 2,6-di-*tert*-butyl analogue,[4] gave mainly the 4-oxocyclohexadienyl complex **7c** (eq 1).



(1)

Scheme 2



The above observations can be summarized as follows. The first step, **1** → **5**, seems to be fast in all cases and was found to be complete when the first spectrum was recorded. Alkyl substitution in the phenol slows both steps in the reaction sequences **5** → **6** → **7**. With phenol only mixtures of mainly **5**/**6** and **6**/**7** or, finally, pure **7**, depending on the stoichiometry, can be obtained. With phenol as well as with carvacrol the second step, **5** → **6**, is separated from the first only by means of stoichiometry, whereas with 2,4-di-*tert*-butylphenol substitution of the second methoxo group by phenoxo is slow. Since **5c** is observed in the presence of free 2,4-di-*tert*-butylphenol and needs about 1 day to convert to **6c**, it follows that not only the equilibrium **1** + phenol ⇌ **5** but also the equilibrium **5** + phenol ⇌ **6** is to the right. Reaction of **5** to give **6** and rearrangement of **6** to **7** were slow enough to allow product isolation only in the case of 2,4-di-*tert*-butylphenol. Therefore, only for **5c** and **6c** were attempts made to isolate pure compounds. In order to assess the molecular geometry of a phenoxy-bridged derivative, **5c** was characterized by X-ray diffraction.

Complex **5c** crystallized as dark red crystals from ether. Structure determination was performed at 203 K. Table 2 gives selected structural parameters of the

(6) Koelle, U.; Kossakowski, J.; Boese, R. *J. Organomet. Chem.* **1989**, *378*, 449.

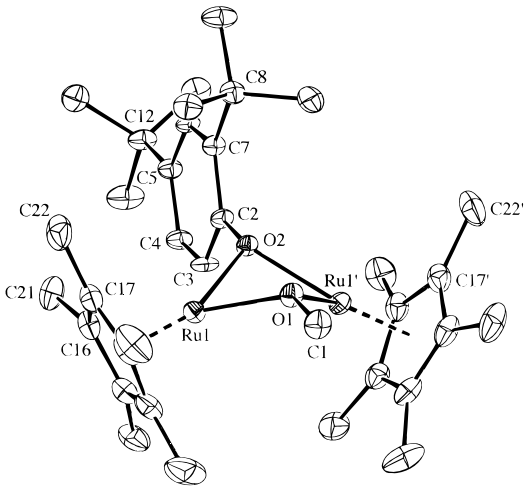


Figure 1. PLATON representation (30% probability ellipsoids) of the molecules **5c**, showing the atom-numbering scheme. For geometrical parameters, see Table 2.

Table 2. Comparison of the Molecular Geometries of 1 and 5c

	5c	1[6]
	Distances (Å)	
Ru−Ru	298.3	295.5(1)
Ru−O	204.0(3), 208.5(3)	205.5(5), 205.7(4)
Ru···Cp*	174.15	174.7
O−C	1.406(8) (OMe), 1.374(7) (OPh)	143.7(10)
	Angles (deg)	
O−Ru−O	71.5(1)	70.9(2)
Ru−O−Ru	91.4(2), 94.0(2)	91.9(2)
Ru−O−C	124.7, 126.1	124.3(4), 123.7(4)
O−Ru−Cp*	143.6, 144.8	145.0, 144.0
Ru−Ru−Cp*	154	150.0
Ru,O,O′/Cp*	91.2	92.3
Ru,O,O′/Ru′,O,O′	126.2	123.8

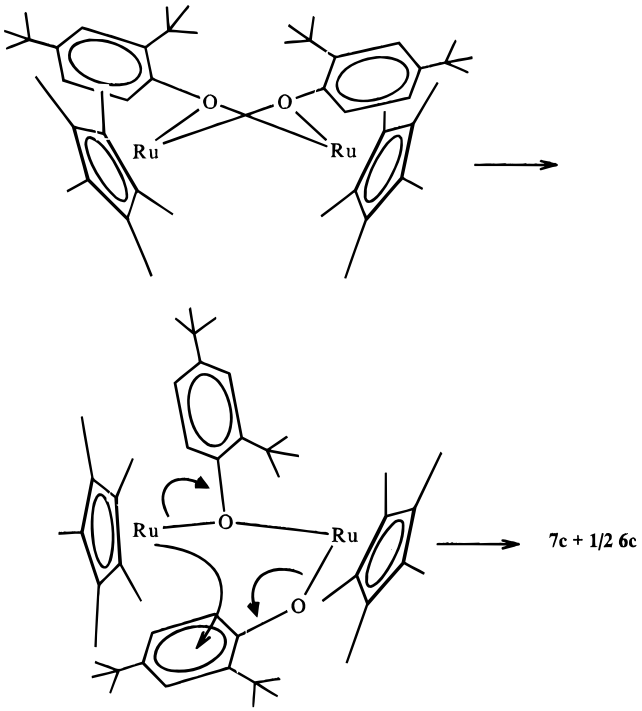
complex in comparison to analogous data for **1**; Figure shows an ORTEP representation of the molecule.

As can be seen from Table 2, all key parameters are very similar for the two molecules, in particular the folded Ru−O−Ru−O rhombus with an Ru−Ru separation of about 3 Å, which in the present complexes is considered as nonbonding. The longer Ru−O distances in **5c** pertain to bonds to the phenolic oxygen. The vectors O1−C1 and O2−C2 from the bridging oxygens to methyl and arene carbon atoms, respectively, are nearly collinear, making an angle of 9°. The arene ring of the 2,4-di-*tert*-butylphenol is contained in a crystallographic mirror plane bisecting the Ru−Ru vector. The 2-*tert*-butyl groups point "upward", away from the Cp* methyl groups, to give minimum steric interference.

The nearly identical geometries of **1** and **5c** further support our view that the particular folding of the Ru−O−Ru−O rhombus has its origin in electronic (overlap) factors, as was deduced from calculations on the monomeric complexes Cp*RuL(OR)[7] and is resistant to steric factors as long as the bulk of the OR groups allows the formation of the complex type. It is noteworthy that a second possible configuration with one R group in an axial position, as has been inferred from VT NMR spectra for the complex $[Cp^*Ru(S\text{-}t\text{-}Bu)]_2$,[8] obviously does not offer a sterically more favorable alternative in the present case. Thus, cooling of **6c** to −90 °C at 500 MHz proton frequency in toluene-d_8 solution gave no indication for exchange broadening of signals.

A look at models discloses that *tert*-butyl groups in the 2,6-positions would severely interfere with Cp* methyl hydrogens. Experiments to exchange the OMe group in **1** with 2,4,6-tri-*tert*-butylphenol under the same conditions as were used for the other phenols gave no reaction over 1 week (apart from small amounts of $(Cp^*Ru)_2(\mu\text{-}CO)(\mu\text{-}H)_2$, a product frequently encountered in substitution-induced decomposition of **1**[9]). Thus, the particular substitution pattern exhibited by a 2,4-di-*tert*-butylphenoxy group seems to slow down sterically the conversion of the σ- into the π-oxocyclohexadienyl complex, but it is still small enough to fit the geometry of the folded dimer.

Scheme 3



Since the rearrangement **6** → **7**, in cases where it could be observed separately, seems not to depend on the presence of excess phenol, it is believed to be intramolecular. The necessary first step is the opening of a Ru−O bond. From the fact that mixed σ-OMe−σ-OPh complexes do not rearrange, or do so only very slowly, it follows that the Ru−OPh bond is preferably broken, when two phenoxo groups are in the bridge. The second step, i.e., π-coordination of the now singly bonded O−Ph to the other Ru, is most probably the one which is hindered by sterically demanding substituents at the phenol ring.

Opening of a Ru−O bond will be facilitated by polar solvents, as well as anions such as Cl^-, both acting as donors toward the unsaturated Ru. In fact, an equilibrium between **1** and $[Cp^*RuCl]_4$ was established whose position depends on the solubility and electrophilicity of the reactants.[10] This observation may give a clue to

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(9) Kang, B.-S.; Koelle, U.; Thewalt, U. *Organometallics* **1991**, *10*, 2569.

the puzzling fact that reaction of $[Cp^*RuCl]_4$ with lithium 2,4-di-*tert*-butylphenolate gave only **7c** (eq 1), whereas lithium 2,4-di-*tert*-butylphenolate and **8** cleanly gave **6c**. In a metathetical reaction starting from $[Cp^*RuCl]_4$, Cl^- ions present will either stabilize a monomeric $Cp^*Ru-\sigma$-phenolate, which collapses to **7c**, or will catalyze $\sigma \rightarrow \pi$ rearrangement of an intermediate σ-complex by the above mechanism. Prolinate anion in contrast, which is generated from metathesis of **8** with phenolate, cannot stabilize a monomeric $Cp^*Ru-\sigma$-phenolate; therefore, the reaction leads directly to the dimer. The reaction of Scheme 2 was found as the best way to prepare the pure dimer **6c**; **5c** is best obtained by reaction of **1** and the lithium phenolate in ether in the correct stoichiometry.

Oxocyclohexadienyl complexes **7**, apart from reactions outlined in Scheme 1 and eq 1, can be prepared alternatively by reacting **1** with the respective phenol in ether in the presence of CF_3SO_3H to give the cationic phenol complex, which is subsequently deprotonated with BuLi to give **7**.

Experimental Section

All manipulations were conducted under exclusion of air using nitrogen and anhydrous, nitrogen-saturated solvents. NMR spectra were recorded on Bruker SY 80 and Varian UNITY 500 instruments.

Bis(pentamethylcyclopentadienyl)(μ-2,4-di-*tert*-butylphenolato)(μ-methoxo)diruthenium (5c). To 145 mg (0.27 mmol) of $[Cp^*RuOMe]_2$ (**1**) in 30 mL of ether was added 115 mg (0.54 mmol) of lithium 2,4-di-*tert*-butylphenolate and the mixture stirred for 2 h. The ether solution was filtered through Celite, concentrated to 4 mL, and stored at −78 °C; 102 mg (0.14 mmol, 52%) of dark red crystals separated. ^{13}C NMR (benzene-d_6): δ 168.2 (C_{ipso}), 142.3 (C2), 137.1 (C4), 126.0, 122.6, 121.7 (C3,5,6), 30.8, 32.2, 34.6, 35.7 (^{t}Bu), 70.2, 11.0 (Cp*), 71.0 (OMe). Anal. Calcd for $C_{35}H_{54}O_2Ru_2$: C, 59.3; H, 7.7. Found: C, 59.6; H, 7.9.

Bis[(pentamethylcyclopentadienyl)(μ-2,4-di-*tert*-butylphenolato)ruthenium] (6c). A slurry of 200 mg (0.57 mmol) of Cp*Ru(prolinate)[5] in 20 mL of THF was cooled to −78 °C, and 121 mg (0.57 mmol) of lithium 2,4-di-*tert*-butylphenolate was added. When the mixture was warmed, a reaction was observed at −15 °C. The color turned mauve red, and the prolinate complex dissolved. When all had dissolved, the solvent was evaporated *in vacuo* and the residue was extracted with ether. The extracts were filtered through Celite, concentrated to 4 mL, and cooled to −78 °C; 164 mg (0.19 mmol, 65%) of **6c** separated as a dark red powder. ^1H NMR: see Table 1. ^{13}C NMR (benzene-d_6): δ 168.8 (C_{ipso}), 143.1 (C2), 136.9 (C4), 126.7, 123.7, 121.7 (C3,5,6), 30.1, 32.0, 35.2, 36.0 (^{t}Bu), 69.8, 10.2 (Cp*). Anal. Calcd for $C_{48}H_{72}O_2Ru_2$: C, 65.27; H, 8.22. Found: C, 61.73; H, 8.23.

Table 3. Crystallographic Data for 5c

formula, fw	$C_{35}H_{54}O_2Ru_2$, 708.96
space group	*Pnma* (orthorhombic, No. 62)
a, b, c (Å); V (Å^3)	11.704(4), 16.021(5), 17.886(4); 3354(2)
d_{calcd} (g/cm^3)	1.404
Z	4
$F(000)$	1472
μ(Mo Kα) (cm^{-1}), T (K)	9.1, 203
scan mode, scan range (deg)	ω, $3 \le \theta \le 27$
total no. of rflns	6153
no. of unique observns with $I > \sigma(I)$	2558
no. of variables	196
R, R_w	0.0045, 0.0045
weighting factor w	$w = 1/\sigma^2(F_o)$
GOF	1.156
maximal residual density (e/Å^3)	0.59

Crystal Structure Determination of 5c. A dark red crystal of approximate dimensions 0.25 × 0.45 × 0.15 mm was mounted on an ENRAF-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Crystal data and parameters of data collection and structure refinement are collected in Table 3. The Ru atoms were located by direct methods using SHELXS86.[11] The remaining atom positions resulted from subsequent cycles of refinement and difference Fourier syntheses.[12] In the final least-squares full-matrix refinement all non-hydrogen atoms were refined with anisotropic thermal displacement parameters and hydrogen atoms were included as riding atoms with an idealized geometry (C−H = 0.98 Å, $B_H = 1.3B_C$).

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Supporting Information Available: Listings of atom coordinates, anisotropic thermal displacement factors, bond distances, and bond angles for **5c** (9 pages). Ordering information is given on any current masthead page.

OM9601211

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(12) MolEN: An Interactive Structure Solution Procedure; ENRAF-Nonius, Delft, The Netherlands, 1990.