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Ligand addition to $[Cp^{\wedge}RuCl]_4$—molecular structure of $[Cp^{\wedge}Ru(C_2H_4)Cl]_2$

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Abstract

$[Cp^{\wedge}RuCl]_4$ (**1a**) ($Cp^{\wedge} = \eta^5$-C_5Me_4Et) reacts with pyridine or ethylene by *trans* addition and cleavage to yield the dimers $[Cp^{\wedge}RuL(Cl)]_2$. The pyridine adduct has been oxidized to the known mixed valence complex $[(Cp^{\wedge}Ru(py))_2(\mu$-$Cl)_2]X$.

Introduction

$Cp^{*}RuCl$ (**1b**) ($Cp^{*} = \eta^5$-C_5Me_5), a versatile synthon for the preparation of $Cp^{*}RuL_2$- and other half-sandwich and sandwich complexes [1–6] has recently been shown by an X-ray structural determination to be tetrameric in the solid state [1]. The analogous $Cp^{\wedge}$ ($Cp^{\wedge} = \eta^5$-C_5Me_4Et) derivative (**1a**) which shows better crystallinity, has a largely identical structure [7]. By virtue of the lone pairs of triply-bridging chloride each Ru in the tetramer adopts an 18-electron configuration in a pseudooctahedral environment. However, the tetramer is easily cleaved by donor/acceptor ligands L; with L = CO, diolefin, or bipyridine, complexes of type $Cp^{\wedge}(^{*})RuL_2Cl$ are formed [2,7]. We found that with stoichiometric amounts of a monodentate ligand cleavage can be held at the dimer stage, yielding stable dimeric addition products.

Results

Complex **1b** was reported to react with pyridine [5,6] to give a π-sandwich cation $[Cp^{*}Ru(\pi$-$C_5H_5N)]^+$, which is readily transformed into a coordination complex $Ru(C_5H_5N)_6{}^{2+}$ in solution [6]. The decomposition is prevented by alkyl substitution; e.g. more stable π-complexes are formed from 2,6- and 3,5-lutidines.

We find that reaction of **1a** with a stoichiometric amount of pyridine in pentane at ambient temperature gives a 60% yield (after recrystallization from ether) of a complex of composition $Cp^{\wedge}Ru(py)Cl$ (**2**). **2** shows ^1H NMR resonances (in THF-d_8) at δ 1.65, 1.20 and 0.80 for $Cp^{\wedge}$, and characteristic multiplets at δ 8.8

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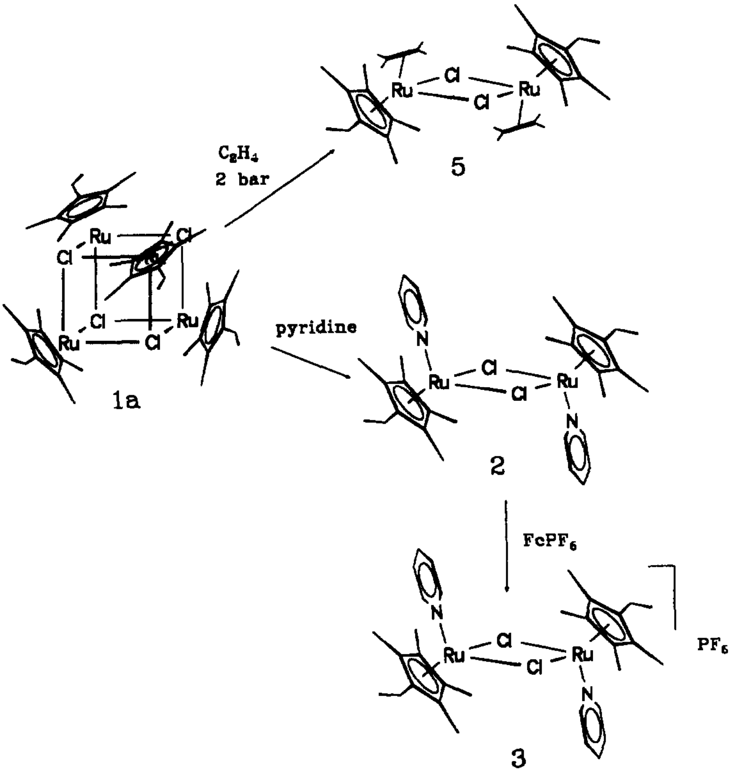


Scheme 1.

(α), 7.45 (γ) and 7.1 (β) for σ-coordinated pyridine, at distinctly higher field than those reported for the ligand in $Ru(C_5H_5N)_6{}^{2+}$ [6]. In the mass spectrum the highest mass peak is found at m/z 572, corresponding to $(Cp^\wedge RuCl)_2$. The dark yellow, quite air sensitive, crystals gave satisfactory analysis for the composition as shown in Scheme 1. We did not observe formation of $Ru(pyridine)_6{}^{2+}$ or of a $Cp^\wedge$ Ru(π-pyridine) complex under these conditions.

The dimeric nature of the adduct **2**, formulated as $[Cp^\wedge Ru(py)Cl]_2$, is inferred from its oxidation to the mixed-valence cation $[(Cp^\wedge Ru(py)Cl)_2]PF_6$ (**3**). Thus, treatment of **2** in THF with a solution of $FcPF_6$ in MeOH gave **3**, after work-up, as a dark green solid. The ^1H NMR spectrum of **3** shows broad signals in the range δ 8–3 and 11–8.4 ppm for $Cp^\wedge$ and pyridine, respectively, in agreement with the paramagnetic nature of the complex, and has a correct CHN analysis.

The Cp^* analogue of complex **3** was obtained fortuitously by Chaudret et al. [6] by an oxidation/decomposition reaction from THF solutions containing **1a** and pyridine, and was identified by an X-ray structural study, which revealed a *trans* disposition of py and Cp^* ligands with respect to a planar Ru–Cl–Ru–Cl rhombus. Since oxidation with ferricenium salt is believed to be largely an outer sphere electron transfer reaction, the neutral Ru^{II}/Ru^{II} precursor must have the same stereochemistry as the mixed valence Ru^{II}/Ru^{III} salt.

As has been extensively demonstrated by Fagan et al. [1], diolefins always cleave **1b** to give the monomeric diolefin complex $Cp^*Ru(diol)Cl$. We have observed the

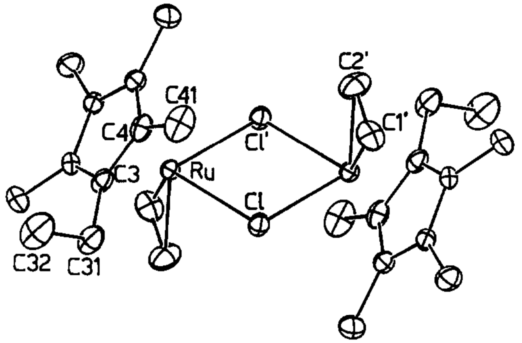


Fig. 1. ORTEP representation of $[\mathrm{Cp}^{\wedge}\mathrm{Ru(C_2H_4)Cl}]_2$ (**5**).

same reaction for 2,3-dimethylbutadiene and **1a**, which gives Cp^ Ru(dimethylbutadiene)Cl (**4**). Application of a 2 bar pressure of ethylene to a pentane solution of **1a**, leads to a colour change from brown yellow to red. Its ^{1}H NMR spectrum indicates product **5** has an ethylene : Cp^ ratio of 1 : 1, suggesting a dimer. Fagan [1] considered a polymeric nature for the less soluble Cp* analogue, which in his case could not be freed from residual starting material. The higher solubility of the Cp^ complex allowed brown-red crystals suitable for an X-ray structural determination to be obtained from ether/pentane at low temperature.

Structure of 5

Complex **5** crystallizes in the space group $P2_1/c$ with $Z = 2$. An ORTEP view of the molecule is shown in Fig. 1 and bond lengths and angles are given in Table 1. The molecule posesses an inversion center with a planar Ru–Cl–Ru–Cl arrangement. Tilting and rotation of the Et group is such that crystallographic inversion is maintained. The projection of the ethylene C=C bond vector on to the Ru–Cl–

Table 1

Bond lengths (Å) and bond angles (°) in **5**

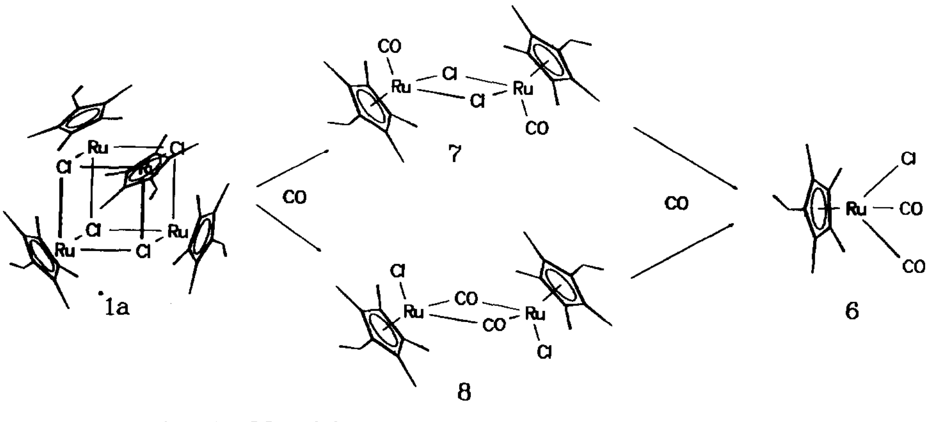
Ru–Ru	3.7834(5)	Ru–C5	2.250(3)
Cl–Cl′	3.198(2)	Ru–C6	2.160(3)
Ru–Cl	2.4750(8)	Ru–C7	2.139(3)
Ru–Cl′	2.4788(8)	C1–C2	1.369(6)
Ru–C1	2.194(3)	C3–C4	1.443(5)
Ru–C2	2.194(4)	C3–C7	1.428(5)
Ru–C3	2.141(3)	C4–C5	1.406(5)
Ru–C4	2.230(3)	C5–C6	1.428(5)
		C6–C7	1.447(4)
Cl–Ru–Cl	80.41(3)	Cl–Ru–C1	84.2(1)
Cl–Ru–C1	114.2(1)	Cl–Ru–C2	99.5(1)
Cl–Ru–C2	84.4(1)	Cl–Ru–C3	153.9(1)
Cl–Ru–C3	97.05(9)	Cl–Ru–C4	115.4(1)
Cl–Ru–C4	89.60(9)	Cl–Ru–C5	93.89(9)
Cl–Ru–C5	116.08(9)	Cl–Ru–C6	105.54(9)
Cl–Ru–C6	152.34(9)	Cl–Ru–C7	143.70(9)
Cl–Ru–C7	134.2(1)	C1–Ru–C2	36.4(2)

Ru–Cl plane is nearly parallel (4.9 ° deviation) to the Cl–Cl vector. The dihedral angle between planes Ru–Cl–Cl and Ru–C=C is 84 °, so that the Ru maintains a close to octahedral coördination. The Ru · · · Ru separation of 3.78 Å rules out any direct contact between the metal atoms, and is typical for edge sharing bioctahedral dimers in which the metal–metal distance is dominated by ligand repulsion [9]. Ru–Cp bond distances are in the range frequently observed for RuCp* with Ru–Cp center 1.815(4) Å. The Ru–ethylene distances (Ru–C(1), Ru–C(2) 2.194 Å) are relatively short, but nevertheless the olefinic double bond (C(1)–C(2) 1.37 Å) is also at the short end of the range for coordinated olefins [10]. Two examples with a comparable set of ligands around Ru are Ru(η^5-C_8H_{11})(PMe_3)(η^3-OC-$OCH_2CH{=}CH_2$) [11] with Ru–C = 2.20, 2.22, C=C 1.37 Å, and the dimeric [Cp*Ru(η^3-$OC_2H_4CH{=}CH_2$)]$_2$ [12], with Ru–C = 2.16, 2.14, C=C 1.42 Å. Whereas in the first example Ru is coordinated, in addition to a π-cyclic η^5-ligand, to oxygen and phosphorus atoms in the latter case coordination is to two oxygen atoms, similar to the two chlorine atoms in **5**. Nevertheless the C=C distance in **5** indicates that there is not much back-bonding, as appears to be the case for the acrylic acid complex, and the olefin acts mostly as a σ-donor, whereas in the butenoxo complex there seems to be more back-bonding. Clearly factors other than the nature of the co-ligands are important for the olefin bonding in these complexes.

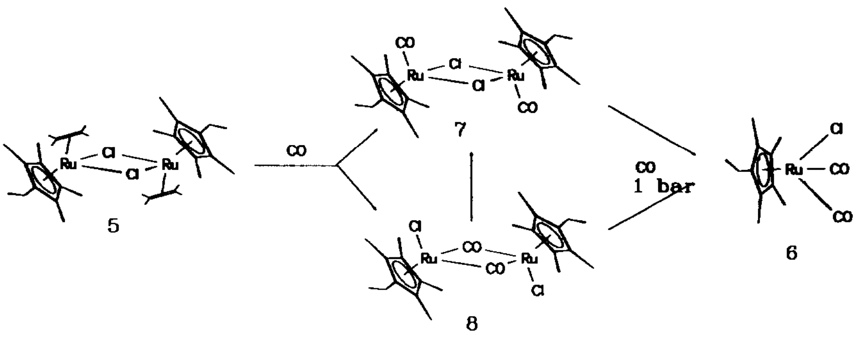
The pair of compounds **3**/**5** provides an example of a type of organometallic complex in which a rather hard pyridine and a much softer olefin ligand yield the same coordination geometry despite the possibility of alternatives such as $CpRuL_2Cl$ in both cases. Cp*Ru(py)$_2$Cl is not known, but the analogous bipy complex is very readily formed [2a]. Likewise Cp*Ru(1,5-COD)Cl is a fairly stable and readily-formed compound [2], though with ethylene, even under 4 bar, no cleavage to a monomeric diolefin complex has been observed [1].

Reaction with CO and dppm (Scheme 2–4)

With carbon monoxide as a π-ligand again, only the mononuclear complex Cp*Ru(CO)$_2$Cl (**6**) is known, and is readily formed if less than 1 bar of CO pressure is applied to **1a** [1,2]. We monitored the reaction of **1a** with less CO by IR



Scheme 2. Reaction with CO and dppm.



Scheme 3.

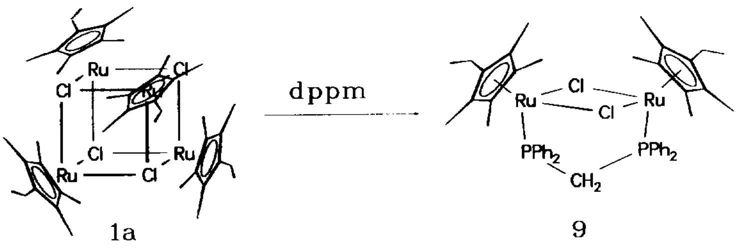
spectrometry; when CO was added to a pentane solution of **1a** in stoichiometric quantity, i.e. 1 mol CO per mol dimer, a strong IR band at 1937 cm^{-1} appeared along with a weaker band at 1804 and two still weaker absorptions at 1979 and 2036 cm^{-1}. A gradual increase in the amount of CO caused the first two bands to disappear to give way to the second two. The latter two bands are clearly those from the dicarbonyl **6**, whereas the first two can be assigned to two different monocarbonyls, viz. a Cl-bridged species **7** and a CO-bridged species **8**. Since some **6** is formed even with less than a stoichiometric amount CO, the mono- and di-carbonyls appear to be in equilibrium under these conditions, and no attempts were made to isolate either **7** or **8** from this reaction mixture.

In a further experiment the ethylene complex **5** was treated with a stoichiometric amount of CO in pentane at ambient temperature (see Scheme 3). The IR spectrum of the solution again exhibited bands at 1937 and 1804 cm^{-1}, with the latter dominating. With time and addition of more than stoichiometric CO the 1937 band strengthens at the expense of the 1804 band, indicating the formation of only **7**. Use of 1 bar pressure of CO finally produced **6**.

Since **7** is formed under these conditions more readily than starting from **1a**, the reaction can be stopped at the stage of **7** and the monocarbonyl crystallized from solution and characterized by NMR and mass spectroscopy. The experiment shows that substitution of ethylene by CO is easier than cleavage of the dimer to give an ethylene–carbonyl monomer. The latter is expected to yield the dimeric dicarbonyl **6**, rather than **7** or **8**, on reaction with further CO. The initial formation of **8** and its disappearance in the later stages of the reaction suggests that the CO-bridged complex is the product of kinetic control, and is formed by ethylene-substitution more easily than by cleavage of **1a**.

Another ligand which can stabilize the dimeric form is bis(diphenylphosphino)methane (dppm). The Cp* analogue of $[Cp^{\wedge}Ru(\mu\text{-}Cl)]_2$ dppm (**9**) was obtained previously as one of the products of cleavage of the mixed valence dimer $(Cp^{*}Ru)_2(\mu\text{-}Cl)_3$ with dppm (Scheme 4) [2a]. Complex **9** is formed directly and in high yield from **1a** and dppm. It should be noted that in this case the $Cp^{\wedge}$ and dppm phosphorus atoms must be in a *cis* disposition. A folded butterfly geometry of the Ru–Cl–Ru–Cl core seems possible.

It appears that stronger π-acceptor ligands tend to produce $Cp^{*}RuL_2X$-type complexes, whereas σ-donors can stabilize the dimeric $[Cp^{*}RuL(\mu\text{-}X)]_2$-type. This latter type can be regarded as a versatile synthon, since further cleavage with a



Scheme 4.

different donor ligand L′ may provide easy access to complexes Cp*RuLL′X with a chiral Ru center.

Experimental

All experiments were conducted under nitrogen in anhydrous, nitrogen-saturated solvents. ^1H and ^{13}C NMR spectra were recorded on a Bruker SY 80 and WH 270 spectrometer and IR spectra on a Perkin–Elmer 842 instrument. Mass spectra were obtained at 70 eV with a Varian CH-5 DF spectrometer. Elemental analyses were by Analytische Laboratorien, Engelskirchen (FRG).

Tetrakis(chloro(tetramethylethylcyclopentadienyl)ruthenium) (1a)

To a solution of 0.29 g (0.51 mmol) of $(Cp^{\wedge}RuOMe)_2$ in 30 ml of pentane was added 0.12 g (1.1 mmol) of Me_3SiCl. Within a few minutes the solution became brown and a brown solid separated. After 30 min the solution was evaporated to dryness, the residue was extracted twice with pentane and the extracts filtered and cooled to −80 °C, at which the product separated as a brownish yellow solid. Yield 0.19 g (67%). ^1H NMR (C_6D_{12}): δ 2.25 (q, 2H, CH_2), 0.95 (t, 3H, Me), 1.56 (pseudo s, 12H, Me) ppm. MS (m/z, $I_{rel.}$): 572 (100, M^+) 286 (21, $M/2$), 250 (56, $M/2$ − HCl), 248 (49, $Cp^{\wedge}$Ru − 2H).

Bis[(μ-chloro)(pyridine)(tetramethylethylcyclopentadienyl)ruthenium)] (2)

To a solution of 0.21 g (0.73 mmol Ru) of **2** in 20 ml of pentane was added 60 μl (0.72 mmol) of pyridine. Within a few minutes a red precipitate separated. After 1 h at ambient temperature the solvent was evaporated *in vacuo*, the residue extracted with ether and the extract filtered. The concentrated filtrate was cooled to −30 °C, at which the product separated as golden-yellow microcrystals. Yield was 0.15 g (57%). ^1H NMR (THF-d_8): δ py: 8.8 (m, 4H, H_α), 7.3 (m, 6H, H_β, H_τ), $Cp^{\wedge}$: 1.65 (q, 2H, CH_2), 0.80 (t, 3H, Me), 1.20 (pseudo s, 12H, Me) ppm. MS (m/z, $I_{rel.}$): 572 (100, M^+ − 2py) 494 (90, $(Cp^{\wedge}Ru)_2$ − 8H), 250 (85, $Cp^{\wedge}$Ru − H). Anal. Found: C, 52.30; H, 5.98. $C_{32}H_{44}N_2Cl_2Ru_2$ (729.1) calc.: C, 52.67; H, 6.03%.

Bis[(μ-chloro)(pyridine)(tetramethylethylcyclopentadienyl)ruthenium)]hexafluorophosphate (3)

To a solution of 0.15 g (0.41 mmol Ru) of **2** in 20 ml of THF was added dropwise 0.07 g of Cp_2FePF_6 in 20 ml of methanol. The colour changed from red to green-yellow. After 1 h at ambient temperature the solution was evaporated to dryness *in vacuo*, the residue washed twice with pentane to remove ferrocene and then extracted with dichloromethane. The filtered extract was concentrated to 5 ml and layered with 5 ml of ether. When the ether was allowed to diffuse into the dichloromethane phase at −30 °C a dark-green solid separated, and was isolated by decantation and dried under vacuum. Yield 0.05 g (30%). ^{1}H NMR (CD_2Cl_2) δ 8.4–11.2 (br, py), 8.0–3.0 (br, Cp^) ppm. IR (KBr): 842 cm^{-1} (PF_6^-). Anal. Found: C, 43.77; H, 4.99; N, 3.36. $C_{32}H_{44}N_2Cl_2PF_6Ru_2$ (874.0) calc.: C, 43.94; H, 5.03; N, 3.20%.

Chloro(2,3-dimethylbutadiene)(tetramethylethylcyclopentadienyl)ruthenium (4)

To an ice-cooled solution of 0.21 g (0.18 mmol Ru) of **1a** in 30 ml of pentane was added ca. 0.3 ml (3 mmol) of 2,3-dimethylbutadiene. After a few minutes a precipitate had formed. The mixture was stirred for a further 1 h at ambient temperature and the solvent was then evaporated and the residue extracted with ether. The extract was filtered, concentrated to 5 ml, and kept at −30 °C to deposit crystals. Yield 0.2 g (73%). ^{1}H NMR (THF-d_8): δ dimethylbutadiene: 3.1 (d, 2H) 2.43 (d, 2H), 1.95 (s, 6H); Cp^: 2.1 (q, 2H, CH_2), 1.07 (t, 3H, Me), 1.64 (pseudo s, 12H, Me) ppm. MS (m/z, $I_{rel.}$): 572 (100, $(Cp^\wedge RuCl)_2$) 492 (90, $(Cp^\wedge Ru)_2 - 8H$), 248 (85, $Cp^\wedge Ru - 3H$). Anal. Found: C, 55.19; H, 7.40. $C_{17}H_{27}ClRu$ (367.5) calc.: C, 55.43; H, 7.33%.

Bis[(μ-chloro)(ethylene)(tetramethylethylcyclopentadienyl)ruthenium)] (5)

A 2 bar pressure of ethylene was applied to a stirred solution of 0.30 g (1.04 mmol Ru) of **1a** in 30 ml of pentane cooled by acetone/dry ice. After 0.5 h the cooling bath was removed and stirring continued at room temperature for 6 h, during which a red precipitate had formed. The supernatant liquid was decanted, the residue extracted with ether, and the extract filtered and set aside to crystallize under a slight ethylene pressure at −20 °C for 6 d. Yield 0.22 g (66%). ^{1}H NMR (cyclohexane-d_{12}): δ 4.14 (s, 4H, ethylene), 1.77 (q, 4H), 1.32 (pss, 24H), 0.92 (t, 6H) Cp^ ppm. MS (m/z, $I_{rel.}$): 572 (100, $(Cp^\wedge RuCl)_2 = M$), 492 (60, $M - 8H$), 248 (80, $Cp^\wedge Ru - 3H$). Anal. Found: C, 49.57; H, 6.62, Cl, 11.05. $C_{13}H_{21}ClRu$ (313.8) calc.: C, 49.75; H, 6.74; Cl, 11.30%.

Bis[(μ-chloro)(carbonyl)(tetramethylethylcyclopentadienyl)ruthenium)] (7)

To a solution of 0.13 g **5** (0.41 mmol Ru) in 30 ml pentane a total of 75 ml CO (3.1 mmol) was added from a syringe. The colour of the solution changed from red to red-violet and finally during 6 h back again to red. The solvent was evaporated off *in vacuo*, the residue extracted with pentane, and the extract filtered and then cooled to −20 °C, to give 0.1 g (75%) of **7** as darkbrown crystals. ^{1}H NMR (C_6D_6): δ Cp^ 1.94 (q, 2H), 1.49 (s, 6H), 1.46 (s, 6H), 0.76 (t, 3H) ppm. MS (m/z, $I_{rel.}$): 628 (6, M^+), 599 (18, $M - CHO$), 572 (100, $(Cp^\wedge RuCl)_2$), 536 (15, $(Cp^\wedge RuCl)_2 - HCl$). IR (KBr): 1931 cm^{-1} (pentane): 1937 cm^{-1}. Anal. Found: C, 46.02; H, 5.37; Cl, 11.43. $C_{12}H_{17}ClORu$ (313.8) calc.: C, 45.93; H, 5.46; Cl, 11.30%.

Bis(tetramethylethylcyclopentadienyl)ruthenium-bis-μ-chloro-μ-diphenylphosphinomethane (9)

To a solution of 0.30 g of **1a** (1.05 mmol Ru) in 30 ml of ether was added 0.19 g (0.49 mmol) of dppm. After 6 h at ambient temperature the colour of the solution had changed from dark yellow to dark red. The solvent was removed in vacuo and the residue extracted with 5 ml toluene. The extract was chromatographed on Al_2O_3 (7% H_2O); toluene eluted an orange species, which was isolated by evaporation of the toluene and dissolved in pentane. Cooling to −50 °C afforded 0.34 g (70%) of **9** as red needles. ^1H NMR (CD_2Cl_2) δ: Cp^ 0.79 (t, 6H), 1.23, 1.33 (s, 24H), 1.63 (q, 4H), CH_2 3.61 (bm, 2H), Ph 7.15, 7.48 (m, 20H) ppm. The complex did not volatilize in the mass spectrometer.

Structure determination

Data collection was performed at room temperature on an Enraf–Nonius CAD4 diffractometer using Mo-K_α radiation (λ 0.7093 Å, graphite monochromator). A single crystal with approximate dimensions $0.2 \times 0.2 \times 0.5$ mm was sealed under N_2 in a glass capillary. Unit cell dimensions were obtained from least-squares refinement of 25 accurately centered reflections.

Crystal data. Monoclinic, space group $P2_1/c$ (No. 14), a 8.816(3), b 13.738(2), c 11.683(1) Å, β 109.35(2)°, V 1335(1) $Å^3$, $Z = 2$, $d_{calc.}$ 1.561 g cm^{-3}, μ(Mo-K_α) 13.2 cm^{-1}, $F(000)$ 640. 2657 reflections with $3 < \theta < 24°$ were collected (ω scan). After an empirical absorption correction symmetry equivalent reflections were averaged. 1781 independent reflections with $I > 2\sigma(I)$ were used for structure solution by Patterson and difference Fourier methods and subsequent refinement [13]. Hydrogen atoms were included in structure factor calculations (standard geometry, 0.98 Å, riding model). Refinement with anisotropic temperature factors for non hydrogen atoms (136 refined parameters) converged at R 0.023, R_w 0.030 ($w = 1/\sigma^2(F_o)$), *GOF* 1.092. Highest residual electron density was 0.37 e/$Å^3$. The atomic coordinates for nonhydrogen atoms are listed in Table 2. Supplementary material can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, W-7514 Eggenstein-

Table 2

Positional parameters, with esd's in parentheses [a] for compound **5**

Atom	x	y	z	B(iso)
Ru	0.07245(3)	0.04424(2)	0.16251(2)	2.167(5)
Cl	0.0080(1)	−0.10988(6)	0.04676(7)	2.96(2)
C1	−0.1388(4)	0.1238(3)	0.1722(4)	4.24(9)
C2	−0.1660(4)	0.0263(3)	0.1805(40	4.75(9)
C3	0.2408(4)	−0.0152(2)	0.3243(3)	3.01(7)
C4	0.3283(4)	−0.0028(3)	0.2405(3)	3.17(7)
C5	0.3279(4)	0.0965(3)	0.2110(3)	2.84(7)
C6	0.2399(4)	0.1488(2)	0.2740(3)	2.62(7)
C7	0.1924(4)	0.0795(3)	0.3491(3)	2.86(7)
C31	0.2221(5)	−0.1076(3)	0.3861(4)	4.5(1)
C32	0.3635(6)	−0.1262(4)	0.5022(5)	7.7(1)
C41	0.4117(4)	−0.0831(3)	0.1959(4)	5.3(1)
C51	0.4081(4)	0.1421(3)	0.1279(3)	4.21(9)
C61	0.2233(4)	0.2563(3)	0.2761(3)	3.93(8)
C71	0.1210(5)	0.1046(3)	0.4456(3)	4.57(9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)(a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} = ac(\cos\beta)B_{1,3})$.

Leopoldshafen (Germany) citing CSD-55785, the journal and the names of the authors.

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