

Co-ordinatively Unsaturated Pentamethylcyclopentadienyl Ruthenium(II) Chloro and Methoxy Complexes

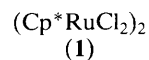
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(Cp*RuOMe)₂, (2), (Cp* = η⁵-C₅Me₅) has been prepared from (Cp*RuCl₂)₂, (1), in MeOH and converted to (Cp*RuCl)₄, (3), in pentane with Me₃SiCl; both complexes (2) and (3) readily react to give Cp*RuL₂X complexes on addition of the appropriate ligands L.

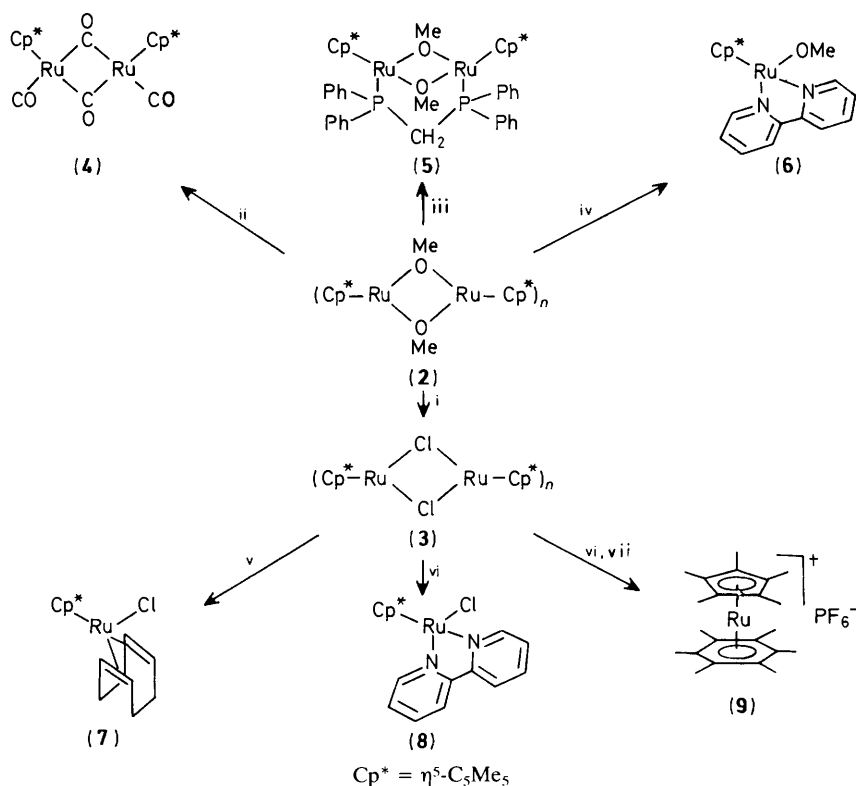
Since the discovery of (Cp*RuCl₂)₂[†] in 1984¹ several groups²⁻⁶ have exploited the synthetic potential of this material for the synthesis of organometallic, in particular Cp*Ru complexes (Cp* = C₅Me₅). Co-ordinatively unsaturated Ru^{II} species should be able to play a key role since they

are expected to be easily converted into a plethora of Cp*Ru complexes under mild conditions. As a continuation of our work on Cp* (halogeno) half-sandwich complexes (Cp*MX)_n of Co, Ni, and Fe⁷⁻¹⁰ we report here a novel route to analogous compounds of Ru.



A brown suspension of (1) in MeOH was stirred in the presence of solid K₂CO₃ at ambient temperature, and within 6 h gave an intense cherry red solution from which a complex

[†] Note added in proof: recent X-ray structure determinations have disclosed (1) and (2) to be dimeric (U. Koelle, R. Boese, N. Klaff, and G. H. Herberich, to be published) and (3) to be a tetramer in the solid state (see ref. 3 in B. K. Campion, R. H. Heyn, and T. D. Tilley, *J. Chem. Soc., Chem. Commun.*, 1988, 278).



Scheme 1. Reagents and conditions: i, Me_3SiCl ; ii, CO, 60%; iii, dppm, 70%; iv, 2,2'-bipyridine; v, 1,5-cyclo-octadiene, 60%; vi, evaporation of pentane, C_6Me_6 melt, 160 °C; vii, $\text{NH}_4\text{PF}_6 \cdot \text{H}_2\text{O}$, 50%.

with the analytical composition of (2) was isolated. The highly air sensitive, diamagnetic compound is soluble in all solvents including hydrocarbons. When extracted into and crystallized from pentane the ^1H n.m.r. spectrum of (2) shows two signals at δ 1.62 and 4.82 (C_6D_6) in the intensity ratio 5 : 1 assigned to Cp^* and MeO protons, respectively, no further co-ordinated solvent being present. Addition of CD_3OD causes rapid exchange of the OMe groups and liberation of MeOH. According to the mass spectrum, where the highest mass appears at m/z 536,‡ (2) is dimeric.

The formation of (2) is proposed to proceed according to equation (1) though the oxidation products of MeOH have not yet been identified. Reduction of (1) in MeOH has frequently been observed in the presence of acceptor ligands¹⁻³ like phosphines and alkenes, leading to $\text{Cp}^*\text{RuL}_2\text{X}$, but reduction of (1) by 'bare' MeOH at the relatively mild potential of the $\text{Cp}^*\text{Ru}^{\text{III/II}}$ couple§ is new. Neutralization of the HCl formed on methanolysis of the Ru-Cl bond in (1) is most likely the driving force. Likewise, the deprotonation of a Ru-OMe group, which must occur in the course of reaction (1), is promoted by the base. Other Brønsted bases like F^- (KF-MeOH) or OH^- (KOH-MeOH) also effect reaction (1) although in a less clean fashion. Reaction (1) was extended

‡ Mass spectral data for (2): m/z (rel. to ^{101}Ru) 536 (60%, M_2^+), 505 (73%, $M_2 - \text{MeOH}$), 470 (100%, $[\text{Cp}^*\text{Ru}]_2 - \text{H}_2$).

§ A two-step reversible wave in the cyclic voltammogram of (1) is observed at 0.09 and -0.08 V vs. standard calomel electrode (SCE), in MeOH corresponding to a $\text{Cp}^*\text{RuCl}_2/\text{Cp}^*\text{RuCl}$ couple (U. Koelle, unpublished work).

along the series of primary alcohols up to Bu^nOH and was found to proceed similarly albeit in lower yield.

Methoxy complex (2) reacts readily with acceptor as well as pronounced donor ligands (2,2'-bipyridine) to give e.g. (4)–(6) (Scheme 1).¶ The formation of complex (4) on treatment of (2) with CO involves a further redox step. Reaction with bis(diphenylphosphino)methane (dppm), apart from the expected product $\text{Cp}^*\text{Ru}(\text{dppm})\text{OMe}$, gives mainly the dimeric complex (5) with bridging phosphine. The reaction of (3) with dppm, not shown in the Scheme 1, is completely analogous.

An instantaneous colour change from red to pale yellow upon addition of Me_3SiCl to a pentane solution of (2) indicates the formation of the chloro complex (3), a pentane soluble,

¶ Selected data for (4): ^1H n.m.r. (CDCl_3) δ 1.87 (s, Cp^*); i.r. (hexane) ν_{CO} 1745, 1925 cm^{-1} ; spectral data in accordance with ref. 11.

(5): ^1H n.m.r. (C_6D_6) δ 1.49 (30H, s, Cp^*), 3.98 (6H, s, OMe), 3.17 (2H, t, $J_{\text{P-H}}$ 10.0 Hz, CH_2), 7.0 (12H, m, Ph), 7.5 (8H, m, Ph).

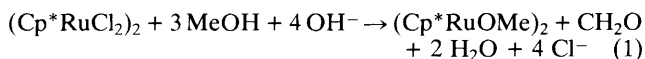
(6): ^1H n.m.r. [$(\text{CD}_3)_2\text{CO}$] δ 1.65 (15H, s, Cp^*), 3.33 (3H, s, OMe), 9.24 (2H, d, $J_{3,4}$ 5.6 Hz, H_3, H_3'), 7.8 (t), 7.55(t), 7.3 (d, 6H, $\text{H}_4, \text{H}_4', \text{H}_5, \text{H}_5', \text{H}_6, \text{H}_6'$).

(7): Spectral data in accordance with ref. 5.

(8): ^1H n.m.r. (CD_2Cl_2) δ 1.61 (15H, s, Cp^*), 7.39 (2H, ddd, H_4, H_4'), 7.70 (2H, dt, H_5, H_5'), 8.00 (2H, br. d, H_6, H_6'), 9.22 (2H, br. d, H_2, H_2' , $J_{3,4}$ 5.6, $J_{3,5}$ 1.4, $J_{4,5}$ 8.1, $J_{4,6}$ 1.6, $J_{5,6}$ 8.2 Hz); m.s. m/z (rel. to ^{101}Ru) 544 (100%, $[\text{Cp}^*\text{RuCl}]_2$), 470 (73%, $[\text{Cp}^*\text{Ru}]_2 - \text{H}_2$), 428 (46%, M^+), 397 (30%, $M^+ - \text{Cl}$).

(9): ^1H n.m.r. (CDCl_3) δ 2.07 (18H, s, C_6Me_6), 1.62 (15H, s, Cp^*); i.r. (KBr) ν 835 vs cm^{-1} (PF_6^-).

highly air sensitive material, characterized by a ^1H n.m.r. signal at δ 1.56 (Cp^*) (C_6D_{12}). The mass spectrum of (**3**) again shows the highest peak at m/z 542, corresponding to the dimer. Further characterization of (**3**) has been achieved through complexation reactions outlined in Scheme 1. The synthetic potential of (**3**) as a source of the $\text{Cp}^*\text{Ru}^{\text{II}}$ unit is illustrated by the formation of the fully methylated cationic sandwich complex (**9**), which proceeds in hydrocarbon solution or in a melt of hexamethylbenzene at about 160°C without promotion by a Lewis acid. Other $\text{Cp}^*\text{Ru}^{\text{II}}$ fragments, e.g. $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]\text{PF}_6$, which readily gave arene complexes with benzene and lower methylated benzenes, in our hands failed, under all conditions, to complex to hexamethylbenzene.



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