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Synthesis and some reactivity of pentamethylcyclopentadienyl-ruthenium complexes with an $SnCl_3$ ligand. X-Ray crystal structure of $[(C_5Me_5)Ru(SnCl_3)(COD)]$

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Abstract

The reaction of [Cp*RuCl(COD)] (**3**) with $SnCl_2$ affords the first pentamethylcyclopentadienyl-ruthenium tin complex [Cp*Ru($SnCl_3$)(COD)] (**4**) (COD = 1,5-cyclooctadiene) which was characterized by an X-ray crystal structure. The reaction of [{Cp*RuCl}$_4$] (**2**) with hex-1-ene in the presence of $SnCl_2$ yields [Cp*Ru($SnCl_3$)(1,3-hexadiene)] (**5**) fully characterized by ^1H and ^{13}C NMR spectroscopies. A similar reaction with methylcyclohexene yields $[Cp^*Ru(\eta^6\text{-}C_6H_5CH_3)]^+$ whereas no reaction is observed with methylcyclohexane. Finally, the reaction of catalytic amounts of the Cp*Ru($SnCl_3$) fragment with norbornene yields the *t*-ROMP polymer, whereas the reaction with phenylacetylene leads to triphenyl-benzene isomers and oligomers.

Keywords: Ruthenium; $SnCl_3^-$ as a ligand; Pentamethylcyclopentadienyl complex; X-ray structure

1. Introduction

Electrophilic metal complexes are attracting a lot of interest because of their high activity in reactions involving transformation of hydrocarbons. For example, early transition metals and lanthanoid derivatives are widely used in polymerization and C-H activation reactions [1,2].

Cationic derivatives of the late transition metals display similar electrophilic properties [3,4] which leads to new selective reactions involving oligomerization [5a] or polymerization of olefins [5b]. Furthermore, cationic palladium [3] and platinum [4] derivatives have been shown to activate the C–H bond of alkanes and, in the case of palladium, isomerization of 3,3-dimethylbut-1-ene through methyl migration.

For some years we have been studying the reactivity of an electrophilic ruthenium fragment, Cp^*Ru^+ (**1**), prepared by protonation of [{Cp*Ru(OMe)}$_2$] by triflic acid. This fragment shows a very high reactivity towards functional hydrocarbons [6] which leads to reaction or aromatization involving cyclization or C–H, C–O [7], C–X (X = Cl, S) [8] and even C–C [7] bond activation. The best example of this reactivity was the selective aromatization of the A [9] or the B [10] ring of steroids through demethylation. However, the reactivity of this fragment towards linear alkenes or dienes is much more complex as a result of the availability of three coordination sites [11]. For example, the reaction of **1** with 1,5-hexadiene gives products from (i) oligomerization reactions, (ii) cyclization and dehydrogenation into benzene, and (iii) metathesis. Similarly, the reaction of **1** with neohexene leads to isomerization into 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene, to oligomers and to a new cracking reaction leading to C_{17} hydrocarbons and methane. In addition, fragment **1** is insoluble in nonpolar solvents such as alkanes and reactive in virtually all other solvents. This made study of the reactivity of **1** towards saturated hydrocarbons difficult. In order to circumvent these problems, we studied the preparation of new electrophilic neutral fragments with only two vacant coordination sites. In this respect, the preparation of a $Cp^*RuSnCl_3$ fragment was attractive. Indeed, $SnCl_3$, through its π-acceptor properties and *trans*-influence, is known to activate platinum complexes for reactions involving hydrogen transfer [12], such as hydrogenation,

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dehydrogenation and hydroformylation, including the thermal dehydrogenation of cyclooctane by $[Pt(SnCl_3)\{P(OMe)_3\}_2]$ [13]. The ruthenium chemistry involving $SnCl_3$ is poorly developed, but it is promising, since, for example, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ catalyzes the formation of acetic acid from methanol alone [14].

We describe here the preparation and some reactions of ruthenium complexes containing Cp^* and $SnCl_3$.

2. Preparation of ruthenium complexes with $SnCl_3$: synthesis of $[Cp^*Ru(SnCl_3)(COD)]$ 4

The strategy adopted to prepare these complexes was the reaction of $[\{Cp^*RuCl\}_4]$ (**2**) [15] with $SnCl_2$ in the presence of the reactive hydrocarbons. With 1,5-cyclooctadiene at room temperature in THF **2** gives first the known $[Cp^*RuCl(COD)]$ (**3**) [16] which was isolated and then allowed to react further with $SnCl_2$. The reaction proceeded smoothly at room temperature in THF to give an orange solution from which orange crystals of $[Cp^*Ru(SnCl_3)(COD)]$ (**4**) were obtained. The molecular structure of **4** determined by X-ray diffraction is shown in Fig. 1, with atomic coordinates in Table 1 and important bond lengths and angles in Table 2. The molecule adopts a distorted piano-stool configuration. The Ru–Sn distance (2.5855(4) Å) is short but comparable to other Ru–Sn distances [17]. The Ru–C bonds to the cyclooctadiene are ca. 2.25 Å, a classical value for such complexes. The molecule has a quasi-symmetry plane through Sn, Ru and the centroid of the Cp^*. The cyclooctadiene molecule is orientated such that half of it (C_2, C_3, C_4, C_5) points towards Sn, which explains the spectroscopic properties.

The ^1H NMR spectrum in $CDCl_3$ shows a singlet with satellites ($J_{H-Sn} = 24$ Hz; the different couplings to ^{117}Sn and ^{119}Sn are not resolved) at δ 1.84 (15H) for the Cp^* and a series of multiplets of equal intensity (2H) at δ 3.72, 3.44, 2.74, 2.34 and 1.99 attributed to the olefinic and alkyl protons of the cyclooctadiene, respectively. One signal of intensity 2 is missing, probably hidden by the Cp^* signal. Selective decoupling experiments show that the signal at δ 3.44 is coupled to the signals at δ 3.72 and 2.34. We propose that the signal at δ 3.44 corresponds to the protons of C_2 and C_5 and that at 3.72 to those of C_1 and C_6. The signal at δ 2.34 corresponds to the protons of C_3 and C_4 coupled to those of C_2 and C_5 and they are therefore mutually transoid. The signals at δ 2.74 and 1.99 correspond to the different protons of C_7 and C_8. The ^{13}C NMR spectrum in acetone-d_6 is very simple, showing the Cp^* at δ 9.51 ($C_5\mathit{Me}_5$, $J_{C-H} = 128$ Hz) and 95.22 (C_5Me_5) and the olefinic carbons of COD at δ 72.38 ($J_{C-H} = 158$ Hz) and 81.88 ($J_{C-H} = 154$ Hz). One signal for the alkyl carbon atoms appears at δ 31.05, whereas the other is hidden by the acetone signal.

This experiment clearly demonstrates that $SnCl_2$ can insert into the Ru–Cl bond of Cp^*Ru derivatives. A similar experiment was carried out with the 16-electron derivative $[Cp^*RuCl(PCy_3)]$ [18]. The reaction proceeded rapidly at room temperature and the solution changed from blue to yellow as soon as the $SnCl_2$ is added. A mixture of compounds was obtained, among which is $[Cp^*Ru(SnCl_3)(PCy_3)]$ as supported by NMR data. The coordination of tin is attested by the observation of tin satellites in the ^1H NMR spectrum for the Cp^* signal (δ 1.91, $J_{H-Sn} = 21$ Hz, $J_{H-P} = 1$ Hz) and in ^{31}P NMR for the phosphorus atom of the phosphines

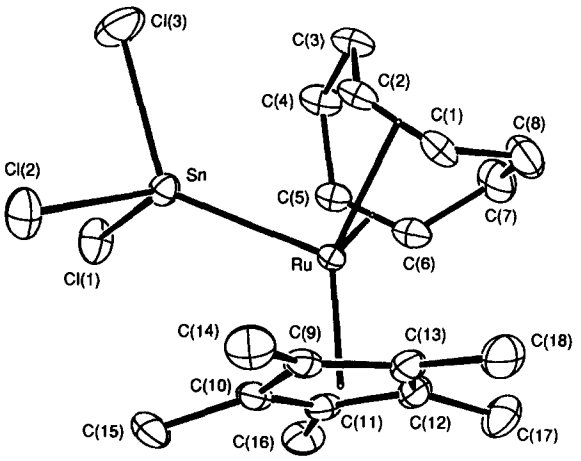


Fig. 1. An ORTEP view of $[Cp^*Ru(SnCl_3)(COD)]$ **4** with the atom-labelling scheme. H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 1
Fractional atomic coordinates for **4**

Atom	x	y	z
Sn	0.25247(2)	0.70243(3)	0.13594(2)
Cl(1)	0.0799(1)	0.7969(2)	0.1002(1)
Cl(2)	0.3220(1)	0.8349(1)	0.26005(8)
Cl(3)	0.3328(1)	0.8463(2)	0.04773(9)
Ru	0.25875(2)	0.44643(3)	0.14138(2)
C(1)	0.3959(3)	0.3657(5)	0.0926(3)
C(2)	0.3881(3)	0.4952(5)	0.0642(3)
C(3)	0.3458(3)	0.5333(5)	−0.0288(3)
C(4)	0.2253(3)	0.5524(5)	−0.0528(3)
C(5)	0.1660(3)	0.4791(5)	0.0058(3)
C(6)	0.1786(3)	0.3458(5)	0.0209(3)
C(7)	0.2521(4)	0.2578(6)	−0.0196(3)
C(8)	0.3640(4)	0.2467(5)	0.0360(3)
C(9)	0.3086(3)	0.4287(4)	0.2848(2)
C(10)	0.2005(3)	0.4733(4)	0.2653(3)
C(11)	0.1390(3)	0.3768(4)	0.2130(3)
C(12)	0.2062(3)	0.2672(4)	0.2048(3)
C(13)	0.3099(3)	0.2997(4)	0.2505(3)
C(14)	0.3982(4)	0.4949(5)	0.3449(3)
C(15)	0.1547(4)	0.5874(5)	0.3073(3)
C(16)	0.0213(3)	0.3832(5)	0.1826(3)
C(17)	0.1704(4)	0.1327(5)	0.1713(4)
C(18)	0.4011(4)	0.2050(5)	0.2695(3)

(δ 49.96, $J_{P-^{119}Sn} = 373$ Hz, $J_{P-^{117}Sn} = 357$ Hz). Curiously, perhaps for steric reasons, this compound is not stable and all attempts to isolate it as a solid led to mixtures which were not separated.

3. Reactivity of the $Cp^*Ru(SnCl_3)$ fragment towards unsaturated hydrocarbons

After the reaction of $SnCl_2$ with monochloro complexes containing an extra ligand, we carried out the reaction of the tetramer $[\{Cp^*RuCl\}_4]$ with $SnCl_2$ in the presence of various hydrocarbons to test the reactivity of the $Cp^*Ru(SnCl_3)$ fragment.

3.1. Reaction with hex-1-ene

As a first test, we treated $[\{Cp^*RuCl\}_4]$ in the presence of $SnCl_2$ with 1-hexene since olefins are known to be oligomerized or polymerized by Lewis acid fragments. The reaction was carried out at 100°C in a closed vessel. GC analysis of the reaction solution did not show the formation of any oligomer, but a new yellow organometallic complex $[Cp^*Ru(SnCl_3)(\eta^4\text{-hexa-1,3-diene})]$ (**5**) was formed in 50% isolated yield. The complex shows in the ^1H NMR spectrum a singlet for the Cp^* at δ 1.88 with tin satellites ($J_{H-Sn} = 19$ Hz) and several multiplets at δ 0.64 (ddd, $J_{H1-H3} = 9.0$ Hz, $J_{H1-H2} = 2.7$ Hz, $J_{H1-H4} = 0.8$ Hz, H_1), 1.04 (t, $J = 7.1$ Hz, CH_3), 1.56 (m, H_5 and CH_2), 2.20 (ddd, $J_{H2-H3} = 7.2$ Hz, $J_{H2-H4} = 0.7$ Hz, H_2), 4.29 (m, H_3) and 4.48 (dd, $J_{H4-H5} = 7.9$ Hz, $J_{H_4-H3} = 5.2$ Hz, H_4) (see Fig. 2) attributed to the protons of a coordinated 1,3-hexadiene. Selective decoupling experiments were used to infer these assignments.

The ^{13}C NMR spectrum shows the Cp^* at δ 10.41 (q, $J_{C-H} = 128$ Hz, C_5Me_5) and 94.43 (s, C_5Me_5) and the hexadiene at δ 16.98 (q, $J_{C-H} = 126$ Hz, $CH_2CHCHCHCH_2CH_3$), 25.93 (t, $J_{C-H} = 126.5$ Hz; $CH_2CHCHCHCH_2CH_3$), 38.29 (t, $J_{C-H} = 159$ Hz; $CH_2CHCHCHCH_2CH_3$), 66.30 (d, $J_{C-H} = 152$ Hz; $CH_2CHCHCHCH_2CH_3$), 81.96 (d, $J_{C-H} = 167$ Hz;

Table 2
Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for **4**

Ru–Sn	2.5855(4)		
Sn–Cl(1)	2.390(1)	Ru–M(12) [a]	2.158(4)
Sn–Cl(2)	2.396(1)	Ru–M(56) [a]	2.137(4)
Sn–Cl(3)	2.387(2)	Ru–Cp	1.882(4)
C(1)–C(2)	1.379(7)	C(5)–C(6)	1.370(7)
C(2)–C(3)	1.513(5)	C(6)–C(7)	1.529(8)
C(3)–C(4)	1.542(6)	C(7)–C(8)	1.541(7)
C(4)–C(5)	1.508(6)	C(8)–C(1)	1.505(7)
C(9)–C(10)	1.444(5)	C(9)–C(14)	1.502(6)
C(10)–C(11)	1.416(6)	C(10)–C(15)	1.506(7)
C(11)–C(12)	1.428(6)	C(11)–C(16)	1.505(5)
C(12)–C(13)	1.431(6)	C(12)–C(17)	1.497(6)
C(13)–C(9)	1.412(6)	C(13)–C(18)	1.501(6)
Ru–Sn–Cl(1)	115.34(3)	Cl(1)–Sn–Cl(2)	98.81(5)
Ru–Sn–Cl(2)	121.72(3)	Cl(1)–Sn–Cl(3)	96.49(5)
Ru–Sn–Cl(3)	127.79(4)	Cl(2)–Sn–Cl(3)	90.11(4)
Sn–Ru–M(12) [a]	94.7(1)	M(12)–Ru–M(56) [a]	82.4(2)
Sn–Ru–M(56) [a]	97.0(1)	M(12)–Ru–Cp [a,b]	131.1(2)
Sn–Ru–Cp	115.6(1)	M(56)–Ru–Cp [a,b]	126.7(2)
Sn–Ru–C(1)	112.1(1)	Sn–Ru–C(2)	77.9(1)
Sn–Ru–C(5)	79.4(1)	Sn–Ru–C(6)	114.9(1)
Sn–Ru–C(9)	96.6(1)	Sn–Ru–C(10)	83.9(1)
Sn–Ru–C(11)	108.4(1)	Sn–Ru–C(12)	144.3(1)
Sn–Ru–C(13)	132.8(1)		
C(2)–C(1)–C(8)	124.7(4)	C(4)–C(5)–C(6)	122.1(4)
C(1)–C(2)–C(3)	123.0(4)	C(5)–C(6)–C(7)	124.1(4)
C(2)–C(3)–C(4)	115.1(4)	C(6)–C(7)–C(8)	113.2(4)
C(3)–C(4)–C(5)	113.6(4)	C(7)–C(8)–C(1)	113.4(4)
C(13)–C(9)–C(10)	106.8(3)	C(9)–C(10)–C(11)	108.6(4)
C(10)–C(11)–C(12)	107.7(3)	C(11)–C(12)–C(13)	107.7(4)
C(12)–C(13)–C(9)	108.9(4)		

[a] M(12) and M(56) are the midpoints of C(1)–C(2) and C(5)–C(6) bond lengths, respectively.
[b] Cp is the centroid of the cyclopentadienyl ring [C(9)C(10)C(11)C(12)C(13)].

$CH_2CHCHCHCH_2CH_3$), 87.15 (d, $J_{C-H} = 161$ Hz; $CH_2CHCHCHCH_2CH_3$).

These spectroscopic data demonstrate unambiguously that hex-1-ene has been dehydrogenated to hexa-1,3-diene. GC analysis does not show any hexane, which suggests an elimination of dihydrogen rather than hydrogen transfer. The diene molecule is then firmly bound to ruthenium, which prevents any further catalytic reaction. This reaction is very different from the oligomerization observed in the presence of Cp^*Ru^+ and suggests a reduced electrophilicity for the $Cp^*Ru(SnCl_3)$ fragment.

3.2. Reaction with methylcyclohexene

A reaction similar to the previous one can be carried out at 100°C for 20 h in the presence of 4-methylcyclohexene. We did not observe any catalytic reaction but the well-known complexes $[Cp^*Ru(\eta^6\text{-}C_6H_6)]^+$ and $[Cp^*Ru(\eta^6\text{-}C_6H_5CH_3)]^+$ were formed. This reaction is similar to that of the Cp^*Ru^+ fragment and probably involves decoordination of the $SnCl_3$ group. It proceeds by dihydrogen elimination rather than by hydrogen transfer, since dihydrogen was detected by GC analysis. An extension of this reaction towards methylcyclohexane dehydrogenation has been attempted but did not lead to any conclusive result.

3.3. Reaction with norbornene

The reaction between $[\{Cp^*RuCl\}_4]$, $SnCl_2$ and norbornene at room temperature in THF led after 16 h at room temperature, to a viscous solution from which polynorbornene was isolated in 70% yield upon addition of methanol and further recrystallization from THF/methanol (the reaction was carried out under catalytic conditions with 190 equiv. monomer/equiv. (2)). The polymer is almost all *trans* (*trans*:*cis* ca. 95:5) as deduced from the observation of a multiplet at δ 5.22 and a broad signal at δ 2.31 in the ^1H NMR spectrum. In IR spectroscopy, absorptions at 963 and 760 cm^{-1} are characteristic of δ C–H vibrations of *trans* and *cis* double bonds, respectively. In the present case the band at 963 cm^{-1} is predominant.

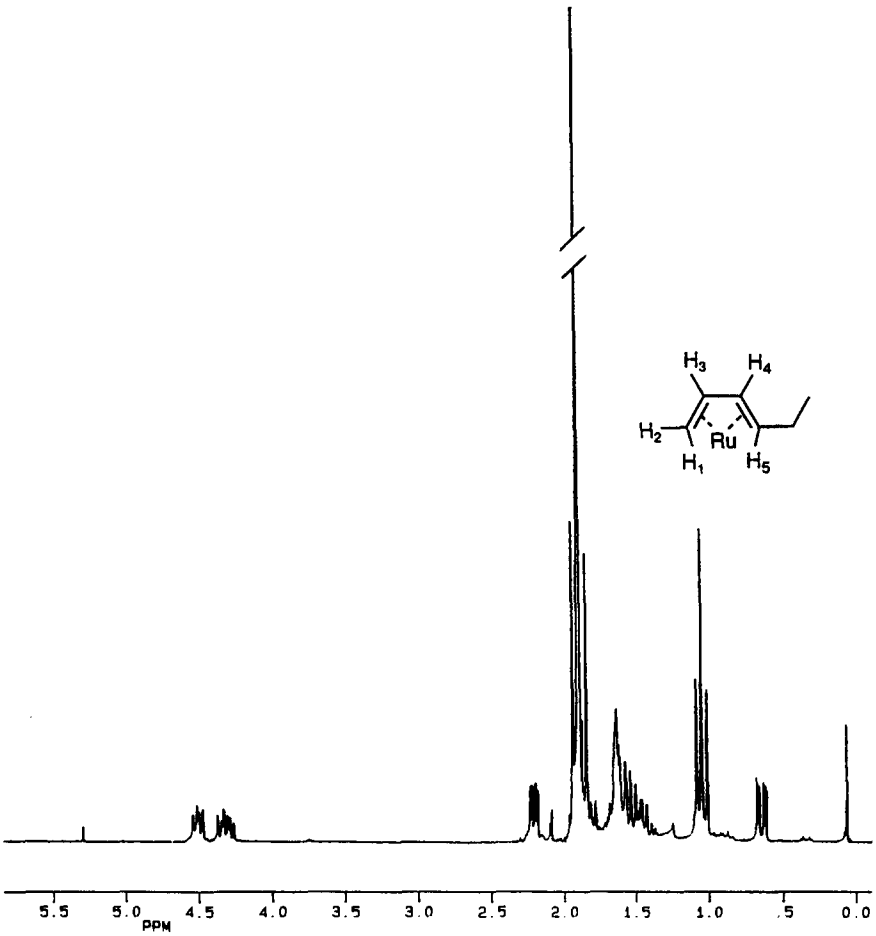


Fig. 2. ^1H NMR ($CDCl_3$, 200 MHz) of $[Cp^*Ru(SnCl_3)(\eta^4\text{-hexadiene})]$ **5**. A scheme is included to show the labelling of hydrogen atoms used in the discussion.

3.4. Reaction with phenylacetylene

Finally, we studied the reaction of $[\{Cp^*RuCl\}_4]/SnCl_2$ towards phenylacetylene at 100°C for 15 h (molar ratio 1 : 42). From the oligomeric mixture, we were able to isolate a yellow solid characterized by GC-MS and ^1H NMR spectroscopy as of two triphenylbenzene isomers (yield 35%).

In conclusion, we have shown that the hydrocarbon-soluble electrophilic $Cp^*Ru(SnCl_3)$ fragment can be synthesized and used for further reactivity. The reactions with unsaturated hydrocarbons clearly show the difference in reactivity between $Cp^*RuSnCl_3$ and Cp^*Ru^+. The presence of only two available coordination sites probably explain why the $Cp^*RuSnCl_3$ fragment is a catalyst for the trimerisation of phenylacetylene whereas Cp^*Ru^+ shows a strong affinity for aromatic rings. However, the Lewis acidity is presumably much less than that of the Cp^*Ru^+ fragment, which accounts for the lack of the olefin oligomerization reaction. Finally, both fragments are able to react with cyclohexene and norbornene. However, aromatisation is much more difficult in the case of $Cp^*RuSnCl_3$ and the polymerisation of norbornene occurs with a different selectivity.

4. Experimental details

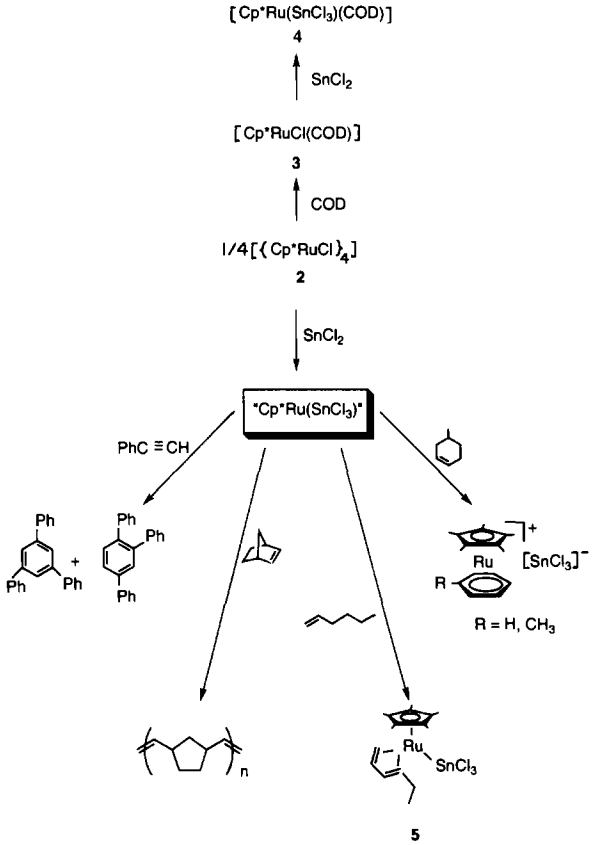
Microanalyses were performed at the microanalysis service of the Laboratoire de Chimie de Coordination. NMR spectra were recorded on a Bruker AC200 (at 200.13 MHz for ^1H, at 50.324 MHz for ^{13}C and 81.015 MHz for ^{31}P) spectrometer operating in the Fourier transform mode. All manipulations were carried out under argon using standard Schlenk techniques. THF was distilled from sodium benzophenone while pentane was dried over calcium hydride and thoroughly degassed under argon before use.

Activation experiments were carried out in closed Fischer–Porter bottles equipped with Swagelok fittings that can connect directly to an injection valve of an IGS 16 Intersmat GC.

The starting materials $[\{Cp^*RuCl\}_4]$ and $[Cp^*RuCl(PCy_3)]$ were prepared by literature procedures [15,18].

4.1. $[Cp^*Ru(SnCl_3)(COD)]$ (4)

To a THF solution (8 ml) of $[Cp^*RuCl(COD)]$ (276 mg, 0.73 mmol) was added $SnCl_2$ (138 mg, 0.73 mmol). The resulting mixture was stirred at room temperature



Scheme 1. Some reactions of the $Cp^*RuSnCl_3$ fragment.

for 8 h. The volume was then reduced and 5 ml of pentane were added. The orange solid which precipitated was isolated by filtration and rinsed twice with 2 ml of pentane. Yellow crystals of **4** were obtained by slow diffusion of gaseous pentane into a chloroform solution (yield 44%, 181 mg). Anal. Calc. for $C_{18}H_{27}Cl_3RuSn$: C, 37.96; H, 4.78%. Found.: C, 37.49; H, 4.60%.

4.2. Crystal-structure determination for [Cp*Ru(SnCl$_3$)(COD)] (4)

4.2.1. Crystal data

$C_{18}H_{27}Cl_3RuSn$, orange–red crystal, $0.35 \times 0.15 \times 0.10$ mm^3, $M = 569.5$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.930(1)$, $b = 10.091(1)$, $c = 15.793(2)$ Å, $\beta = 101.34(1)°$, $U = 2020.3(4)$ Å^3, $Z = 4$, $F(000) = 1120$, $Dc = 1.872$ g cm^{-3}.

4.2.2. Data collection

The unit-cell parameters were obtained from the least-squares fitting of the setting values of 25 reflections in the range $13.2 < \theta < 19.6°$. 4394 unique data were collected at 20°C on an Enraf-Nonius CAD4 automatic diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), ω–2θ scan mode, *hkl* range 0–16, 0–12, −20–20 ($3 < 2\theta < 54°$), were corrected for Lorentz and polarisation effects. Three reflections measured every 2 h showed no significant intensity variations. Empirical absorption corrections [19] were applied (ψ-scan method), $\mu = 23.7$ cm^{-1} (maximum and minimum transmission factors 0.999 and 0.844).

4.2.3. Structure solution and refinement

The structure was solved by Patterson techniques and refined by full-matrix least-squares method using 3014 data with $I > 3\ \sigma(I)$, 209 variable parameters, $R = \Sigma(|Fo| - |Fc|)/\Sigma|Fo| = 0.022$, $R' = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2} = 0.022$, $w = 1/\sigma^2(Fo)$, an isotropic extinction parameter g refined to 1.6×10^{-8}, goodness of fit $S = 1.49$ ($S = \Sigma w(|Fo| - |Fc|)^2/(No - Nv)$, where No and Nv are the number of observations and refined parameters, respectively). All nonhydrogen atoms were refined anisotropically and H atoms were included in the model in idealised geometry (C–H 0.97 Å, $U_{iso} = 0.09$ Å^2, for methyl and $U_{iso} = 0.06$ Å^2 for others). The largest shift-to-error ratio in the final refinement was 0.006 and the largest peak in the final Fourier difference map was 0.56 e Å^{-3}. Neutral atomic scattering factors were taken from Ref. [20]. Table 1 lists the fractional atomic coordinates.

All calculations were carried out using a MicroVax 3400 computer running MolEN package [21], SHELXS-86 [22] and SHELX-76 [23] programs. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atoms coordinates, thermal parameters, all bond lengths and angles and least-squares planes calculations.

4.3. Reaction of $SnCl_2$ with [Cp*RuCl(PCy$_3$)]

To a THF (10 ml) solution of [Cp*RuCl(PCy$_3$)] (275 mg, 0.5 mmol) was added $SnCl_2$ (94 mg, 0.5 mmol). The colour changed immediately from blue to yellow. The mixture was stirred for 30 min at room temperature. The solution was filtered and concentrated. A yellow powder was isolated by addition of pentane and shown to be a mixture of compounds that could not be separated.

4.4. [Cp*Ru(SnCl$_3$)(η^4-hexadiene)] (5)

To a THF (8 ml) solution of [{Cp*RuCl}$_4$] (165 mg, 0.15 mmol) were added $SnCl_2$ (111 mg, 0.59 mmol) and hex-1-ene (75 μl, 0.6 mmol). The resulting solution was transferred to a Fischer–Porter bottle and heated for 18 h at 100°C. The solution was then filtered and reduced in volume to 4 ml. Addition of pentane (4 ml) resulted in a microcrystalline yellow solid (yield 50%, 165 mg).

Anal. Calc. for $C_{16}H_{25}Cl_3RuSn$: C, 35.36; H, 4.64%. Found: C, 35.03; H, 4.69%.

4.5. Reaction of $SnCl_2$ with [{Cp*RuCl}$_4$] and methylcyclohexene

[{Cp*RuCl}$_4$] (70 mg, 0.064 mmol), $SnCl_2$ (49 mg, 0.26 mmol) and methylcyclohexene (1.5 ml, 13 mmol) were dissolved into 15 ml of THF. The solution was transferred to a Fisher–Porter bottle and was heated to 100°C for 18 h. The solution was filtered and the volatile products recovered and analyzed by GC. Only THF and methylcyclohexene were detected. NMR analysis of the residue showed the formation of [Cp*Ru(η^6-$C_6H_5CH_3$)]$^+$ and [Cp*Ru(η^6-C_6H_6)]$^+$ (in a 2:1 ratio) characterized by comparison with authentic samples [24].

4.6. Polymerization of norbornene

To a THF (10 ml) solution of [{Cp*RuCl}$_4$] (127 mg, 0.12 mmol) were added $SnCl_2$ (88 mg, 0.46 mmol) and norbornene (2.15 g, 22.8 mmol). The solution was stirred at room temperature for 16 h. The polymer was precipitated by addition of MeOH and recrystallized from a mixture THF/MeOH.

4.7. Oligomerization of phenylacetylene

To a THF (10 ml) solution of [{Cp*RuCl}$_4$] (245 mg, 0.22 mmol) were added $SnCl_2$ (170 mg, 0.90 mmol)

and phenylacetylene (0.93 g, 9 mmol). The resulting solution was transferred to a Fischer–Porter bottle and heated for 15 h at 100°C. The solution was then filtered and the solvent was removed under vacuum. The residue was extracted with diethyl ether and evaporated to dryness. Dissolution in CH_2Cl_2 and addition of MeOH produced a methanol-insoluble oligomeric yellow solid and a methanol-soluble fraction corresponding to the triphenylbenzene isomers.

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