Trimethylenemethane Complexes of Ruthenium, Osmium and Rhodium *via* the Compound $CH_2{=}C(CH_2SnMe_3)_2$ *

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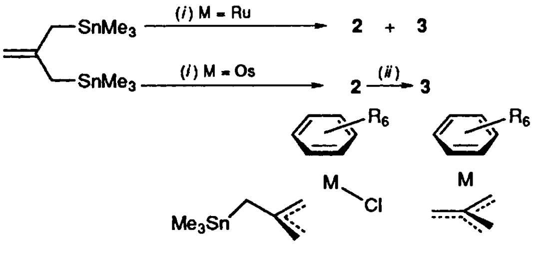
The compound $CH_2{=}C(CH_2SnMe_3)_2$ **1** was readily made (61% yield) from K_2(tmm) (tmm = trimethylenemethane) and $SnMe_3Cl$. It serves as a new and efficient entry to tmm metal complexes. The arene complexes [$\{MCl_2(arene)\}_2$] (M = Ru or Os) reacted with **1** to give allylmetal complexes [$MCl\{CH_2C(CH_2SnMe_3)CH_2\}$(arene)] **2a**–**2e** and sandwich-like compounds [M(tmm)(arene)] **3a**–**3e** (M = Ru, arene = C_6H_6 **a**, C_6Me_6 **b**, or *p*-$MeC_6H_4CHMe_2$ **c**; M = Os, arene = C_6H_6 **d** or *p*-$MeC_6H_4CHMe_2$ **e**). The cymene complexes **3c** and **3e** can also be made using the combination $CH_2{=}C(CH_2Cl)_2$–Mg–tetrahydrofuran as tmm source. Treatment of [$\{RhI_2(C_5Me_5)\}_2$] with **1** produced [Rh(tmm)(C_5Me_5)] in high yield, and the carbonyl compounds [$\{MCl_2(CO)_3\}_2$] (M = Ru or Os) afforded the tricarbonyl complexes [$M(CO)_3$(tmm)] (M = Ru or Os) in good yields. X-Ray crystal structure determinations have been made for **2a**, **3a** and [$Ru(CO)_3$(tmm)]. The data for the last two show the tmm ligand to be more firmly bonded in the arene complex.

Several main routes to trimethylenemethane (tmm) metal complexes have been described.[1] Most synthetic approaches to this chemistry use 'Y'-shaped C_4 fragments as precursors for the tmm ligand, such as $CH_2{=}C(CH_2Cl)_2$,[2,3] methylenecyclopropane,[4] functionalized allylsilanes,[5] and the trimethylenemethane dianion $[C(CH_2)_3]^{2-}$ in Li_2(tmm).[6,7] The tmm ligand may also form at a metal centre *via* oxidative coupling of allene and methylene ligands.[8] In a preliminary communication we reported the reaction of [$\{RuCl_2(arene)\}_2$] with Li_2(tmm) to give sandwich-like compounds [Ru(tmm)(arene)] (arene = C_6H_6 or C_6Me_6).[9] We also mentioned the use of $CH_2{=}C(CH_2SnMe_3)_2$ **1** as ligand source. As we shall detail in this paper, this reagent allows improved or altogether new syntheses and promises to have wide applicability.

Results and Discussion

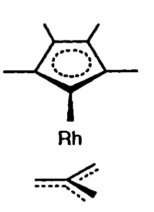
Sandwich-type Complexes.—The tin compound **1** has been made previously from $CH_2{=}C(CH_2Cl)_2$ and $LiSnMe_3$.[10] It can be obtained more conveniently from K_2(tmm) and $SnMe_3Cl$ in pentane–tetrahydrofuran (thf). When (arene)ruthenium dihalides are treated with **1** mixtures of allyl complexes **2a**–**2c** and trimethylenemethane complexes **3a**–**3c** are formed (Scheme 1) which can be separated by column chromatography. The complexes **2** and **3** can be obtained in *ca.* 50% yield, depending on the reaction conditions. Short reaction times in the solvent CH_2Cl_2 allow **2** to be isolated in good yields. In the case of the osmium complexes, treatment with **1** at room temperature gives the allyl compounds **2d** and **2e** which only on heating afford the trimethylenemethane complexes **3d** and **3e**. In the case of the rhodium electrophile [$\{RhI_2(C_5Me_5)\}_2$] a slow room-temperature reaction with **1** produces the tmm rhodium complex **4** in *ca.* 80% yield.

As the above examples show, the tin reagent **1** can be used with advantage when the reducing power of the reagent Li_2(tmm) turns out to be detrimental. Sometimes the combination of $CH_2{=}C(CH_2Cl)_2$–Mg–thf can also be used as a less strongly reducing source of the tmm ligand.[3] Treating this combination with the soluble compounds [$\{MCl_2(p\text{-}MeC_6H_4CHMe_2)\}_2$] (M = Ru or Os) does indeed give good yields of the tmm complexes **3c** and **3e**. Unfortunately, this reagent is not suitable for sparingly soluble precursors such as [$\{RuCl_2(C_6H_6)\}_2$] where it gives only minor yields of **3a**.



M	arene		
Ru	C_6H_6	**2a**	**3a**
Ru	C_6Me_6	**2b**	**3b**
Ru	*p*-$MeC_6H_4CHMe_2$	**2c**	**3c**
Os	C_6H_6	**2d**	**3d**
Os	*p*-$MeC_6H_4CHMe_2$	**2e**	**3e**

Scheme 1 (*i*) [$\{MCl_2(arene)\}_2$], (*ii*) slight warming in nitromethane



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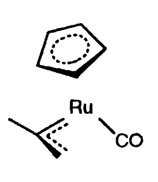

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The purified compounds **2** exist in only one isomeric form, as shown by NMR spectroscopy. Two isomers might have been expected, an *exo* isomer with the allyl group (or C^2 of the allyl) pointing towards the arene ring and an *endo* isomer pointing away from the arene region.[11] According to an X-ray crystal structure determination of **2a**, the energetically favourable *exo*

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: bar = 10^5 Pa.

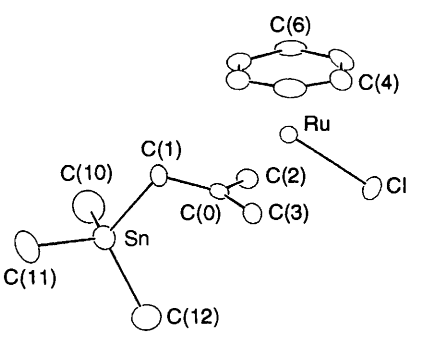


Fig. 1 An ORTEP plot (30% probability ellipsoids) of complex **2a**

isomer is present (Fig. 1). The geometry in the C_4 fragment corresponds to that of the methylallyl ligand in *e.g. exo*-**5**.[12]

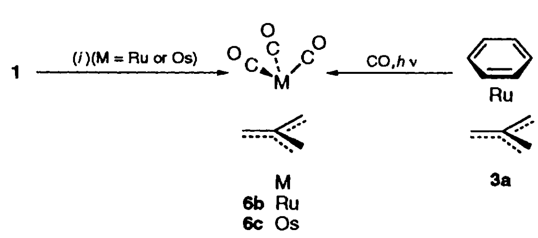
All tmm metal complexes **3a**–**3e** are volatile *in vacuo*; **3a** undergoes sublimation at *ca.* 40 °C (10^{-6} bar). The ^{13}C NMR spectra show the expected resonance due to the central carbon atom at $\delta \approx 105$. For the methylene carbon atoms we observe *cis*- and *trans*-^3J(CH) couplings. An X-ray crystal structure determination of **3a** shows a sandwich-like complex with an approximately staggered conformation.[9] The arene ligand is planar within experimental accuracy and no significant alternation of the C–C bond lengths in the ring is observed. The crystal structure of the homologous osmium complex **3d** is isotypic to that of **3a**. A discussion of the molecular parameters does not seem justified because of the low quality of the structure solution.

Tricarbonyl Complexes.—Until now the higher homologues **6b** and **6c** of the first tmm complex [Fe(CO)$_3$(tmm)][2] **6a** have remained unknown. They can readily be synthesized from **1** and [{MCl$_2$(CO)$_3$}$_2$] (M = Ru or Os) (Scheme 2). Like **6a** they are rather volatile, boiling at *ca.* 140 °C; decomposition occurs above *ca.* 160 °C. In principle there is a further way to **6b**, starting from the benzene complex **3a** which is susceptible to photochemical decomplexation of its arene ligand. After irradiation of **3a** in thf solution under an atmosphere of carbon monoxide, the characteristic ν(CO) bands of **6b** appear in the IR spectrum and a ^1H NMR spectrum of the unpurified product shows the characteristic singlet of **6b**. However, this reaction was not optimized and yields were not determined.

In the ^{13}C NMR spectra of the three tricarbonyl compounds **6a**–**6c** we observe the vicinal coupling constants *cis*- and *trans*-^3J(CH) for the methylene carbon atoms. The structure of **6b** was determined by X-ray crystallography, and shows a staggered conformation (Fig. 2) like that observed for the iron complex **6a** in an electron diffraction study.[13] The tmm ligand is less firmly bonded to the central metal atom than it is in the arene complex **3a**;[9] the distances M–C_{tmm} are lengthened by *ca.* 0.03 Å (average 2.06 and 2.23 in **6b** compared to 2.03 and 2.19 Å in **3a**). This *trans* effect parallels observations in cyclooctadiene complexes where the ligand is bonded more strongly to the arenemetal fragment Ru(C_6Me_6) than to the Ru(CO)$_3$ fragment.[14]

Experimental

Synthesis.—Experiments were carried out in a dry, oxygen-free nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Alumina used for chromatography columns was obtained from Woelm (ICN-Adsorbentien) and deactivated with 7% water. Irradiations were carried out with a high-pressure mercury lamp (TQ 150, Original Hanau, 150 W). The compounds [{RuCl$_2$(C$_6$H$_6$)}$_2$],[15] [{RuCl$_2$(C$_6$Me$_6$)}$_2$],[14] [{RuCl$_2$(*p*-MeC$_6$H$_4$CHMe$_2$)}$_2$],[14] [{OsCl$_2$(C$_6$H$_6$)}$_2$],[16] [{OsCl$_2$(*p*-MeC$_6$H$_4$CHMe$_2$)}$_2$],[17] [{RuCl$_2$(CO)$_3$}$_2$],[18] [{OsCl$_2$(CO)$_3$}$_2$],[19] [{RhI$_2$(C$_5$Me$_5$)}$_2$][20] and K$_2$(tmm)[21] were prepared by methods previously described. The NMR data for the new compounds are given in Table 1.



Scheme 2 (*i*) [{MCl$_2$(CO)$_3$}$_2$]

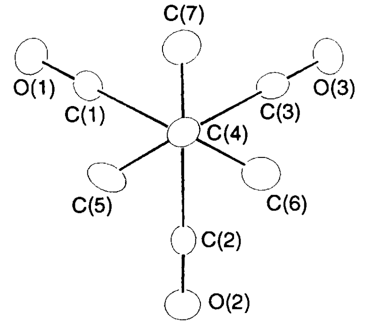


Fig. 2 An ORTEP plot (30% probability ellipsoids) of complex **6b** [the metal atom is hidden by C(4)]

2-*Methylene*-1,3-*bis*(*trimethylstannyl*)*propane* **1**. The compound SnMe$_3$Cl (82.4 g, 414 mmol) in hexane (530 cm^3) was added dropwise to a stirred suspension of K$_2$(tmm) (27.4 g, 207 mmol) in hexane (150 cm^3). After 1 h thf (10 cm^3) was added and stirring was continued for 2 h. The suspension was filtered through Kieselgur, the residue carefully dissolved in ethanol and extracted with hexane. The combined hexane fractions were concentrated under reduced pressure, filtered over alumina (8 × 4 cm) and eluted with hexane (500 cm^3). The solvent was removed under reduced pressure and the residue distilled (51 °C, *ca.* 10^{-3} bar) to give compound **1** (48.0 g, 61%) as a spectroscopically pure colourless oil ($d \approx 1.6$ g cm^{-3}). Its ^1H NMR data were consistent with the values reported earlier.[10]

Reactions of (*arene*)*ruthenium halides with* CH$_2$=C(CH$_2$SnMe$_3$)$_2$. (*i*) A suspension of [{RuCl$_2$(C$_6$H$_6$)}$_2$] (0.45 g, 0.89 mmol) in thf (50 cm^3) was stirred with compound **1** (0.50 cm^3, 0.80 g, 2.10 mmol) for 30 h. The solvent was evaporated *in vacuo*, the residue dissolved in toluene and added to a column filled with alumina. Elution with the same solvent gave a light yellow band containing [Ru(tmm)(C$_6$H$_6$)] **3a**; recrystallization from pentane afforded light yellow needles (0.18 g, 42%). Further elution with thf gave an intense yellow band containing [RuCl{CH$_2$C(CH$_2$SnMe$_3$)CH$_2$}(C$_6$H$_6$)] **2a** (0.33 g, 42%), obtained as yellow platelets from thf at −78 °C, m.p. of **2a** 159 °C (Found: C, 36.1; H, 4.9%; *M* 434. $C_{13}H_{21}ClRuSn$ requires C, 36.1; H, 4.9%), m.p. of **3a** 165–166 °C (Found: C, 51.4; H, 5.2%; *M* 234. $C_{10}H_{12}Ru$ requires C, 51.5; H, 5.2%).

(*ii*) A CH$_2$Cl$_2$ (200 cm^3) solution of [{RuCl$_2$(C$_6$Me$_6$)}$_2$] (0.52 g, 0.77 mmol) was stirred with compound **1** (1.28 g, 3.35 mmol) for 1 h at room temperature. Work-up as described above gave [Ru(tmm)(C$_6$Me$_6$)] **3b** (0.14 g, 29%) as light yellow *crystals* and [RuCl{CH$_2$C(CH$_2$SnMe$_3$)CH$_2$}(C$_6$Me$_6$)] **2b** (0.43 g, 54%) as intense yellow *microcrystals*. A higher yield of **3b** was obtained by stirring a suspension of [{RuCl$_2$(C$_6$Me$_6$)}$_2$] (1.18 g, 1.76 mmol) in MeCN (60 cm^3) with **1** (1.1 cm^3, 1.76 g, 4.60 mmol) for 24 h. Work-up as described above gave **3b** (0.61 g, 55%); no **2b** was found. M.p. of **2b** 95 °C (Found: C, 44.3; H, 6.5. $C_{19}H_{33}ClRuSn$ requires C, 44.2; H, 6.4%); of **3b** 183–184 °C (Found: C, 60.5; H, 7.6%; *M* 318. $C_{16}H_{24}Ru$ requires C, 60.5; H, 7.6%).

(*iii*) A CH$_2$Cl$_2$ solution (50 cm^3) of [{RuCl$_2$(*p*-MeC$_6$H$_4$CHMe$_2$)}$_2$] (0.31 g, 0.50 mmol) was stirred with compound **1** (0.6 cm^3, 0.96 g, 2.52 mmol) for 10 min at room temperature. Work-up as described above gave [Ru(tmm)(*p*-MeC$_6$H$_4$CHMe$_2$)] **3c**

Table 1 Hydrogen-1 and carbon-13 NMR data[a] for the complexes

Complex	^1H (δ)	^{13}C (δ)
2a[b]	0.11 [s, 9 H, Me_3Sn, J(SnH) 52, 54], 1.26 (s, 2 H, CH_2Sn), 2.12 (s, 2 H, 2 CH_{anti}, J(SnH) 8], 3.97 (s, 2 H, 2 CH_{syn}), 5.31 (s, 6 H, C_6H_6)	−9.8 [q, Me_3Sn, J(CH) 129], 23.3 [t, CH_2Sn, J(CH) 131], 52.6 [t, CH_2, J(CH) 158], 77.0 [d, C_6H_6, J(CH) 174], 112.7 (s, CC_3)
2b[b]	0.12 [s, 9 H, Me_3Sn, J(SnH) 52, 54], 1.33 (s, 2 H, CH_2Sn), 2.05 (s, 18 H, C_6Me_6), 2.36 (s, 2 H, 2 CH_{anti}), 2.89 (s, 2 H, 2 CH_{syn})	−9.9 [q, Me_3Sn, J(CH) 129], 15.8 [q, C_6Me_6, J(CH) 128], 21.7 [t, CH_2Sn, J(CH) 131], 49.7 [t, CH_2, J(CH) 154], 94.9 (s, C_6Me_6), 113.0 (s, CC_3)
2c[b]	0.06 [s, 9 H, Me_3Sn, J(SnH) 51, 54], 1.26 (s, 2 H, CH_2Sn), 1.30 [d, 6 H, Me_2CH, J(HH) 6], 2.16 [s, 2 H, 2 CH_{anti}, J(SnH) 8], 2.36 (s, 3 H, Me), 2.6–3.0 [m, 1 H, Me_2CH, J(HH) 6], 3.49 (s, 2 H, 2 CH_{syn}), 4.4–4.9 [m, 4 H, $(AB)_2$, C_6H_4]	−9.8 [q, Me_3Sn, J(CH) 129], 19.7 [q, Me, J(CH) 133], 23.7 [q, Me_2CH, J(CH) 127 + t, CH_2Sn, J(CH) 133], 32.0 [d, Me_2CH, J(CH) 130], 54.1 [t, CH_2, J(CH) 159], 83.8 [dm C^2 or C^3 of C_6H_4, J(CH) 171], 84.4 [dm, C^2 or C^3 of C_6H_4, J(CH) 169], 103.3 (s, C^1 of C_6H_4), 112.9, 114.0 (s, CC_3 and C^4 of C_6H_4)
2d[b]	0.20 [s, 9 H, Me_3Sn, J(SnH) 52, 54], 1.49 (s, 2 H, CH_2Sn), 2.24 [s, 2 H, 2 CH_{anti}, J(SnH) 9], 4.20 (s, 2 H, 2 CH_{syn}), 5.44 (s, 6 H, C_6H_6)	−9.6 [q, Me_3Sn, J(CH) 129], 24.5 [t, CH_2Sn, J(CH) 130], 43.5 [t, CH_2, J(CH) 158], 78.6 [d, C_6H_6, J(CH) 176], 107.8 (s, CC_3)
2e[b]	0.14 [s, 9 H, Me_3Sn, J(SnH) 52, 54], 1.34 [d, 6 H, Me_2CH, J(HH) 7], 1.41 (s, 2 H, CH_2Sn), 2.32 (s, 2 H, 2 CH_{anti}), 2.50 (s, 3 H, Me), 2.7–3.1 [m, 1 H, Me_2CH, J(HH) 7], 3.69 (s, 2 H, 2 CH_{syn}), 4.6–5.0 [m, 4 H, $(AB)_2$, C_6H_4]	−9.7 [q, Me_3Sn, J(CH) 129], 19.9 [q, Me, J(CH) 128], 23.9 [q, Me_2CH, J(CH) 127], 24.8 [t, CH_2Sn, J(CH) 127], 32.2 [d, Me_2CH, J(CH) 129], 45.1 [t, CH_2, J(CH) 153], 75.9 [dm, C^2 or C^3 of C_6H_4, J(CH) 171], 76.4 [dm, C^2 or C^3 of C_6H_4, J(CH) 173], 97.4 (s, C^1 of C_6H_4), 107.1, 107.8 (s, CC_3 and C^4 of C_6H_4)
3a[c]	1.51 (s, 6 H, tmm), 4.97 (s, 6 H, C_6H_6)	40.7 [ttt, $C(CH_2)_3$, J(CH) 157, 10, 5], 80.8 [d, C_6H_6, J(CH) 172], 103.5 (s, CC_3)
3b[c]	0.95 (s, 6 H, tmm), 2.03 (s, 18 H, C_6Me_6)	18.4 [q, C_6Me_6, J(CH) 127], 40.2 [ttt, $C(CH_2)_3$, J(CH) 155, 10, 5], 91.6 (s, C_6Me_6), 105.0 (s, CC_3)
3c[c]	1.01 [d, 6 H, Me_2CH, J(HH) 7], 1.36 (s, 6 H, tmm), 1.92 (s, 3 H, Me), 1.9–2.4 [m, 1 H, Me_2CH, J(HH) 7], 4.91–5.16 [m, 4 H, $(AB)_2$, C_6H_4, J(HH) 6.5, 13]	22.0 [q, Me, J(CH) 129], 23.9 [q, Me_2CH, J(CH) 129], 33.1 [d, Me_2CH, J(CH) 128], 40.3 [ttt, $C(CH_2)_3$, J(CH) 157, 10, 5], 80.2 [dm, C^2 or C^3 of C_6H_4, J(CH) 171], 80.6 [dm, C^2 or C^3 of C_6H_4, J(CH) 169], 95.2, 103.6, 104.5 (s, CC_3, C^1 and C^4 of C_6H_4)
3d[c]	1.55 (s, 6 H, tmm), 4.69 (s, 6 H, C_6H_6)	[d]30.1 (impurity, ?), 32.2 [$C(CH_2)_3$], 71.7 (C_6H_6), 91.0 (s, CC_3)
3e[c]	1.02 [d, 6 H, Me_2CH, J(HH) 7], 1.41 (s, 6 H, tmm), 2.1–2.4 [m, 1 H, Me_2CH, J(HH) 7], 2.13 (s, 3 H, Me), 4.66–4.90 [m, 4 H, $(AB)_2$, C_6H_4]	21.9 [q, Me, J(CH) 129], 24.1 [q, Me_2CH, J(CH) 126], 31.9 [tm, $C(CH_2)_3$, J(CH) 155], 33.0 [d, Me_2CH, J(CH) 130], 70.5 [dm, C^2 or C^3 of C_6H_4, J(CH) 172], 71.8 [dm, C^2 or C^3 of C_6H_4, J(CH) 172], 86.8, 90.7, 94.6 (s, CC_3, C^1 and C^4 of C_6H_4)
4[c]	1.61 [d, 6 H, tmm, J(RhH) 1.5], 2.04 (s, 15 H, C_5Me_5)	11.8 [q, C_5Me_5, J(CH) 127], 44.3 [td, $C(CH_2)_3$, J(CH) 158, J(RhC) 14], 94.6 [d, C_5Me_5, J(RhC) 6], 109.1 [d, $C(CH_2)_3$, J(RhC) 4]
6a[e]	1.56 (s, tmm)	54.5 [ttt, $C(CH_2)_3$, J(CH) 160.5, 10, 5], 105.5 (s, CC_3), 211.7 [s, $Fe(CO)_3$]
6b[c]	1.66 (s, tmm)	48.1 [ttt, $C(CH_2)_3$, J(CH) 158.5, 10, 5], 110.0 (s, CC_3), 197.2 [s, $Ru(CO)_3$]
6c[c]	1.65 (s, tmm)	40.0 [ttt, $C(CH_2)_3$, J(CH) 157, 10, 5], 107.2 (s, CC_3), 177.0 [s, $Os(CO)_3$]

[a] Chemical shifts (δ) in ppm, measured at room temperature, coupling constants in Hz. [b] Measured in $CDCl_3$. [c] Measured in C_6D_6. [d] Hydrogen-1 decoupled. [e] Redetermined, in C_6D_6.

(0.03 g, 10%) as a spectroscopically pure, light yellow oil and $[RuCl\{CH_2C(CH_2SnMe_3)CH_2\}(p\text{-}MeC_6H_4CHMe_2)]$ **2c** (0.18 g, 37%) as yellow needles. M.p. of **2c** 87–89 °C (Found: C, 41.6; H, 5.9%; *M* 488. $C_{17}H_{29}ClRuSn$ requires C, 41.8; H, 6.0%).

Reactions of (arene)osmium halides with $CH_2{=}C(CH_2SnMe_3)_2$. (*i*) a MeCN suspension (50 cm^3) of $[\{OsCl_2(C_6H_6)\}_2]$ (0.66 g, 0.98 mmol) was stirred with compound **1** (1.0 cm^3, 1.6 g, 4.19 mmol) for 24 h. Work-up as described above gave $[OsCl\{CH_2C(CH_2SnMe_3)CH_2\}(C_6H_6)]$ **2d** (0.50 g, 49%) as yellow *microcrystals*, m.p. 169–170 °C (Found: C, 30.05; H, 4.05%; *M* 522. $C_{13}H_{21}ClOsSn$ requires C, 29.9; H, 4.1%). A $MeNO_2$ solution (10 cm^3) of **2d** (0.19 g, 0.36 mmol) was heated in the dark at 50–55 °C for 3 d. After evaporation of the solvent *in vacuo* the residue was extracted with pentane. Filtration over alumina and recrystallization from pentane gave $[Os(tmm)(C_6H_6)]$ **3d** (0.03 g, 26%) as white *crystals*.

(*ii*) A CH_2Cl_2 (25 cm^3) solution of $[\{OsCl_2(p\text{-}MeC_6H_4CHMe_2)\}_2]$ (0.18 g, 0.23 mmol) was stirred with compound **1** (0.4 cm^3, 0.64 g, 1.68 mmol) for 3 h at room temperature. After evaporation of the solvent, extraction with hexane (150 cm^3), filtration and cooling to −78 °C, $[OsCl\{CH_2C(CH_2SnMe_3)CH_2\}(p\text{-}MeC_6H_4CHMe_2)]$ **2e** (0.20 g, 73%) was obtained as yellow needles, m.p. 101.5–102.5 °C (Found: C, 35.6; H, 5.0%; *M* 578. $C_{17}H_{29}ClOsSn$ requires C, 35.3; H, 5.1%). A CD_3NO_2 solution of **2e** was warmed to *ca.* 35 °C, and after 6 h the ^1H NMR spectrum showed resonances for the starting material **2e**, $[Os(tmm)(p\text{-}MeC_6H_4CHMe_2)]$ **3e** and $SnMe_3Cl$.

Reactions with $CH_2{=}C(CH_2Cl)_2$ *and* Mg. (*i*) To a thf suspension (15 cm^3) of $[\{RuCl_2(p\text{-}MeC_6H_4CHMe_2)\}_2]$ (0.30 g, 0.49 mmol) and Mg (0.10 g, 3.99 mmol) a thf solution (6 cm^3) of $CH_2{=}C(CH_2Cl)_2$ (0.139 cm^3, 0.15 g, 1.20 mmol) was added dropwise. After stirring at room temperature until the solution had turned deep brown (1–2 h), methanol (0.5 cm^3) was added to stop the reaction. Evaporation of the solvent *in vacuo* and purification by column chromatography over alumina with pentane as eluent gave a yellowish band containing $[Ru(tmm)(p\text{-}MeC_6H_4CHMe_2)]$ **3c** (0.13 g, 47%) as a light yellow, spectroscopically pure oil.

(*ii*) A thf suspension (5 cm^3) of $[\{OsCl_2(p\text{-}MeC_6H_4CHMe_2)\}_2]$ (0.16 g, 0.21 mmol) and Mg (0.05 g, 2.18 mmol) was treated with $CH_2{=}C(CH_2Cl_2)$ (0.055 cm^3, 0.09 g, 0.70 mmol) and stirred for 7 h at room temperature. Purification by column chromatography with pentane as described above gave a nearly colourless eluate which afforded $[Os(tmm)(p\text{-}MeC_6H_4CHMe_2)]$ **3e** (0.09 g, 55%) as a nearly colourless, spectroscopically pure oil.

Reaction of $[\{RhI_2(C_5Me_5)\}_2]$ *with* $CH_2{=}C(CH_2SnMe_3)_2$. A thf suspension (20 cm^3) of $[\{RhI_2(C_5Me_5)\}_2]$ (0.27 g, 0.27 mmol) was stirred with compound **1** (0.2 cm^3, 0.32 g, 0.84 mmol) for 5 d at room temperature. After evaporation of the solvent *in vacuo*, the product was extracted with toluene and filtered over alumina; repeated purification by column chromatography over alumina with pentane as eluent gave a light yellow band containing $[Rh(tmm)(C_5Me_5)]$ **4** (0.13 g, 82%). Recrystallization from pentane at −78 °C afforded analytically pure yellow *crystals*, m.p. 93–94 °C (Found: C, 57.4; H, 7.1%; *M* 292. $C_{14}H_{21}Rh$ requires C, 57.5; H, 7.2%).

Reactions of $[\{MCl_2(CO)_3\}_2]$ (M = Ru *or* Os) *with*

$CH_2=C(CH_2SnMe_3)_2$. (*i*) The compound $[\{RuCl_2(CO)_3\}_2]$ (1.81 g, 3.53 mmol) was dissolved in thf (30 cm^3) with stirring (10 min), then added to a thf solution (2 cm^3) of **1** (2.69 g, 7.05 mmol). After stirring for 20 min, the solvent was evaporated *in vacuo* (*ca.* 0.05 bar), the residue extracted with pentane and added to a column filled with alumina (10 × 3 cm). Elution with the same solvent (*ca.* 200 cm^3) and removal of the solvent under reduced pressure (*ca.* 0.13 bar) gave $[Ru(CO)_3(tmm)]$ **6b** (1.04 g, 61%) as a colourless oil. Two-fold recrystallization from pentane at −78 °C afforded a spectroscopically pure oil (0.82 g), m.p. 20–22 °C, *M* 240.

(*ii*) During 1.5 h a solution of compound **1** (2 cm^3, 3.2 g, 8.38 mmol) in CH_2Cl_2 (50 cm^3) was added dropwise to a suspension of $[\{OsCl_2(CO)_3\}_2]$ (2.99 g, 4.34 mmol) in CH_2Cl_2 (150 cm^3) giving a slightly yellow solution. After evaporation of the solvent at a bath temperature of *ca.* 50 °C and drying at room temperature (*ca.* 0.13 bar) the product was extracted with pentane and filtered over alumina (10 × 3 cm). Elution with pentane (150 cm^3) and removal of the solvent at *ca.* 0.13 bar gave $[Os(CO)_3(tmm)]$ **6c** (1.38 g, 48%) as a colourless oil. Two-fold recrystallization from pentane left 1.01 g of analytically pure *microcrystals*, m.p. 42.5–44 °C (Found: C, 25.5; H, 1.9%; *M* 330. $C_7H_6O_3Os$ requires C, 25.6; H, 1.8%).

Arene-displacement Reaction.—A thf solution (50 cm^3) of $[Ru(tmm)(C_6H_6)]$ **3a** (0.09 g) was saturated with carbon monoxide and irradiated for 36 h under an atmosphere of CO. The slightly yellow solution turned white and dark insoluble material formed. After removal of the solvent *in vacuo* and filtration over alumina in pentane, the IR spectrum of the

Table 2 Selected bond lengths (Å) and angles (°) for $[RuCl\{CH_2C(CH_2SnMe_3)CH_2\}(C_6H_6)]$ **2a**

Ru–C(0)	2.205(7)	C(0)–C(3)	1.423(9)
Ru–C(2)	2.196(7)	Sn–C(1)	2.175(8)
Ru–C(3)	2.201(7)	Sn–C(10)	2.06(1)
Ru–C(4)	2.234(8)	Sn–C(11)	2.17(1)
Ru–C(5)	2.240(8)	Sn–C(12)	2.12(1)
Ru–C(6)	2.252(7)	C(4)–C(5)	1.43(1)
Ru–C(7)	2.151(8)	C(4)–C(9)	1.40(1)
Ru–C(8)	2.185(8)	C(5)–C(6)	1.41(1)
Ru–C(9)	2.243(8)	C(6)–C(7)	1.42(1)
Ru–Cl	2.446(2)	C(7)–C(8)	1.40(1)
C(0)–C(1)	1.50(1)	C(8)–C(9)	1.43(1)
C(0)–C(2)	1.43(1)		
C(1)–C(0)–C(2)	122.9(6)	C(3)–Ru–Cl	84.8(2)
C(1)–C(0)–C(3)	120.1(7)	C(4)–Ru–Cl	90.0(2)
C(2)–C(0)–C(3)	116.5(6)	Cl–Ru–C(5)	89.0(3)
C(0)–Ru–C(2)	37.8(3)	Cl–Ru–C(6)	114.8(3)
C(0)–Ru–C(3)	37.7(2)	Cl–Ru–C(7)	152.1(3)
C(2)–Ru–C(3)	66.8(3)	Cl–Ru–C(8)	154.9(2)
C(0)–Ru–Cl	103.2(2)	Cl–Ru–C(9)	117.1(3)
C(2)–Ru–Cl	86.1(2)		

Table 3 Selected bond lengths (Å) and angles (°) for $[Ru(CO)_3(tmm)]$ **6b**

Ru–C(1)	1.915(5)	C(4)–C(5)	1.436(8)
Ru–C(2)	1.937(6)	C(4)–C(7)	1.380(9)
Ru–C(3)	1.920(6)	O(1)–C(1)	1.134(6)
Ru–C(4)	2.055(5)	O(2)–C(2)	1.121(6)
Ru–C(5)	2.221(5)	O(3)–C(3)	1.148(7)
Ru–C(6)	2.230(6)	C(4)–C(6)	1.413(9)
Ru–C(7)	2.225(6)		
C(1)–Ru–C(2)	96.9(2)	C(3)–Ru–C(7)	100.7(2)
C(1)–Ru–C(3)	97.1(2)	C(4)–Ru–C(5)	39.0(2)
C(1)–Ru–C(4)	120.3(2)	C(4)–Ru–C(6)	38.2(2)
C(1)–Ru–C(5)	96.8(2)	C(4)–Ru–C(7)	37.3(2)
C(1)–Ru–C(6)	158.6(2)	C(5)–Ru–C(6)	65.3(2)
C(1)–Ru–C(7)	98.2(2)	C(5)–Ru–C(7)	64.8(2)
C(2)–Ru–C(3)	94.8(2)	C(6)–Ru–C(7)	64.2(2)
C(2)–Ru–C(4)	119.4(2)	Ru–C(1)–O(1)	178.3(5)
C(2)–Ru–C(5)	96.0(2)	Ru–C(2)–O(2)	176.8(5)
C(2)–Ru–C(6)	96.7(2)	Ru–C(3)–O(3)	178.3(5)
C(2)–Ru–C(7)	156.8(2)	C(5)–C(4)–C(6)	114.7(5)
C(3)–Ru–C(4)	122.3(2)	C(5)–C(4)–C(7)	115.6(5)
C(3)–Ru–C(5)	161.2(2)	C(6)–C(4)–C(7)	116.0(5)
C(3)–Ru–C(6)	98.3(2)		

Table 4 Data for crystal-structure analyses

	2a	**3a**	**3d**	**6b**
Empirical formula	$C_{13}H_{21}ClRuSn$	$C_{10}H_{12}Ru$	$C_{10}H_{12}Os$	$C_7H_6O_3Ru$
M	432.53	233.28	322.41	239.19
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	*Pbca* (no. 61)	$Pna2_1$ (no. 33)		$P\bar{1}$ (no. 2)
a/Å	12.567(5)	17.686(4)	17.561(4)	5.765(4)
b/Å	11.863(5)	8.012(2)	8.005(1)	7.096(3)
c/Å	20.657(13)	6.119(1)	6.106(1)	10.323(3)
α/°				81.89(3)
β/°				84.46(4)
γ/°				82.03(4)
Z	8	4		2
U/Å^3	3080(4)	867.1(4)		412.7(5)
T/K	248	293	293	203
D_c/g cm^{-3}	1.87	1.79		1.92
λ/Å	0.7107 (Mo-Kα)	0.7093 (Mo-Kα)	0.5609 (Ag-Kα)	1.5406 (Cu-Kα)
μ/cm^{-1}	27.44	17.05		154.20
Approximate crystal size/mm	0.1 × 0.1 × 0.4	0.2 × 0.2 × 0.5	0.1 × 0.1 × 0.2	
2θ range/°	6–48	6–60		16–130
F(000)	1680.0	464.0		232.0
No. of data collected	2962	1964		1386
No. of unique data	2699	1291		1233
No. with $I > n\sigma(I)$, N_o	1675	1199		1173
n	3	1		1
No. of variables, N_v	146	100		101
R^a	0.044	0.019		0.043
R'^b	0.056	0.026		0.059
Largest peak/e Å^{-3}	1.02	0.53		1.07

[a] $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $\Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|$.

Table 5 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms in $[RuCl\{CH_2C(CH_2SnMe_3)CH_2\}(C_6H_6)]$ **2a**

Atom	*x*	*y*	*z*
Sn	5619.2(7)	321.0(7)	7030.9(4)
Ru	8054.9(6)	1296.6(6)	5099.7(3)
Cl	9529(2)	2532(2)	5407(1)
C(0)	7112(7)	1174(7)	5997(4)
C(1)	6086(8)	528(9)	6024(5)
C(2)	8126(8)	661(8)	6097(4)
C(3)	7118(7)	2315(7)	5785(4)
C(4)	8340(10)	1701(9)	4058(5)
C(5)	8990(9)	760(10)	4230(5)
C(6)	8525(9)	−214(8)	4504(5)
C(7)	7427(9)	−204(8)	4658(4)
C(8)	6777(9)	700(9)	4469(5)
C(9)	7240(10)	1663(9)	4157(5)
C(10)	6290(10)	−1180(10)	7321(7)
C(11)	3900(10)	290(10)	7103(6)
C(12)	6220(10)	1690(10)	7586(7)

Table 6 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms in $[Ru(tmm)(C_6H_6)]$ **3a**

Atom	*x*	*y*	*z*
Ru	6249.8(1)	3239.5(2)	2500
C(0)	7085(2)	4858(4)	1675(6)
C(1)	6522(2)	5898(4)	2640(10)
C(2)	7440(2)	3724(6)	3126(8)
C(3)	6867(2)	4133(5)	−390(7)
C(4)	5063(2)	3116(4)	3550(10)
C(5)	5506(2)	2639(5)	5313(7)
C(6)	6025(2)	1390(5)	5085(8)
C(7)	6094(2)	563(4)	3115(9)
C(8)	5651(2)	1003(5)	1340(8)
C(9)	5115(2)	2310(7)	1571(7)

Table 7 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms in $[Ru(CO)_3(tmm)]$ **6b**

Atom	*x*	*y*	*z*
Ru	2 093.5(9)	1 919.3(7)	2 344.7(4)
O(1)	5 250(10)	2 577(9)	−180(6)
O(2)	−970(10)	−721(8)	1 397(6)
O(3)	5 360(10)	−1 284(9)	3 816(6)
C(1)	4 080(10)	2 300(10)	760(7)
C(2)	210(10)	200(10)	1 749(7)
C(3)	4 150(10)	−100(10)	3 247(8)
C(4)	460(10)	4 230(10)	3 222(8)
C(5)	−430(10)	4 560(10)	1 946(8)
C(6)	−340(20)	2 660(10)	4 062(8)
C(7)	2 800(20)	4 430(10)	3 246(9)

pentane solution was identical with that of $[Ru(CO)_3(tmm)]$ **6b** in the same solvent.

Instrumentation.—Proton NMR spectra were recorded on a Bruker WP-80 PET spectrometer at 80 MHz, ^{13}C NMR spectra on a Bruker WH-270 spectrometer at 67.88 MHz, infrared spectra on a Perkin Elmer 1720 X FTIR spectrometer and mass spectra on a MAT CH 5-DF (Varian) spectrometer at 70 eV (*ca.* 1.12×10^{-17} J). Melting points were measured under nitrogen and are uncorrected. Elemental analyses were carried out by Analytische Laboratorien Engelskirchen.

X-Ray Crystallography.—Details of the structure analyses are in Table 4.

(*i*) Crystals of compound **2a** were grown from thf at −78 °C, of **3a** by slow evaporation of the solvent toluene, and of **6b** by sublimation on the diffractometer in a sealed capillary under reduced pressure. Diffracted intensities (Wyckoff ω scans) were collected on an Enraf-Nonius CAD4 diffractometer. Three check reflections showed no crystal decay. Corrections for Lorentz, polarization, and absorption effects were applied. The latter correction was based on a semiempirical method using azimuthal scan data for **2a** and **3a**,[22] or the program DIFABS for **6b**.[23] The structures of the complexes were solved by conventional heavy-atom methods, and successive Fourier-difference syntheses were used to locate all non-hydrogen atoms. All hydrogen atoms on the C_4H_6 ligand in **2a** and **6b** were located in a single Fourier-difference map and idealized to C–H 0.98 Å with $B_H = 1.3B_C$ in **2a** and 3.0 $Å^2$ in **6b**. All other hydrogen atoms were included with calculated positions (C–H 0.98 Å) and fixed thermal parameters ($B_H = 1.3B_C$). Refinements were carried out by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms, while the hydrogen atoms were allowed to ride on their carbon atoms. A weighting scheme of the form $w = 1/\sigma^2(F)$ was used.

(*ii*) Crystals of compound **3d** were grown from hexane by slow evaporation of the solvent. The cell parameters were similar to those of **3a** and should be sufficient to establish an isostructural relationship between **3a** and **3d**. During data collection three check reflections showed more than 50% intensity loss in the first 12 h. As a consequence of the combined effects of radiation-induced decay and X-ray absorption a satisfactory solution of the structure was not obtained.

Calculations were performed using the SDP system of programs[24] and the ORTEP program[25] was used to obtain the drawings. Tables 5–7 report the positional parameters for the non-hydrogen atoms. Selected bond distances and angles are listed in Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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