Bimetallic Polymers

Isolation of [1]Ruthenocenophanes: Synthesis of Polyruthenocenylstannanes by Ring-Opening Polymerization[**]

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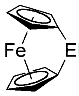
Strained [1]ferrocenophanes **1**[1] have attracted considerable attention over the past decade because of their interesting structures and reactivity and their ability[2] to function as precursors of high-molecular-weight polyferrocenes through ring-opening polymerization (ROP). Studies of the unusual properties of the resulting metallopolymers **2**[3] as well as



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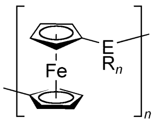

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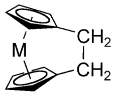

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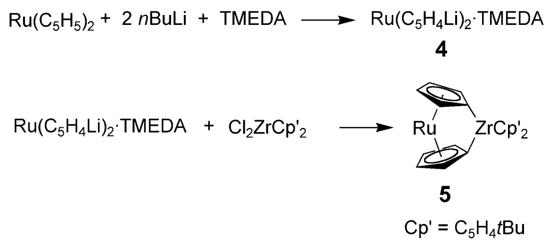
fundamental interest in strained organometallic rings,[4] have inspired the synthesis and study of a range of new [1]ferrocenophanes **1** with either main-group[5] or d- or f-block elements[6] in the bridge. A feature of these strained molecules is the presence of a tilting of the cyclopentadienyl rings which can result in a dihedral angle of up to 32°. The expansion of this chemistry to allow the incorporation of other metals into analogous strained organometallic monomers is of considerable interest but has been much slower to develop. Rare examples of strained and potentially polymerizable species studied to date include silicon-bridged bis(benzene)chromium complexes,[7] [2]cobaltocenophanes,[8] and [2]ruthenocenophanes **3** (M = Ru) with a CH_2CH_2 bridge.[9] In the latter case, the species were shown to exhibit a significantly higher ring tilt and degree of strain than their iron analogues, as a result of the larger size of the ruthenium atom which forces the Cp rings further apart.[9,10] Herein we report the first examples of [1]ruthenocenophanes together with preliminary studies of their ROP behavior.

Attempts to synthesize silicon-bridged [1]ruthenocenophanes by reaction of the *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) adduct of dilithiated ruthenocene $Ru(C_5H_4Li)_2 \cdot TMEDA$ (**4**) with Cl_2SiMe_2 have been reported to result in the formation of dimeric and oligomeric species.[11,12] Introduction of larger elements such as zirconium or tin as the bridging atoms might be expected to lead to less-strained and therefore more-stable [1]ruthenocenophanes. We attempted to prepare the zirconium-bridged [1]ruthenocenophane by the reaction of **4** with $[Cl_2ZrCp'_2]$ ($Cp' = C_5H_4tBu$) in Et_2O at low temperature. Recrystallization of the crude reaction product from hexanes at −55 °C afforded **5** as a pale yellow powder in 35 % yield (Scheme 1).



Scheme 1. Synthesis of **4** and **5**.

The identity of **5** was confirmed by ^1H NMR and ^{13}C NMR spectroscopy, and by mass spectrometry. The ^1H NMR spectrum indicates a ring-strained structure with a set of two pseudotriplets at $\delta = 4.52$ and 4.86 ppm, which we assigned to the α and β H atoms of the Cp ring bound to ruthenium. The ^{13}C NMR spectrum shows an unusual downfield shift for the signal of the *ipso*-C atom of the ruthenocene Cp ring at $\delta = 162.5$ ppm. The same is observed for the analogous iron compound **1** ($ER_n = ZrCp'_2$),[6a] in which the corresponding shift is $\delta = 159.0$ ppm. For strained [1]ferrocenophanes the signals for the *ipso*-Cp carbon atoms are usually shifted upfield relative to those for unstrained compounds.

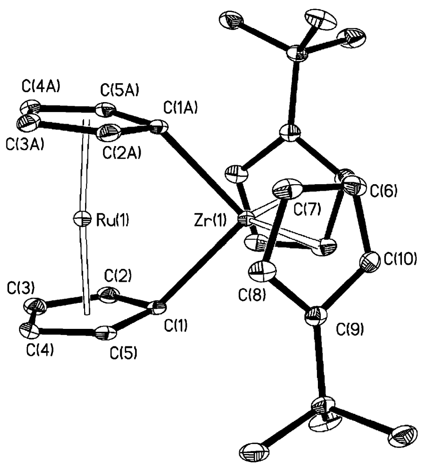
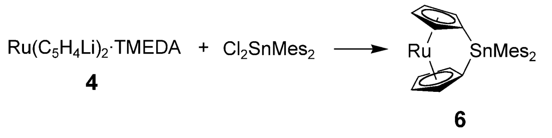


Figure 1. Structure of **5** in the solid state, hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ru(1)···Zr(1) 295.04(4), Ru(1)-C(1) 214.6(2), Ru(1)-C(2) 216.9(3), Ru(1)-C(3) 221.3(3), Ru(1)-C(4) 221.0(4), Ru(1)-C(5) 215.5(2), Zr(1)-C(1) 214.6(2), Zr(1)-C(6) 249.5(2), Zr(1)-C(7) 252.9(2), Zr(1)-C(8) 258.5(2), Zr(1)-C(9) 262.5(2), Zr(1)-C(10) 254.0(2); C(1)-Zr(1)-C(1A) 92.3(1).

To probe the structure of **5**, an X-ray crystal structure determination of a single crystal grown from hexanes at −30 °C was conducted (Figure 1).[13] As expected from the larger size of the ruthenium atom in comparison to the iron atom, **5** shows more strain than the corresponding iron compound **1** ($ER_n = ZrCp'_2$). The tilt angle α for **5** is 10.4°, which is significantly greater than for the analogous iron compound (6°),[6a] but the increase in tilt is not as high as expected when compared with **3**[10]. Another feature indicating the strain in **5** is the $Cp_{centroid}$-Ru-$Cp_{centroid}$ angle θ which is 175° as opposed to 177.3° in **1** ($ER_n = ZrCp'_2$). The angle β between the planes of the Cp rings and the Zr–C(1) bond is 41°, which is slightly larger than in **1** ($ER_n = ZrCp'_2$, 40.1°).[6a] The constrained geometry in **5** forces the Ru atom and the Zr atom into close contact. The Ru–Zr distance is 295.04(4) pm, close to distances found for Ru–Zr single bonds ($[Cp_2Zr\{Ru(CO)_2Cp\}_2]$: Zr–Ru = 293.8(1), 294.9(1) pm;[14] $[Cp_2Zr\{Ru(CO)_2Cp\}OtBu]$: Zr–Ru = 291.0(1) pm).[15] The electronic nature of this interaction is currently under theoretical investigation.

To determine if **5** can be polymerized thermally, a DSC (differential scanning calorimetry) experiment was carried out. It showed a melt endotherm at 188 °C; a ROP exotherm could not be detected. On heating the monomer to 200 °C in a sealed tube for 4 days, only unconverted starting material was recovered. Compound **5** is also unreactive towards anionic initiators such as MeLi.

Tin-bridged [1]ferrocenophanes can be isolated with bulky substituents and are sufficiently strained to undergo ROP.[5b] To synthesize a tin-bridged [1]ruthenocenophane, **4** was treated with Cl_2SnMes_2 at low temperature in Et_2O. A ^1H NMR spectrum of the crude reaction mixture showed broad peaks owing to the formation of presumably oligomeric material. However, signals attributable to the tin-bridged [1]ruthenocenophane **6** could also be detected in the mixture. When the reaction was carried out in THF instead of Et_2O, **6** was formed as the main product. Extraction of the crude reaction mixture with hexanes and repeated recrystallizations from Et_2O led to the isolation of **6** in 13 % yield (Scheme 2).[16]



Scheme 2. Synthesis of **6** (Mes = 2,4,6-trimethylphenyl).

The identity of **6** was confirmed by NMR and UV/Vis spectroscopy and mass spectrometry. Signals attributable to the α and β H atoms of the Cp ring are detected in the ^{1}H NMR spectrum at $\delta = 5.03$ and 4.30 ppm, respectively. At $\delta = 0.73$ ppm the separation of these signals ($\Delta\delta_{Cp}$) is larger than in the analogous iron compound **1** ($ER_n = SnMes_2$), for which $\Delta\delta_{Cp}$ is 0.13 ppm.[5b] This increasing separation has been attributed to an increased tilt angle α in several other cases, but in this study we could not confirm this trend. On the contrary, we found that in some cases $\Delta\delta_{Cp}$ decreases with increasing α: The [2]ruthenocenophane **3** (M = Ru, $\alpha = 29.6(5)^\circ$) shows a separation of 0.38 ppm for the hydrogen atoms of the Cp ring,[12] whereas for the analogous [2]ferrocenophane **3** (M = Fe, $\alpha = 21.6(5)^\circ$)[17] this value increases to $\delta = 0.88$ ppm.[12] The same can be observed for **5** (**5**: $\Delta\delta_{Cp} = 0.34$ ppm; **1** ($ER_n = ZrCp'_2$): $\Delta\delta_{Cp} = 0.37$ ppm). The shift of the ^{13}C NMR signal for the Cp *ipso*-carbon atom of **6** ($\delta = 31.8$ ppm) seems to follow the usual trend: The signal is shifted upfield relative to that for the corresponding iron complex **1** ($ER_n = SnMes_2$, $\delta = 38.2$ ppm).

Also indicating the strain in **6** is the UV/Vis spectrum in CH_2Cl_2 (Figure 2) which shows a band at 363 nm ($\varepsilon_{max} = 436\,L\,mol^{-1}\,cm^{-1}$). For comparison, ruthenocene shows an absorption band at 322 nm, which can be resolved into two bands when measured at 77 K (339 nm, $\varepsilon_{max} = 120\,L\,mol^{-1}\,cm^{-1}$ and 308 nm, $\varepsilon_{max} = 160\,L\,mol^{-1}\,cm^{-1}$). These bands have been assigned to the $^1A_{1g}\rightarrow{}^1E_{1g}$ and $^1A_{1g}\rightarrow{}^1E_{2g}$ transitions, respectively.[18] For strained ferrocenophanes it has been shown that the longer wavelength band is red-shifted and the absorption coefficient of this band increases with the amount of ring tilt.[5,19] Compound **5** only shows a weak shoulder in the same wavelength region. This behavior is also observed for [1]ruthenocenophanes.

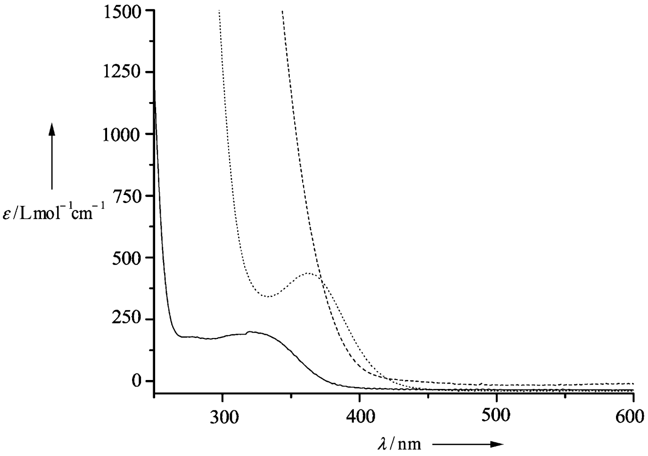


Figure 2. UV/Vis spectra of ruthenocene (——), **5** (•••••), and **6** (-----) in CH_2Cl_2.

To determine the solid-state structure of **6** an X-ray diffraction study was carried out on single crystals grown from nBu_2O (Figure 3).[13] Complex **6** is isostructural with **1** ($ER_n = SnMes_2$) and crystallizes in the space group $P2_1/c$ with three independent molecules (designated $\mathbf{6^I}$, $\mathbf{6^{II}}$, $\mathbf{6^{III}}$) in the asymmetric unit. The three molecules mainly differ in the rotation of the mesityl groups around the Sn–C bond. The tilt angles α are 20.9(3), 20.2(3), and 20.8(4)°, which are significantly higher than in **1** ($ER_n = SnMes_2$, $\alpha = 15.3(2)$, 14.5(2), and 15.7(3)°).[5b] The β angles ($\mathbf{6^I}$ 34.7, 35.5; $\mathbf{6^{II}}$ 35.7, 35.6; $\mathbf{6^{III}}$ 35.6, 35.3°) are comparable to **1** ($ER_n = SnMes_2$, $\alpha = 35.3(2)$). As expected, the angle θ between the Cp-ring centroids and the central Ru atom in **6** ($\theta = 164.3$, 164.9, and 164.5°) is smaller than in the analogous iron compound **1** ($ER_n = SnMes_2$, $\theta = 167.5(2)$, 168.0(2), and 167.3(2)°) and therefore also indicates the higher strain in **6**. The average Sn–C bond lengths ($Sn-C_{Mes}$: 216.9(7) pm; $Sn-C_{Cp}$: 219.3(7) pm) are consistent with values typically found for such bonds. As in the case of **5**, the Ru and the bridging Sn atom are forced into close contact with the distance Ru–Sn being 299.63(7), 299.36(7), and 299.26(8) pm. These distances are longer than the values normally found for Ru–Sn single bonds,[20] but shorter than the long distances in $[Ru_6C(CO)_{16}SnCl_3]_2^-$ in which a five-coordinate tin atom asymmetrically bridges two ruthenium atoms (Ru–Sn = 314.0(2), 258.1(3), 310.2(2), and 258.3(3) pm).[21] Based on these findings an interaction between the two elements cannot be ruled out.

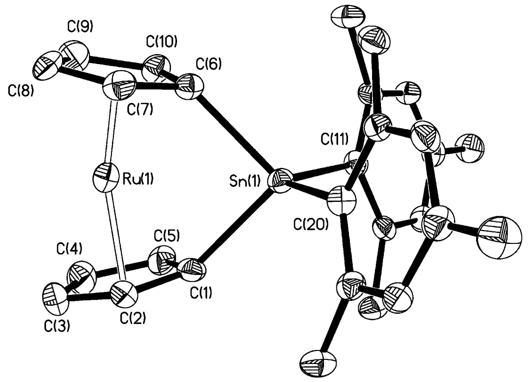
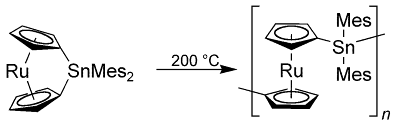


Figure 3. Structure of **6** in the solid state. Only one of the three independent molecules in the unit cell is depicted, hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ru(1)···Sn(1) 299.63(7), Ru(1)-C(1) 213.0(6), Ru(1)-C(2) 215.0(7), Ru(1)-C(3) 221.3(8), Ru(1)-C(4) 221.4(7), Ru(1)-C(5) 215.2(6), Ru(1)-C(6) 215.5(6), Ru(1)-C(7) 215.4(7), Ru(1)-C(8) 221.5(7), Ru(1)-C(9) 220.8(8), Ru(1)-C(10) 214.6(7), Sn(1)-C(1) 219.7(6), Sn(1)-C(6) 218.1(6), Sn(1)-C(11) 217.0(6), Sn(1)-C(20) 217.4(6), C(1)-Sn(1)-C(6) 91.2(2), C(11)-Sn(1)-C(20) 116.7(2).

A DSC study of **6** showed no melt transition, but a ROP exotherm was detected at 181 °C. On heating **6** in a sealed tube at 200 °C for 4.5 h, the polymeric material **7** was obtained after precipitation from THF into methanol (Scheme 3). The structure of **7** was confirmed by NMR spectroscopy. The ^{1}H NMR spectrum of **7** shows peaks for the H atoms of the Cp



6 **7**

Scheme 3. Ring-opening polymerization of **6**.

ring as well as the mesityl ligands, which are typically broad as expected for a polymer. The most prominent feature of the ^{13}C NMR spectrum of **7** is the signal for the Cp *ipso*-carbon atom at $\delta = 76.9$ ppm, which shows a significant downfield shift relative to that of the monomer **6** ($\delta = 31.8$ ppm). GPC analysis in THF versus polystyrene standards showed the material to be of high molecular weight with a relatively broad molecular-weight distribution ($M_n = 2.7 \cdot 10^5$, $M_w/M_n = 2.28$). The polymer **7** is stable to air, moderately soluble in organic solvents such as toluene, CH_2Cl_2 and THF, and insoluble in hexanes and methanol. DSC analysis showed a glass transition temperature (T_g) of 221 °C. Thermogravimetric analysis of **7** showed decomposition starting at 270 °C. The ceramic yield at 900 °C was 32 %.

Further studies of the reactivity of **5** and **6** are in progress. Current work is also focused on the synthesis of other examples of [1]ruthenocenophanes with different bridging elements and the study of the properties of the resulting ring-opened polymers, which should differ substantially from those based on ferrocene.

Experimental Section

4: TMEDA (4.12 mL, 27.3 mmol) and *n*BuLi (1.6 M solution in hexanes, 21.2 mL, 33.9 mmol) were added to a suspension/solution of ruthenocene (3.11 g, 13.5 mmol) in hexanes (100 mL), and the mixture was stirred at room temperature for 60 h. The resulting light yellow precipitate was collected by filtration, washed with hexanes until the washings were colorless, and dried in vacuo (4.05 g, 84 %). The solid should be stored at −30 °C.

5: Solid $[Cl_2ZrCp'_2]$[22] (1.32 g, 3.26 mmol) was added to a suspension of **4** (1.17 g, 3.26 mmol) in Et_2O (50 mL) at −70 °C. The solution was allowed to warm to room temperature overnight and the solvent was then removed in vacuo. Extraction with hot hexanes, filtration, and concentration of the resulting solution yielded **5** as a pale yellow powder (650 mg, 35 %) on storage at −55 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 5.92$ (t, ^3J(H, H) = 5.1 Hz, 4H; Cp*t*Bu), 5.33 (t, ^3J(H, H) = 5.1 Hz, 4H; Cp*t*Bu), 4.86 (t, ^3J(H, H) = 3 Hz, 4H; Cp), 4.52 (t, ^3J(H, H) = 3 Hz, 4H; Cp), 1.31 ppm (s, 18H; *t*Bu); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 162.5$ (s; *ipso* CpRu), 138.3 (s; *ipso*-CpZr), 104.8 (s; CpZr), 104.6 (s; CpZr), 87.1 (s; CpRu), 74.4 (s; CpRu), 33.3 (s; $C(\mathit{C}H_3)_3$), 33.2 ppm (s; $\mathit{C}(CH_3)_3$); MS: *m*/*z* (%): 562 (100) [M^+], 547 (15) [$M^+ - CH_3$], 506 (25) [$M^+ - C_4H_8$], 232 (56) [$RuCp_2^+$]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 310 nm (shoulder); elemental analysis: calcd for $C_{28}H_{34}RuZr$ (%): C 59.75, H 6.09; found: C 59.58, H 6.32.

6: Compound **4** (1.0 g, 2.78 mmol) in THF (6 mL) was added to a suspension of finely ground Cl_2SnMes_2[23] (1.3 g, 3.04 mmol) in THF (2 mL) at −70 °C. The mixture was stirred at low temperature for 4 h and then allowed to slowly reach −30 °C. The solution was taken out of the cold bath, and the solvent removed in vacuo. Extraction of the residue with hexanes (50 mL) and removal of the solvent gave a crude product, which was repeatedly recrystallized from Et_2O to give **6** as a pale yellow powder (210 mg, 13 %). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.79$ (s, $^4J(^{117/119}Sn,^1H) = 22.0$ Hz, 4H; *m*-H), 5.03 (t, ^3J(H,H) = 2.4 Hz, 4H; Cp), 4.30 (t, ^3J(H,H) = 2.4 Hz, 4H; Cp), 2.75 (s, $^4J(^{117/119}Sn,^1H) = 6.9$ Hz, 12H; *o*-CH_3), 2.14 ppm (s, 6H; *p*-CH_3); ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): $\delta = 145.7$ (s, $^2J(^{117/119}Sn,^{13}C) = 42$ Hz; *o*-Mes), 139.6 (s, $^4J(^{117/119}Sn,^{13}C) = 11$ Hz; *p*-Mes), 136.8 (s, $^1J(^{119}Sn,^{13}C) = 406$ Hz, $^1J(^{117}Sn,^{13}C) = 392$ Hz; *ipso*-Mes), 129.4 (s, $^3J(^{119}Sn,^{13}C) = 50$ Hz, $^3J(^{117}Sn,^{13}C) = 48$ Hz; *m*-Mes), 79.8 (s, $^3J(^{117/119}Sn,^{13}C) = 34$ Hz, Cp), 77.9 (s, $^2J(^{117/119}Sn,^{13}C) = 49$ Hz; Cp), 31.8 (s, $^1J(^{119}Sn,^{13}C) = 398$ Hz, $^1J(^{117}Sn,^{13}C) = 380$ Hz; *ipso* Cp), 25.6 (s, $^3J(^{119}Sn,^{13}C) = 42$ Hz, $^3J(^{117}Sn,^{13}C) = 40$ Hz; *o*-CH_3), 21.4 ppm (s, $^5J(^{117/119}Sn,^{13}C) = 7$ Hz; *p*-CH_3); ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C) $\delta = -112.5$ ppm; MS: *m*/*z*:(%) 586 (6) [M^+], 467 (23) [$M^+ - Mes$], 349 (100) [$M^+ - 2\,Mes + H$], 232 (48) [$RuCp_2^+$]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 363 nm (436 L mol^{-1} cm^{-1}); elemental analysis: calcd for $C_{28}H_{30}RuSn$ (%): C 57.36, H 5.16; found: C 57.21, H 5.51.

7: **6** (130 mg, 0.22 mmol) was sealed in an evacuated tube and heated to 200 °C for 4.5 h. The crude polymer was purified by repeated precipitation from THF into methanol to yield **7** as a white powder, which was dried in vacuo (59 mg, 45 %). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.72$ (s, 4H; *m*-H), 4.71 (s, 4H; Cp), 4.65 (s, 4H; Cp), 2.37 (s, 12H; *o*-CH_3), 2.12 ppm (s, 6H; *p*-CH_3); ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): $\delta = 144.5$ (s, $^2J(^{117/119}Sn,^{13}C) = 33$ Hz; *o*-Mes), 141.6 (s; *ipso*-Mes) 138.2 (s; *p*-Mes), 129.0 (s; *m*-Mes), 77.9 (s; Cp), 76.9 (s; *ipso*-Cp), 75.2 (s, $J(^{117/119}Sn,^{13}C) = 36$ Hz; Cp), 26.9 (s, $^3J(^{117/119}Sn,^{13}C) = 32$ Hz; *o*-CH_3), 21.5 ppm (s; *p*-CH_3); ^{119}Sn NMR (111.8 MHz, C_6D_6, 25 °C): $\delta = -133.0$ ppm; GPC (THF, versus polystyrene): $M_n = 2.7 \times 10^5$, $M_w/M_n = 2.28$; elemental analysis: calcd for $C_{28}H_{30}RuSn$ (%): C 57.36, H 5.16; found: C 57.67, H 5.38.

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Keywords: cyclopentadienyl ligands · ring-opening polymerization · ruthenium · stannanes · strained molecules

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[10] For **3** the difference in the tilt angle α between the planes of the Cp ligands for the Ru and Fe species is 8°. (**3** (M = Ru): $\alpha = 29.6(5)°$, **3** (M = Fe): $\alpha = 21.6(5)°$); see references [9] and [17].

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[13] Crystallographic data for $C_{28}H_{34}RuZr$ (**5**): monoclinic $C2/c$, $a = 19.0368(4)$, $b = 9.5493(4)$, $c = 15.1497(4)$ Å, $\beta = 124.306(2)°$, $V = 2274.9(1)$ Å^3, $Z = 4$, $\mu = 1.135\ \mathrm{mm^{-1}}$, $\rho_{calcd} = 1.643\ \mathrm{Mg\,m^{-3}}$, 150(1) K, Nonius Kappa-CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), pale yellow crystal ($0.30 \times 0.22 \times 0.16\ \mathrm{mm^3}$). Of 9615 reflections collected ($5.1 \leq 2\theta \leq 55.0°$), 2617 were independent ($R_{int} = 0.0296$), and 2279 were observed with $F_o \geq 4\sigma(F_o)$. Solution and refinement with SHELXTL-PC v6.12, non-hydrogen atoms were refined with anisotropic parameters, hydrogen atoms were refined on calculated positions using a riding model, $R1 = 0.0256$, $wR2 = 0.0628$, ($R1 = \Sigma(F_o - F_c)/\Sigma F_o$ observed data, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data), GOF = 1.102, $\Delta\rho_{max} = 0.896$ e Å^{-3}. Crystallographic data for $C_{28}H_{30}RuSn$ (**6**): monoclinic $P2_1/c$, $a = 17.8377(4)$, $b = 12.4501(3)$, $c = 31.9136(7)$ Å, $\beta = 93.826(1)°$, $V = 7071.6(3)$ Å^3, $Z = 12$, $\mu = 1.712\ \mathrm{mm^{-1}}$, $\rho_{calcd} = 1.652\ \mathrm{Mg\,m^{-3}}$, 150(1) K, Nonius Kappa-CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), pale yellow crystal ($0.26 \times 0.26 \times 0.03\ \mathrm{mm^3}$). Of 36931 reflections collected ($5.1 \leq 2\theta \leq 55.0°$) 16057 were independent $R_{int} = 0.0657$, and 10129 were observed with $F_o \geq 4\sigma(F_o)$. Solution and refinement as for **5**, $R1 = 0.0557$, $wR2 = 0.1296$, ($R1 = \Sigma(F_o - F_c)/\Sigma F_o$ observed data, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data), GOF = 1.015, $\Delta\rho_{max} = 1.47$ e Å^{-3}. CCDC-231377 (**6**) and -231378 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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