

# Facile Syntheses of Selenium- and Tellurium-Containing Metal Cubanes, $[\text{Cp}^*\text{M}(\mu_3\text{-E})]_4$ ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ; $\text{M} = \text{Rh}, \text{Ir}, \text{Ga}$ ; $\text{E} = \text{Se}, \text{Te}$ ), and X-ray Crystal Structures of $[\text{Cp}^*\text{RhSe}]_4$ , $[\text{Cp}^*\text{IrSe}]_4$ , $[\text{Cp}^*\text{RhTe}]_4$ , $[\text{Cp}^*\text{IrTe}]_4$ , and $[\text{Cp}^*\text{GaTe}]_4$

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Reactions of  $(\text{Cp}^*\text{MCl}_2)_2$  ( $\text{M} = \text{Rh}, \text{Ir}, \text{Ga}$ ) with  $\text{E}(\text{SiMe}_3)_2$  ( $\text{E} = \text{Se}, \text{Te}$ ) give in all cases complexes with tetrameric structures, which were identified by IR, NMR, and mass spectra, elemental analyses and X-ray single-crystal structure determinations. The reactions were carried out at room temperature, forming the products within a few minutes. After evaporation of solvent and  $\text{SiMe}_3\text{Cl}$ , the red-brown heterocubanes were isolated in nearly quantitative yields.  $[\text{Cp}^*\text{GaTe}]_4$  crystallizes in the monoclinic space group  $C2/m$ , and the other four compounds crystallize in the triclinic space group  $P\bar{1}$  with the following unit cell dimensions:  $a = 11.283(2)$  Å,  $b = 11.395(2)$  Å,  $c = 18.880(5)$  Å,  $\alpha = 81.39(1)^\circ$ ,  $\beta = 80.84(1)^\circ$ ,  $\gamma = 65.24(1)^\circ$ ,  $Z = 2$  ( $[\text{Cp}^*\text{RhSe}]_4$ , **1**);  $a = 11.365(7)$  Å,  $b = 11.451(9)$  Å,  $c = 18.98(2)$  Å,  $\alpha = 81.37(6)^\circ$ ,  $\beta = 80.81(4)^\circ$ ,  $\gamma = 65.07(3)^\circ$ ,  $Z = 2$  ( $[\text{Cp}^*\text{IrSe}]_4$ , **2**);  $a = 11.724(1)$  Å,  $b = 12.072(1)$  Å,  $c = 17.935(2)$  Å,  $\alpha = 88.61(1)^\circ$ ,  $\beta = 77.40(1)^\circ$ ,  $\gamma = 83.99(1)^\circ$ ,  $Z = 2$  ( $[\text{Cp}^*\text{RhTe}]_4$ , **3**);  $a = 11.664(3)$  Å,  $b = 12.071(3)$  Å,  $c = 18.076(4)$  Å,  $\alpha = 88.82(2)^\circ$ ,  $\beta = 77.22(2)^\circ$ ,  $\gamma = 84.32(2)^\circ$ ,  $Z = 2$  ( $[\text{Cp}^*\text{IrTe}]_4$ , **4**);  $a = 22.225(8)$  Å,  $b = 15.966(7)$  Å,  $c = 15.406(9)$  Å,  $\beta = 112.34(3)^\circ$ ,  $Z = 4$ , ( $[\text{Cp}^*\text{GaTe}]_4$ , **5**).

## Introduction

Organometallic compounds  $(\text{RMER}')_x$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ;  $\text{E} = \text{N}, \text{P}, \text{As}$ ;  $\text{R} = \text{alkyl}, \text{aryl}$ ) have been receiving attention due to their potential use as precursors of group 13–15 materials. In contrast, there are only a few examples known of isoelectronic compounds  $(\text{RME})_x$  of groups 13 and 16. This is surprising, since  $\text{InS}$  and  $\text{In}_2\text{S}_3$  have interesting electronic and optoelectronic properties.<sup>1–3</sup> The synthesis of the first selenium and tellurium heterocubanes of aluminum<sup>4</sup> spurred the investigation of a simple and general route for the preparation of these compounds.

Although the coordination chemistry of selenium and tellurium compounds has been developed in the last decade by the work of Fenske et al.,<sup>5,6</sup> the prediction of the size and structure of the clusters was nearly impossible. Systematic investigations of selenium- or tellurium-containing metal heterocubanes were almost unknown. In contrast, many investigations on O-, N-, and S-containing clusters have been reported and a number of structures of these compounds are well-known.<sup>7–9</sup>

A few examples of structurally characterized selenium and tellurium cubanes are known.<sup>10–12</sup> These were preferentially prepared by (a) thermal decomposition of transition-metal chalcogenide clusters, (b) reactions of metal chlorides with  $\text{LiSeH}$ , or (c) redox reactions. These methods are not generally applicable for generating heterocubanes. Only the recently published results by Houser et al. showed a straightforward route to ruthenium cubanes containing S, Se, and Te.<sup>13</sup>

Herein we report the reaction of  $(\text{Cp}^*\text{MCl}_2)_2$  with readily available  $\text{E}(\text{SiMe}_3)_2$  ( $\text{E} = \text{Se}, \text{Te}$ ) yielding a series of new heterocubanes.  $\text{Se}(\text{SiMe}_3)_2$  and  $\text{Te}(\text{SiMe}_3)_2$  function as chalcogenide transfer reagents with elimination of  $\text{SiMe}_3\text{Cl}$ .

## Results and Discussion

Heterocubanes of rhodium, iridium, and gallium are formed from the reaction of dimeric pentamethylcyclopentadienyl-substituted metal dichlorides with bis-(trimethylsilyl)selenium or -tellurium (Scheme 1).

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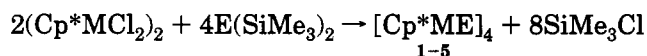
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Table 1. IR and <sup>1</sup>H NMR Data and Melting Points

	1	2	3	4	5
IR, cm <sup>-1</sup>	363	378	366	350	364
NMR, δ	1.92	1.99	1.86	1.88	1.82
mp, °C	185	178	178	165	>250

## Scheme 1



E = Se, M = Rh (1), Ir (2); E = Te, M = Rh (3),

Ir (4), Ga (5)

The formation of the heterocubanes proceeds readily at room temperature in nearly quantitative yields. All compounds are air and moisture sensitive. IR studies of the five compounds show a characteristic frequency at ca. 360 cm<sup>-1</sup>. In addition to the frequency at 364 cm<sup>-1</sup> for compound 5, two further absorptions at 430 and 272 cm<sup>-1</sup> are found. Comparable bands were also observed in the aluminum analogues [Cp\*AlSe]<sub>4</sub> and [Cp\*AlTe]<sub>4</sub>.<sup>4</sup>

The <sup>1</sup>H NMR spectra consist in all cases of one singlet, confirming the equal nature of the methyl groups (Table 1).

Compounds 1-5 have also been characterized by mass spectra (EI) and elemental analyses. The data are in good agreement with the theoretical data.

Transition-metal-chalcogenide cubanes are important because of their well-known capability as one electron carriers. In many biological processes iron-sulfur and iron-molybdenum-sulfur cubanes play an important role as electron donors and acceptors, e.g. in photosynthesis.<sup>14,15</sup> It will be interesting to study the effect of variation of either the transition metal or chalcogenide, as they will change the redox potential of the system. Furthermore, for the active center of nitrogenase an iron-sulfur and iron-molybdenum-sulfur cubane was postulated. In a recent work by Sellman and Cramer it was shown that the structure is formed of two cubanes with common squares.<sup>16,17</sup> We believe that the synthesis of the new heterocubanes will be helpful in studying the unknown details of this structure.

Compound 5 could function as a precursor for GaTe. Another point of interest is that the Cp\*Ga fragment is isolobal with Cd and Hg. CdSe and HgSe are interesting compounds for the formation of optoelectronic devices, and Cp\*GaTe may have comparable properties.

**X-ray Structures of Compounds 1-5.** Figure 1 shows the structure of the isomorphous compounds 1-4. Due to the small differences in the atomic radii of rhodium and iridium structures, 1 and 2, 3 and 4, respectively, are even isostructural. In the crystals of 3 and 4 there is one uncoordinated THF molecule in the asymmetric unit.

All compounds crystallize in space group  $P\bar{1}$ , although there is a noncrystallographic 4 axis through the

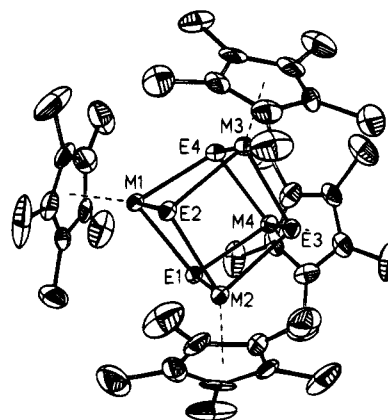


Figure 1. Crystal structure of the isomorphous compounds 1-4.

Table 2. Mean, Minimum, and Maximum Values of the Bond Angles (deg)

	1	2	3	4	5
M, E	Rh, Se	Ir, Se	Rh, Te	Ir, Te	Ga, Te
∠E-M-E (mean)	82.5	81.5	81.2	81.5	99.9
∠E-M-E (min)	82.0	81.1	79.9	81.2	96.6
∠E-M-E (max)	83.4	82.3	82.7	81.9	102.5
∠M-E-M (mean)	97.0	97.9	98.2	97.3	78.5
∠M-E-M (min)	96.0	97.0	97.2	98.5	76.9
∠M-E-M (max)	97.9	98.7	100.1	97.9	81.0

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1

Rh(1)-Se(2)	2.4546(13)	Rh(1)-Se(1)	2.4651(13)
Rh(1)-Se(4)	2.4710(14)	Rh(2)-Se(2)	2.4518(13)
Rh(2)-Se(1)	2.4612(14)	Rh(2)-Se(3)	2.4681(13)
Rh(3)-Se(2)	2.4552(13)	Rh(3)-Se(3)	2.4616(13)
Rh(3)-Se(4)	2.4659(14)	Rh(4)-Se(1)	2.4622(13)
Rh(4)-Se(3)	2.4625(14)	Rh(4)-Se(4)	2.4695(13)
Se(2)-Rh(1)-Se(1)	82.30(4)	Se(2)-Rh(1)-Se(4)	82.67(4)
Se(1)-Rh(1)-Se(4)	82.10(4)	Se(2)-Rh(2)-Se(1)	82.43(4)
Se(2)-Rh(2)-Se(3)	82.01(4)	Se(1)-Rh(2)-Se(3)	83.25(4)
Se(2)-Rh(3)-Se(3)	82.08(4)	Se(2)-Rh(3)-Se(4)	82.77(4)
Se(3)-Rh(3)-Se(4)	82.28(4)	Se(1)-Rh(4)-Se(3)	83.35(4)
Se(1)-Rh(4)-Se(4)	82.19(4)	Se(3)-Rh(4)-Se(4)	82.19(4)
Rh(2)-Se(1)-Rh(4)	96.16(5)	Rh(2)-Se(1)-Rh(1)	96.92(4)
Rh(4)-Se(1)-Rh(1)	97.68(4)	Rh(2)-Se(2)-Rh(1)	97.44(4)
Rh(2)-Se(2)-Rh(3)	97.87(4)	Rh(1)-Se(2)-Rh(3)	96.98(5)
Rh(3)-Se(3)-Rh(4)	97.52(5)	Rh(3)-Se(3)-Rh(2)	97.27(4)
Rh(4)-Se(3)-Rh(2)	95.98(5)	Rh(3)-Se(4)-Rh(4)	97.23(5)
Rh(3)-Se(4)-Rh(1)	96.27(5)	Rh(4)-Se(4)-Rh(1)	97.33(4)

midpoints of two metal-element faces. Interestingly the isomorphous compound [η<sup>5</sup>-Cp\*IrS]<sub>4</sub><sup>9</sup> crystallizes in  $I\bar{4}$ , while the space group of [η<sup>5</sup>-Cp\*IrS]<sub>2</sub>[η<sup>5</sup>-Cp\*RhS]<sub>2</sub><sup>9</sup> is  $P\bar{1}$ . The molecules 1-4 do not form regular cubes. The element-metal-element angles are about 16° smaller than the metal-element-metal angles (see Table 2). Corresponding to the different atomic radii, the smaller element atoms cause smaller angles at the metal atoms. The faces of the cube are not quite planar (mean deviation about 0.09 Å). The element atoms are pulled slightly into the cube.

5 (see Figure 2) is the third example of a gallium-chalcogenide heterocubane which has been characterized by X-ray single-crystal determination and is the first gallium-tellurium heterocubane. The other compounds known are [Bu<sup>t</sup>GaS]<sub>4</sub><sup>18</sup> and [Bu<sup>t</sup>GaSe]<sub>4</sub>.<sup>19</sup> In 5

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**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for 2

Ir(1)—Se(1)	2.489(2)	Ir(1)—Se(4)	2.492(2)
Ir(1)—Se(2)	2.499(2)	Ir(2)—Se(3)	2.482(2)
Ir(2)—Se(1)	2.492(2)	Ir(2)—Se(2)	2.501(2)
Ir(3)—Se(3)	2.483(2)	Ir(3)—Se(4)	2.494(2)
Ir(3)—Se(2)	2.496(2)	Ir(4)—Se(3)	2.482(2)
Ir(4)—Se(1)	2.490(2)	Ir(4)—Se(4)	2.495(2)
Se(1)—Ir(1)—Se(4)	82.27(7)	Se(1)—Ir(1)—Se(2)	81.21(8)
Se(4)—Ir(1)—Se(2)	81.46(7)	Se(3)—Ir(2)—Se(1)	81.52(7)
Se(3)—Ir(2)—Se(2)	81.52(7)	Se(1)—Ir(2)—Se(2)	81.10(8)
Se(3)—Ir(3)—Se(4)	81.20(8)	Se(3)—Ir(3)—Se(2)	81.62(7)
Se(4)—Ir(3)—Se(2)	81.49(7)	Se(3)—Ir(4)—Se(1)	81.55(7)
Se(3)—Ir(4)—Se(4)	81.21(8)	Se(1)—Ir(4)—Se(4)	82.18(7)
Ir(1)—Se(1)—Ir(4)	97.17(7)	Ir(1)—Se(1)—Ir(2)	98.65(8)
Ir(4)—Se(1)—Ir(2)	97.58(8)	Ir(3)—Se(2)—Ir(1)	97.88(8)
Ir(3)—Se(2)—Ir(2)	97.28(7)	Ir(1)—Se(2)—Ir(2)	98.12(8)
Ir(4)—Se(3)—Ir(2)	98.07(7)	Ir(4)—Se(3)—Ir(3)	98.61(8)
Ir(2)—Se(3)—Ir(3)	98.12(7)	Ir(1)—Se(4)—Ir(3)	98.09(8)
Ir(1)—Se(4)—Ir(4)	96.96(7)	Ir(3)—Se(4)—Ir(4)	97.97(8)

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for 3

Rh(1)—Te(1)	2.605(2)	Rh(1)—Te(4)	2.608(2)
Rh(1)—Te(2)	2.628(2)	Rh(2)—Te(1)	2.610(3)
Rh(2)—Te(3)	2.611(2)	Rh(2)—Te(2)	2.622(2)
Rh(3)—Te(4)	2.608(3)	Rh(3)—Te(3)	2.619(3)
Rh(3)—Te(2)	2.651(2)	Rh(4)—Te(1)	2.582(2)
Rh(4)—Te(3)	2.607(2)	Rh(4)—Te(4)	2.609(2)
Te(1)—Rh(1)—Te(4)	81.48(7)	Te(1)—Rh(1)—Te(2)	80.61(7)
Te(4)—Rh(1)—Te(2)	80.30(7)	Te(1)—Rh(2)—Te(3)	82.06(7)
Te(1)—Rh(2)—Te(2)	80.62(7)	Te(3)—Rh(2)—Te(2)	81.22(7)
Te(4)—Rh(3)—Te(3)	81.34(7)	Te(4)—Rh(3)—Te(2)	79.88(7)
Te(3)—Rh(3)—Te(2)	80.53(7)	Te(1)—Rh(4)—Te(3)	82.68(7)
Te(1)—Rh(4)—Te(4)	81.90(7)	Te(3)—Rh(4)—Te(4)	81.55(7)
Rh(4)—Te(1)—Rh(1)	97.98(7)	Rh(4)—Te(1)—Rh(2)	97.27(7)
Rh(1)—Te(1)—Rh(2)	99.26(8)	Rh(2)—Te(2)—Rh(1)	98.38(8)
Rh(2)—Te(2)—Rh(3)	97.97(8)	Rh(1)—Te(2)—Rh(3)	98.48(8)
Rh(4)—Te(3)—Rh(2)	96.63(8)	Rh(4)—Te(3)—Rh(3)	97.82(8)
Rh(2)—Te(3)—Rh(3)	99.03(8)	Rh(3)—Te(4)—Rh(1)	100.07(8)
Rh(3)—Te(4)—Rh(4)	98.06(8)	Rh(1)—Te(4)—Rh(4)	97.21(7)

**Table 6.** Selected Bond Lengths (Å) and Angles (deg) for 4

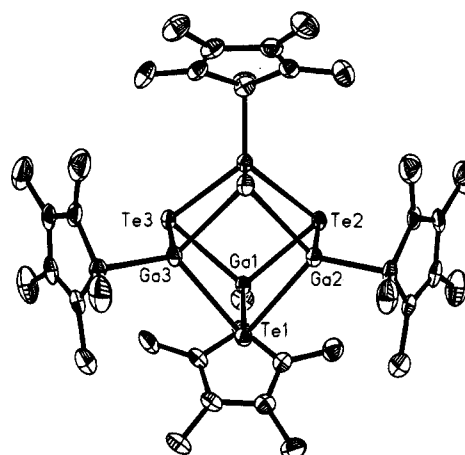
Ir(1)—Te(1)	2.6257(13)	Ir(1)—Te(4)	2.6329(14)
Ir(1)—Te(2)	2.6390(13)	Ir(2)—Te(1)	2.6214(13)
Ir(2)—Te(3)	2.6308(14)	Ir(2)—Te(2)	2.6367(13)
Ir(3)—Te(3)	2.6261(13)	Ir(3)—Te(4)	2.6274(13)
Ir(3)—Te(2)	2.6433(14)	Ir(4)—Te(1)	2.6221(14)
Ir(4)—Te(3)	2.6286(13)	Ir(4)—Te(4)	2.6313(13)
Te(1)—Ir(1)—Te(4)	81.36(4)	Te(1)—Ir(1)—Te(2)	81.20(4)
Te(4)—Ir(1)—Te(2)	81.39(4)	Te(1)—Ir(2)—Te(3)	81.87(4)
Te(1)—Ir(2)—Te(2)	81.32(4)	Te(3)—Ir(2)—Te(2)	81.43(4)
Te(3)—Ir(3)—Te(4)	81.88(4)	Te(3)—Ir(3)—Te(2)	81.39(4)
Te(4)—Ir(3)—Te(2)	81.41(4)	Te(1)—Ir(4)—Te(3)	81.90(4)
Te(1)—Ir(4)—Te(4)	81.46(4)	Te(3)—Ir(4)—Te(4)	81.76(4)
Ir(2)—Te(1)—Ir(4)	97.65(4)	Ir(2)—Te(1)—Ir(1)	98.51(4)
Ir(4)—Te(1)—Ir(1)	98.21(4)	Ir(2)—Te(2)—Ir(1)	97.79(4)
Ir(2)—Te(2)—Ir(3)	97.78(5)	Ir(1)—Te(2)—Ir(3)	97.73(5)
Ir(3)—Te(3)—Ir(4)	97.63(4)	Ir(3)—Te(3)—Ir(2)	98.36(5)
Ir(4)—Te(3)—Ir(2)	97.26(4)	Ir(3)—Te(4)—Ir(4)	97.53(4)
Ir(3)—Te(4)—Ir(1)	98.28(5)	Ir(4)—Te(4)—Ir(1)	97.80(4)

the cube lies on a mirror plane through the atoms Te(2), Te(3), Ga(2), and Ga(3). There is half an uncoordinated THF molecule in the asymmetric unit. The cube of **5** is more distorted than those in **1–4**. Here the Ga atom is smaller than the Te atom so that the Ga—Te—Ga angles are about 22° smaller than the Te—Ga—Te angles and the Ga atoms are pulled into the cube. In contrast to  $\eta^5$ -coordinated Cp\* rings in [Cp\*AlTe]<sub>4</sub>,<sup>4</sup> the Cp\* rings in **5** are  $\sigma$ -bonded. **5** is the third structurally characterized compound with Ga—Te bonds, but its structure is not comparable to the structures of [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Ga—TeSi(SiMe<sub>3</sub>)<sub>3</sub><sup>20</sup> and [(Bu<sup>t</sup>CH<sub>2</sub>)<sub>2</sub>Ga—TePh]<sub>2</sub>.<sup>21</sup>

**Table 7.** Selected Bond Lengths (Å) and Angles (deg) for 5

Ga(1)—Te(1)	2.652(2)	Ga(1)—Te(3)	2.6729(10)
Ga(1)—Te(2)	2.6865(10)	Ga(2)—Te(2)	2.656(2)
Ga(2)—Te(1)	2.6917(10)	Ga(3)—Te(3)	2.650(2)
Ga(3)—Te(1)	2.6905(10)		
Te(1)—Ga(1)—Te(3)	102.52(3)	Te(1)—Ga(1)—Te(2)	102.26(3)
Te(3)—Ga(1)—Te(2)	97.45(4)	Te(2)—Ga(2)—Te(1)	102.01(3)
Te(1) <sup>†</sup> —Ga(2)—Te(1)	96.59(4)	Te(3)—Ga(3)—Te(1)	102.09(3)
Te(1)—Ga(3)—Te(1) <sup>†</sup>	96.64(4)	Ga(1)—Te(1)—Ga(3)	76.92(3)
Ga(1)—Te(1)—Ga(2)	77.22(3)	Ga(3)—Te(1)—Ga(2)	80.98(4)
Ga(2)—Te(2)—Ga(1)	77.23(3)	Ga(1) <sup>†</sup> —Te(2)—Ga(1)	79.83(4)
Ga(3)—Te(3)—Ga(1)	77.25(3)	Ga(1)—Te(3)—Ga(1) <sup>†</sup>	80.32(4)

<sup>a</sup> Symmetry transformation used to generate equivalent atoms: (†) *x*,  $-y$ , *z*.

**Figure 2.** Crystal structure of compound **5**.

**Conclusions.** We describe a facile procedure for the preparation of pentamethylcyclopentadienyl-substituted selenium- and tellurium-containing metal cubanes. It is obvious that other heterocubanes of the type [Cp\**M*-( $\mu_3$ -E)]<sub>4</sub> may be obtained by following this route. Compounds **1–5** might be interesting precursors for materials science.

## Experimental Section

All manipulations were carried out on a conventional vacuum line using standard Schlenk or syringe techniques and a glovebox under an atmosphere of dry nitrogen. Solvents were dried and purified prior to use, followed by distillation under an atmosphere of nitrogen.

Infrared spectra were recorded on a Bio-Rad Digilab FTS 7; only selected, characteristic frequencies are given. Nuclear magnetic resonance spectra were recorded on a Bruker WP 80 SY or an AM 250 spectrometer. Elemental analyses were carried out at our institute. Mass spectra were recorded on Finnigan MAT 8230 and Varian MAT CH5 spectrometers.

The pentamethylcyclopentadienyl-substituted metal dichlorides and bis(trimethylsilyl)selenium and -tellurium were prepared according to literature methods.<sup>22–24</sup>

**General Procedure.** A 100 mL flask was charged with Cp\**M*Cl<sub>2</sub> (1.5 mmol; *M* = Rh, Ir, Ga) and toluene (40 mL). Then Se(SiMe<sub>3</sub>)<sub>2</sub> (0.68 g, 3.0 mmol) or Te(SiMe<sub>3</sub>)<sub>2</sub> (1.37 g, 3.0 mmol) were added with a syringe at room temperature. The color changed immediately to red or brown. The reaction mixture

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Table 8. Crystal Data and Structure Refinement Details for 1–5

	1	2	3	5	5
formula	C <sub>40</sub> H <sub>60</sub> Rh <sub>4</sub> Se <sub>4</sub>	C <sub>40</sub> H <sub>60</sub> Ir <sub>4</sub> Se <sub>4</sub>	C <sub>40</sub> H <sub>60</sub> Rh <sub>4</sub> Te <sub>4</sub> C <sub>4</sub> H <sub>8</sub> O	C <sub>40</sub> H <sub>60</sub> Ir <sub>4</sub> Te <sub>4</sub> C <sub>4</sub> H <sub>8</sub> O	C <sub>40</sub> H <sub>60</sub> Ga <sub>4</sub> Te <sub>4</sub> C <sub>4</sub> H <sub>8</sub> O
<i>M<sub>r</sub></i>	1268.36	1625.52	1535.02	1892.18	1402.26
cryst syst	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>m</i>
<i>a</i> (Å)	11.283(2)	11.365(7)	11.724(1)	11.664(3)	22.225(8)
<i>b</i> (Å)	11.395(2)	11.451(9)	12.072(1)	12.071(3)	15.966(7)
<i>c</i> (Å)	18.880(5)	18.980(20)	17.935(2)	18.076(4)	15.406(9)
$\alpha$ (deg)	81.39(1)	81.37(6)	88.61(1)	88.82(2)	90
$\beta$ (deg)	80.84(1)	80.81(4)	77.40(1)	77.22(2)	112.34(3)
$\gamma$ (deg)	65.24(1)	65.07(3)	83.99(1)	84.32(2)	90
<i>V</i> (Å <sup>3</sup> )	2166.8(8)	2202(3)	2463.6(4)	2470(1)	5056(4)
<i>Z</i>	2	2	2	2	4
<i>D<sub>x</sub></i> (g cm <sup>-3</sup> )	1.944	2.452	2.069	2.544	1.842
$\mu$ (mm <sup>-1</sup> )	4.883	15.382	3.668	13.088	4.400
<i>F</i> (000)	1232	1488	1456	1712	2688
cryst size (mm)	0.05 × 0.1 × 0.1	0.3 × 0.3 × 0.4	0.05 × 0.1 × 0.1	0.1 × 0.2 × 0.2	0.15 × 0.25 × 0.4
2 $\theta$ range (deg)	8–45	7–45	8–45	8–45	8–45
range of <i>hkl</i>	-11 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 12, -19 ≤ <i>l</i> ≤ 20	-11 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 20	-12 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 13, -17 ≤ <i>l</i> ≤ 19	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 19	-23 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 17, -16 ≤ <i>l</i> ≤ 16
no. of rflns coll	8194	11 309	8206	11 957	4526
no. of indep rflns	5699	5739	6430	6479	3455
<i>R</i> (int)	0.0671	—	0.0656	0.0651	0.0507
<i>T<sub>min</sub></i>	0.791	0.449	0.672	0.473	0.514
<i>T<sub>max</sub></i>	0.926	0.922	0.759	0.940	0.770
no. of data	5693	5733	6427	6476	3450
no. of params.	453	454	623	593	330
restraints	0	1880	2933	3012	224
<i>S</i>	1.030	1.061	1.013	1.025	1.050
<i>R</i> 1 ( <i>F</i> > 4 $\sigma$ ( <i>F</i> ))	0.0362	0.0444	0.0938	0.0475	0.0282
w <i>R</i> 2 (all data)	0.0936	0.1229	0.2466	0.1268	0.0743
largest diff peak and hole (e Å <sup>-3</sup> )	0.85, -0.90	2.45, -1.85	6.98, -1.88	2.13, -1.74	0.65, -0.71

was stirred for 2 h; the solvent and SiMe<sub>3</sub>Cl were removed in vacuo. **1** and **2** were recrystallized from toluene; **3–5** were recrystallized from THF.

[Cp\***Rh**Se]<sub>4</sub> (**1**): yield 0.85 g (89%); mp 185 °C. Anal. Calcd for C<sub>40</sub>H<sub>60</sub>Rh<sub>4</sub>Se<sub>4</sub>: C, 37.87; H, 4.77. Found: C, 37.6; H, 4.9. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  1.92. EI (MS): *m/z* 1270 (M<sup>+</sup>). IR (Nujol, CsI):  $\nu$  363 br cm<sup>-1</sup>.

[Cp\***Ir**Se]<sub>4</sub> (**2**): yield 1.13 g (93%); mp 178 °C. Anal. Calcd for C<sub>40</sub>H<sub>60</sub>Ir<sub>4</sub>Se<sub>4</sub>: C, 29.55; H, 3.72. Found: C, 28.5; H, 3.8. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  1.99. EI (MS): *m/z* 1626 (M<sup>+</sup>). IR (Nujol, CsI):  $\nu$  466 br, 378 sst, 227 st cm<sup>-1</sup>.

[Cp\***Rh**Te]<sub>4</sub> (**3**): yield 1.80 g (97%); mp 165 °C. Anal. Calcd for C<sub>40</sub>H<sub>60</sub>Rh<sub>4</sub>Te<sub>4</sub>: C, 32.81; H, 4.12. Found: C, 36.2; H, 4.8. <sup>1</sup>H NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>DN):  $\delta$  1.88. EI (MS): *m/z* 1464 (M<sup>+</sup>). IR (Nujol, CsI):  $\nu$  578 m, 536 br, 397 br, 350 br cm<sup>-1</sup>.

[Cp\***Ir**Se]<sub>4</sub> (**4**): yield 2.18 g (96%); mp 178 °C. Anal. Calcd for C<sub>40</sub>H<sub>60</sub>Ir<sub>4</sub>Se<sub>4</sub>: C, 26.41; H, 3.31. Found: C, 25.2; H, 3.4. <sup>1</sup>H NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.86. EI (MS): *m/z* 1822 (M<sup>+</sup>). IR (Nujol, CsI):  $\nu$  535 m, 464 m, 366 br cm<sup>-1</sup>.

[Cp\***Ga**Te]<sub>4</sub> (**5**): yield 0.55 g (83%); mp >250 °C. Anal. Calcd for C<sub>40</sub>H<sub>60</sub>Ga<sub>4</sub>Te<sub>4</sub>: C, 36.12; H, 4.55. Found: C, 35.7; H, 5.2. <sup>1</sup>H NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.82. EI (MS): *m/z* 1332 (M<sup>+</sup>). IR (Nujol, CsI):  $\nu$  585 sst, 430 sst, 364 br, 272 sst, 227 st cm<sup>-1</sup>.

**X-ray Structure Determination for 1–5.** Data were collected at -120 °C on a Siemens-Stoe-Huber diffractometer for **1** and **3–5** and on a Siemens-Stoe-AED2 instrument for **2**. Monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) was used in all cases. Semiempirical absorption correction was employed. The structures were solved by direct methods.<sup>25</sup> All non-hydrogen atoms were refined anisotropically.<sup>26</sup> For the hydrogen atoms the riding model was used. The structures

were refined against *F*<sup>2</sup> with a weighting scheme of  $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$  with  $P = (F_o^2 + 2F_c^2)/3$ . The *R* values are defined as  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{0.5}$  and  $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ .

The THF molecules in **3–5** are disordered. They were refined as five-membered carbon rings with distant restraints and restraints for the anisotropic displacement parameters. In the structures of **3** and **4** also one Cp\* group is disordered and was refined with restraints.

Because of weak data the structure of **3** is not well determined and several high residual density peaks are found. Only because of the similarities of **1–4** is this structure reported here.

For **2** an extinction correction ( $F_c^* = kF_c[1 + 0.001x(F_c^2)^{0.5} / (\sin 2\theta)]^{-0.25}$  with  $x = 0.00030(8)$ ) was applied.

The crystal data for the structures of **1–5** are summarized in Table 8.

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**Supplementary Material Available:** For **1–5**, tables of crystal data and structure refinement details, atomic coordinates, displacement parameters, and bond distances and angles and figures giving additional views of the structures (46 pages). Ordering information is given on any current masthead page.

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