

Scheme 2. Reactions of **1** ( $X^1, X^2 = O$ ; a), **8** ( $X^1, X^2 = N-NH-Ts$ ; b), **9** ( $X^1, X^2 = N-NNa-Ts$ ; c, d), and **10** ( $X^1 = H, X^2 = Me-SO_3$ ; f). a)  $Al_2O_3$ , b)  $MeLi, Et_2O, 0^\circ C$ . c)  $125^\circ C$ . d)  $h\nu, THF, 20^\circ C$ . e) Preparative gas chromatography, Carbowax,  $160^\circ C$ . f)  $KOtBu$ .

The rearrangements observed for **1** and its derivatives, such as the tosyl hydrazone **8** or the methanesulfonate **10**, are summarized in Scheme 2. Compound **1**, which is stable at room temperature, undergoes rearrangement within a few minutes in the presence of  $Al_2O_3$  (neutral, activity I) to give quantitatively **11**,<sup>[4]</sup> from which the  $C_{10}H_{10}$  isomer **12**<sup>[5]</sup> may be obtained. When **8** was allowed to react with excess  $MeLi$  in  $Et_2O$  at  $0^\circ C$ ,<sup>[6]</sup> we obtained tricyclo[5.3.0.0<sup>4,8</sup>]deca-2,5,9-triene **13**,<sup>[7]</sup> instead of the expected isomer **2**. The pyrolysis products obtained by heating **9** (sodium salt of **8**) without a solvent to  $120^\circ C$  were trapped at 10 K in an argon matrix in the window of an IR spectrometer; 7-(2-propynyl)-1,3,5-cycloheptatriene **14**<sup>[8]</sup> and 7-(1,2-propadienyl)-1,3,5-cycloheptatriene **15**, formed in a

Table 1. Spectroscopic data for the compounds **1**, **5**, **11**, **17**, and **18**. <sup>1</sup>H-NMR: 300 MHz,  $CDCl_3$ ; <sup>13</sup>C-NMR: 75.46 MHz,  $CDCl_3$ .

**1**: IR (film):  $\tilde{\nu} = 1755\text{ cm}^{-1}$ ; <sup>1</sup>H-NMR:  $\delta = 1.63$  (s, 2H), 2.45 (s, 2H), 2.95–2.97 (d, 2H,  $J = 5.8$  Hz), 6.11–6.22 (m, 4H); <sup>13</sup>C-NMR:  $\delta = 23.9$  (d), 43.0 (d), 45.8 (t), 52.1 (d), 126.8 (d), 132.5 (d), 212.4 (s); UV ( $H_2CCN$ ):  $\lambda_{max}(\epsilon) = 275\text{ nm}$  (3870)

**5**: IR (KBr):  $\tilde{\nu} = 1680\text{ cm}^{-1}$ ; <sup>1</sup>H-NMR:  $\delta = 2.03$ –2.12 (m, 2H), 2.33–2.42 (m, 3H), 2.73 (d, 1H,  $J = 7.5$  Hz), 2.78 (d, 1H,  $J = 7.5$  Hz), 2.84 (d, 1H,  $J = 5.75$  Hz), 2.92 (d, 1H,  $J = 13.3$  Hz), 2.98 (d, 1H,  $J = 13.3$  Hz), 3.89–4.04 (m, 8H); <sup>13</sup>C-NMR:  $\delta = 38.8$  (t), 42.9 (d), 44.2 (t), 47.3 (d), 51.7 (t), 53.5 (d), 64.2 (d), 64.4 (t), 64.5 (t), 64.7 (t), 106.7 (s), 114.7 (s), 207.0 (s)

**11**: IR (film):  $\tilde{\nu} = 1700\text{ cm}^{-1}$ ; <sup>1</sup>H-NMR (500 MHz):  $\delta = 1.80$ –1.83 (dd, 1H,  $J = 4.9, 10.3$  Hz), 2.13–2.17 (m, 1H), 2.17–2.23 (dd, 1H,  $J = 19.2, 8.0$  Hz), 2.45–2.53 (dd, 1H,  $J = 19.2, 10.6$  Hz), 2.55–2.59 (ddd, 1H,  $J = 5.4, 6.4, 4.9$  Hz), 3.24–3.32 (m, 1H), 5.80–5.84 (dd, 1H,  $J = 10.6, 5.6$  Hz), 6.03–6.05 (ddd, 1H,  $J = 10.6, 5.6, 1.1$  Hz), 6.17–6.27 (m, 2H); UV ( $CDCl_3$ ):  $\lambda_{max}(\epsilon) = 258\text{ nm}$  (4200)

**17**: <sup>1</sup>H-NMR:  $\delta = 2.54$ –2.61 (dd, 1H,  $J = 18.6, 9.3$  Hz), 2.70–2.90 (m, 1H,  $J = 9.3$  Hz), 3.12–3.27 (dd, 1H,  $J = 18.6, 9.3$  Hz), 5.36–5.38 (dd, 1H,  $J = 9.7, 3.7$  Hz), 6.01–6.09 (m, 2H), 6.19 (s, 2H), 6.23–6.25 (dd, 1H,  $J = 11.1, 6.2$  Hz), 6.43–6.48 (dd, 1H,  $J = 11.1, 6.2$  Hz); UV (*n*-hexane):  $\lambda_{max} = 318\text{ nm}$

**18**: <sup>1</sup>H-NMR:  $\delta = 3.06$ –3.10 (m, 1H), 3.30 (d, 2H,  $J = 4, 4$  Hz), 5.00–5.04 (dd, 1H,  $J = 9.7, 4.4$  Hz), 5.92–5.96 (m, 1H), 6.00–6.06 (m, 2H), 6.19–6.21 (br, 1H), 6.43–6.48 (dd, 1H,  $J = 11.5, 5.7$  Hz), 6.52–6.58 (dd, 1H,  $J = 11.5, 5.7$  Hz); UV (*n*-hexane):  $\lambda_{max} = 276\text{ nm}$

ratio of 2 : 1 (<sup>1</sup>H-NMR spectrum), were detected. Compounds **14** and **15** were also obtained by irradiation of a solution of **9** in degassed THF at room temperature. Upon heating (GC), compound **15** undergoes rearrangement to give 2-methylenebicyclo[3.2.2]nona-3,6,8-triene **16**.<sup>[9]</sup>

The reaction of **10** with  $KOtBu$  leads to the two unknown dihydroazulenes **17** and **18**, the structures of which were established from the spectroscopic data (Table 1) and from the observation that both compounds undergo oxidation with chloranil to give azulene. Two further isomeric dihydroazulenes were obtained in about 15% yield but could not be separated and identified.

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**1**, 104291-26-1; **3**, 53578-24-8; **4**, 104291-23-8; **5**, 104291-24-9; **7**, 104291-25-0; **8**, 104291-27-2; **9**, 104291-28-3; **10**, 104291-30-7; **11**, 15719-07-0; **13**, 16749-40-9; **14**, 14760-05-5; **15**, 104291-29-4; **16**, 38898-40-7; **17**, 104291-31-8; **18**, 104291-32-9.

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## Synthesis and Structure of $[(C_5Me_5)_2M_2Se_3]$ : Formation of a $\mu, \eta^2$ -Tetraselenide Ligand at the M–M Double Bond of $[(C_5Me_5)_2M_2(\mu-CO)_2]$ (M = Co, Rh)\*\*

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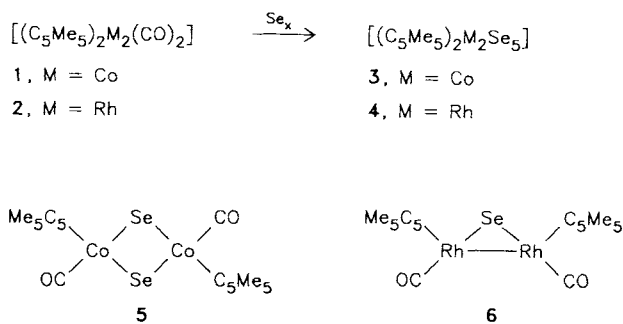
A rational synthesis of chalcogen-rich cyclopentadienyl transition-metal complexes has been achieved by addition of elemental sulfur or selenium to the M–M triple bond of the complexes  $[(C_5Me_5)_2M_2(CO)_4]$  (M = Cr, Mo, W).<sup>[1]</sup> Substitution of all the CO groups leads, via labile addition adducts,<sup>[2]</sup> to complexes having one- and two-atom chalcogen ligands displaying a variety of coordinations. Bridging ligands with more than two atoms are not formed in these reactions, however, even though they are well documented for sulfur (but not for selenium).<sup>[3]</sup> We report here the synthesis of a complex containing a tetraselenide ligand by stepwise addition of selenium to the M–M double bond of  $[(C_5Me_5)_2M_2(\mu-CO)_2]$  (M = Co, Rh).

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[\*\*] Reactivity of the M–M Multiple Bond in Metal Carbonyl Derivatives, Part 12.—Part 11: I. Bernal, M. Draux, H. Brunner, B. Hoffmann, J. Wachter, *Organometallics* 5 (1986) 655.

The reaction of the  $\text{Co}_2$  and  $\text{Rh}_2$  complexes **1** and **2**, respectively, with an excess of gray selenium in toluene (18 h, room temperature) affords, after chromatography on  $\text{Al}_2\text{O}_3$ , the carbonyl-free, diamagnetic complexes **3** (violet-brown) and **4** (dark green), respectively. Whereas the formation of **3** occurs surprisingly smoothly (80% yield), **4** (19% yield) is obtained along with two, as yet unidentified, likewise CO-free products. The  $^1\text{H-NMR}$  spectra<sup>[4]</sup> of **3** and **4** support a symmetrical structure. Each of the  $^{77}\text{Se-NMR}$  spectra<sup>[4]</sup> contains two groups of relatively broad signals having no fine structure (intensity ratio 3:2), the chemical shifts of which are strikingly similar to those of organic tetraselenides.<sup>[5]</sup> Less informative are the very weak IR absorptions between  $\tilde{\nu}=300$  and  $400\text{ cm}^{-1}$ , the region of M–Se–M and Se–Se vibrations.



An X-ray structure analysis<sup>[6]</sup> revealed the presence of two types of selenide ligands in **4**: a  $\text{Se}^{2\ominus}$  and a nearly planar  $\text{Se}_4^{2\ominus}$  ligand are situated in the same plane (deviation  $\leq 0.009\text{ \AA}$ ), which intersects the midpoint of the Rh–Rh axis and is perpendicular to it (Fig. 1). Owing to the eighteen-electron rule, the two ligands contribute eight electrons to the electron count of the two Rh atoms, which thereby achieve a noble-gas configuration when the five electrons of the  $\text{C}_5\text{Me}_5$  ligands are included, without the necessity of a metal–metal bond. The Se–Se distances in the  $\text{Se}_4^{2\ominus}$  ligands are nearly identical and their average value (2.37  $\text{\AA}$ ) is similar to those in trigonal selenium.<sup>[7]</sup> The relatively small Se1–Se4–Se5 angle (98.6(1) $^\circ$ ) appears to be determined by the size of the ring. Se1, Se2, and Se3

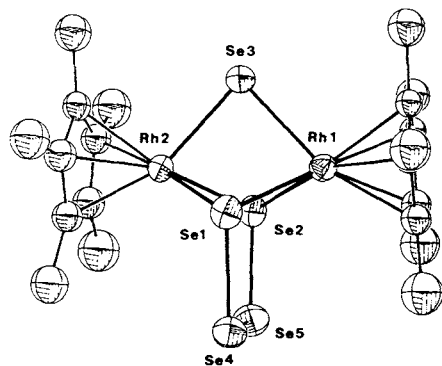


Fig. 1. Crystal structure of **4** (ORTEP plot). Selected bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ]: Rh1–Se1 2.481(2), Rh1–Se2 2.460(2), Rh1–Se3 2.476(2), Rh2–Se1 2.479(2), Rh2–Se2 2.464(2), Rh2–Se3 2.473(2), Se1–Se4 2.373(2), Se2–Se5 2.370(2), Se4–Se5 2.368(2), Se1...Se2 3.115(2), Se1...Se3 3.102(2); Se1–Rh1–Se2 78.2(1), Rh1–Se1–Rh2 86.4(1), Rh1–Se2–Rh2 87.2, Rh1–Se3–Rh2 86.6(1), Rh1–Se1–Se4 105.2(1), Se1–Se4–Se5 98.6(1), Se2–Se5–Se4 99.5(1), Se2–Se1–Se3 60.3(0). Only one of the two independent, nearly identical molecules is shown.

form a nearly equilateral triangle with separations of about 3.101  $\text{\AA}$ , which are much less than the sums of the van der Waals radii of two Se atoms (3.80  $\text{\AA}$ ). Interactions of this order of magnitude are sufficient, for example, to dimerize two  $[\text{W}(\text{CO})_5(\eta^2\text{-Se}_2)]^\ominus$  molecules to form a molecule with  $\text{Se}_4^{2\ominus}$  bridges.<sup>[8]</sup> This tendency is further revealed, albeit less strongly, in the molecular lattice of **4**, in which neighboring molecules are linked together to form chains by means of intermolecular interactions ( $d_{\text{Se-Se}}=3.50\text{ \AA}$ ) between Se3 of one molecule and Se4/Se5 of another.

These structural findings might explain the ready formation of the complexes **3** and **4**. The reaction of **1** with  $\text{S}_8$  affords only a small yield of  $[(\text{C}_5\text{Me}_5)_2\text{Co}_2\text{S}_4]^{19}$ . A Se analogue of the  $\mu\text{-}\eta^1,\eta^2\text{-S}_2$  ligand that characterizes this compound, namely,  $[(\text{triphos})_2\text{Rh}_2\text{Se}_4][\text{PPh}_4]_2$  (triphos =  $\text{H}_3\text{CC}(\text{CH}_2\text{PPh}_2)_3$ ), is also known.<sup>[10]</sup> In the case of **3** and **4**, instead, a planar  $\text{Se}_4/\text{Se}$  ligand system is formed, which can be viewed alternatively as an  $\eta^3\text{-Se}_5$  ligand. Comparable sulfur ligands are not planar.<sup>[11]</sup>

The stability of the polyselenide ligands in **3** and **4** is so pronounced that the dark brown diselenium adduct **5**,<sup>[4]</sup> obtained from **1** at  $0^\circ\text{C}$ , and the known monoselenium adduct **6**<sup>[12]</sup> undergo reaction at room temperature in toluene to afford mixtures from which **3** and **4**, respectively, may be isolated. Since **5** and **6** also undergo reaction with selenium in toluene to give **3** and **4** in appreciably better yields, the reactions **1**  $\rightarrow$  **3** and **2**  $\rightarrow$  **4** may be interpreted as occurring by stepwise addition of selenium to the M–M double bond with subsequent CO substitution.

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