Synthesis and Characterization of Cubane-Like Cr_4E_4 (E = S, Se) Clusters − Molecular Structures of $(\eta^5\text{-}RC_5H_4)_4Cr_4E_4$ (E = S, R = MeCO, MeO_2C, EtO_2C; E = Se, R = H)

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Treatment of the Cr–Cr singly-bonded dimers $[\eta^5\text{-}RC_5H_4Cr(CO)_3]_2$ (**1**, R = MeCO; **2**, R = MeO_2C; **3**, R = EtO_2C) with excess sulfur in refluxing THF gave the cubane Cr_4S_4 clusters $(\eta^5\text{-}RC_5H_4)_4Cr_4S_4$ (**4**, R = MeCO; **5**, R = MeO_2C; **6**, R = EtO_2C). The cubane Cr_4S_4 cluster **4** reacted with excess 2,4-dinitrophenylhydrazine to produce the hydrazone derivative $[\eta^5\text{-}2,4\text{-}(NO_2)_2C_6H_3NHN{=}C(Me)C_5H_4]_4Cr_4S_4$ (**7**). The singly-bonded dimers of $[\eta^5\text{-}RC_5H_4Cr(CO)_3]_2$ (**8**, R = Me; **9**, R = EtO_2C), in the presence of excess selenium, reacted similarly to the linear Cr_2Se complexes $[\eta^5\text{-}RC_5H_4Cr(CO)_2]_2Se$ (**10**, R = Me; **11**, R = EtO_2C), which reacted with an equimolar quantity of selenium to afford the cubane Cr_4Se_4 clusters $(\eta^5\text{-}RC_5H_4)_4Cr_4Se_4$ (**12**, R = Me; **13**, R = EtO_2C). A particularly interesting phenomenon is the cross-assembled reaction of the linear Cr_2Se complexes $[\eta^5\text{-}MeC(O)C_5H_4Cr(CO)_2]_2Se$ (**14**) and $[CpCr(CO)_2]_2Se$ (**15**) in the presence of excess selenium in THF that gave rise to a series of cubane Cr_4Se_4 clusters $[\eta^5\text{-}MeC(O)C_5H_4]_nCp_{4-n}Cr_4Se_4$ (**16**, n = 0; **17**, n = 1; **18**, n = 2; **19**, n = 3; **20**, n = 4). The possible pathway for the cross-assembled reaction is suggested. Furthermore the new clusters were characterized by elemental analysis and spectroscopy, and in the case of **4**–**6** and **16** also by X-ray diffraction techniques.

Introduction

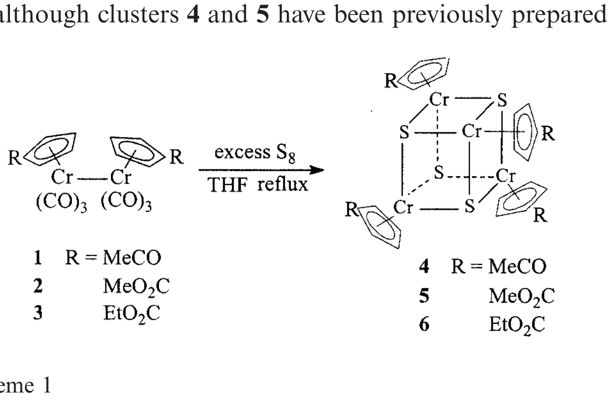
Transition-metal cubane-like cluster complexes containing μ_3-E chalcogen elements (where E = S, Se) have attracted much attention, largely due to their unique structures and novel properties,[1−4] and particularly because of the biological functions played by cubane subclusters, such as Fe_4S_4 and $MoFe_3S_4$, in metalloenzymes of nitrogenase and [Fe]-only hydrogenase.[5−8] Among these transition metal clusters, the Cr_4E_4 cluster complexes (where E = μ_3-S, μ_3-Se) have been studied to a smaller extent, although the parent clusters and the Me-substituted Cp derivatives $Cp_4Cr_4E_4$ (where E = S,[3] E = Se[9]) and $(\eta^5\text{-}MeC_5H_4)_4Cr_4E_4$ (where E = S,[10] E = Se[11]) have been known for many years. In this paper we report the synthesis and spectroscopic characterization of a series of cubane Cr_4E_4 clusters (E = S, Se), $(\eta^5\text{-}RC_5H_4)_4Cr_4S_4$ [where R = MeCO, MeO_2C, EtO_2C, 2,4-$(NO_2)_2C_6H_3NHN{=}CMe$], $(\eta^5\text{-}RC_5H_4)_4Cr_4Se_4$ (where R = Me, EtO_2C) and $[\eta^5\text{-}MeC(O)C_5H_4]_nCp_{4-n}Cr_4Se_4$ (n = 0−4), along with the crystal structures of cubane clusters $(\eta^5\text{-}RC_5H_4)_4Cr_4S_4$ (where R = MeCO, MeO_2C, EtO_2C) and $Cp_4Cr_4Se_4$.

Results and Discussion

Synthesis and Characterization of $(\eta^5\text{-}RC_5H_4)_4Cr_4S_4$ [4, R = MeCO; 5, R = MeO_2C; 6, R = EtO_2C; 7, R = 2,4-$(NO_2)_2C_6H_3NHN{=}CMe$]

The Cr−Cr singly-bonded dimers $[\eta^5\text{-}RC_5H_4Cr(CO)_3]_2$ (**1**, R = MeCO;[12] **2**, R = MeO_2C;[12] **3**, R = EtO_2C[13]) were found to react with an excess amount of elemental sulfur in THF at reflux for 12 h to give cubane clusters **4−6** in 81−95 % yields (see Scheme 1), while the functional transformation reaction of cubane cluster **4** with excess 2,4-dinitrophenylhydrazine in CH_2Cl_2 at room temperature for 24 h afforded the phenylhydrazone derivative **7** in 63 % yield (see Scheme 2).

For the above preparations, it is worth pointing out that (i) although clusters **4** and **5** have been previously prepared



Scheme 1

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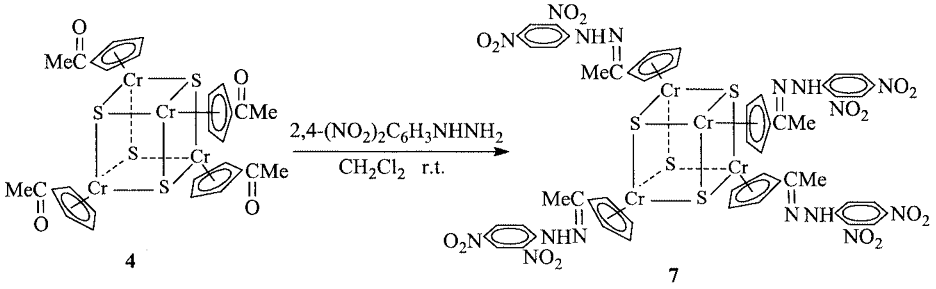


Scheme 2

by another method, the yields were rather low (29 % and 42 %, respectively) and their structures were characterized by combustion analysis and spectroscopy, but not confirmed by X-ray diffraction analysis;[14] and (ii) cluster **7** was the solely isolated product during the course of our study on the functional transformation reactions of the acetyl groups in cluster **4**. The other attempted functional transformation reactions, such as with $NaBH_4$ and with Grignard reagents followed by hydrolysis, led to serious decomposition of the starting cluster **4** and no corresponding hydroxy-containing cluster derivatives were isolated.

The new clusters **6** and **7** were characterized by combustion analysis, IR and ^1H NMR spectroscopy and the structures of clusters **4−6** were further confirmed by X-ray crystallographic studies. Similarly to clusters **4** and **5**,[14] the IR spectra of **6** and **7** showed one absorption band at 1708 and 1616 cm^{-1} for the ester C=O and hydrazone C=N groups, while the ^1H NMR spectra of **6** and **7** displayed two singlets at lower and higher fields, attributed respectively to H^2/H^5 and H^3/H^4 protons in the functionally substituted Cp rings.[15]

The ORTEP drawings of **4−6** are shown in Figures 1−3, while the selected bond lengths and angles are presented in Table 1.

Figures 1−3 show the molecular structures of clusters **4−6**, which are similar to those of the methyl analogs (η^5-$MeC_5H_4)_4Cr_4S_4$,[10] in which the cubane-like Cr_4S_4 cluster core carries four substituted Cp ligands coordinated in an η^5-manner to four chromium atoms. The bond lengths of Cr−Cr are 2.8042−2.8298 Å for **4**, 2.8214−2.8589 Å for **5** and 2.7946−2.8337 Å for **6**, whereas those of Cr−S are 2.2390−2.2540 Å for **4**, 2.2584−2.2747 Å for **5** and 2.2347−2.2478 Å for **6**. The bond angles of Cr−S−Cr are 77.27−78.08° for **4**, 77.03−78.21° for **5** and 77.02−78.49° for **6**, while those of S−Cr−S are 100.69−101.39° for **4**, 100.21−101.95° for **5** and 100.5−101.89° for **6**. The C(1)−C(6) bond of **4** [1.483(11) Å], the C(5)−C(6) bond of **5** [1.494(6) Å] and the C(1)−C(6) bond of **6** [1.477(9) Å] are all shorter than a normal C−C single bond, presumably due to conjugation between the π-electron systems of the functional substituents and the cyclopentadienyl rings.

Table 1. Selected bond lengths (Å) and angles (°) for **4−6**

	4	**5**	**6**
Bond lengths			
Cr(1)−Cr(2)	2.8166(18)	2.8379(11)	2.8337(13)
Cr(1)−Cr(3)	2.8042(19)	2.8296(10)	2.7978(12)
Cr(1)−Cr(4)	2.8298(17)	2.8421(12)	2.7946(14)
Cr(2)−Cr(3)	2.8212(17)	2.8589(11)	2.8098(14)
Cr(2)−Cr(4)	2.8212(17)	2.8394(11)	2.8005(14)
Cr(3)−Cr(4)	2.8183(18)	2.8214(12)	2.8175(13)
Cr(1)−S(1)	2.247(2)	2.2637(12)	2.2477(17)
Cr(1)−S(3)	2.248(2)	2.2584(12)	2.2466(17)
Cr(2)−S(1)	2.241(2)	2.2747(12)	2.2462(17)
Cr(2)−S(2)	2.252(2)	2.2669(12)	2.2423(16)
Bond angles			
S(3)−Cr(1)−Cr(2)	98.37(7)	99.01(4)	98.14(5)
S(1)−Cr(1)−S(3)	101.39(9)	100.74(5)	101.89(6)
S(3)−Cr(1)−Cr(3)	51.30(6)	51.41(3)	51.52(4)
S(1)−Cr(1)−Cr(3)	51.19(6)	98.67(4)	51.45(4)
Cr(2)−Cr(1)−Cr(4)	59.95(4)	59.99(2)	59.68(3)
Cr(1)−S(1)−Cr(2)	77.75(8)	77.41(4)	78.18(5)
Cr(2)−S(2)−Cr(4)	77.52(8)	77.65(4)	77.30(5)
Cr(4)−S(3)−Cr(1)	78.08(8)	77.88(4)	77.08(6)
Cr(3)−S(3)−Cr(1)	77.27(8)	77.42(4)	77.00(6)

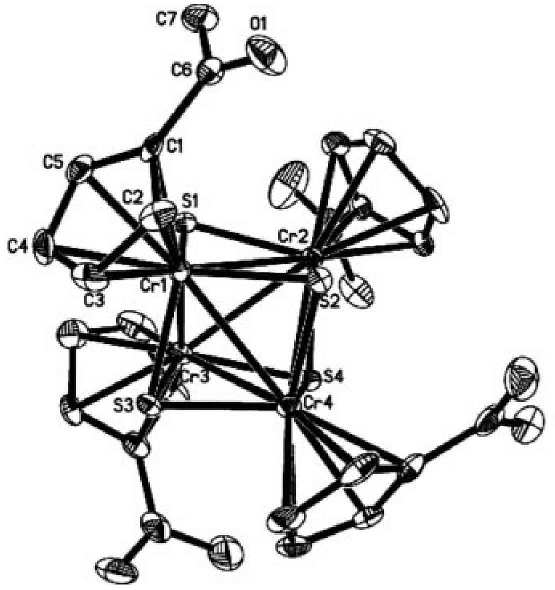


Figure 1. Molecular structure of **4** showing the atom-labeling scheme

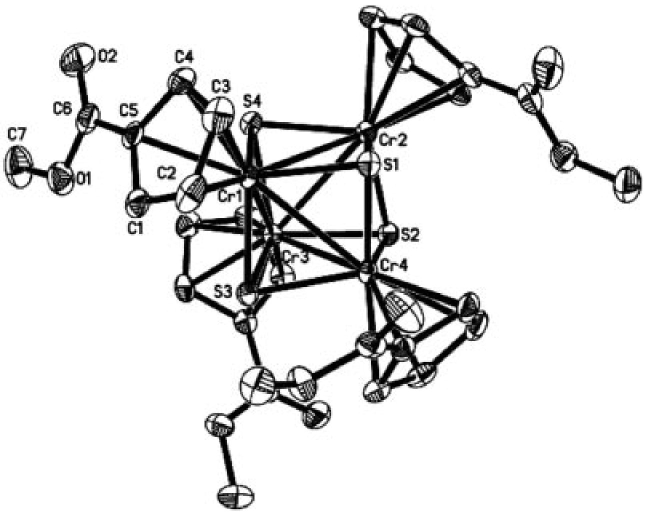


Figure 2. Molecular structure of **5** showing the atom-labeling scheme

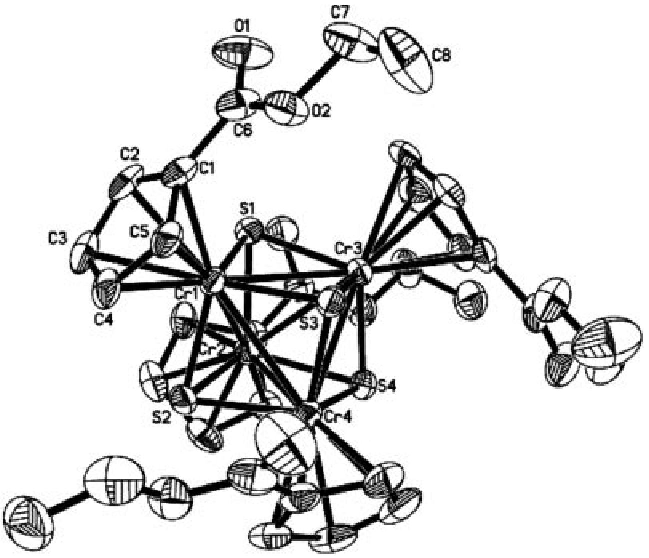
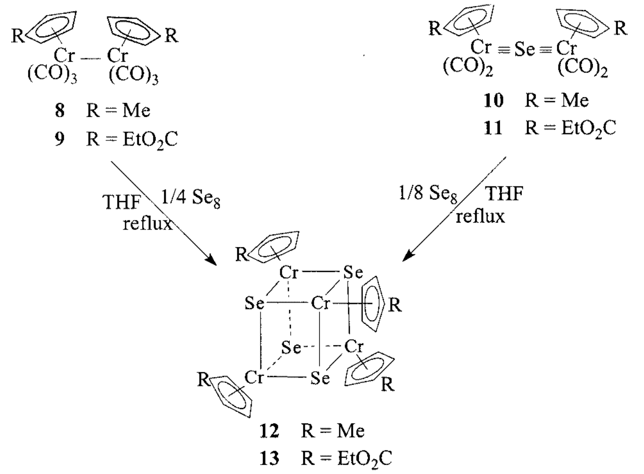


Figure 3. Molecular structure of **6** showing the atom-labeling scheme

Synthesis and Characterization of (η^5-$RC_5H_4)_4Cr_4Se_4$ (12, R = Me; 13, R = EtO_2C) and [η^5-$MeC(O)C_5H_4]_nCp_{4-n}$-Cr_4Se (16, *n* = 0; 17, *n* = 1;18, *n* = 2; 19, *n* = 3; 20, *n* = 4)

When the Cr−Cr singly-bonded dimers [η^5-$RC_5H_4Cr(CO)_3]_2$ (**8**, R = Me;[16] **9**, R = EtO_2C[13]) were refluxed with an equimolar amount of elemental selenium in THF for 8 h or when the linear complexes [η^5-$RC_5H_4Cr(CO)_2]_2Se$ (**10**, R = Me;[17] **11**, R = EtO_2C[17]) were treated with an equimolar quantity of selenium in refluxing THF for 8 h, the corresponding cubane Cr_4Se_4 clusters **12** and **13** were obtained in excellent yield (see Scheme 3).

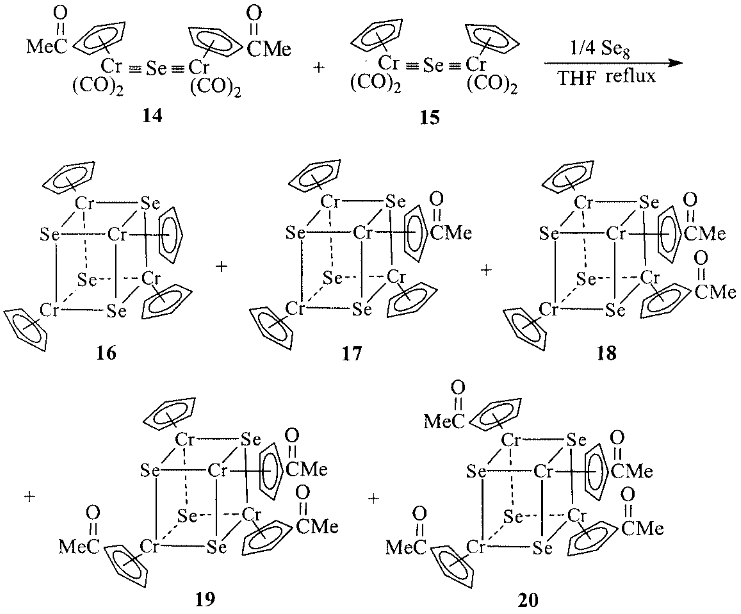


Scheme 3

More interestingly, when an equimolar mixture of the linear acetyl-substituted complex [η^5-$MeC(O)C_5H_4Cr$-$(CO)_2]_2Se$ (**14**)[4] and its parent complex $[CpCr(CO)_2]_2Se$ (**15**)[18] were treated with elemental selenium in refluxing THF for 8 h, a series of Cr_4Se_4 cubane clusters with the general formula [η^5-$MeC(O)C_5H_4]_nCp_{4-n}Cr_4Se_4$ (**16−20**, *n* = 0−4) were produced in total 97 % yield (see Scheme 4).

At present, we do not know how clusters **16−20** are formed from the reaction described in Scheme 4. We initially thought that the complicated reaction might be similar to that of the linear complexes **10** or **11** with selenium and that cubane clusters **16** and **20** were formed from the corresponding reaction of complexes **14** or **15** with selenium, and clusters **17−19** were then produced by ligand exchange between **16** and **20**. However, our experiment showed that the attempted reaction between **16** and **20** in THF at reflux did not afford any cubane clusters bearing mixed-Cp ligands. Therefore, we further suggested that clusters **16−20** could possibly be formed by self-tetramerization and cross-tetramerization of the highly unsaturated species η^5-$MeC(O)C_5H_4CrSe$ and CpCrSe, generated in situ from the thermolysis of the mixture of **14**, **15** and elemental selenium. This is because the molar ratio of the five products **16−20** is approximately 1:4:6:4:1, which is consistent with the combinatory rule of tetramerization of the two highly unsaturated fragments η^5-$MeC(O)C_5H_4CrSe$ and CpCrSe. However, this pathway is mainly speculative and the detailed mechanism for the cross-assembled reaction needs to be further studied. This cross-assembled reaction is particularly interesting, since it provides evidence for the mechanism for the production of the cubane Cr_4Se_4 clusters[19] and it can also furnish the novel cubane clusters with mixed-Cp ligands.

While the cubane clusters **12**,[11] **16**[9] and **20**[4] have been previously prepared by other methods, clusters **13**, **17−19** are new and were characterized by combustion analysis, IR, ^1H NMR spectroscopy and ^{77}Se NMR spectroscopy. The IR spectra of **13** and **17−19** display one absorption band



Scheme 4

in the region 1666−1668 cm^{-1} for the ketone carbonyls. The ^{1}H NMR spectra of **13** and **17−19** show one singlet for the five protons of each Cp ring and two singlets for the H^2/H^5 and H^3/H^4 protons of each substituted Cp ring.[15] It is worthy of note that the ^{1}H NMR signals of the mixed-Cp cluster **18** appear in the normal range, whereas the signals displayed by **17** and **19** are in the low-field region (12−28 ppm), probably due to traces of paramagnetic species, such as $(CpCr)_mSe_n$ and $(RCpCr)_mSe_n$, generated from the decomposition of the corresponding cubane clusters.

^{77}Se NMR spectroscopy is an important tool for characterizing Se-containing complexes.[20] To examine the influence of different Cp ligands upon ^{77}Se NMR behavior, the ^{77}Se NMR spectra of **12**, **13** and **17−19** were determined. Only one singlet in the range 1009−1241 ppm, which corresponds to the μ$_3$-Se atoms, was observed. This means that the magnetic environments around the four μ$_3$-Se atoms in each of the cubane clusters are basically the same, even for the mixed-Cp clusters **17−19**. The ^{77}Se chemical shifts of these clusters are in the order **12** < **17** < **18** < **19** < **13**, which is consistent with the electron-releasing effect of the methyl group and the electron-withdrawing effects of the acetyl and ethoxycarbonyl groups.

Although cluster **16** has been previously prepared,[9] we were the first to confirm its structure by using X-ray crystal-diffraction techniques. This is probably due to its low solubility in common solvents for crystal growing. Figure 4

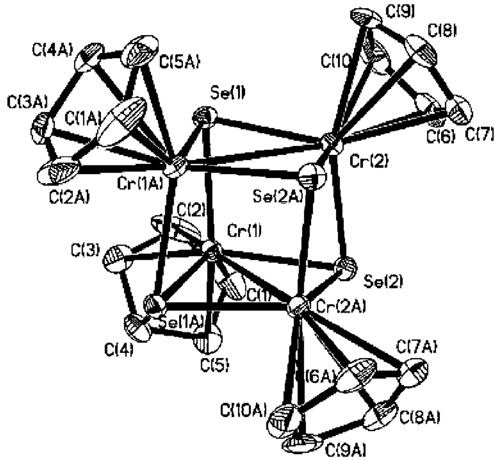


Figure 4. ORTEP drawing of cluster **16**

Table 2. Selected bond lengths (Å) and angles (°) for **16**

Bond lengths			
Se(1)−Cr(2)	2.3983(13)	Se(2)−Cr(2)	2.3972 (14)
Se(1)−Cr(1)	2.3984(13)	C(1)−Cr(1)	2.233(6)
Se(2)−Cr(1)	2.3957(13)	Cr(2)−C(6)	2.245(5)
Bond angles			
Cr(2)−Se(1)−Cr(1)	79.42(3)	C(1)−Cr(1)−Se(1)	115.0(3)
Cr(2)−Se(1)−Cr(1A)	76.32(3)	Se(2)−Cr(1)−Se(1)	98.52(3)
Cr(1)−Se(2)−Cr(2A)	76.56(3)	Se(2)−Cr(1)−Cr(2A)	51.72(3)
Cr(1)−Se(2)−Cr(2)	79.50(3)	Se(1)−Cr(1)−Cr(2A)	99.41(4)
C(1)−Cr(1)−Se(2)	87.5(2)	Se(2)−Cr(2)−Se(1)	98.48(3)

shows the ORTEP drawing of cluster **16** and Table 2 lists selected bond lengths and angles. Similarly to the methyl derivative,[11] cluster **16** comprises a cubane Cr_4Se_4 cluster core that carries four Cp ligands coordinated in an η^5-fashion to four Cr atoms. The Cr−Cr and Cr−Se bond lengths and the Cr−Se−Cr and Se−Cr−Se bond angles are 2.9683 Å, 2.3957−2.4055 Å, 76.32−79.50° and 98.48−103.12°, respectively. Thus, the cubane Cr_4Se_4 cluster core is just slightly distorted. This molecule has an alternating fourfold axis of symmetry.

Experimental Section

General: All reactions were carried out under an atmosphere of highly purified nitrogen gas using standard Schlenk or vacuum-line techniques. Solvents for preparative use were dried and distilled under nitrogen from Na/benzophenone ketyl or CaH_2 prior to use. Commercial sulfur powder, selenium powder, and 2,4-dinitrophenylhydrazine were used as received. $[\eta^5\text{-}RC_5H_4Cr(CO)_3]_2$ (where R = Me,[16] MeCO,[12] MeO_2C,[12] EtO_2C[13]), $[CpCr(CO)_2]_2Se$[18] and $[\eta^5\text{-}MeC(O)C_5H_4Cr(CO)_2]_2Se$[4] were prepared according to literature procedures. All reactions were monitored by thin layer chromatography (TLC) at intervals. The preparative TLC was carried out on a glass column (2 × 10 cm) packed with silica gel G and glass plates (25 × 20 × 0.25 cm) coated with silica gel H (10−40 μm). Samples for characterization were recrystallized from mixed dichloromethane and hexane. IR spectra were recorded on a Bruker Vector 22 infrared spectrophotometer. While ^1H NMR spectra were recorded on a Bruker AC-P 200 NMR spectrometer, ^{77}Se NMR spectra were taken from a Varian Unity-Plus 400 NMR spectrometer with Ph_2Se_2 as external standard and chemical shifts were referenced to Me_2Se (δ = 0 ppm). Elemental analysis was performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

Preparation of $(\eta^5\text{-}MeCOC_5H_4)_4Cr_4S_4$ (4): A 100-mL Schlenk flask equipped with a magnetic stir bar was charged with $[\eta^5\text{-}MeCOC_5H_4Cr(CO)_3]_2$ (0.423 g, 0.87 mmol), sulfur powder (0.070 g, 2.19 mmol) and THF (20 mL). The mixture was stirred at reflux for 12 h. The solvent was removed under vacuum and the residue was extracted in a minimum volume of dichloromethane, which was then subjected to TLC separation using acetone/petroleum ether (v/v, 1:2) as eluent. Compound **4** (0.287 g, 86 %) was obtained as a black solid from the green band and it was identified by comparing its melting point, ^1H NMR and IR spectra with those of the spectroscopically characterized sample.[14]

Preparation of $(\eta^5\text{-}MeO_2CC_5H_4)_4Cr_4S_4$ (5): The same procedure as for the preparation of **4** was followed, but $[\eta^5\text{-}MeO_2CC_5H_4Cr(CO)_3]_2$ (0.450 g, 0.87 mmol) was employed to give **5** (0.342 g, 95 %) as a black solid, which was also identified by comparing its melting point, ^1H NMR and IR spectra with those of the spectroscopically characterized sample.[14]

Preparation of $(\eta^5\text{-}EtO_2CC_5H_4)_4Cr_4S_4$ (6): The same procedure as for the preparation of **4** was followed, but $[\eta^5\text{-}EtO_2CC_5H_4Cr(CO)_3]_2$ (0.490 g, 0.90 mmol) was employed to give **6** (0.321 g, 81 %) as a black solid. M.p. 186−188 °C. ^1H NMR ($CDCl_3$): δ = 1.32 (t, J = 8.0 Hz, 12 H, 4 CH_3), 4.24 (q, J = 8.0 Hz, 8 H, 4 CH_2), 4.76 (s, 8 H, 4 H^3, 4 H^4), 5.28 (s, 8 H, 4 H^2, 4 H^5). IR (KBr disk): $\tilde{\nu}$ = 1708 (s) (C=O) cm^{-1}. $C_{32}H_{36}Cr_4O_8S_4$ (884.85): calcd. C 43.44, H 4.10; found C 42.85, H 4.13.

Preparation of $[\eta^5\text{−}2,4\text{-}(NO_2)_2C_6H_3NHN{=}CMeC_5H_4]_4Cr_4S_4$ (7): A 2,4-dinitrophenylhydrazine solution (2 mL, ca. 4 mmol), which was prepared by dissolving 1.0 g of 2,4-dinitrophenylhydrazine in 5 mL of 98 % H_2SO_4, 10 mL of H_2O and 35 mL of 95% EtOH, was added to a solution of **4** (0.382 g, 0.50 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was washed carefully by anhydrous ethyl alcohol and was then extracted with a minimum volume of CH_2Cl_2. This extract was subjected to TLC separation using CH_2Cl_2 as eluent. Compound **7** (0.467 g, 63 %) was obtained as a black solid from the main band. M.p. 242−244 °C. ^1H NMR ($CDCl_3$): δ = 1.53 (s, 12 H, 4 CH_3), 4.93 (s, 8 H, 4 H^3, 4 H^4), 5.64 (s, 8 H, 4 H^2, 4 H^5), 7.80 (m, 4 H, 4 H^6 of benzene ring), 8.20−8.50 (m, 4 H, 4 H^5 of benzene ring), 9.14 (s, 4 H, 4 H^3 of benzene ring), 11.20 (s, 4 H, 4 NH) ppm. IR (KBr disk): $\tilde{\nu}$ = 3312 (vs) (N−H), 1616 (s) (C=N) cm^{-1}. $C_{52}H_{44}Cr_4N_{16}O_{16}S_4$ (1485.24): calcd. C 42.05, H 2.99, N 15.32; found C 41.74, H 3.51, N 15.09.

Preparation of $(\eta^5\text{-}MeC_5H_4)_4Cr_4Se_4$ (12). Method (i): A mixture of $[\eta^5\text{-}MeC_5H_4Cr(CO)_3]_2$ (0.215 g, 0.50 mmol), selenium powder (0.079 g, 1.00 mmol) and THF (20 mL) was refluxed for 8 h, causing a color change from brown red to dark green. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. CH_2Cl_2 was removed under vacuum and the residue was recrystallized from a mixed CH_2Cl_2/hexane solvent to give 0.202 g (96%) of **12** as a black solid. M.p. 179−180 °C. ^1H NMR ($CDCl_3$): δ = 2.57 (s, 12 H, 4 CH_3), 30.07 (s, 8 H, 4 H^2, 4 H^5), 30.45 (s, 8 H, 4 H^3, 4 H^4) ppm. ^{77}Se NMR ($CDCl_3$): δ = 1009 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 1630 (m), 1490 (m), 1449 (s), 1371 (m), 1038 (m), 1024 (s), 802 (vs) cm^{-1}. $C_{24}H_{28}Cr_4Se_4$ (840.30): calcd. C 34.30, H 3.36; found C 34.18, H 3.31. **Method (ii):** A mixture of $[\eta^5\text{-}MeC_5H_4Cr(CO)_2]_2Se$ (0.227 g, 0.50 mmol), selenium powder (0.040 g, 0.50 mmol) and THF (20 mL) was refluxed for 8 h. The same workup as that described in method (i) gave 0.200 g (95%) of **12**.

Preparation of $(\eta^5\text{-}EtO_2CC_5H_4)_4Cr_4Se_4$ (13). Method (i): The same procedure as Method (i) for **12** was followed, but $[\eta^5\text{-}EtO_2CC_5H_4Cr(CO)_3]_2$ (0.273 g, 0.50 mmol) was utilized to give 0.260 g (97%) of **13** as a black solid. M.p. 169−170 °C. ^1H NMR ($CDCl_3$): δ = 1.32 (t, J = 7.0 Hz, 12 H, 4 CH_3), 4.14 (q, J = 7.0 Hz, 8 H, 4 CH_2), 4.95 (s, 8 H, 4 H^3, 4 H^4), 5.83 (s, 8 H, 4 H^2, 4 H^5) ppm. ^{77}Se NMR ($CDCl_3$): δ = 1241 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 1705 (s) (C=O) cm^{-1}. $C_{32}H_{36}Cr_4O_8Se_4$ (1072.45): calcd. C 35.84, H 3.38; found C 35.41, H 3.16. **Method (ii):** The same procedure as Method (ii) for **12** was followed, but $[\eta^5\text{-}EtO_2CC_5H_4Cr(CO)_2]_2Se$ (0.285 g, 0.50 mmol) was used to afford 0.257 g (96%) of **13**.

Preparation of $[\eta^5\text{-}MeC(O)CC_5H_4]_nCp_{4-n}Cr_4Se_4$ (n = 0, 16; n = 1, 17; n = 2, 18; n = 3, 19; n = 4, 20): A 100-mL Schlenk flask was charged with $[CpCr(CO)_2]_2Se$ (0.212 g, 0.50 mmol), $[\eta^5\text{-}MeC(O)C_5H_4Cr(CO)_2]_2Se$ (0.255 g, 0.50 mmol), selenium powder (0.158 g, 2 mmol) and THF (30 mL). The mixture was stirred at reflux for 8 h, resulting in a color change from brown red to dark green. The mixture was centrifuged to give a clear centrifugate, which was concentrated to ca. 10 mL and was then subjected to TLC separation using acetone/CH_2Cl_2/petroleum ether (v/v/v, 1:3:3) as eluent to develop four brown-green bands.

$[\eta^5\text{-}MeC(O)C_5H_4]Cp_3Cr_4Se_4$ (17): Compound **17** (0.096 g, 23 %) was obtained from the first band (R_f = 0.81) as a black solid. M.p. 202−203 °C. ^1H NMR ($CDCl_3$): δ = 2.17 (s, 3 H, CH_3), 12.27 (s, 2 H, H^3, H^4), 13.17 (s, 15 H, 3 C_5H_5), 15.20 (s, 2 H, H^2, H^5) ppm.

Table 3. Crystal data and structural refinements details for **4**, **5**, **6** and **16**

	4	**5**	**6**	**16**
Empirical formula	$C_{28}H_{28}Cr_4O_4S_4$	$C_{28}H_{28}Cr_4O_8S_4$	$C_{32}H_{36}Cr_4O_8S_4$	$C_{10}H_{10}Cr_2Se_2$
Formula mass	764.74	828.74	884.85	392.10
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a(Å)	9.728(3)	10.009(4)	10.384(3)	17.875(7)
b (Å)	9.642(3)	10.798(4)	12.048(4)	8.240(3)
c(Å)	31.097(9)	16.592(6)	15.051(5)	16.184(7)
α (°)	90	73.296(5)	85.127(6)	90
β (°)	97.823(5)	77.332(6)	76.690(5)	116.087(6)
γ (°)	90	66.133(5)	77.264(6)	90
V (Å^3)	2889.7(13)	1559.7(9)	1786.1(10)	2140.9(15)
Z	4	2	2	8
$D_{calcd.}$ (g cm^{-3})	1.758	1.765	1.645	2.433
μ (Mo-K_α) (mm^{-1})	1.788	1.673	1.467	8.782
F(000)	1552	840	904	1488
Reflections collected	14600	6456	9101	4296
Independent reflections	5109	5462	6863	1895
R_{int}	0.0906	0.0225	0.0306	0.0349
2θ$_{max}$ (°)	50.00	50.06	52.88	50.04
Data/restraints/parameters	5109/0/366	5462/0/397	6863/0/434	1895/0/127
R	0.0619	0.0345	0.0529	0.0308
Rw	0.1250	0.0777	0.1065	0.0700
Gooodness of fit	1.074	0.999	0.986	1.042
Largest difference peak and hole/e·Å^{-3}	0.722 and −0.740	0.373 and −0.396	0.456 and −0.428	0.516 and −0.713

^{77}Se NMR (CDCl$_3$): δ = 1148(s) ppm. IR (KBr disk): ṽ = 1667 (s) (C=O) cm^{-1}. $C_{22}H_{22}Cr_4OSe_4$ (826.24): calcd. C 31.98, H 2.68; found C 31.93, H 2.54.

[η^5-MeC(O)C$_5$H$_4$]$_2$Cp$_2$Cr$_4$Se$_4$ (18): Compound **18** (0.158 g, 36 %) was obtained from the second band (R_f = 0.72) as a black solid. M.p. 214−215 °C. ^{1}H NMR (CDCl$_3$): δ = 2.19 (s, 6 H, 2 CH$_3$), 5.27 (s, 4 H, 2 H^3, 2 H^4), 5.33 (s, 10 H, 2 C$_5$H$_5$), 6.13 (s, 4 H, 2 H^2, 2 H^5) ppm. ^{77}Se NMR (CDCl$_3$): δ = 1178 (s) ppm. IR (KBr disk): ṽ = 1668 (s) (C=O) cm^{-1}. $C_{24}H_{24}Cr_4O_2Se_4$ (868.28): calcd. C 33.20, H 2.79; found C 33.21, H 2.76.

[η^5-MeC(O)C$_5$H$_4$]$_3$CpCr$_4$Se$_4$ (19): Compound **19** (0.112 g, 25 %) was obtained from the third band (R_f = 0.60) as a black solid. M.p. 188−189 °C. ^{1}H NMR (CDCl$_3$): δ = 2.18 (s, 9 H, 3CH$_3$), 22.17 (s, 6 H, 3 H^3, 3 H^4), 23.75 (s, 5 H, C$_5$H$_5$), 27.22 (s, 6 H, 3 H^2, 3 H^5) ppm. ^{77}Se NMR (CDCl$_3$): δ = 1224 (s) ppm. IR (KBr disk): ṽ = 1666 (s) (C=O) cm^{-1}. $C_{26}H_{26}Cr_4O_3Se_4$ (910.31): calcd. C 34.31, H 2.88; found C 34.33, H 2.77.

[η^5-MeC(O)C$_5$H$_4$]$_4$Cr$_4$Se$_4$ (20): Compound **20** (0.031 g, 7 %) was obtained from the fourth band (R_f = 0.45) identified by comparing its IR and ^{1}H NMR spectra with those of the fully characterized sample.[4] The immovable base band was collected and refluxed with 10 mL of bromobenzene for 10 min. Once it had cooled to room temperature, the mixture was filtered and the filtrate was centrifuged to give a clear centrifugate, from which Cp$_4$Cr$_4$Se$_4$ (**16**)[9] (0.025 g, 6 %) was obtained.

Attempted Cp/η^5-MeC(O)C$_5$H$_4$ Ligand Exchange Between Cp$_4$Cr$_4$Se$_4$ and [η^5-MeC(O)C$_5$H$_4$]$_4$Cr$_4$Se$_4$: A mixture consisting of Cp$_4$Cr$_4$Se$_4$ (0.078 g, 0.10 mmol) and **20** (0.095 g, 0.10 mmol) in THF (20 mL) was stirred at reflux for 10 h. The resulting mixture was concentrated to ca. 5 mL and was subjected to TLC separation using acetone/CH$_2$Cl$_2$/petroleum ether (v/v/v, 1:3:3) as eluent to develop only one brown-green band. Compound **20** (0.079 g, 82 %) was recovered from this band, while Cp$_4$Cr$_4$Se$_4$ (0.052 g, 67 %) was recovered from the immovable band. No ligand exchange products of [η^5-MeC(O)CC$_5$H$_4$]$_n$Cp$_{4-n}$Cr$_4$Se$_4$ (n = 1−3, **17−19**) were produced.

Crystal Structure Determination of 4−6 and 16: Single crystals of **4−6** and **16**, suitable for X-ray diffraction analysis, were grown by slow evaporation of an acetone/hexane solution at room temperature. Each single crystal was glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature, using graphite monochromator Mo-K_α radiation (λ = 0.71073 Å) in the ω-2θ scanning mode. Absorption correction was performed using the SADABS method. The structure was solved by direct methods using the SHELXS-97[21a] program and refined by full-matrix least-squares techniques (SHELXL-97[21b]) on F^2. Hydrogen atoms were located by using the geometric method. The crystal data and structural refinement details are listed in Table 3. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.[22] CCDC-228444, -228445, -228446 and -228990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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