

Synthesis, spectroscopic characterization and reactivities of linear and butterfly chromium/selenium complexes containing substituted cyclopentadienyl ligands: crystal structures of $[\{\eta^5\text{-MeC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}]$ and $[\{\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2]$

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Abstract

The Cr–Cr singly-bonded dimers $[\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_3\}_2]$ (**1**, R = Me; **2**, R = CO₂Et) reacted with an equivalent of elemental selenium in THF at room temperature to give the linear Cr₂Se complexes $[\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}]$ (**3**, R = Me; **4**, R = CO₂Et), whereas the linear Cr₂Se complex (**5**, R = MeCO) reacted with excess NaBH₄, Ph₃P=CHPh or 2,4-dinitrophenylhydrazine under respective conditions to afford the linear Cr₂Se derivatives $[\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}]$ (**6**, R = MeCH(OH); **7**, R = PhCH=CMe; **8**, R = 2,4-(NO₂)₂C₆H₃NHN=CMe). Similarly, while the butterfly Cr₂Se₂ complexes $[\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2]$ (**9**, R = Me; **10**, R = CO₂Et) could be produced either by reaction of dimers **1** and **2** with an excess amount of elemental selenium, or by reaction of the linear complexes **3** and **4** with an equivalent of elemental selenium, the butterfly Cr₂Se₂ derivatives $[\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2]$ (**12**, R = MeCH(OH); **13**, R = PhCH=CMe; **14**, R = 2,4-(NO₂)₂C₆H₃NHN=CMe) were yielded by reaction of the butterfly Cr₂Se₂ complex (**11**, R = MeCO) with an excess quantity of NaBH₄, Ph₃P=CHPh and 2,4-dinitrophenylhydrazine. Both the linear complexes **3**, **4**, **6–8** and the butterfly complexes **9**, **10**, **12–14** are new, which have been fully characterized by elemental analysis, spectroscopy and X-ray crystallography.

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Keywords: Organochromium complex; Selenium complex; Synthesis; Reactivity; Crystal structures

1. Introduction

The linear Cr₂Se and butterfly Cr₂Se₂ compounds are of great interest, because of their unique structures, high reactivity and the practical applications as building blocks in synthesis of Cr/Se-containing organometallic and cluster complexes [1–4]. Recently, we reported the synthesis of some linear Cr₂Se and but-

terfly Cr₂Se₂ compounds with substituted cyclopentadienyl ligands and their skeleton transformation reactions leading to the corresponding cubane-like Cr₄Se₄ clusters [5]. As part of this project, we wish to report in this article the synthesis and structural characterization of another new linear Cr₂Se and butterfly Cr₂Se₂ complexes $[\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}]$ and $[\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2]$ (R = Me, CO₂Et, MeCH(OH), PhCH=CMe, 2,4-(NO₂)₂C₆H₃NHN=CMe). Interestingly, some of these products are the first examples prepared so far by functional transformation reactions of the functionally substituted Cp rings in the corresponding linear Cr₂Se and butterfly Cr₂Se₂ starting materials.

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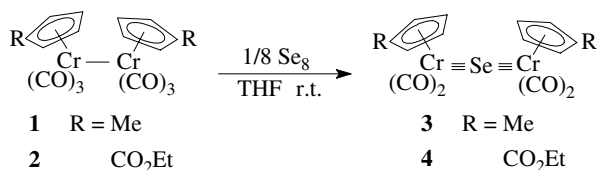
E-mail address: lsong@nankai.edu.cn (L.-C. Song).

2. Results and discussion

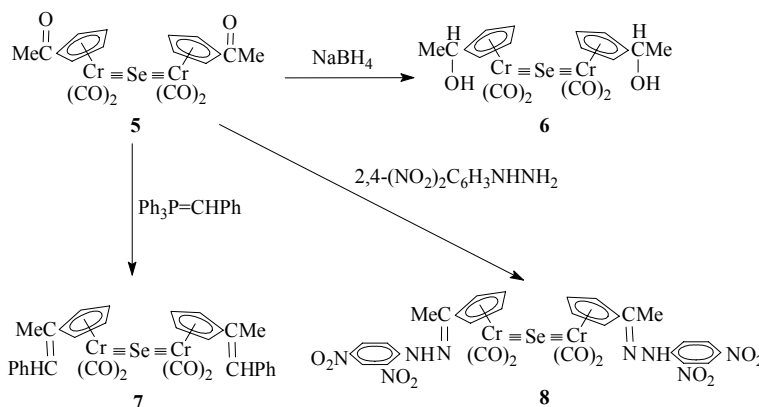
2.1. Synthesis and characterization of linear complexes [$\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}$] (**3**, $\text{R} = \text{Me}$; **4**, $\text{R} = \text{CO}_2\text{Et}$; **6**, $\text{R} = \text{MeCH}(\text{OH})$; **7**, $\text{R} = \text{PhCH}=\text{CMe}$; **8**, $\text{R} = 2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{NHN}=\text{CMe}$)

The linear complexes containing substituted Cp ligands **3** and **4** could be prepared by reaction of the Cr–Cr singly-bonded dimers [$\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_3\}_2$] (**1**, $\text{R} = \text{Me}$ [6]; **2**, $\text{R} = \text{CO}_2\text{Et}$ [7]) with an equivalent of elemental selenium (Scheme 1), whereas the linear complexes **6–8** were prepared through functional transformation reactions of the linear complex [$\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}$] (**5**, $\text{R} = \text{MeCO}$) [5] with an excess amount of reducing agent NaBH_4 , Wittig reagent $\text{Ph}_3\text{P}=\text{CHPh}$ or 2,4-dinitrophenylhydrazine, respectively (Scheme 2).

Products **3**, **4** and **6–8** are new and have been fully characterized by elemental analysis, IR, ^1H NMR, ^{77}Se NMR and X-ray diffraction analysis. The IR spectra of **3**, **4** and **6–8** displayed several absorption bands in the region $1999\text{--}1874\text{ cm}^{-1}$ for their terminal carbonyls, whereas those of **4**, **7** and **8** showed an additional absorption band in the range $1712\text{--}1616\text{ cm}^{-1}$ for their $\text{C}=\text{O}$, $\text{C}=\text{C}$ and $\text{C}=\text{N}$ double bonds. The ^1H NMR spectra of **3**, **4** and **6–8** showed two singlets or two doublets for the four protons in each of the substituted Cp rings. For **3** the upfield signal can be assigned to H^2/H^5 close to the substituent and the down field one



Scheme 1.



Scheme 2.

to H^3/H^4 remote from the substituent, while for **4** and **6–8** the assignment should be opposite, since the substituent of methyl group is a typical electron-releasing group and the others are somewhat electron-withdrawing. The ^{77}Se NMR spectra of **3**, **4** and **6–8** each exhibited one singlet for $\mu_2\text{-Se}$ atom in the highly deshielded range from 2563.1 to 2614.3 ppm. Such ^{77}Se NMR data are comparable with that of the reported parent linear complex [$\{\text{CpCr}(\text{CO})_2\}_2\text{Se}$] [8]. The highly deshielding $\mu_2\text{-Se}$ in such linear complexes presumably originates from the involvement of the π -electrons of Se in the unusual cumulated $\text{Cr} \equiv \text{Se} \equiv \text{Cr}$ linkage [9].

The molecular structure of **3** was unequivocally confirmed by X-ray diffraction techniques. The ORTEP drawing of **3** is shown in Fig. 1 and Table 1 lists its selected bond lengths and angles. As can be seen in Fig. 1, **3** consists of an essentially linear Cr–Se–Cr skeleton, two methyl-substituted Cp rings and four terminal carbonyls. The bond angle around Se (178.70°) in **3** is much larger than that ($167.90(8)^\circ$) in its MeO_2C -substituted homolog [$\{\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}$] [5], but almost the same as that (178.28°) in its parent complex [$\{\text{CpCr}(\text{CO})_2\}_2\text{Se}$] [2]. The Cr–Se bond lengths of **3** (2.211(2) and 2.210(2) Å) are nearly identical to

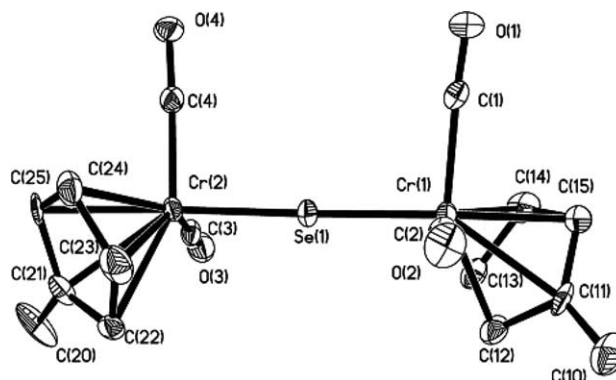
Fig. 1. Molecular structure of **3** showing the atom labeling scheme.

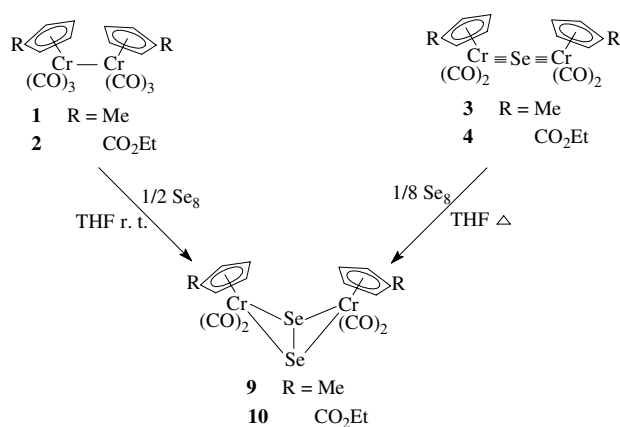
Table 1
Selected bond lengths (Å) and angles (deg) for **3**

| Bond lengths | | | |
|-------------------|-----------|-------------------|-----------|
| Cr(1)–Se(1) | 2.211(2) | Cr(2)–C(4) | 1.835(18) |
| Cr(2)–Se(1) | 2.210(2) | Cr(2)–C(21) | 2.211(15) |
| Cr(1)–C(1) | 1.874(19) | C(10)–C(11) | 1.510(13) |
| Cr(1)–C(11) | 2.236(14) | C(20)–C(21) | 1.540(13) |
| Bond angles | | | |
| Cr(2)–Se(1)–Cr(1) | 178.70(6) | C(14)–Cr(1)–Se(1) | 120.9(5) |
| C(1)–Cr(1)–C(2) | 90.9(8) | C(15)–Cr(1)–Se(1) | 157.8(5) |
| C(1)–Cr(1)–Se(1) | 94.9(5) | C(4)–Cr(2)–C(3) | 90.2(9) |
| C(2)–Cr(1)–Se(1) | 93.2(5) | C(4)–Cr(2)–Se(1) | 95.3(5) |

those of its parent complex (2.206(1) and 2.211 Å), but slightly longer than that of the MeO₂C-substituted homolog (2.1935(16) Å). Apparently, the considerable shortening of the Cr–Se bond lengths in comparison with the sum of the covalent radii of chromium (r_{Cr} 1.46 Å) [10] and selenium (r_{Se} 1.17 Å) [11] atoms in the linear Cr≡Se≡Cr structural moieties is consistent with triple bonding between chromium and selenium atoms in the linear Cr≡Se≡Cr units of such complexes.

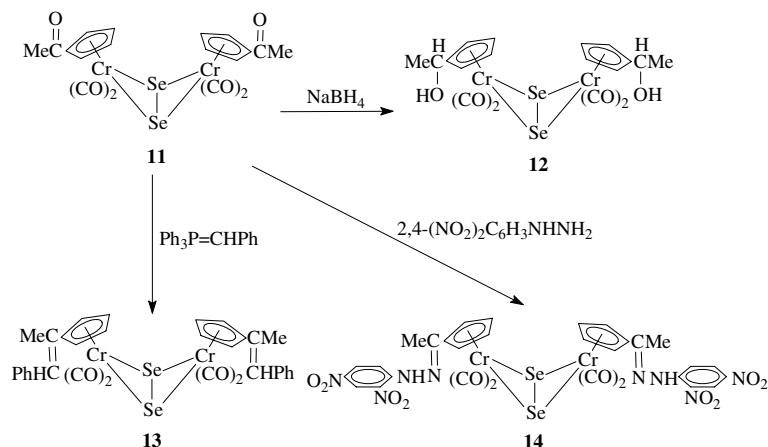
2.2. Synthesis and characterization of butterfly complexes [$\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] (**9**, R = Me; **10**, R = CO₂Et; **12**, R = MeCH(OH); **13**, R = PhCH=CMe; **14**, R = 2,4-(NO₂)₂C₆H₃NHN=CMe)

While the butterfly complexes **9** and **10** could be prepared either by reaction of the Cr–Cr singly-bonded dimers **1** and **2** with an excess quantity of elemental selenium or by reaction of the linear complexes **3** and **4** with an equivalent of elemental selenium (Scheme 3), the butterfly complexes **12–14** could be produced, through functional transformation reactions of the butterfly complex [$\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] (**11**, R = MeCO) [5] with excess NaBH₄, Ph₃P=CHPh and 2,4-dinitrophenylhydrazine, respectively (Scheme 4).



Scheme 3.

All the new butterfly complexes **9**, **10** and **12–14** have been fully characterized by elemental analysis, IR, ¹H NMR, ⁷⁷Se NMR and X-ray crystallography. In fact, the IR and ¹H NMR spectra of these butterfly complexes are very similar to the corresponding those of the linear complexes **3**, **4** and **6–8**, since they all contain terminal carbonyls and the same substituted Cp rings attached to chromium atoms. For example, the IR spectra of **9**, **10** and **12–14** showed two or three absorption bands for their terminal carbonyls, while those of **10**, **13** and **14** each displayed an additional absorption band for their respective C=O, C=C and C=N functional groups. In addition, the ¹H NMR spectra of **9**, **10** and **12–14** also displayed two signals for the four protons in each of the two substituted Cp rings, as well as corresponding signals for their hydrogen-containing R groups. However, it is noteworthy that the ⁷⁷Se NMR spectra of the butterfly complexes **9**, **10** and **12–14** displayed only one singlet for μ₂-Se₂ atoms in the highly shielded range from –265.5 to –202.4 ppm. This implies that the two Se atoms in



Scheme 4.

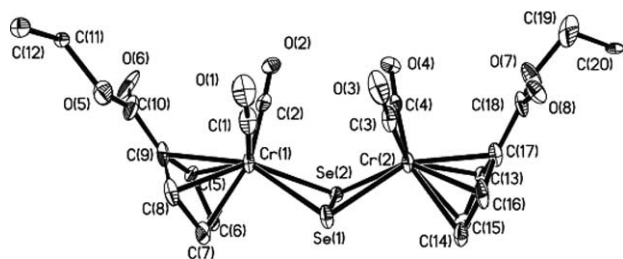
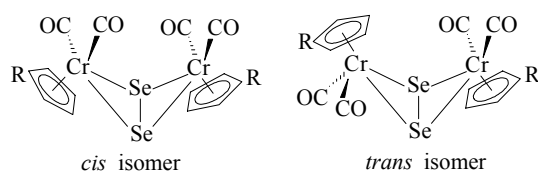


Fig. 2. Molecular structure of **10** showing the atom labeling scheme.

these complexes have virtually the same magnetic environment.

The molecular structure of **10** has been further confirmed by X-ray diffraction analysis. Fig. 2 shows that it comprises two substituted Cp ligands η^5 -EtO₂CC₅H₄, four terminal carbonyls, and a butterfly Cr₂Se₂ skeleton. The dihedral angle between two butterfly wings Cr(1)Se(1)Se(2) and Cr(2)Se(1)Se(2) is 119.69°. The Se–Se bond length (2.252(2) Å), Se–Cr bond lengths (2.533(2)–2.543(2) Å), Se–Cr–Se bond angles (52.61(6)°, 52.75(6)°) and the other geometric parameters involved in butterfly skeleton are very close to the corresponding those in its parent complex [$\{\text{CpCr}(\text{CO})_2\}_2\text{Se}_2$] [2]. In principle, the butterfly Cr₂Se₂ complexes may have two isomers, *cis* and *trans*, in terms of favorably relative arrangement of Cp or R-substituted Cp and CO ligands (Scheme 5). The X-ray diffraction study of **10** revealed that it exists only as *cis*-isomer and it possesses a C₂ symmetric axis, which passes through the two mid points of the two Se(1)–Se(2) and Cr(1)–Cr(2) bonds (see Table 2).



Scheme 5.

Table 2
Selected bond lengths (Å) and angles (deg) for **10**

| Bond lengths | | | |
|-------------------|-----------|-------------------|-----------|
| Cr(1)–Se(1) | 2.539(3) | Cr(2)–C(3) | 1.808(18) |
| Cr(2)–Se(1) | 2.533(2) | Cr(2)–Se(1) | 2.533(2) |
| Cr(1)–C(1) | 1.820(17) | Cr(2)–Se(2) | 2.536(2) |
| Cr(1)–Se(2) | 2.543(2) | Se(1)–Se(2) | 2.252(2) |
| Bond angles | | | |
| Se(1)–Cr(1)–Se(2) | 52.61(6) | Se(2)–Cr(2)–Cr(1) | 39.31(5) |
| Se(1)–Cr(1)–Cr(2) | 39.10(5) | Se(2)–Se(1)–Cr(2) | 63.69(7) |
| Se(2)–Cr(1)–Cr(2) | 39.18(5) | Se(2)–Se(1)–Cr(1) | 63.78(7) |
| Se(1)–Cr(2)–Se(2) | 52.75(6) | Se(1)–Se(2)–Cr(2) | 63.57(7) |
| Se(1)–Cr(2)–Cr(1) | 39.21(6) | Cr(2)–Se(2)–Cr(1) | 101.51(8) |

3. Experimental

All reactions were carried out under an atmosphere of highly purified nitrogen using standard Schlenk or vacuum-line techniques. Solvents for preparative use were dried and distilled under nitrogen from Na/benzophenone ketyl or CaH₂ prior to use. Commercial NaBH₄, selenium powder, and 2,4-dinitrophenylhydrazine were used as received. Ph₃(CH₂Ph)PBr [12], *n*-BuLi [13], [$\{\eta^5\text{-RC}_5\text{H}_4\text{Cr}(\text{CO})_3\}_2$] (R = Me [6], CO₂Et [7]), [$\{\eta^5\text{-MeC}(\text{O})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}\}$] [5] and [$\{\eta^5\text{-MeC}(\text{O})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] [5] were prepared according to literature procedures. All reactions were monitored by thin layer chromatography (TLC) at intervals. Column chromatography under nitrogen and preparative TLC were 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), respectively. Samples for characterization were recrystallized in 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, ⁷⁷Se NMR spectra were taken from a Varian Unity-Plus 400 NMR spectrometer with Ph₂Se₂ as external standard and chemical shifts are referenced to Me₂Se (δ = 0). Elemental analysis was performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

3.1. Preparation of [$\{\eta^5\text{-MeC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}\}$ (**3**)

A 100 ml Schlenk flask equipped with a magnetic stir-bar was charged with 0.215 g (0.50 mmol) of [$\{\eta^5\text{-MeC}_5\text{H}_4\text{Cr}(\text{CO})_3\}_2$], 0.040 g (0.50 mmol) of gray selenium powder and 20 ml of THF. The mixture was stirred at room temperature for ca. 15 min to produce an orange–red solution. After solvent was removed under vacuum, the residue was extracted with dichloromethane, which was then subjected to column chromatography using CH₂Cl₂/petroleum ether (*v/v* = 1:2) as eluent. From the orange–red band was obtained 0.222 g (98%) of **3** as a brown–red solid, m.p. 64–65 °C. Anal. Found: C, 42.71; H, 3.13. Calc. for C₁₆H₁₄Cr₂O₄Se: C, 42.40; H, 3.11%. IR (KBr disk): $\nu_{\text{C=O}}$ 1975s, 1951vs, 1895vs, 1882vs cm⁻¹. ¹H NMR (CDCl₃): δ 1.91 (s, 6H, 2CH₃), 4.72 (s, 4H, 2H², 2H⁵), 4.89 (s, 4H, 2H³, 2H⁴). ⁷⁷Se NMR (CDCl₃): δ 2580.9 (s).

3.2. Preparation of [$\{\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}\}$ (**4**)

The same procedure as preparation of **3** was followed, but 0.273 g (0.50 mmol) of [$\{\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Cr}(\text{CO})_3\}_2$] was employed to give 0.281 g (99%) **4** as a black–red solid, m.p. 58–59 °C. Anal. Found: C, 42.14; H, 3.18. Calc. for C₂₀H₁₈Cr₂O₈Se: C,

42.20; H, 3.19%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 1999s, 1954vs, 1934s, 1916s; $\nu_{\text{C}=\text{O}}$ 1712s cm^{-1} . ^1H NMR (CDCl_3): δ 1.25 (t, $J = 6.9$ Hz, 6H, 2CH₃), 4.18 (q, $J = 6.9$ Hz, 4H, 2CH₂), 5.02 (s, 4H, 2H³, 2H⁴), 5.57 (s, 4H, 2H², 2H⁵). ^{77}Se NMR (CDCl_3): δ 2572.9 (s).

3.3. Preparation of [$\{\eta^5\text{-MeCH(OH)C}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}$] (**6**)

The Schlenk flask described above was charged with 0.102 g (0.20 mmol) of [$\{\eta^5\text{-MeC(O)C}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}$] in 10 ml of THF and 0.030 g (0.80 mmol) of NaBH₄ in 10 ml of MeOH. The mixture was stirred at room temperature for 3 h. After removal of the solvents under reduced pressure, the residue was extracted with CH₂Cl₂, which was then subjected to column chromatography using CH₂Cl₂/petroleum ether ($v/v = 1:2$) as eluent. From the green band was obtained 0.076 g (74%) of **6** as a blue–black solid, m.p. 86–87 °C. Anal. Found: C, 42.49; H, 3.70. Calc. for C₁₈H₁₈Cr₂O₆Se: C, 42.12; H, 3.53%. IR (KBr disk): $\nu_{\text{O-H}}$ 3332vs; $\nu_{\text{C}\equiv\text{O}}$ 1938s, 1874m cm^{-1} . ^1H NMR (DMSO): δ 1.20 (s, 6H, 2CH₃), 3.10 (s, 2H, 2CH), 4.20 (d, $J = 6.7$ Hz, 2H, 2OH), 5.02 (d, 4H, 2H³, 2H⁴), 5.51 (d, 4H, 2H², 2H⁵). ^{77}Se NMR (CDCl_3): δ 2563.1 (s).

3.4. Preparation of [$\{\eta^5\text{-PhCH=C(Me)C}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}$] (**7**)

The Schlenk flask was charged with 0.346 g (0.80 mmol) of Ph₃(CH₂Ph)PBr, and 15 ml of THF. To the resulting solution cooled to 0 °C was added 0.80 mmol of *n*-BuLi in hexane. The mixture was stirred for 4 h to give a brown–red solution containing the Wittig reagent Ph₃P=CHPh [14] and then 0.102 g (0.20 mmol) of [$\{\eta^5\text{-MeC(O)C}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}$] in 10 ml of THF was added. The new mixture was stirred for additional 4 h. After removal of the solvents under reduced pressure, the residue was extracted with CH₂Cl₂, which was then subjected to column chromatography using CH₂Cl₂/petroleum ether ($v/v = 1:3$) as eluent. From the brown–yellow band was obtained 0.082 g (62%) of **7** as a brown–yellow solid, m.p. 84–85 °C. Anal. Found: C, 58.81; H, 4.13. Calc. for C₃₂H₂₆Cr₂O₄Se: C, 58.46; H, 3.99%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 1936s, 1883m; $\nu_{\text{C}=\text{C}}$ 1633vs cm^{-1} . ^1H NMR (CDCl_3): δ 1.32 (s, 6H, 2CH₃), 4.44 (s, 2H, 2CH), 5.09 (s, 4H, 2H³, 2H⁴), 5.74 (s, 4H, 2H², 2H⁵), 7.26–7.40 (m, 10H, 2C₆H₅). ^{77}Se NMR (CDCl_3): δ 2570.8(s).

3.5. Preparation of [$\{\eta^5\text{-2,4-(NO}_2\text{)}_2\text{C}_6\text{H}_3\text{NHNC(Me)C}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}$] (**8**)

To a solution of 0.102 g (0.20 mmol) of [$\{\eta^5\text{-MeC(O)C}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}$] in 15 ml of THF was dropped 8 ml (ca. 1.30 mmol) of 2,4-dinitrophenylhydrazine solu-

tion (prepared by dissolving 1.0 g of 2,4-dinitrophenylhydrazine in 5 ml of 98% H₂SO₄, 7 ml of H₂O and 23 ml of 95% EtOH). The mixture was stirred at room temperature for 3 h. The resulting red precipitate was filtered, and washed thoroughly with H₂O, ethyl alcohol and petroleum ether, respectively. The residue was extracted with CH₂Cl₂ and subjected to TLC separation using CH₂Cl₂ as eluent. From the brown–green band was obtained 0.113 g (65%) **8** as a brown–yellow solid, m.p. 152–153 °C. Anal. Found: C, 41.88; H, 2.75; N, 13.11. Calc. for C₃₀H₂₂Cr₂N₈O₁₂Se: C, 41.44; H, 2.55; N, 12.89%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 1973vs, 1904vs; $\nu_{\text{C}=\text{N}}$ 1616vs cm^{-1} . ^1H NMR (CDCl_3): δ 2.28 (s, 6H, 2CH₃), 6.04 (s, 4H, 2H³, 2H⁴), 6.58 (s, 4H, 2H², 2H⁵), 8.00 (d, $J = 9.9$ Hz, 2H, 2H⁶ of benzene ring), 8.31 (d, $J = 10.4$ Hz, 2H, 2H⁵ of benzene ring), 9.12 (s, 2H, 2H³ of benzene ring), 11.25 (s, 2H, 2NH). ^{77}Se NMR (CDCl_3): δ 2614.3 (s).

3.6. Preparation of [$\{\eta^5\text{-MeC}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}_2$] (**9**)

Method (i): A mixture of 0.215 g (0.50 mmol) of [$\{\eta^5\text{-MeC}_5\text{H}_4\text{Cr(CO)}_3\}_2$], 0.158 g (2.00 mmol) of selenium powder and 20 ml of THF was stirred at room temperature for 10 h, causing a color change from dark green to brown–green. The solvent was removed under vacuum and the residue was subjected to column chromatography using acetone/petroleum ether ($v/v = 1:4$) as eluent. A brown–green band was collected, from which 0.223 g (84%) of **9** was obtained as a brown–green solid, m.p. 132–133 °C. Anal. Found: C, 36.26; H, 2.64. Calc. for C₁₆H₁₄Cr₂O₄Se₂: C, 36.11; H, 2.65%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 1906s, 1847s cm^{-1} . ^1H NMR (CDCl_3): δ 1.97 (s, 6H, 2CH₃), 4.77 (s, 4H, 2H², 2H⁵), 4.94 (s, 4H, 2H³, 2H⁴). ^{77}Se NMR (CDCl_3): δ –202.4 (s).

Method (ii): A mixture of 0.227 g (0.50 mmol) of [$\{\eta^5\text{-MeC}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}$], 0.040 g (0.50 mmol) of selenium powder and 20 ml of THF was stirred at ca. 45 °C for 1.5 h, resulting in a color change from brown–red to brown–green. The same workup as that in Method (i) gave 0.194 g (73%) of **9**.

3.7. Preparation of [$\{\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Cr(CO)}_2\}_2\text{Se}_2$] (**10**)

Method (i): The same procedure as Method (i) for **9** was followed, but 0.273 g (0.50 mmol) of [$\{\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Cr(CO)}_3\}_2$] was utilized to give 0.276 g (85%) of **10** as a brown–green solid, m.p. 119–120 °C. Anal. Found: C, 36.94; H, 2.81. Calc. for C₂₀H₁₈Cr₂O₈Se₂: C, 37.06; H, 2.80%. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 1958vs, 1873vs; $\nu_{\text{C}=\text{O}}$ 1713 s cm^{-1} . ^1H NMR (CDCl_3): δ 1.32 (t, $J = 7.0$ Hz, 6H, 2CH₃), 4.26 (q, $J = 7.0$ Hz, 4H, 2CH₂), 4.69 (s, 4H, 2H³, 2H⁴), 5.20 (s, 4H, 2H², 2H⁵). ^{77}Se NMR (CDCl_3): δ –265.5 (s).

Method (ii): The same procedure was followed as Method (ii) for **9**, but 0.285 g (0.50 mmol) of [$\{\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}\}$] was employed. **10**: 0.223 g (69%).

3.8. Preparation of [$\{\eta^5\text{-MeCH}(\text{OH})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] (**12**)

The same procedure as preparation of **6** was followed, but 0.118 g (0.20 mmol) of [$\{\eta^5\text{-MeC}(\text{O})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] was used to give 0.076 g (64%) of **12** as a deep green solid, m.p. 135–136 °C. Anal. Found: C, 36.11; H, 2.96. Calc. for $\text{C}_{18}\text{H}_{18}\text{Cr}_2\text{O}_6\text{Se}_2$: C, 36.50; H, 3.06%. IR (KBr disk): $\nu_{\text{O-H}}$ 3329vs; $\nu_{\text{C=O}}$ 1938s, 1871m cm^{-1} . ^1H NMR (DMSO): δ 1.25 (s, 6H, 2CH₃), 3.09 (s, 2H, 2CH), 4.21 (d, $J = 9.3$ Hz, 2H, 2OH), 5.62 (d, 4H, 2H³, 2H⁴), 6.15 (d, 4H, 2H², 2H⁵). ^{77}Se NMR (CDCl_3): δ -237.0 (s).

3.9. Preparation of [$\{\eta^5\text{-PhCH}=\text{C}(\text{Me})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] (**13**)

The same procedure as preparation of **7** was followed, but 0.118 g (0.20 mmol) of [$\{\eta^5\text{-MeC}(\text{O})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] was used to afford 0.081 g (55%) of **13** as a brown–green solid, m.p. 128–129 °C. Anal. Found: C, 51.96; H, 3.40. Calc. for $\text{C}_{32}\text{H}_{26}\text{Cr}_2\text{O}_4\text{Se}_2$: C, 52.19; H, 3.56%. IR (KBr disk): $\nu_{\text{C=O}}$ 1936s, 1873m; $\nu_{\text{C=C}}$ 1635vs cm^{-1} . ^1H NMR (CDCl_3): δ 1.68 (s, 6H, 2CH₃), 4.42 (s, 2H, 2CH), 4.94 (s, 4H, 2H³, 2H⁴), 5.58 (s, 4H, 2H², 2H⁵), 7.31–7.46 (m, 10H, 2C₆H₅). ^{77}Se NMR (CDCl_3): δ -242.4 (s).

3.10. Preparation of [$\{\eta^5\text{-2,4-(NO}_2)_2\text{C}_6\text{H}_3\text{NHNC}(\text{Me})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] (**14**)

The same procedure as preparation of **8** was followed, but 0.118 g (0.20 mmol) of [$\{\eta^5\text{-MeC}(\text{O})\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\}_2\text{Se}_2$] was used to give 0.074 g (39%) of **14** as a brown–yellow solid, m.p. 172–173 °C. Anal. Found: C, 38.39; H, 2.50; N, 12.00. Calc. for $\text{C}_{30}\text{H}_{22}\text{Cr}_2\text{N}_8\text{O}_{12}\text{Se}_2$: C, 37.99; H, 2.34; N, 11.81%. IR (KBr disk): $\nu_{\text{N-H}}$ 3310m; $\nu_{\text{C=O}}$ 1999s, 1952vs, 1907vs; $\nu_{\text{C=N}}$ 1616vs cm^{-1} . ^1H NMR (CDCl_3): δ 2.18 (s, 6H, 2CH₃), 5.37 (s, 4H, 2H³, 2H⁴), 5.97 (s, 4H, 2H², 2H⁵), 8.04 (d, $J = 9.8$ Hz, 2H, 2H⁶ of benzene ring), 8.35 (d, $J = 10.8$ Hz, 2H, 2H⁵ of benzene ring), 9.15 (s, 2H, 2H³ of benzene ring), 11.14 (s, 2H, 2NH). ^{77}Se NMR (CDCl_3): δ -261.2 (s).

3.11. X-ray crystal structure determinations of **3** and **10**

Single crystals of **3** and **10** suitable for X-ray diffraction analysis were grown by slow evaporation of a hexane solution of **3** and toluene/hexane for **10** at -10 °C. Each of the single crystals was glued to a glass fiber and

Table 3
Crystal data and structural refinements details for **3** and **10**

| | 3 | 10 |
|--|--|--|
| Formula | $\text{C}_{16}\text{H}_{14}\text{Cr}_2\text{O}_4\text{Se}$ | $\text{C}_{20}\text{H}_{18}\text{Cr}_2\text{O}_8\text{Se}_2$ |
| Formula weight | 453.23 | 648.26 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | C_2/c | C_2/c |
| a (Å) | 10.462(2) | 29.135(8) |
| b (Å) | 8.0690(16) | 23.194(7) |
| c (Å) | 21.116(4) | 6.8770(18) |
| α (°) | 90 | 90 |
| β (°) | 102.84(3) | 103.045(5) |
| γ (°) | 90 | 90 |
| V (Å ³) | 1738.1(6) | 4527(2) |
| Z | 4 | 8 |
| D_{calc} (g cm^{-3}) | 1.732 | 1.902 |
| $F(000)$ | 896 | 2544 |
| μ (Mo $K\alpha$) (mm^{-1}) | 3.358 | 4.220 |
| Temperature (K) | 293(2) | 293(2) |
| Scan type | ω -2 θ | ω -2 θ |
| $2\theta_{\text{max}}$ (°) | 50 | 50.04 |
| Data/restraints/parameters | 2040/14/203 | 3592/3/317 |
| R | 0.0406 | 0.0739 |
| R_w | 0.1394 | 0.1681 |
| Goodness-of-fit | 1.090 | 0.950 |
| Largest differential peak and hole ($\text{e} \text{ \AA}^{-3}$) | 0.546 -0.698 | 0.982 -0.966 |

mounted on a Bruker SMART 1000 automated diffractometer, respectively. Data were collected at room temperature, using Mo $K\alpha$ graphite-monochromated radiation ($\lambda = 0.71073$ Å) in the ω -2 θ scanning mode. Absorption corrections were performed using SADABS. The structures were solved by direct methods using the SHELXTL-97 program and refined by full-matrix least-squares techniques (SHELXTL-97) on F^2 . Hydrogen atoms were located by using the geometric method. All calculations were performed on a Bruker Smart computer. Details of the crystals, data collections, and structure refinements are summarized in Table 3.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 228065 and 217180 for compounds **3** and **10**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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References

- [1] W.A. Herrmann, *Angew. Chem. Int. Ed. Engl.* 25 (1986) 56.
- [2] L.Y. Goh, W. Chen, E. Sinn, *J. Chem. Soc., Chem. Commun.* (1985) 462.
- [3] W. Chen, L.Y. Goh, E. Sinn, *Organometallics* 7 (1988) 2020.
- [4] W.A. Herrmann, J. Rohrmann, H. Nöth, CH.K. Nanila, I. Bernal, M. Draux, *J. Organomet. Chem.* 284 (1985) 189.
- [5] L.-C. Song, H.-W. Cheng, Q.-M. Hu, *Organometallics* 23 (2004) 1072.
- [6] R. Birdwhistell, P. Hackett, A.R. Manning, *J. Organomet. Chem.* 157 (1978) 239.
- [7] L.-C. Song, J.-Q. Wang, Q.-M. Hu, *Chin. J. Struct. Chem.* 14 (1995) 15.
- [8] P.A.W. Dean, L.Y. Goh, I.D. Gay, R.D. Sharma, *J. Organomet. Chem.* 533 (1997) 1.
- [9] (a) N.P. Luthra, J.D. Odom, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Organic Selenium and Tellurium Compounds*, Wiley, New York, 1986, p. 189;
(b) H.C.E. McFarlane, W. McFarlane, in: J. Mason (Ed.), *Multinuclear NMR*, Plenum, New York, 1987, p. 421.
- [10] L. Pauling, *The Nature of the Chemical Bond*, third ed., Cornell University Press, Ithaca, NY, 1960.
- [11] V.G. Andrianov, B.P. Biryukov, Yu.T. Struchkov, *Zh. Strukt. Khim.* 10 (1969) 1129.
- [12] M. Grayson, P.T. Keough, *J. Am. Chem. Soc.* 82 (1960) 3919.
- [13] H. Gilman, F.W. Moore, O. Baine, *J. Am. Chem. Soc.* 63 (1941) 2479.
- [14] E. Band, E.L. Muetterties, *Chem. Rev.* 98 (1979) 639.