

Novel Organometallic Macrocycles Containing Linear Cr₂E Structural Units: Synthesis and Characterization of $\{[(\text{CO})_2\text{Cr}\equiv\text{E}\equiv\text{Cr}(\text{CO})_2][\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2\}_n$ (E = Se, S; n = 1, 2)

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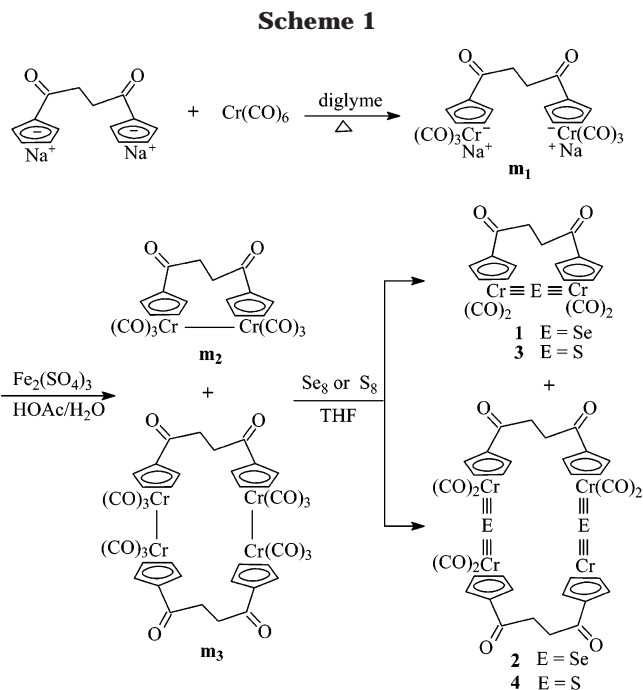
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Summary: The four novel organometallic macrocyclic compounds $\{[(\text{CO})_2\text{Cr}\equiv\text{Se}\equiv\text{Cr}(\text{CO})_2][\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2\}_n$ (**1**, n = 1; **2**, n = 2) and $\{[(\text{CO})_2\text{Cr}\equiv\text{S}\equiv\text{Cr}(\text{CO})_2][\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2\}_n$ (**3**, n = 1; **4**, n = 2) were prepared via a facile "one pot" synthetic route. While a possible pathway leading to such macrocycles is suggested, products **1–4** have been characterized by elemental analysis and spectroscopy and, for **1**, by X-ray crystallography.

We have been interested in the synthesis and structural characterization of organometallic macrocycles, since macrocycles, particularly those with organometallic structural units, are of great importance in theory and practical applications.^{1,2} So far, we have reported three new types of macrocycles, which include the first type of those containing linear M₂Hg (M = Cr, Mo, W) structural moieties,³ the second type of those containing tetrahedral M₂FeS (M = Mo, W) cluster cores,⁴ and the third type of those containing butterfly cluster cores (for example, Fe₂S₂).⁵ Herein we report the synthesis and structural characterization of another new type of macrocycle, which contains the linear Cr≡E≡Cr (E = Se, S) structural unit.

The designed synthetic route leading to such macrocycles, for instance **1–4**, is shown in Scheme 1, which is believed to involve three elementary reactions. The first one is actually the previously reported ligand exchange reaction between the succinoyl-bridged bis-(cyclopentadienylsodium) salt $[\text{NaC}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2$ and Cr(CO)₆ to give the corresponding bis(Cr/Na) salt $[\text{NaCr}(\text{CO})_3]_2[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2$ (**m**₁).³ The second one includes both the intramolecular oxidative coupling of one molecule of **m**₁ and the intermolecular oxidative coupling of two molecules of **m**₁ under the action of



solution of Fe₂(SO₄)₃ in HOAc and H₂O to produce the Cr–Cr singly bonded macrocycles $[(\text{CO})_3\text{Cr}-\text{Cr}(\text{CO})_3][\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2$ (**m**₂) and $\{[(\text{CO})_3\text{Cr}-\text{Cr}(\text{CO})_3][\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_2]_2\}_2$ (**m**₃), respectively. In fact, such oxidative coupling can be expected, since the M/Na salt $(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_3\text{MNa}$ (M = Cr, Mo, W) under the action of Fe₂(SO₄)₃/HOAc/H₂O was reported to undergo oxidative coupling to give the singly bonded complexes $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_3\text{M}]_2$,^{6a} while a mixture of $(\eta^5\text{-R}^1\text{C}_5\text{H}_4)(\text{CO})_3\text{MNa}$, $(\eta^5\text{-R}^2\text{C}_5\text{H}_4)(\text{CO})_3\text{MNa}$, and Fe₂(SO₄)₃/HOAc/H₂O could occur in oxidative coupling to produce the singly bonded complexes $[(\eta^5\text{-R}^1\text{C}_5\text{H}_4)(\text{CO})_3\text{M}]_2$, $[(\eta^5\text{-R}^2\text{C}_5\text{H}_4)(\text{CO})_3\text{M}]_2$, and $[(\eta^5\text{-R}^1\text{C}_5\text{H}_4)(\text{CO})_3\text{M}][(\eta^5\text{-R}^2\text{C}_5\text{H}_4)(\text{CO})_3\text{M}]$ (M = Mo, W).^{6b} Furthermore, although the Cr–Cr singly bonded macrocycles **m**₂ and **m**₃ were unable to be separated and fully characterized by conventional methods due to their insufficient solubility in common organic solvents and extreme air sensitivity (it is inflammable in air), the IR spectrum and particularly the ESI mass spectrum of the mixture⁷ obtained by reaction of **m**₁ with Fe₂(SO₄)₃

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/HOAc/H₂O followed by an appropriate workup (vide infra) indicated the presence of the singly bonded macrocycles **m**₂ and **m**₃. For example, the IR spectrum showed three absorption bands around 2000 cm⁻¹ for their terminal carbonyls and one absorption band at 1653 (s) cm⁻¹ for their diketone groups, whereas the ESI mass spectrum displayed a fragment ion at *m/z* 428 derived from the molecular ion of monomeric macrocycle **m**₂ by loss of two CO ligands and the molecular ion of **m**₃ at *m/z* 968. The third elementary reaction involved is the insertion reaction of elemental selenium or sulfur into **m**₂ and **m**₃ to afford the Cr≡E≡Cr (E = Se, S) structural unit containing macrocycles {[Cr(CO)₂Cr≡E≡Cr(CO)₂][η⁵-C₅H₄C(O)CH₂]₂]_n (**1**, *n* = 1; **2**, *n* = 2) and {[Cr(CO)₂Cr≡S≡Cr(CO)₂][η⁵-C₅H₄C(O)CH₂]₂]_n (**3**, *n* = 1; **4**, *n* = 2). This is also believable, since the insertion reaction of elemental E (E = Se, S) with the Cr–Cr singly bonded complexes [η⁵-RC₅H₄(CO)₃Cr]₂ is a well-known process to produce the corresponding linear Cr₂–E complexes [η⁵-RC₅H₄(CO)₂Cr]₂E (E = Se,⁸ S⁹) and particularly the macrocycles **1–4** have been fully characterized (vide infra).

As a typical experiment, the preparation of **1** and **2** was performed as follows. A mixture of 0.440 g (2 mmol) of Cr(CO)₆ and 0.258 g (1 mmol) of [NaC₅H₄C(O)CH₂]₂ in 15 mL of diglyme was refluxed for 5 h and then cooled to ca. 0 °C. To this mixture was added a solution consisting of 1.67 g (4.2 mmol) of Fe₂(SO₄)₃, 4 mL of acetic acid, and 9 mL of H₂O, and then the new mixture was stirred at room temperature for 0.5 h to give a green suspension. After solvents were removed by evaporation at reduced pressure, the green solid was washed sequentially with distilled water, ethyl alcohol, and petroleum ether. To the washed and vacuum-dried green solid were added 0.158 g (2 mmol) of selenium powder and 30 mL of THF. The mixture was stirred at room temperature for 0.5 h to give an orange solution, which was subjected to TLC separation using 2/5 (v/v) acetone/petroleum ether (30–60 °C) as eluent to give **1** (*R*_f = 0.65, 0.142 g, 28%) and **2** (*R*_f = 0.50, 0.112 g, 22%). Similarly, **3** and **4** were obtained in 27% and 24% yields, respectively, when using 0.064 g (2 mmol) of sulfur powder instead of selenium powder.

Macrocycles **1–4** have been fully characterized by elemental analysis and spectroscopy.¹⁰ The IR spectra of **1–4** each showed one absorption band in the range 1672–1665 cm⁻¹ characteristic of their diketone groups and three absorption bands in the region 2007–1906 cm⁻¹ typical of their terminal carbonyls. The ¹H NMR spectra of **1–4** all displayed one singlet in the region 2.81–3.10 ppm for their CH₂ groups and two singlets in the range 4.47–5.76 ppm for their substituted Cp rings, the upfield one being assigned to H³ and H⁴ protons of the Cp rings remote from the electron-withdrawing succinoyl substituent and the downfield one being attributed to H² and H⁵ protons close to the succinoyl group.¹¹ The ⁷⁷Se NMR spectra of **1** and **2**

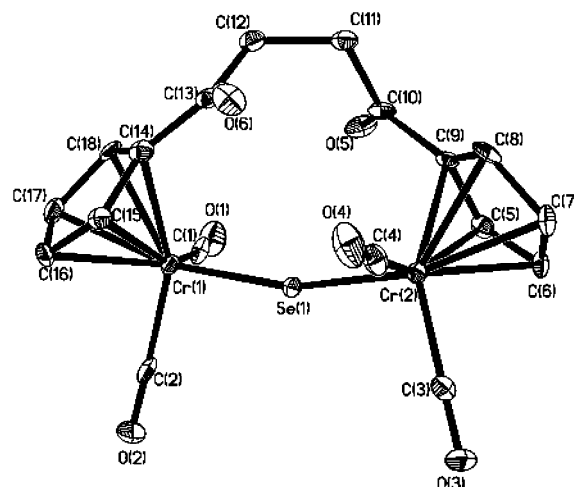


Figure 1. ORTEP drawing of **1** (thermal ellipsoids at the 30% probability level). Selected bond lengths (Å) and angles (deg): Se(1)–Cr(1) = 2.2217(16), Se(1)–Cr(2) = 2.2135(17), Cr(1)–C(1) = 1.883(11), Cr(2)–C(3) = 1.877(10), C(10)–O(5) = 1.212(10); Cr(1)–Se(1)–Cr(2) = 163.08(6), O(2)–C(2)–Cr(1) = 177.7(8), O(3)–C(3)–Cr(2) = 178.6(8), C(9)–C(10)–O(5) = 118.6(8).

exhibited one singlet at 2693.9 and 2589.2 ppm for their Se atoms, respectively. It follows that the two Se atoms in **2** have identical magnetic environments, and the ⁷⁷Se NMR chemical shifts of **1** and **2** are very close to those of their noncyclic analogues [(η⁵-RC₅H₄)Cr(CO)₂]₂Se (R = H (2574 ppm),¹² Me (2580.9 ppm),¹³ MeCO (2589.8 ppm),^{8b} MeO₂C (2604.6 ppm^{8b})). In addition, it is worth pointing out that the ESI mass spectrum of dimeric macrocycle **2** showed its molecular ion at *m/z* 1016, whereas the mass spectrum of dimeric macrocycle **4** displayed its molecular ion at *m/z* 921.

Fortunately, the structure of **1** has been confirmed by X-ray diffraction analysis.¹⁴ Figure 1 shows that **1**

(10) Characterization data for **1–4** are as follows. **1**: mp 62–63 °C. Anal. Calcd for C₁₈H₁₂Cr₂O₆Se: C, 42.62; H, 2.39. Found: C, 42.72; H, 2.62. IR (KBr disk): ν_{C=O} 1999 (m), 1973 (vs), 1906 (s); ν_{C–O} 1665 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 2.81 (s, 4H, 2CH₂), 4.47 (s, 4H, 2H³, 2H⁴), 5.76 (s, 4H, 2H², 2H⁵). ⁷⁷Se NMR (CDCl₃): δ 2693.9 (s). **2**: mp 71–72 °C. Anal. Calcd for C₃₆H₂₄Cr₄O₁₂Se₂: C, 42.62; H, 2.39. Found: C, 42.87; H, 2.49. IR (KBr disk): ν_{C=O} 1978 (vs), 1940 (s), 1908 (s); ν_{C–O} 1666 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 3.10 (s, 8H, 4CH₂), 4.71 (s, 8H, 4H³, 4H⁴), 5.66 (s, 8H, 4H², 4H⁵). ⁷⁷Se NMR (CDCl₃): δ 2589.2 (s). ESI MS (*m/z*): 1016 (M⁺, ⁸⁰Se), 960 (M⁺ – 2CO), 880 (M⁺ – 2CO – Se), 664 (M⁺ – 5CO – 2Se – Cr). **3**: mp 132 °C dec. Anal. Calcd for C₁₈H₁₂Cr₂O₆S: C, 46.96; H, 2.63. Found: C, 47.00; H, 2.83. IR (KBr disk): ν_{C=O} 2005 (s), 1970 (vs), 1939 (s); ν_{C–O} 1665 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 2.81 (s, 4H, 2CH₂), 4.60 (s, 4H, 2H³, 2H⁴), 5.73 (s, 4H, 2H², 2H⁵). **4**: mp 146 °C dec. Anal. Calcd for C₃₆H₂₄Cr₄O₁₂S₂: C, 46.96; H, 2.63. Found: C, 46.54; H, 2.86. IR (KBr disk): ν_{C=O} 2007 (vs), 1963 (vs), 1923 (vs); ν_{C–O} 1672 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 3.11 (s, 8H, 4CH₂), 4.81 (s, 8H, 4H³, 4H⁴), 5.64 (s, 8H, 4H², 4H⁵). ESI MS (*m/z*): 921 (M⁺), 697 (M⁺ – 8CO).

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(14) Crystal data for **1**: *M*_r = 507.24, monoclinic, *C*2/*c*, *a* = 27.496(11) Å, *b* = 11.788(5) Å, *c* = 11.791(5) Å, β = 107.335(8)°, *V* = 3648(3) Å³, *Z* = 8, *D*_{calcd} = 1.847 Mg/m³, *F*(000) = 2000, μ = 3.219 mm⁻¹, Mo Kα radiation (λ = 0.710 73 Å), 2θ_{max} = 46.54°, scan mode ω–2θ, 5753 collected reflections, 2457 independent reflections, *R* = 0.0546, *R*_w = 0.1283. The structure was solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were included but not refined. The calculations were performed using the SHELXTL-97 program.

(7) Some characterization data for the mixture of **m**₂ and **m**₃: IR (KBr disk) ν_{C=O} 2008 (m), 1945 (vs), 1917 (s); ν_{C–O} 1653 cm⁻¹; ESI MS (*m/z*) 428 (M⁺ – 2CO) and 372 (M⁺ – 4CO) for **m**₂, 968 (M⁺), 856 (M⁺ – 4CO), 744 (M⁺ – 8CO), and 664 (M⁺ – 9CO – Cr) for **m**₃.

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consists of an essentially linear Cr–Se–Cr skeleton, four terminal carbonyls, and the succinoyl-bridged bis-(cyclopentadienyl) ligand. This molecule could be regarded as a 17-membered macrocycle, if all the carbon atoms of the two Cp rings C(5) through C(9) and C(14) through C(18) are all involved in counting the ring size. The bond angle around Se ($163.08(6)^\circ$) in macrocycle **1** is obviously smaller than those in their noncyclic analogues $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)\text{Cr}(\text{CO})_2]_2\text{Se}$ ($167.90(8)^\circ$),^{8b} $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Cr}(\text{CO})_2]_2\text{Se}$ ($178.70(6)^\circ$),¹³ and $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ ($178.3(1)^\circ$),^{8a} whereas the average Cr–Se bond length ($2.2176(16)$ Å) of **1** is close to those of $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)\text{Cr}(\text{CO})_2]_2\text{Se}$ ($2.1935(16)$ Å),^{8b} $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Cr}(\text{CO})_2]_2\text{Se}$ ($2.2105(2)$ Å),¹³ and $[\text{CpCr}(\text{CO})_2]_2\text{Se}$ ($2.22085(1)$ Å).^{8a} In addition, it is worthy of note that the considerable shortening of the Cr–Se bond lengths in comparison with the sum of the covalent radii of chromium ($r_{\text{Cr}} = 1.46$ Å)¹⁵ and selenium ($r_{\text{Se}} = 1.17$ Å)¹⁶ atoms is in agreement with triple bonding between chromium and selenium atoms in those Cr≡Se≡Cr units of such complexes. This molecule is C_{2v} symmetric, which has a C_2 axis passing through the Se(1) atom and the midpoint of the C(11)–C(12) bond.

In conclusion, we have prepared and characterized

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four novel organometallic macrocycles **1–4**, which contain both the inorganic functionality of linear Cr≡E≡Cr (E = Se, S) structural moieties and the organic diketo functionality of succinoyl groups. In view of the rich chemistry of those functionalities,^{8b,11,17} it is expected that macrocycles **1–4** can be used as a new type of versatile synthon for preparing a wide variety of organometallic macrocycles. Further studies concerning the functional transformations of such functionalities, as well as the new applications of the mixed Cr–Cr singly bonded macrocycles **m**₂ and **m**₃ for synthesis of other organometallic macrocycles, are also in progress.

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Supporting Information Available: Text describing the synthesis and characterization of complexes **1–4** and a CIF file giving details of the structural determination of **1**, including atomic coordinates, equivalent isotropic displacement parameters, bond lengths and angles, and data collection and processing parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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