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A Basic Strategy for Functionalization of Metal Cyclopentadienyl Complexes: Synthesis, Characterization, and Reactivity of Linear, Butterfly, and Cubic Chromium/Selenium Complexes Containing Functionally Substituted Cyclopentadienyl Ligands

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The first examples of linear, butterfly, and cubic Cr/Se complexes containing functionally substituted Cp ligands have been successfully synthesized by skeleton and functional transformations of the prefunctionalized Cp metal precursors. For example, (i) the prefunctionalized Cp metal precursors $[\eta^5\text{-RC}_5\text{H}_4\text{Cr(CO)}_3]_2$ (**1**, R = MeCO; **2**, R = MeO_2C) reacted with elemental selenium under the given conditions to afford linear complexes $[\eta^5\text{-RC}_5\text{H}_4\text{Cr(CO)}_2]_2\text{Se}$ (**3**, R = MeCO; **4**, R = MeO_2C), butterfly complexes $[\eta^5\text{-RC}_5\text{H}_4\text{Cr(CO)}_2]_2\text{Se}_2$ (**5**, R = MeCO; **6**, R = MeO_2C), and cubane clusters $(\eta^5\text{-RC}_5\text{H}_4)_4\text{Cr}_4\text{Se}_4$ (**7**, R = MeCO; **8**, R = MeO_2C), whereas the linear complexes **3**/**4** reacted with elemental selenium under appropriate conditions to produce butterfly complexes **5**/**6** or cubane clusters **7**/**8**; (ii) thermolysis of a THF solution of butterfly complex **5** or **6** gave rise to cubane cluster **7** or **8**, whereas the THF solution of two butterfly complexes $[\text{CpCr(CO)}_2]_2\text{Se}_2$ and **6** under reflux afforded cubane clusters $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)_n\text{Cp}_{4-n}\text{Cr}_4\text{Se}_4$ ($n = 0$, $\text{Cp}_4\text{Cr}_4\text{Se}_4$; $n = 1$, **9**; $n = 2$, **10**; $n = 3$, **11**; $n = 4$, **8**); (iii) while cluster **7** reacted with excess NaBH_4 to give secondary hydroxy derivative $[\eta^5\text{-MeCH(OH)C}_5\text{H}_4]_4\text{Cr}_4\text{Se}_4$ (**12**), it reacted with Grignard reagent MeMgI and subsequent hydrolysis of the addition intermediate to afford tertiary hydroxy derivative $[\eta^5\text{-Me}_2\text{C(OH)-C}_5\text{H}_4]_4\text{Cr}_4\text{Se}_4$ (**13**); and (iv) the functional transformation of cluster **7** under the action of Wittig reagent $\text{Ph}_3\text{P{=}CHPh}$ produced cubane cluster $[\eta^5\text{-PhCH{=}C(Me)C}_5\text{H}_4]_4\text{Cr}_4\text{Se}_4$ (**14**), whereas the condensation reaction of **7** with 2,4-dinitrophenylhydrazine yielded phenylhydrazone derivative $[\eta^5\text{-2,4-(NO}_2)_2\text{C}_6\text{H}_3\text{NHNC(Me)C}_5\text{H}_4]_4\text{Cr}_4\text{Se}_4$ (**15**). Possible pathways for the reactions leading to functionalized cubane clusters **7**−**11** are suggested. Furthermore, ^{77}Se NMR techniques were utilized to characterize the new functionalized complexes, whereas single-crystal X-ray diffraction was employed to confirm the structures of complexes **4**, **7**, **8**, **11**, and **12**.

Introduction

There has been increasing current interest in metal complexes bearing ligands with an “external” functionality that is not ligated to the central metal. The “external” functionality, in contrast to “internal” functionality,[1] is known to play an important role in the synthesis of novel metal complexes[2−4] and in the accomplishment of the biological function of metal enzymes,[5,6] as well as in catalysis and molecular recognition.[7] This study focuses on organometallic complexes and clusters containing functionally substituted cyclopentadienyl ligands. It is expected that such fundamental studies in this area will ultimately achieve great success since the parent cyclopentadienyl ligand and its substituted derivatives are important and ubiquitous in transition metal chemistry.

In principle, there are two basic strategies for functionalization of metal-Cp compounds, the first involving direct functionalization of the metal-Cp complexes[8] and the second being based on the transformation of prefunctionalized Cp-metal complex precursors.[3,9] Recently, Rauchfuss and co-workers carried out a study on the first strategy regarding direct functionalization of the

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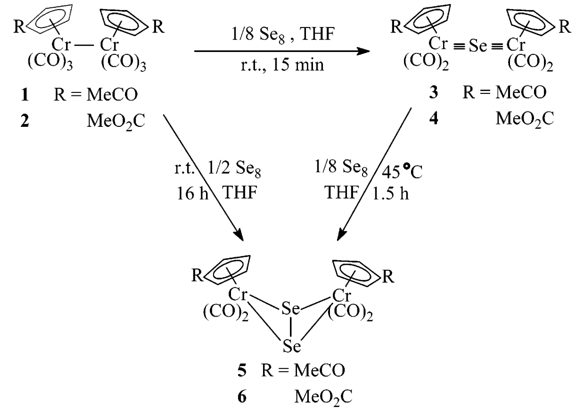
Cp-metal cubane-like cluster $Cp_4Fe_4(CO)_4$, based on their initial considerations that the second strategy is less easily applied to clusters since the functional group on the prefunctionalized Cp ligands can be incompatible with clusterification processes.[4] To examine the suitability of the two strategies for synthesizing cubane clusters containing functionally substituted Cp ligands, we chose to study the cubane Cr_4Se_4 clusters. This is because such clusters are closely related to the active site in biomolecules, such as high potential proteins and ferredoxins.[5] In addition, the parent compound $Cp_4Cr_4Se_4$ of such clusters can be easily prepared.[10] Now, we have found that the second strategy is well suited for preparing functionalized cyclopentadienyl Cr_4Se_4 clusters from the prefunctionalized Cp-metal complex precursors, whereas the first strategy, in contrast to the feasible case for $Cp_4Fe_4(CO)_4$,[4] cannot be applied to direct functionalization of $Cp_4Cr_4Se_4$ under similar metalation and Friedel−Crafts acylation conditions to give the corresponding cubane-like cluster complexes. This article will mainly describe the synthesis, characterization, and reactions of the functionalized Cp cubane Cr_4Se_4 clusters $(\eta^5\text{-}RC_5H_4)_nCp_{4-n}Cr_4Se_4$ ($n = 1-4$), the functionalized Cp linear Cr_2Se complexes $[\eta^5\text{-}RC_5H_4Cr(CO)_2]_2Se$, and butterfly Cr_2Se_2 complexes $[\eta^5\text{-}RC_5H_4Cr(CO)_2]_2Se_2$. Furthermore, the mechanistic pathways for production of the Cr_4Se_4 cubane clusters are also described.

Results and Discussion

Synthesis and Characterization of Linear, Butterfly, and Cubic Complexes Containing Functionalized Cp Ligands 3−6. We found that the Cr−Cr singly bonded dimers containing functionalized Cp ligands $[\eta^5\text{-}RC_5H_4Cr(CO)_3]_2$ (**1**, R = MeCO; **2**, R = MeO_2C)[11] reacted with 1 equiv of elemental selenium in THF at room temperature for ca. 15 min to give the linear Cr_2Se complexes $[\eta^5\text{-}RC_5H_4Cr(CO)_2]_2Se$ (**3**, R = MeCO; **4**, R = MeO_2C) in nearly quantitative yield. Further reaction of **3** or **4** with 1 equiv of elemental selenium in THF at ca. 45 °C for 1.5 h and reaction of **1** or **2** with an excess amount of elemental selenium in THF at room temperature for 16 h resulted in formation of the butterfly Cr_2Se_2 complexes $[\eta^5\text{-}RC_5H_4Cr(CO)_2]_2Se_2$ (**5**, R = MeCO; **6**, R = MeO_2C) in high yield (Scheme 1).

While the linear complexes **3** and **4** could be regarded as derived by insertion of a Se atom into the Cr−Cr single bonds of **1** and **2** followed by loss of two CO ligands and concomitant formation of the cumulated Cr≡Se triple bonds between Cr and Se atoms, the butterfly complexes **5** and **6** might be formally viewed as produced from insertion of a Se atom across the cumulated Cr≡Se triple bonds of **3** and **4** and concurrent change to the butterfly Cr_2Se_2 skeleton.[12−14] Either the μ_2-Se or μ_2-Se_2 ligand acts as a 6e donor, and the Cr atoms in **3**−**6** have achieved the noble gas configuration.

Scheme 1[a]



Products **3**−**6** are the first examples of the linear and butterfly Cr/Se complexes containing functionalized Cp ligands, although their parent complexes $[CpCr(CO)_2]_2Se$ and $[CpCr(CO)_2]_2Se_2$ were known.[14−16] The IR spectra of **3**−**6** showed two or three absorption bands in the range 1999−1880 cm^{-1} for their terminal carbonyls and one absorption band in the region 1717−1676 cm^{-1} for their ketonic and ester carbonyls in the functionalized Cp ligands. The ^1H NMR spectra of **3**−**6** displayed two singlets for the four protons in each substituted Cp ring, one singlet at lower field being assigned to H^2/H^5 close to the substituent and the other at higher field attributed to H^3/H^4 remote from the substituent since the substituents attached to the Cp rings are electron-withdrawing.[3]

The ^{77}Se NMR spectra of **3** and **4** each showed one singlet for the μ_2-Se atom in the highly deshielded range from 2589 to 2605 ppm, whereas the spectra of **5** and **6** each displayed one singlet for μ_2-Se_2 atoms in the highly shielded region from −257 to −267 ppm. Such ^{77}Se NMR data of **3**−**6** are comparable with the reported data corresponding to the parent linear and butterfly complexes $[CpCr(CO)_2]_2Se$ and $[CpCr(CO)_2]_2Se_2$, respectively.[17] The highly deshielding μ_2-Se of **3** and **4** probably originates from the involvement of the π-electrons of Se in the unusual cumulated Cr≡Se≡Cr linkage.[18]

The structure of linear complex **4** was confirmed by a single-crystal X-ray diffraction study. The ORTEP drawing of **4** is shown in Figure 1, whereas Table 1 presents its selected bond lengths and angles.

Figure 1 shows that complex **4** consists of an essentially linear Cr−Se−Cr skeleton, two functionalized Cp ligands η^5-$MeO_2CC_5H_4$, and four terminal carbonyls.

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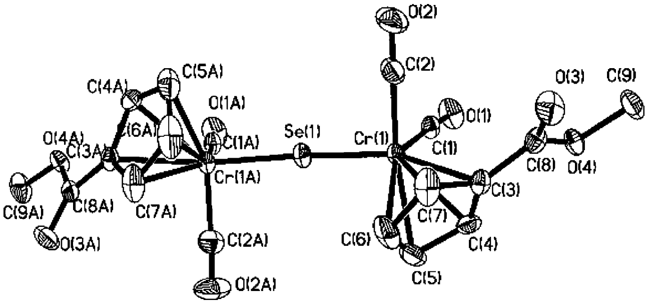


Figure 1. ORTEP drawing of **4** (30% probability ellipsoids, H atoms are omitted).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4

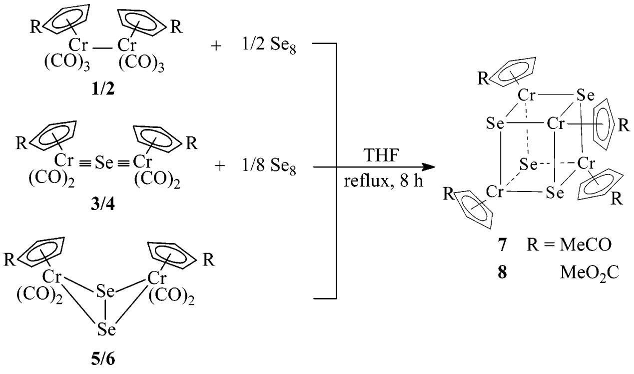
Cr(1)−C(1)	1.873(9)	Cr(1A)−Se(1)	2.1935(16)
Cr(1)−C(2)	1.871(13)	Cr(1)−C(3)	2.169(8)
Cr(1)−Se(1)	2.1935(16)	Cr(1)−C(4)	2.189(9)
C(1)−O(1)	1.111(10)	C(8)−C(3)	1.453(13)
Cr(1)−Se(1)−Cr(1A)	167.90(8)	C(1)−Cr(1)−Se(1)	97.9(2)
C(1)−Cr(1)−C(2)	88.7(5)	C(2)−Cr(1)−C(5)	153.5(6)
C(2)−Cr(1)−C(7)	90.9(5)	Se(1)−Cr(1)−C(5)	100.4(3)
C(2)−Cr(1)−Se(1)	94.5(4)	O(1)−C(1)−Cr(1)	177.7(9)

The bond angle around Se [167.90(8)°] in **4** is much less than the corresponding angle in its parent complex $[\eta^5\text{-CpCr(CO)}_2]_2\text{Se}$ [178.3(1)°], whereas the Cr−Se bond lengths of **4** [2.1935(16) Å] are close to those of its parent complex (2.208(1) and 2.211 Å).[16] It is noteworthy that 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 [19]) and selenium (r_{Se} 1.17 Å [20]) is consistent with triple bonding between chromium and selenium atoms in the linear Cr≡Se≡Cr unit of complex **4**. In addition, the bond length of C(8)−C(3) (1.453 (13) Å) is much shorter than that of a normal C−C single bond, which could be attributed to conjugation between the π-electron systems of the substituted MeO_2C and cyclopentadienyl ring. This molecule possesses C_2 symmetry.

Reactions of Prefunctionalized Cp Precursors 1−6 with Selenium Leading to Functionalized Cp Cubane Cr_4Se_4 Clusters 7 and 8. We further found that when the Cr−Cr singly bonded dimers **1** and **2** with excess elemental selenium, or the linear Cr_2Se complexes **3** and **4** with 1 equiv of selenium, or even the butterfly Cr_2Se_2 complexes **5** and **6** alone were refluxed in THF for 8 h, the corresponding functionalized cubane clusters $(\eta^5\text{-RC}_5\text{H}_4)_4\text{Cr}_4\text{Se}_4$ (**7**, R = MeCO; **8**, R = MeO_2C) could be obtained in excellent yield (Scheme 2).

Products **7** and **8** are the first functionalized Cp cubane Cr_4Se_4 clusters, which were prepared through skeleton transformation of the prefunctionalized Cp-metal precursors by the second synthetic strategy. It should be noted that our attempts failed to obtain such functionalized Cp cubane clusters by the first synthetic strategy. For instance, when parent cubane cluster $Cp_4Cr_4Se_4$ was treated with MeC(O)Cl/$AlCl_3$, acetic anhydride/H_3PO_4, or lithium diisopropylamide (LDA) followed by treatment with $(PhS)_2$ under conditions similar to those of Friedel−Crafts acylation and lithiation of

Scheme 2[a]



[a] The Cr−Cr bonds in the cubane cores of **7** and **8** are omitted for clarity.

ferrocene or $Cp_4Fe_4(CO)_4$,[4,21,22] no expected functionalized cubane cluster complexes of $[\eta^5\text{-MeC(O)C}_5\text{H}_4]_n\text{-Cp}_{4-n}\text{Cr}_4\text{Se}_4$ (n = 1−4) and $(\eta^5\text{-PhSC}_5\text{H}_4)_n\text{Cp}_{4-n}\text{Cr}_4\text{Se}_4$ (n = 1−4) were obtained from the corresponding reaction mixtures.

Products **7** and **8** were fully characterized by elemental analysis, spectroscopy, and X-ray diffraction studies. For example, the IR spectra of **7** and **8** exhibited one absorption band in the range 1664−1716 cm^{-1} assigned to their ketonic and ester carbonyls, and the ^1H NMR spectra showed two singlets at lower and higher fields attributed to H^2/H^5 and H^3/H^4 protons in the functionalized Cp rings. It was previously reported[17] that the solid-state ^{77}Se NMR spectrum of parent cluster $Cp_4Cr_4Se_4$ (due to its insufficient solubility for a solution NMR study) exhibited two singlets at 1018 and 1079 ppm, and it was not clear whether the two shifts represent different $Cp_4Cr_4Se_4$ molecules or different Se environments within a single distorted molecule. However, in contrast to the case of parent cluster $Cp_4Cr_4Se_4$, the solution ^{77}Se NMR spectra of the functionalized derivatives **7** and **8** displayed only one singlet in the range 1244−1227 ppm, which implies that they possess only one single μ_3-Se environment for a single molecule. Fortunately, this has been unambiguously confirmed by their crystal X-ray diffraction analyses. The ORTEP drawings of **7** and **8** are depicted in Figures 2 and 3, while their selected bond lengths and angles are given in Table 2.

As can be seen in Figures 2 and 3, complexes **7** and **8**, similar to their methyl analogue $(\eta^5\text{-MeC}_5\text{H}_4)_4\text{Cr}_4\text{Se}_4$,[23] contain a cubane-like Cr_4Se_4 cluster core, which carries four substituted Cp ligands coordinated to four Cr atoms, respectively. The cubic Cr_4Se_4 cluster core of **7** seems to be idealized, but that of **8** is slightly distorted, which could be seen from their related bond lengths and angles. For example, for **7** the bond lengths of Cr−Se and Cr−Cr are 2.432−2.426 Å and 3.015−3.010 Å, and the bond angles of Se−Cr−Se and Cr−Se−Cr are 102.05−101.75° and 76.76−76.57°, whereas for **8** the bond lengths of Cr−Se and Cr−Cr are 2.394−2.376 Å and 2.985−2.932 Å, and the bond angles of Se−Cr−Se and Cr−Se−Cr are 102.82−100.61° and 77.52−76.02°,

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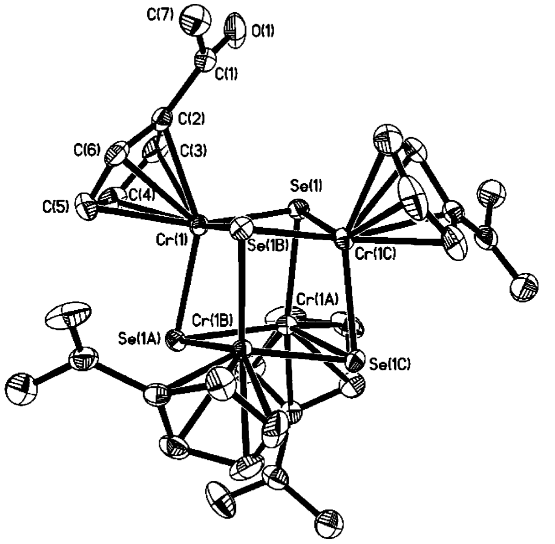

Figure 2. ORTEP drawing of **7** (30% probability ellipsoids, H atoms are omitted).

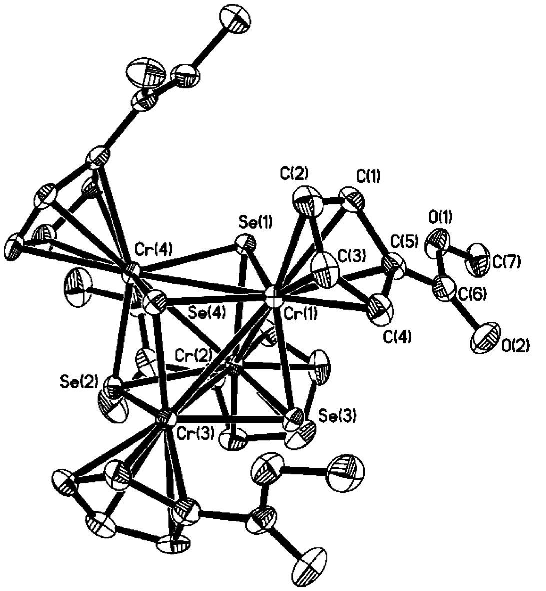

Figure 3. ORTEP drawing of **8** (30% probability ellipsoids, H atoms are omitted).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7, 8, 11, and 12

	7		
Cr(1)−C(2)	2.255(10)	Cr(1)−Cr(1A)	3.010(3)
Cr(1)−Se(1A)	2.426(2)	Cr(1)−Cr(1B)	3.015(3)
Cr(1)−Se(1B)	2.429(3)	O(1)−C(1)	1.279(10)
Cr(1)−Se(1)	2.432(2)	C(1)−C(2)	1.503(14)
C(2)−Cr(1)−Se(1A)	147.1(3)	Se(1B)−Cr(1)−Se(1)	101.75(6)
C(4)−Cr(1)−Se(1A)	88.0(3)	Cr(1A)−Se(1)−Cr(1C)	76.76(6)
Se(1A)−Cr(1)−Se(1B)	101.90(6)	Cr(1A)−Se(1)−Cr(1)	76.57(6)
C(2)−Cr(1)−Se(1)	97.5(3)	Cr(1C)−Se(1)−Cr(1)	76.67(6)
Se(1A)−Cr(1)−Se(1)	102.05(6)	O(1)−C(1)−C(2)	119.0(18)
	8		
Cr(1)−Se(4)	2.3761(13)	Cr(3)−Se(2)	2.3810(13)
Cr(1)−Se(1)	2.3824(13)	Cr(3)−Se(4)	2.3838(13)
Cr(3)−Cr(4)	2.9848(17)	Cr(3)−Se(3)	2.3940(14)
Cr(1)−Cr(4)	2.9326(18)	Se(1)−Se(3)	3.6772(13)
Cr(1)−Cr(3)	2.9521(16)	Se(1)−Se(2)	3.7154(12)
Cr(1)−Cr(2)	2.9669(17)	C(6)−O(1)	1.338(9)
Se(4)−Cr(1)−Se(1)	102.82(5)	Cr(2)−Se(1)−Cr(4)	76.60(4)
Se(4)−Cr(1)−Se(3)	102.47(5)	Cr(2)−Se(1)−Cr(1)	77.14(5)
Se(4)−Cr(4)−Se(2)	100.61(5)	Cr(1)−Se(1)−Se(2)	80.49(4)
Se(4)−Cr(1)−Cr(4)	52.08(4)	Se(3)−Se(1)−Se(2)	60.33(3)
Se(3)−Cr(1)−Cr(4)	99.62(5)	Se(2)−Se(4)−Se(1)	60.35(2)
Se(1)−Cr(1)−Cr(3)	99.54(5)	Cr(1)−Cr(4)−Cr(3)	59.85(4)
	11		
Cr(4)−Se(1)	2.4048(19)	Cr(4)−Se(2)	2.4140(19)
Cr(1)−Se(1)	2.396(2)	Cr(4)−Se(4)	2.4135(19)
Cr(2)−Se(1)	2.406(2)	Cr(1)−C(3)	2.251(12)
Cr(2)−Se(2)	2.4055(19)	Cr(1)−Cr(4)	2.955(3)
Se(2)−Cr(3)	2.410(2)	Cr(2)−Cr(3)	2.944(2)
Cr(1)−Se(1)−Cr(4)	75.97(7)	Se(1)−Cr(1)−Cr(3)	99.96(7)
Cr(1)−Se(1)−Cr(2)	78.34(6)	Cr(4)−Cr(1)−Cr(3)	62.84(5)
Cr(4)−Se(1)−Cr(2)	76.22(7)	Se(3)−Cr(2)−Se(2)	103.74(7)
Se(1)−Cr(1)−Se(3)	99.01(7)	Se(3)−Cr(2)−Cr(3)	52.11(5)
Se(1)−Cr(1)−Se(4)	103.69(8)	Se(1)−Cr(2)−Cr(4)	51.87(5)
Se(2)−Cr(4)−Se(4)	97.54(7)	Cr(3)−Cr(2)−Cr(4)	62.97(6)
	12		
Cr(1A)−Se(1)	2.375(3)	Cr(1)−Cr(1A)	2.957(5)
Cr(1B)−Se(1)	2.384(3)	Cr(1)−Cr(1C)	2.969(4)
Cr(1)−Se(1)	2.386(3)	Cr(1)−Cr(1B)	2.969(4)
Cr(1)−Se(1A)	2.375(3)	C(5)−C(6)	1.533(10)
Se(1C)−Cr(1)	2.384(3)	C(6)−O(1)	1.298(10)
Cr(1A)−Se(1)−Cr(1B)	77.19(10)	Se(1A)−Cr(1)−Cr(1A)	51.77(8)
Cr(1A)−Se(1)−Cr(1)	76.80(10)	Se(1)−Cr(1)−Cr(1A)	51.43(9)
Cr(1B)−Se(1)−Cr(1)	76.98(9)	Se(1A)−Cr(1)−Cr(1C)	51.55(7)
Se(1A)−Cr(1)−Se(1C)	101.67(10)	Se(1)−Cr(1)−Cr(1C)	98.58(8)
C(1)−Cr(1)−Se(1)	86.2(6)	Se(1)−Cr(1)−Cr(1B)	51.49(7)
Se(1A)−Cr(1)−Se(1)	101.93(10)	Cr(1A)−Cr(1)−Cr(1B)	60.13(4)

respectively. Both C(1)−C(2) (1.503 Å) of **7** and C(5)−C(6) (1.488 Å) of **8** are shorter than a normal C−C single bond, due to the same reason for **4** as described above. In addition, it is worthy of note that complexes **7** and **8**, as predicated by the 18-valence-electron (18 VE) rule, are 60-electron clusters, which contain four μ_3-Se atoms (each as a 4e donor) and six Cr−Cr single bonds.

Reaction of Prefunctionalized Cp Precursor 6 with [CpCr(CO)$_2$]$_2$Se$_2$ Leading to Cubane Cr$_4$Se$_4$ Clusters Containing Cp and Functionalized Cp Ligands 9−11. Reaction of an equimolar quantity of prefunctionalized Cp butterfly precursor **6** with its parent butterfly complex [CpCr(CO)$_2$]$_2$Se$_2$ in THF for 8 h produced mainly the cubane clusters containing both Cp and functionalized Cp ligands (η^5-MeO$_2$CC$_5$H$_4$)$_n$-Cp$_{4-n}$Cr$_4$Se$_4$ (n = 1, **9**; n = 2, **10**; n = 3, **11**), along with minor cubane clusters Cp$_4$Cr$_4$Se$_4$ (n = 0) and (η^5-MeO$_2$CC$_5$H$_4$)$_4$Cr$_4$Se$_4$ (n = 4, **8**) in total 96% yield (Scheme 3).

Cubane clusters **9**−**11** contain both Cp and functionalized Cp and were formed through a new type of cross-assembled reaction,[24] namely, coclusterification reaction of two different butterfly complexes. While the IR spectra of **9**−**11** showed one absorption band at ca. 1720 cm^{-1} for their ester's carbonyl functionalities, the ^{1}H NMR spectra of **9**−**11** displayed one singlet for the five protons of each Cp ring and two singlets for H^2/H^5 and H^3/H^4 protons of each substituted Cp ring.[3] It is worth pointing out that most of the mixedCp clusters **9**−**11**, in contrast to parent Cp cluster Cp$_4$Cr$_4$Se$_4$ and functionalized Cp clusters **7** and **8**, displayed ^{1}H NMR signals for Cp and functionalized Cp at much lower field. That is, while **11** showed ^{1}H NMR signals in the normal range, the other two exhibited signals at low field up to 32 ppm, probably due to trace amounts of paramagnetic species such as (CpCr)$_m$Se$_n$ and (RCpCr)$_m$Se$_n$ derived from decomposition of the corresponding cubane clusters.

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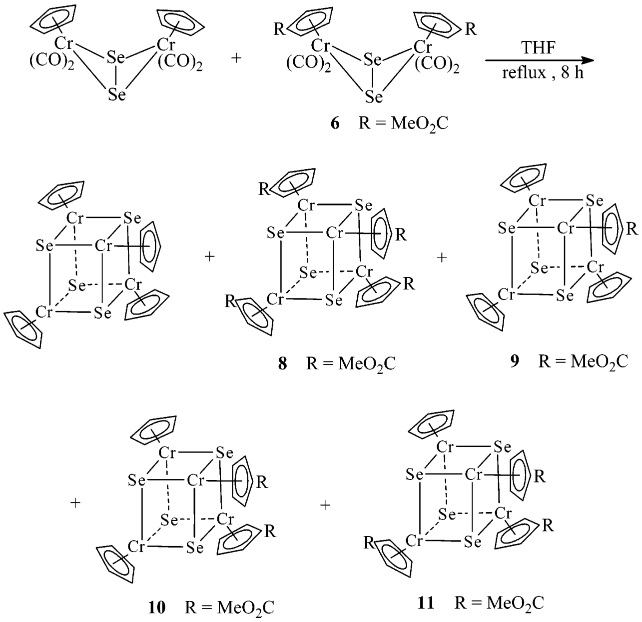
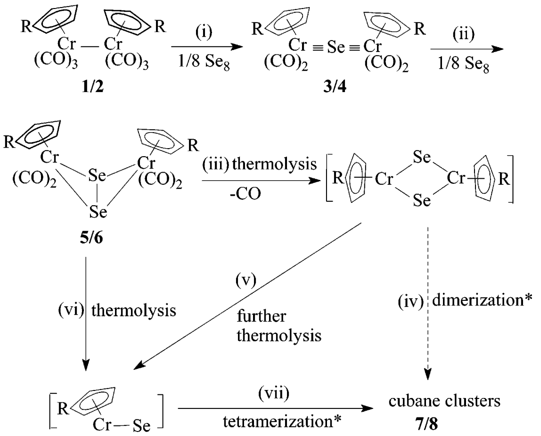
[24] Kabashima, S.; Kuwata, S.; Ueno, K.; Shiro, M.; Hidai, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1128.

Scheme 3[a]



[a] The Cr−Cr bonds in the cubane cores of all the indicated cubane clusters are omitted for clarity.

Scheme 4[a]



[a] Tetramerization occurs through intermolecular coordination of Se to Cr.

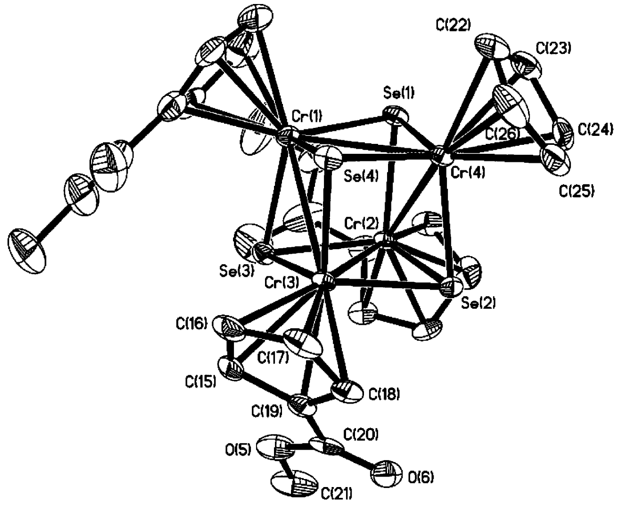


Figure 4. ORTEP drawing of **11** (30% probability ellipsoids, H atoms are omitted).

To examine the influence of different Cp ligands upon ^{77}Se NMR behavior, we determined the ^{77}Se NMR spectra of **9**−**11**. As a result, beyond our expectation, they showed only one singlet (in the range 1105−1216 ppm) for their μ_3-Se atoms. This implies that the difference between Cp and the functionalized Cp is too small to make μ_3-Se environments sufficiently different in these clusters. In addition, the ^{77}Se chemical shifts of $(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)_n\text{Cp}_{4-n}\text{Cr}_4\text{Se}_4$ ($n = 1-4$) increase with the increase of number n, which is in agreement with the fact that the methoxycarbonyl substituent is electron-withdrawing.

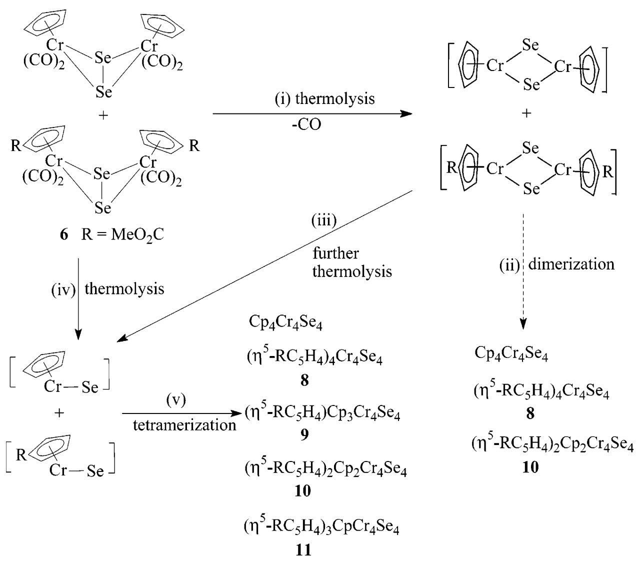
The molecular structure of **11** was determined by X-ray diffraction techniques. The ORTEP drawing of **11** is presented in Figure 4. Selected bond lengths and bond angles are listed in Table 2. This molecule indeed contains a cubane Cr_4Se_4 cluster core that carries one Cp and three MeO_2C-substituted Cp ligands coordinated in an η^5-fashion to four Cr atoms, respectively. The cubic cluster core of **11** is more distorted than that of **8**, apparently due to the presence of the mixed Cp ligands, which can be seen from the bond lengths and bond angles. For example, the values of Cr−Se (2.396−2.414 Å), Cr−Cr (2.970−2.944 Å), Se−Cr−Se (97.54−103.74°), and Cr−Se−Cr (79.63−75.38°) are within a larger region, respectively. However, similar to **8**, this molecule is also a 60-electron cluster, which contains four μ_3-Se 4e ligands and six Cr−Cr single bonds.

Reaction Pathways Leading to Cubane Clusters 7−11. The suggested pathway for production of cubic clusters **7** and **8** is shown in Scheme 4. As can be seen in Scheme 4, the linear complexes **3/4** and butterfly complexes **5/6** are the intermediates for the formation of the cubane clusters **7/8** starting from the Cr−Cr singly bonded dimers **1/2**. This is because we have proved that (i) **1/2** could react with 1 equiv of selenium to give **3/4** (Scheme 1); (ii) **3/4** reacted with 1 equiv of selenium to yield **5/6** (Scheme 1); and (iii) thermolysis of **5/6** yielded **7/8** (Scheme 2). Now, the question is how are the cubane clusters **7/8** formed from butterfly complexes **5/6**? Initially, we thought that **7/8** might be simply produced by dimerization of a highly unsaturated species $(\eta^5\text{-RC}_5\text{H}_4\text{CrSe})_2$ (Scheme 4, step iv), which was generated in situ from butterfly complexes **5/6** by loss of their CO ligands and concomitant cleavage of their Se−Se bonds under thermolysis conditions (Scheme 4, step iii).

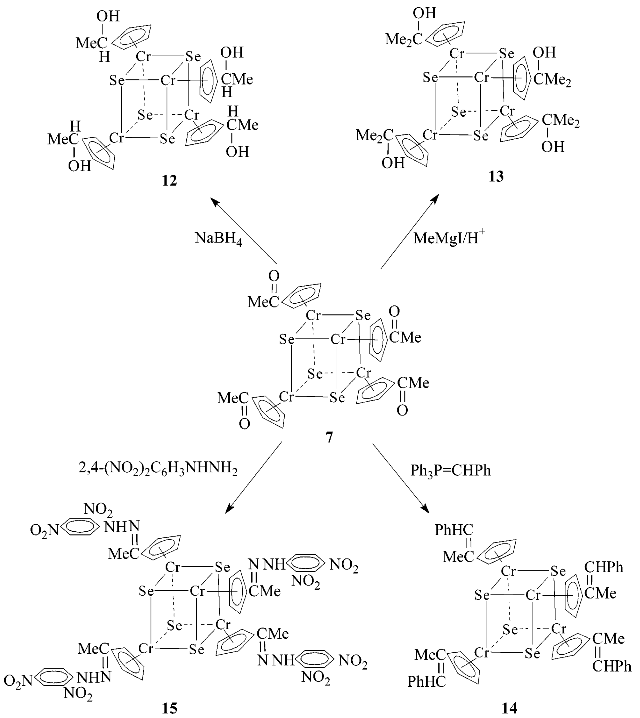
However, **7/8** would also be possibly produced by tetramerization of another highly unsaturated species $\eta^5\text{-RC}_5\text{H}_4\text{CrSe}$ (Scheme 4, step vii), which was derived from further thermolysis of the first unsaturated species $(\eta^5\text{-RC}_5\text{H}_4\text{CrSe})_2$ or directly derived from **5/6** (Scheme 4, steps v and vi).

To prove which pathway is correct, we carried out a study on the above-described cross-assembled reaction between two butterfly complexes, **6** and $[\text{CpCr(CO)}_2]_2\text{Se}_2$. The results indicated that (i) the reaction afforded five cubane products, $Cp_4Cr_4Se_4$ and **8**−**11**, and not three cubane products, $Cp_4Cr_4Se_4$, **8**, and **10**; and (ii) the molar ratio of the five products is ca. 1:4:6:4:1. Therefore, these observations are consistent with the combinatory rule of tetramerization of the two different highly unsaturated fragments CpCrSe and $\eta^5\text{-RC}_5\text{H}_4\text{CrSe}$, which strongly supports the pathway involving steps v and vi for formation of cubane clusters **7** and **8** (Scheme 4).

Scheme 5



Scheme 6[a]



[a] The Cr−Cr bonds in the cubane cores of **7** and **12**−**15** are omitted for clarity.

The possible pathway for production of cubane clusters **8**−**11** and $Cp_4Cr_4Se_4$ from the above-mentioned cross-assembled reaction can be similarly suggested and is shown in Scheme 5. As can be seen in Scheme 5, the highly unsaturated species CpCrSe and η^5-RC_5H_4CrSe may undergo both self-tetramerization to give cubane clusters $Cp_4Cr_4Se_4$/**8** and co-tetramerization to produce cubane clusters **9**−**11**.

It should be pointed out that in order to exclude the possibility that the cubane clusters containing mixed Cp ligands, namely, **9**−**11**, were produced by ligand exchange, we tried the reactions between two cubane clusters, one cluster containing four Cp and the other containing four functionalized Cp, namely, $Cp_4Cr_4Se_4$ and **8**. The results showed that no other cubane cluster bearing mixed Cp ligands was formed, which further supports the suggested pathways described in Schemes 4 and 5.

Finally, it is worthy of note that although the reaction pathways described above appear to be reasonable and are based on a series of experimental evidence, the details still need to be further studied. For instance, the supposed unsaturated species for tetramerization could also have CO ligands such as $CpCrSe(CO)_n$ and η^5-$RC_5H_4CrSe(CO)_n$ (n = 1, 2), which may lose their CO ligands at a given stage during tetramerization.[25]

Functional Transformations of Cluster 7 Leading to Functionalized Cp Cubane Clusters 12−15. The second synthetic strategy directed to functionalized Cp clusters includes not only the above-mentioned skeleton transformations but also the functional transformation reactions of the prefunctionalized Cp clusters.[3,22] Now, we have carried out a series of functional transformations regarding acetyl groups of cubane cluster **7**. For instance, cluster **7** could be reduced by excess $NaBH_4$ in CH_2Cl_2/MeOH at ca. 45 °C to give the secondary hydroxy derivative [η^5-MeCH(OH) $C_5H_4]_4Cr_4Se_4$ (**12**) in 72% yield, whereas it reacted with Grignard reagent MeMgI in THF at room temperature followed by hydrolysis of the addition intermediate to afford the tertiary hydroxy derivative [η^5-$Me_2C(OH)C_5H_4]_4Cr_4Se_4$ (**13**) in 66% yield (Scheme 6). Furthermore, cluster **7** could also undergo olefination with excess Wittig reagent $Ph_3P{=}CHPh$[26] formed in situ from $Ph_3(CH_2Ph)PBr$ in $CHCl_3$/MeOH at reflux or undergo condensation with 2,4-dinitrophenylhydrazine in refluxing $CHCl_3$ to produce olefin derivative [η^5-$PhCH{=}C(Me)C_5H_4]_4Cr_4Se_4$ (**14**) in 67% yield and phenylhydrazone derivative [η^5-2,4-$(NO_2)_2C_6H_3NHNC(Me)C_5H_4]_4Cr_4Se_4$ (**15**) in 52% yield, respectively (Scheme 6).

Apparently, the above-mentioned successful functional transformations of cluster **7**, in contrast to the failure of direct functionalization of parent cluster $Cp_4Cr_4Se_4$, is due to the enhanced chemical stability of the cubic Cr_4Se_4 cluster core caused by functional substituents and good solubility of **7** in common organic solvents. Clusters **12**−**15** have been fully characterized. For example, while the IR spectra of **12**−**15** displayed absorption bands characteristic of their functionalities such as O−H, C=C, C=N, and N−H groups, the ^{77}Se NMR spectra of **12**−**15** showed one singlet in the range 991−1275 ppm for their μ_3-Se atoms. In addition, the ^1H NMR spectra of **12**−**15** displayed two doublets or two singlets for the four protons of each substituted Cp ring, the downfield one being assigned to their H^2/H^5 protons and the upfield one ascribed to their H^3/H^4 protons, respectively. This is consistent with the reported ^1H NMR spectra of a monosubstituted cyclopentadienyl ring in transition metal complexes, which vary greatly in complexity such as a single resonance, an A_2B_2 or A_2BB' pattern, or a multiplet pattern, all depending on the nature of the transition metal and the substituent.[27]

The structure of **12** was unequivocally confirmed by X-ray crystallography. The ORTEP drawing of **12** is shown in Figure 5, while its selected bond lengths and

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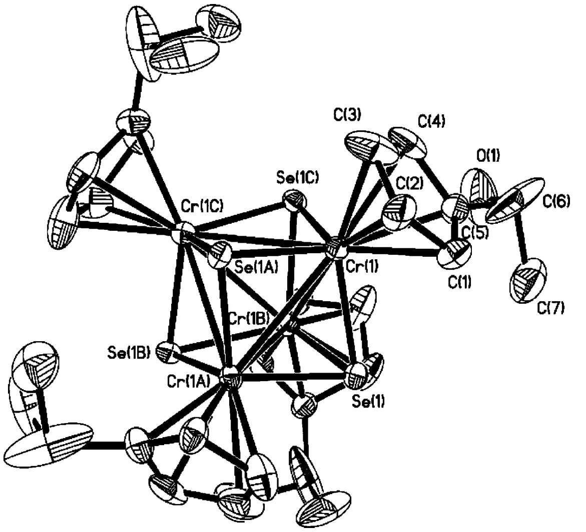

Figure 5. ORTEP drawing of **12** (20% probability ellipsoids, H atoms are omitted).

angles are given in Table 2. Cluster **12** is virtually isostructuctral with its precusor **7**, except the functional ligand acetylcyclopentadienyl in **7** being replaced by α-hydroxyethylcyclopentadienyl. That is, the four C═O double bonds (for example, C(1)−O(1) = 1.279(10) Å) in **7** (Figure 2), after reduction with $NaBH_4$, become four C−O single bonds (for example, C(6)−O(1) = 1.298 (10) Å) in **12** (Figure 5). Particularly noteworthy is that the four carbon atoms attached to hydroxyl groups of **12** are chiral, among which C(6)/C(6A) possess an *R* configuration and C(6B)/C(6C) have an *S* configuration (Figure 5). This molecule has an alternating 4-fold axis of symmetry and thus is optically inactive. In addition, it is worth noting that although the formation of such a tetra-alcohol **12** is very interesting, we do not know, at the present stage, how it formed and what factors made this reduction so highly diasteroselective.

Summary

We have successfully synthesized the first examples of functionalized Cp-containing linear Cr_2Se, butterfly Cr_2Se_2, and cubane Cr_4Se_4 complexes **3**−**15** by a basic strategy for functionalization of metal Cp complexes from the corresponding prefunctionalized Cp-metal precursors. The possible pathways for production of cubane clusters **7**−**11** by skeleton transformations of the Cr−Cr singly bonded dimers **1/2**, linear complexes **3/4**, and butterfly complexes **5/6**, as well as a new type of cross-assembled reaction involving two butterfly complexes **6** and $[CpCr(CO)_2]_2Se_2$ have been proposed. It is noteworthy that direct functionalization of the parent cubane cluster $Cp_4Cr_4Se_4$ with MeC(O)Cl/$AlCl_3$ or acetic anhydride/H_3PO_4 failed to give the acetyl-containing cubane clusters $[MeC(O)C_5H_4]_nCp_{4-n}Cr_4Se_4$ ($n = 1-4$), while the functional transformations of the acetyl-containing cluster **7** with $NaBH_4$, Grignard reagent MeMgI, Wittig reagent $Ph_3P{=}CHPh$, or 2,4-dinitrophenylhydrazine yield the corresponding cubane cluster derivatives **12**−**15**. It should be noted that the various functionalized Cr/Se complexes prepared in this article may have potential usage not only in organometallic and cluster chemistry but also in other areas such as material and life sciences, since they have easily convertible functional groups and/or cubane Cr_4Se_4 cluster cores closely related to the biologically active site of some metal-containing enzymes.[2−6,23]

Experimental Section

General Comments. 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 CaH_2 prior to use. Commercial $NaBH_4$, selenium powder, and 2,4-dinitrophenylhydrazine were used as received. $Ph_3(CH_2Ph)PBr$,[28] n-BuLi,[29] MeMgI,[30] $[\eta^5\text{-}RC_5H_4Cr(CO)_3]_2$ (R = MeCO, MeO_2C),[11] and $[CpCr(CO)_2]_2Se_2$[16] 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 Nicolet 170 SX FT-IR or 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 are referenced to Me_2Se ($\delta = 0$). Elemental analysis was performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

Preparation of $[\eta^5\text{-}MeC(O)C_5H_4Cr(CO)_2]_2Se$ (3). A 100 mL Schlenk flask equipped with a magnetic stir-bar was charged with 0.486 g (1.00 mmol) of $[\eta^5\text{-}MeC(O)C_5H_4Cr(CO)_3]_2$, 0.079 g (1.00 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 in a minium volume of dichloromethane, which was then subjected to column chromatography. Elution with 1:2 (v/v) CH_2Cl_2/petroleum ether gave an orange red band, from which **3** was obtained. **3**: brown red solid, yield 0.490 g (0.96 mmol, 96%); mp 90−91 °C. Anal. Calcd for $C_{18}H_{14}Cr_2O_6Se$: C, 42.45; H, 2.77. Found: C, 42.06; H, 2.72. IR (KBr disk): $\nu_{C\equiv O}$ 1954 (vs), 1914 (m), 1894 (s); $\nu_{C=O}$ 1681 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.19 (s, 6H, $2CH_3$), 4.59 (s, 4H, $2H^3$, $2H^4$), 5.32 (s, 4H, $2H^2$, $2H^5$). ^{77}Se NMR ($CDCl_3$): δ 2589.8 (s).

Preparation of $[\eta^5\text{-}MeO_2CC_5H_4Cr(CO)_2]_2Se$ (4). The same procedure as for the preparation of **3** was followed, but 0.518 g (1.00 mmol) of $[\eta^5\text{-}MeO_2CC_5H_4Cr(CO)_3]_2$ was employed. **4**: brown red solid, yield 0.536 g (0.99 mmol, 99%); mp 80−81 °C. Anal. Calcd for $C_{18}H_{14}Cr_2O_8Se$: C, 39.94; H, 2.61. Found: C, 39.62; H, 2.59. IR (KBr disk): $\nu_{C\equiv O}$ 1999 (s), 1958 (vs), 1925 (vs); $\nu_{C=O}$ 1715 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.71 (s, 6H, $2CH_3$), 4.68 (s, 4H, $2H^3$, $2H^4$), 5.32 (s, 4H, $2H^2$, $2H^5$). ^{77}Se NMR ($CDCl_3$): δ 2604.6 (s).

Preparation of $[\eta^5\text{-}MeC(O)C_5H_4Cr(CO)_2]_2Se_2$ (5). Method i. A mixture of 0.243 g (0.50 mmol) of $[\eta^5\text{-}MeC(O)C_5H_4Cr(CO)_3]_2$, 0.158 g (2.00 mmol) of selenium powder, and 20 mL of THF was stirred at room temperature for 16 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 with 1:2 (v/v) acetone/petroleum ether as eluent. A brown-green band was collected, from which **5** was obtained. **5**: brown green solid, yield 0.241 g (0.41 mmol, 82%); mp 140−141 °C. Anal. Calcd for $C_{18}H_{14}Cr_2O_6Se_2$: C,

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36.75; H, 2.40. Found: C, 36.71; H, 2.50. IR (KBr disk): $\nu_{C\equiv O}$ 1954 (vs), 1890 (vs); $\nu_{C=O}$ 1676 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.24 (s, 6H, 2CH$_3$), 5.02 (s, 4H, 2H^3, 2H^4), 5.60 (s, 4H, 2H^2, 2H^5). ^{77}Se NMR (CDCl$_3$): δ −257.4 (s).

Method ii. A mixture of 0.255 g (0.50 mmol) of [η^5-MeC(O)C$_5$H$_4$Cr(CO)$_2$]$_2$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 0.209 g (0.36 mmol, 71%) of **5**.

Preparation of [η^5-MeO$_2$CC$_5$H$_4$Cr(CO)$_2$]$_2$Se$_2$ (6). Method i. The same procedure as for method i for the preparation of **5** was followed, except that 0.259 g (0.50 mmol) of [η^5-MeO$_2$CC$_5$H$_4$Cr(CO)$_3$]$_2$ was utilized. **6**: brown-green solid, yield 0.260 g (0.42 mmol, 84%); mp 135−136 °C. Anal. Calcd for C$_{18}$H$_{14}$Cr$_2$O$_8$Se$_2$: C, 34.86; H, 2.28. Found: C, 34.68; H, 2.29. IR (KBr disk): $\nu_{C\equiv O}$ 1950 (vs), 1880 (vs); $\nu_{C=O}$ 1717 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.76 (s, 6H, 2CH$_3$), 4.92 (s, 4H, 2H^3, 2H^4), 5.30 (s, 4H, 2H^2, 2H^5). ^{77}Se NMR (CDCl$_3$): δ −266.8 (s).

Method ii. The same procedure was followed as for method ii for **5**, but 0.271 g (0.50 mmol) of [η^5-MeO$_2$CC$_5$H$_4$Cr(CO)$_2$]$_2$Se was utilized. **6**: 0.232 g (0.38 mmol, 75%).

Preparation of [η^5-MeC(O)C$_5$H$_4$]$_4$Cr$_4$Se$_4$ (7). Method i. A green suspension of 0.243 g (0.50 mmol) of [η^5-MeC(O)C$_5$H$_4$Cr(CO)$_3$]$_2$ and 0.158 g (2.00 mmol) of selenium powder in 20 mL of THF was stirred at reflux for 8 h, and then the solvent was removed at reduced pressure to give a brown-black residue, which was extracted with dichloromethane. The extracts were evaporated to dryness and then recrystallized in CH$_2$Cl$_2$/petroleum ether to give product **7**. **7**: greenish black solid, yield 0.224 g (0.24 mmol, 94%); mp 223−224 °C. Anal. Calcd for C$_{28}$H$_{28}$Cr$_4$O$_4$Se$_4$: C, 35.31; H, 2.96. Found: C, 35.33; H, 3.10. IR (KBr disk): $\nu_{C=O}$ 1664 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.23 (s, 12H, 4CH$_3$), 4.95 (s, 8H, 4H^3, 4H^4), 5.78 (s, 8H, 4H^2, 4H^5). ^{77}Se NMR (CDCl$_3$): δ 1226.2 (s).

Method ii. A red suspension of 0.255 g (0.50 mmol) of [η^5-MeC(O)C$_5$H$_4$Cr(CO)$_2$]$_2$Se and 0.040 g (0.50 mmol) of selenium powder in 20 mL of THF was stirred at reflux for 8 h to give a brown-green mixture. The same workup as that for method i afforded 0.226 g (0.24 mmol, 95%) of **7**.

Method iii. A brown-green solution of 0.118 g (0.20 mmol) of [η^5-MeC(O)C$_5$H$_4$Cr(CO)$_2$]$_2$Se$_2$ in 20 mL of THF was stirred at reflux for 8 h, and the same workup as that for method i gave 0.087 g (0.09 mmol, 91%) of **7**.

Preparation of (η^5-MeO$_2$CC$_5$H$_4$)$_4$Cr$_4$Se$_4$ (8). Method i. The same procedure as for method i for the preparation of **7** was followed, but 0.259 g (0.50 mmol) of [η^5-MeO$_2$CC$_5$H$_4$Cr(CO)$_3$]$_2$ was employed. **8**: greenish black solid, yield 0.236 g (0.23 mmol, 93%); mp 202−203 °C. Anal. Calcd for C$_{28}$H$_{28}$Cr$_4$O$_8$Se$_4$: C, 33.09; H, 2.78. Found: C, 32.69; H, 2.73. IR (KBr disk): $\nu_{C=O}$ 1716 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.70 (s, 12H, 4CH$_3$), 4.89 (s, 8H, 4H^3, 4H^4), 5.76 (s, 8H, 4H^2, 4H^5). ^{77}Se NMR (CDCl$_3$): δ 1244.2 (s).

Method ii. The same procedure as for method ii for the preparation of **7** was followed, but 0.271 g (0.50 mmol) of [η^5-MeO$_2$CC$_5$H$_4$Cr(CO)$_2$]$_2$Se was used to afford 0.239 g (0.24 mmol, 94%) of **8**.

Method iii. The same procedure as for method iii for the preparation of **7** was followed, but 0.124 g (0.20 mmol) of [η^5-MeO$_2$CC$_5$H$_4$Cr(CO)$_2$]$_2$Se$_2$ was used to give 0.094 g (0.09 mmol, 92%) of **8**.

Preparation of [η^5-MeO$_2$CC$_5$H$_4$]$_n$Cp$_{4-n}$Cr$_4$Se$_4$ (n = 0, Cp$_4$Cr$_4$Se$_4$; n = 4, 8; n = 1−3, 9−11). A mixture consisting of 0.101 g (0.20 mmol) of [CpCr(CO)$_2$]$_2$Se$_2$, 0.124 g (0.20 mmol) of [η^5-MeO$_2$CC$_5$H$_4$Cr(CO)$_2$]$_2$Se$_2$, and 20 mL of THF was stirred and refluxed for 8 h, resulting in a color change from brown-green to dark green. The mixture was centrifuged to give a clear centrifugate, which was concentrated to ca. 5 mL and then was subjected to TLC separation using 1:2:6 (v/v/v) acetone/CH$_2$Cl$_2$/petroleum ether as eluent to develop four brown-green bands.

From the first band (R_f = 0.75) was obtained 0.040 g (0.05 mmol, 24%) of (η^5-MeO$_2$CC$_5$H$_4$)Cp$_3$Cr$_4$Se$_4$ (**9**) as a black solid, mp 186−187 °C. Anal. Calcd for C$_{22}$H$_{22}$Cr$_4$O$_2$Se$_4$: C, 31.37; H, 2.63. Found: C, 33.53; H, 2.77. IR (KBr disk): $\nu_{C=O}$ 1719 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.54 (s, 3H, CH$_3$), 26.24 (s, 2H, H^3, H^4), 29.19 (s, 15H, 3C$_5$H$_5$), 31.80 (s, 2H, H^2, H^5). ^{77}Se NMR (CDCl$_3$): δ 1105.5 (s).

From the second band (R_f = 0.66) was obtained 0.065 g (0.07 mmol, 36%) of (η^5-MeO$_2$CC$_5$H$_4$)$_2$Cp$_2$Cr$_4$Se$_4$ (**10**) as a black solid, mp 174−175 °C. Anal. Calcd for C$_{24}$H$_{24}$Cr$_4$O$_4$Se$_4$: C, 32.02; H, 2.69. Found: C, 32.23; H, 2.76. IR (KBr disk): $\nu_{C=O}$ 1719 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.55 (s, 6H, 2CH$_3$), 26.93 (s, 4H, 2H^3, 2H^4), 29.60 (s, 10H, 2C$_5$H$_5$), 32.09 (s, 4H, 2H^2, 2H^5). ^{77}Se NMR (CDCl$_3$): δ 1161.2 (s).

From the third band (R_f = 0.55) was obtained 0.048 g (0.05 mmol, 25%) of (η^5-MeO$_2$CC$_5$H$_4$)$_3$CpCr$_4$Se$_4$ (**11**) as a black solid, mp 193−194 °C. Anal. Calcd for C$_{26}$H$_{26}$Cr$_4$O$_6$Se$_4$: C, 32.59; H, 2.73. Found: C, 32.53; H, 2.69. IR (KBr disk): $\nu_{C=O}$ 1718 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.68 (s, 9H, 3CH$_3$), 5.01 (s, 6H, 3H^3, 3H^4), 5.07 (s, 5H, C$_5$H$_5$), 5.87 (s, 6H, 3H^2, 3H^5). ^{77}Se NMR (CDCl$_3$): δ 1215.3 (s).

From the fourth band (R_f = 0.43) was obtained 0.013 g (0.01 mmol, 6%) of (η^5-MeO$_2$CC$_5$H$_4$)$_4$Cr$_4$Se$_4$ (**8**) identified by comparison of its IR and ^{1}H NMR spectra with those of the fully characterized sample described above. The immovable base band was collected and refluxed with 10 mL of bromobenzene for 10 min. After cooling to room temperature, the mixture was filtered and the filtrate was centrifuged to give a clear centrifugate, from which 0.007 g (0.01 mmol, 5%) of Cp$_4$Cr$_4$Se$_4$ was obtained.

Attempted Cp/η^5-RC$_5$H$_4$ Ligand Exchange between Cp$_4$Cr$_4$Se$_4$ and [η^5-RC$_5$H$_4$]$_4$Cr$_4$Se$_4$ (8, R = MeO$_2$C). A mixture consisting of 0.078 g (0.10 mmol) of Cp$_4$Cr$_4$Se$_4$ and 0.102 g (0.10 mmol) of **8** in 20 mL of THF was stirred at reflux for 10 h. The resulting mixture was concentrated to ca. 5 mL, which was subjected to TLC separation using 1:3:3 (v/v/v) acetone/CH$_2$Cl$_2$/petroleum ether as eluent to develop only one brown-green band. From this band 0.086 g (0.08 mmol, 84%) of **8** was recovered, while from the immovable band 0.048 g (0.06 mmol, 62%) of Cp$_4$Cr$_4$Se$_4$ was recovered. No ligand exchange products of [η^5-MeO$_2$CC$_5$H$_4$]$_n$Cp$_{4-n}$Cr$_4$Se$_4$ (n = 1−3, **9**−**11**) were formed.

Preparation of [η^5-MeCH(OH)C$_5$H$_4$]$_4$Cr$_4$Se$_4$ (12). A 100 mL Schlenk flask was charged with 0.190 g (0.20 mmol) of [η^5-MeC(O)C$_5$H$_4$]$_4$Cr$_4$Se$_4$ in 15 mL of CH$_2$Cl$_2$ and 0.061 g (1.60 mmol) of NaBH$_4$ in 15 mL of MeOH. The mixture was stirred at ca. 45 °C for 10 h. After removal of the solvents under reduced pressure, the residue was extracted with CH$_2$Cl$_2$. The extracts were concentrated to ca. 5 mL, which was then subjected to TLC column chromatography. Elution with acetone yielded a green band, from which **12** was obtained. **12**: 0.138 g (0.14 mmol, 72%), brown-green solid; mp 164−165 °C. Anal. Calcd for C$_{28}$H$_{36}$Cr$_4$O$_4$Se$_4$: C, 35.02; H, 3.78. Found: C, 35.16; H, 3.99. IR (KBr disk): ν_{O-H} 3371 (vs) cm^{-1}. ^{1}H NMR (DMSO): δ 1.15 (d, J = 3.0 Hz, 12H, 4CH$_3$), 3.15 (s, 4H, 4CH), 4.20 (d, J = 3.0 Hz, 4H, 4OH), 5.04 (d, 8H, 4H^3, 4H^4), 5.40 (s, 8H, 4H^2, 4H^5). ^{77}Se NMR (CDCl$_3$): δ 996.2 (s).

Preparation of [η^5-Me$_2$C(OH)C$_5$H$_4$]$_4$Cr$_4$Se$_4$ (13). To a deep green solution of 0.190 g (0.20 mmol) of [η^5-MeC(O)C$_5$H$_4$]$_4$Cr$_4$Se$_4$ in 15 mL of THF, while stirring at room temperature, was dropwise added 2 mL (1.6 mmol) of MeMgI/diethyl ether solution. The mixture was stirred at this temperature for 8 h, and then 25 mL (ca. 2 mmol) of diluted HCl was added. The mixture was stirred for an additional 20 min and then was extracted with 3 × 10 mL of CH$_2$Cl$_2$. The extracts were dried over anhydrous Na$_2$SO$_4$. After removal of Na$_2$SO$_4$, the filtrate was concentrated to ca. 5 mL, which was subjected to TLC separation. Elution with 1:3:3 (v/v/v) acetone/CH$_2$Cl$_2$/petroleum ether afforded a brown-green band, from which **13** was obtained. **13**: 0.134 g (0.13 mmol, 66%), brown green solid; mp 178−179 °C. Anal. Calcd for C$_{32}$H$_{44}$Cr$_4$O$_4$Se$_4$: C, 37.81; H,

Table 3. Crystal Data and Structural Refinement Details for 4, 7, 8,11, and 12

	4	**7**	**8**	**11**	**12**
empirical formula	$C_{18}H_{14}Cr_2O_8Se$	$C_{28}H_{28}Cr_4O_4Se_4$	$C_{28}H_{28}Cr_4O_8Se_4$	$C_{26}H_{26}Cr_4O_6Se_4$	$C_{28}H_{36}Cr_4O_4Se_4 \cdot H_2O$
fw	541.25	952.34	1016.34	958.31	978.42
cryst syst	monoclinic	tetragonal	triclinic	triclinic	tetragonal
space group	$C2/c$	$I\bar{4}$	$P\bar{1}$	$P\bar{1}$	$I\bar{4}$
a, Å	10.787(6)	10.809(6)	10.036(3)	9.777(5)	11.068(3)
b, Å	8.057(5)	10.809(6)	10.779(3)	10.028(6)	11.068(3)
c, Å	23.448(14)	13.197(15)	16.581(5)	16.758(10)	12.901(6)
α, deg	90	90	73.849(5)	93.260(9)	90
β, deg	96.548(11)	90	77.721(5)	96.725(9)	90
γ, deg	90	90	65.921(4)	111.474(9)	90
V, Å^3	2025(2)	1542(2)	1562.9(8)	1509.5(15)	1580.3(10)
Z	4	2	2	2	2
d(calcd), Mg/m^3	1.776	2.051	2.160	2.108	2.056
abs coeff, mm^{-1}	2.913	6.126	6.060	6.263	5.982
cryst size, mm	0.24 × 0.12 × 0.06	0.24 × 0.20 × 0.14	0.40 × 0.25 × 0.05	0.30 × 0.20 × 0.15	0.25 × 0.15 × 0.06
F(000)	1072	920	984	924	956
θ range, deg	3.16−25.00	2.44−26.34	2.12−25.02	1.23−25.03	2.42−25.03
no. of reflns	4419	3081	6499	6163	3261
no. of indep reflns	1618 (R_{int}= 0.0787)	1546 (R_{int}= 0.0580)	5473 (R_{int} = 0.041)	5257 (R_{int}=0.0343)	1391 (R_{int}= 0.1027)
index ranges	$-10 \le h \le 12$ $-6 \le k \le 9$ $-27 \le l \le 27$	$-11 \le h \le 12$ $-3 \le k \le 13$ $-16 \le l \le 16$	$-11 \le h \le 9$ $-12 \le k \le 12$ $-19 \le l \le 14$	$-8 \le h \le 11$ $-11 \le k \le 11$ $-19 \le l \le 19$	$-12 \le h \le 13$ $-13 \le k \le 11$ $-14 \le l \le 15$
no. of data/restraints/ params	1618/0/134	1546/6/104	5473/0/379	5257/0/361	1391/3/93
goodness of fit on F^2	1.034	0.992	0.983	1.108	0.982
final R indices (obsd data)	$R_1 = 0.0683$, $wR_2 = 0.1628$	$R_1 = 0.0581$, $wR_2 = 0.1369$	$R_1 = 0.0514$, $wR_2 = 0.1262$	$R_1 = 0.0575$, $wR_2 = 0.1398$	$R_1 = 0.0\ 576$, $wR_2 = 0.1363$
R indices (all data)	$R_1 = 0.1007$, $wR_2 = 0.1799$	$R_1 = 0.0699$, $wR_2 = 0.1436$	$R_1 = 0.0721$, $wR_2 = 0.1407$	$R_1 = 0.0921$, $wR_2 = 0.1545$	$R_1 = 0.1417$, $wR_2 = 0.1713$
largest diff peak and hole, e Å^{-3}	0.993/−0.457	1.943/−1.199	1.287/ −1.883	1.267/−1.027	0.983/−0.495

4.36. Found: C, 38.08; H, 4.46. IR (KBr disk): ν_{O-H} 3375 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 24H, 8CH_3), 4.07 (s, 4H, 4OH), 5.09 (s, 8H, 4H^3, 4H^4), 5.94 (s, 8H, 4H^2, 4H^5). ^{77}Se NMR ($CDCl_3$): δ 1005.7 (s).

Preparation of [η^5-PhCH=C(Me)C_5H_4]$_4$$Cr_4Se_4$ (14). A 100 mL Schlenk flask was charged with 0.190 g (0.20 mmol) of [η^5-MeC(O)C_5H_4]$_4$$Cr_4Se_4$, 0.692 g (1.60 mmol) of Ph_3(CH_2-Ph)PBr, 20 mL of $CHCl_3$, and 0.640 g (16 mmol) of NaOH in 5 mL of MeOH. The mixture was stirred at reflux for 1 h, during which time the in situ generated Wittig reagent Ph_3P=CHPh[28] had completed its reaction with [η^5-MeC(O)C_5H_4]$_4$$Cr_4Se_4$. The mixture was cooled to room temperature, and 30 mL of H_2O was added. The organic layer was separated and dried over anhydrous Na_2SO_4. After removal of Na_2SO_4, the filtrate was reduced to ca. 5 mL, which was subjected to TLC separation. Elution using 1:2:3 (v/v/v) acetone/petroleum ether/CH_2Cl_2 gave a brown-green band, from which **14** was obtained. **14**: 0.168 g (0.13 mmol, 67%), black solid; mp 203−205 °C. Anal. Calcd for $C_{56}H_{52}Cr_4Se_4$: C, 53.86; H, 4.20. Found: C, 53.47; H, 4.09. IR (KBr disk): $\nu_{C=C}$ 1630 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.57 (s, 12H, 4CH_3), 4.79 (s, 4H, 4CH), 5.12 (s, 8H, 4H^3, 4H^4), 5.67 (s, 8H, 4H^2, 4H^5), 7.29−7.40 (m, 20H, 4C_6H_5). ^{77}Se NMR ($CDCl_3$): δ 991.5 (s).

Preparation of [η^5-2,4-(NO_2)$_2$$C_6H_3$NHNC(Me)-$C_5H_4$]$_4$$Cr_4Se_4$ (15). To a deep green solution of 0.190 g (0.20 mmol) of [η^5-MeC(O)C_5H_4]$_4$$Cr_4Se_4$ in 20 mL of $CHCl_3$ was added 9.6 mL (ca. 1.60 mmol) of 2,4-dinitrophenylhydrazine solution (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). The mixture was stirred at reflux for 2 h and then cooled to room temperature. The same workup as that for **14** produced **15**. **15**: 0.174 g (0.10 mmol, 52%), brown solid; mp > 280 °C. Anal. Calcd for $C_{52}H_{44}Cr_4N_{16}O_{16}Se_4$: C, 37.34; H, 2.65; N, 13.40. Found: C, 37.00; H, 2.54; N, 13.16. IR (KBr disk): $\nu_{C=N}$ 1618 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.64 (s, 12H, 4CH_3), 5.15 (s, 8H, 4H^3, 4H^4), 5.68 (s, 8H, 4H^2, 4H^5), 8.31 (d, J = 6.6 Hz, 4H, 4H^6 of benzene ring), 8.66 (d, J = 8.5 Hz, 4H, 4H^5 of benzene ring), 9.41 (s, 4H, 4H^3 of benzene ring), 10.64 (s, 4H, NH). ^{77}Se NMR ($CDCl_3$): δ 1274.7 (s).

X-ray Crystal Structure Determinations of 4, 7, 8, 11, and 12. Single crystals of **4**, **7**, **8**, **11**, and **12** suitable for X-ray diffraction analysis were grown by slow evaporation of a hexane solution of **4**, a hexane/CH_2Cl_2 solution of **7** or **8**, and a hexane/EtOH solution of **12** at room temperature and slow diffusion of hexane into a toluene solution of **11** at room temperature for several days, respectively. Each of the single crystals was glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer, respectively. Data were collected at room temperature, using Mo Kα graphite-monochromated radiation (λ = 0.71073 Å) in the $\omega-2\theta$ 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 (SHELXL-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.

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Supporting Information Available: An X-ray crystallographic file for **4**, **7**, **8**, **11**, and **12** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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