Efficient Demetalation of Fischer Alkoxy- and Amino-Biscarbene Complexes of Chromium via CO-Promoted Sulfuration and Selenylation

Zhaoyan Zheng,[†] Jinzhu Chen,[†] Ning Luo,[†] Zhengkun Yu,*[,†,‡] and Xiuwen Han[§]

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People's Republic of China, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China, and State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People's Republic of China

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CO-promoted sulfuration with elemental sulfur and selenylation with elemental selenium of Fischer biscarbene complexes of chromium have been achieved by means of in-situ-generated SCO and SeCO, efficiently affording thio- and selenocarboxylates. Intramolecular reactivity inversion of the chromium carbene carbon bonds (Cr═C) in an alkoxy−alkoxy biscarbene complex was realized by replacement of the alkoxy group bonded to the more reactive Cr═C carbon atom with an amino moiety. A strained cyclobutenyl ring activates the aminocarbene carbon bond, which thus undergoes oxidation, sulfuration, and selenylation under mild conditions. Demetalation of alkynyl, alkenyl, and alkyl Fischer monocarbene complexes was also investigated by the same method, from which selenium- or sulfur-insertion complexes and seleno- and thiocarboxylates were obtained.

Introduction

Fischer carbene complexes have been successfully employed in a wide range of organic synthesis[1] since they were first reported by Fischer et al.[2] In Fischer-type carbene complexes of the formulas $(OC)_5M{=}C(X)R$ (M = Cr, W; X = a π-donor substituent; and R = a saturated alkyl or unsaturated alkenyl, alkynyl, or aryl group), the multiple bond between the metal and the carbene carbon atom is of great interest in organometallic chemistry and organic synthesis because cleavage of this bond is a key step in a number of reactions of Fischer carbene complexes. Furthermore, both the electronic and structural features of the carbene substituents (X and R) control the electrophilicity of the complex and therefore have a great influence on its chemical reactivity.[3] Some specialized work has been directed toward study of the relationship between the chemical reactivity, electronic properties, and structure of a Fischer carbene complex. Bernasconi studied the mechanism and structure−reactivity relationships in the reactions of Fischer carbene complexes with various nucleophiles.[3a,b,4] Theoretical investigations on the reaction mechanisms and reactivity of Fischer carbene complexes were carried out by means of density functional theory, etc.[5] Wulff recently reported a systematic ESI-MS study of the ionization mechanism of alkenyl and alkynyl group 6 Fischer carbene complexes.[6]

Oxidation has usually been applied to demetalate Fischer alkoxy carbene complexes to organic products.[7] Development of new demetalation procedures for Fischer carbene complexes has been highly desired. Rare examples of sulfuration and selenylation of Fischer carbene complexes were reported in 1974: several Fischer methoxy arylcarbene complexes of chromium were transformed to the corresponding thio- and selenocarboxylates in 7−32% yields by their reactions with elemental sulfur and selenium in diethyl ether or dioxane at refluxing temperatures, respectively.[8] Very recently, we found that the two M═C bonds in unsymmetrical Fischer biscarbene complexes **1** (M = Cr, W) obtained from the reactions of

* Corresponding author. E-mail: zkyu@dicp.ac.cn.
[†] Dalian Institute of Chemical Physics.
[‡] State Key Laboratory of Organometallic Chemistry.
[§] State Key Laboratory of Catalysis.

(1) For selected recent reviews, see: (a) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539. (b) Gómez-Gallego, M.; Mancheño, M. J.; Sierra, M. A. *Acc. Chem. Res.* **2005**, *38*, 44. (c) Herndon, J. W. *Coord. Chem. Rev.* **2005**, *249*, 999. (d) Barluenga, J.; Santamaría, J.; Tomás, M. *Chem. Rev.* **2004**, *104*, 2259. (e) Herndon, J. W. *Coord. Chem. Rev.* **2004**, *248*, 3. (f) Herndon, J. W. *Coord. Chem. Rev.* **2003**, *243*, 3. (g) Dötz, K. H.; Jäkel, C.; Haase, W.-C. *J. Organomet. Chem.* **2001**, *617/618*, 119. (h) Barluenga, J.; Flóréz, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. (i) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (j) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (k) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257. (l) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597. (m) Aumann, R. *Eur. J. Org. Chem.* **2000**, 17.

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(5) Selected literatures, see: (a) Jacobsen, H.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1994**, *98*, 11406. (b) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224. (c) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775. (d) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428. (e) Frenking, G. *J. Organomet. Chem.* **2001**, *635*, 9. (f) Cases, M.; Frenking, G.; Duran, M.; Solà, M. *Organometallics*, **2002**, *21*, 4182. (g) Poater, J.; Cases, M.; Fradera, X.; Duran, M.; Solà, M. *Chem. Phys.* **2003**, *294*, 129.

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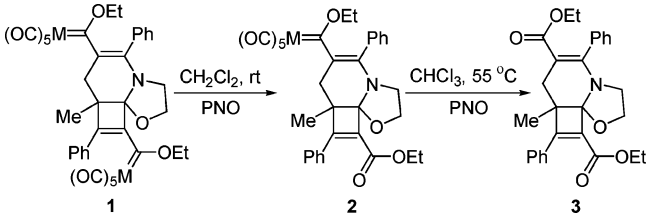
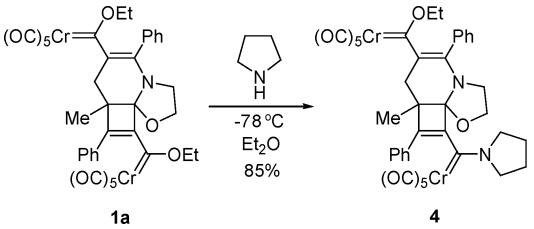
Scheme 1. Stepwise Oxidation of 1[9]



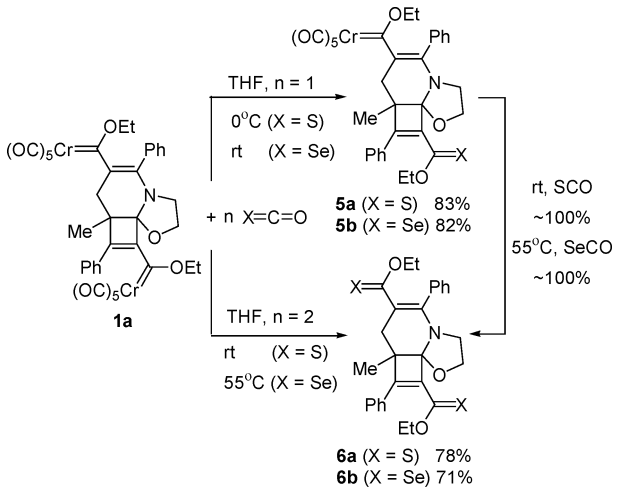
1-alkynyl Fischer carbene complexes $(OC)_5M{=}C(OEt)C{\equiv}CPh$ (M = Cr, W) with 2-isopropenyl-2-oxazoline can exhibit very different reactivity to the oxidant, i.e., pyridine-*N*-oxide (PNO) (Scheme 1).[9] Keeping this in mind, we reasonably expected that **1a** (M = Cr), with two different Cr=C bonds, may be a very ideal molecule that can be used to study the relationship between electronic/structural characteristics and reactivity of Fischer carbene complexes. Thus, the analogue of **1a**, i.e., Fischer alkoxy−amino biscarbene complex **4** was prepared by reacting **1a** with pyrrolidine at −78 °C for a comparative study on the reactivity of their different Cr=C bonds. Oxidation, sulfuration, and selenylation of **1a** and **4** were carried out, respectively, for this purpose. Herein, we report efficient synthesis of thio- and selenocarboxylates by means of CO-promoted sulfuration and selenylation of alkoxy−alkoxy and alkoxy−amino biscarbene complexes **1a** and **4** and a study on the unusual intramolecular reactivity inversion of the Cr=C bonds in these complexes.



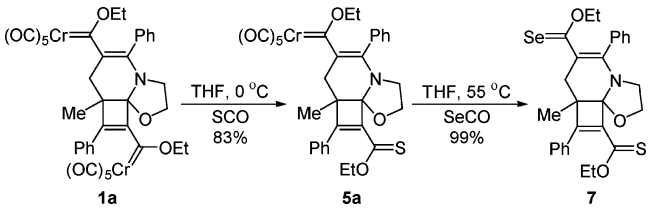
Results and Discussion

In complexes **1**, the M=C bonds additionally stabilized by the vinylogous nitrogen exhibit a reactivity lower than those bonded to the cyclobutenyl ring during oxidation (Scheme 1). With 1.0 equiv of in-situ-generated carbonyl sulfide SCO (i.e., S=C=O, equivalent to S/CO)[10] from the reaction of CO and elemental sulfur and SeCO (i.e., Se=C=O, equivalent to Se/CO)[11] from the reaction of CO and selenium as the chalcogenating reagents, sulfuration (at 0 °C) and selenylation (at room temperature) of complex **1a** under atmospheric pressure of CO afforded thio- and selenocarboxylate monocarbene complexes **5a** and **5b** in 82−83% yields, respectively (Scheme 2). With 2.0 equiv of in-situ-generated XCO (X = S, Se), the reactions of **1a** gave dithiocarboxylate **6a** (78%) at room temperature and diselenocarboxylate **6b** (71%) at 55 °C. The thio- and selenocarboxylate monocarbene complexes **5** were quantitatively converted to the corresponding dithio- and diselenocarboxylates under the stated conditions, respectively (Scheme 2). During

Scheme 2. CO-Promoted Stepwise Sulfuration and Selenylation of 1a



Scheme 3. Synthesis of *Se,S*-Dicarboxylate 7



the reactions, the chromium pentacarbonyl moiety was removed as $Cr(CO)_6$, which had been easily isolated by flash silical gel column chromatography and can be reused for synthesis of the starting Fischer carbene complex **1a**. To the best of our knowledge, this is a rare report on the efficient sulfuration and selenylation of Fischer carbene complexes under mild conditions. Moreover, O,S-, O,Se-, S,O-, Se,O-, S,Se-, and Se,S-hetero-dicarboxylates can be efficiently synthesized with the above-described method via a transformation represented by preparation of Se,S-dicarboxylate **7** (99% yield) (Scheme 3).

Both the Cr=C bonds in Fischer alkoxy-aminocarbene complex **4** underwent oxidation with PNO, CO-promoted sulfuration with sulfur, and selenylation with selenium under mild conditions. Surprisingly, the Cr=C bond additionally stabilized by the vinylogous nitrogen in **4** exhibited a reactivity much higher than the cyclobutenyl-bonded Cr=C bond (Scheme 4), while in complex **1a** the former Cr=C bond is much less reactive than the latter.[9] It should be noted that Fischer aminocarbene complexes are usually difficult to demetalate and only activated Fischer aminocarbene complexes undergo oxidative demetalation with PNO.[12] In the present case, the reactivity of the two Cr=C bonds in **1a** was reversibly altered in **4** by replacement of the ethoxy group attached to the cyclobutenyl-bonded carbene carbon in **1a** with a pyrrolidino group. These results have demonstrated an interesting example showing intramolecular reactivity inversion of transition metal carbene carbon bonds. With 1.0 equiv of PNO and XCO (X = S, Se) in THF at 55 °C, the vinylogous nitrogen-stabilized Cr=C bond in **4** was demetalated first, forming *O*-carboxylate, *S*- and *Se*-carboxylate-monocarbene complexes **8** in 77−95% yields, respectively, while the pyrrolidino/cyclobutenyl-bonded Cr=C bond stayed unchanged. Only under relatively harsh conditions such as at 80 °C in CH_3CN did the pyrrolidino/cyclobutenyl-

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(11) (a) Kondo, K.; Yokoyama, S.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 691. (b) Sonoda, N. *Pure Appl. Chem.* **1993**, *65*, 699. (c) Tian, F. S.; Yu, Z. K.; Lu, S. W. *J. Org. Chem.* **2004**, *69*, 4520.

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Scheme 4. Oxidation, Sulfuration, and Selenylation of 4

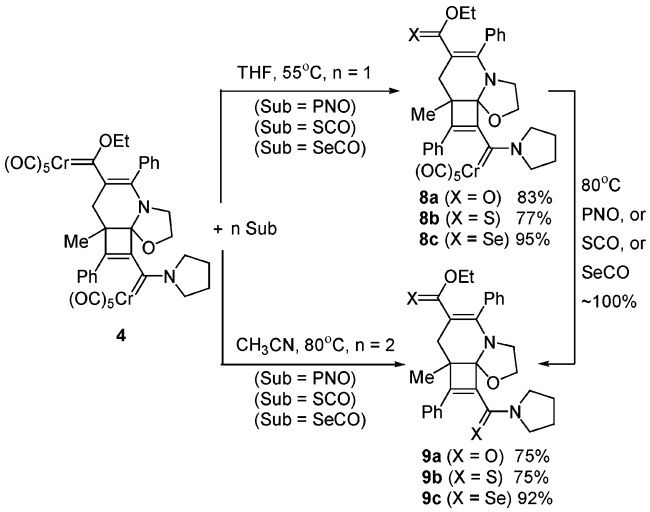
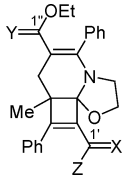


Table 1. $^{13}C\{^1H\}$ NMR Chemical Shifts of C═O, S═C, and Se═C for Compounds 5−9

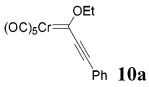
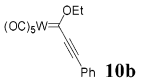
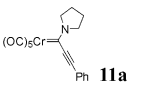
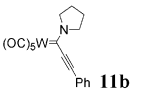
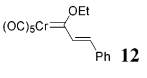
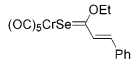
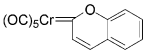
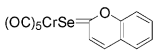
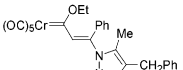
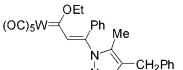
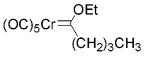
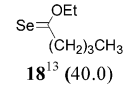


compound	δ(C1′)	δ(C1″)	compound	δ(C1′)	δ(C1″)
1a[9]	345.37 (Cr═C1′)	317.52 (Cr═C1″)	**4**	261.89 (Cr═C1′)	315.26 (Cr═C1″)
3[9]	163.58 (O═C1′)	168.80 (O═C1″)	**8a**	261.17 (Cr═C1′)	169.98 (O═C1″)
5a	202.95 (S═C1′)	313.08 (Cr═C1″)	**8b**	261.15 (Cr═C1′)	211.26 (S═C1″)
5b	210.86 (Se═C1′)	312.60 (Cr═C1″)	**8c**	261.28 (Cr═C1′)	217.59 (Se═C1″)
6a	203.00 (S═C1′)	210.11 (S═C1″)	**9a**	163.56 (O═C1′)	169.19 (O═C1″)
6b	210.97 (Se═C1′)	216.35 (Se═C1″)	**9b**	188.11 (S═C1′)	210.40 (S═C1″)
7	202.91 (S═C1′)	216.23 (Se═C1″)	**9c**	189.68 (Se═C1′)	216.44 (Se═C1″)

bonded Cr═C bond undergo oxidation with PNO, sulfuration with SCO, and selenylation with SeCO, affording dicarboxylates **9** in 75−92% yields (Scheme 4). Further reactions of the carboxylate monocarbene complexes **8** with PNO, SCO, or SCO quantitatively afforded **9**, suggesting that the usually unreactive aminocarbene Cr═C bonds in **4** and **8** are activated by the strained cyclobutenyl ring.

The ^{13}C NMR chemical shifts of the carbene carbon (Cr═C), O═C, S═C, and Se═C moieties in **1a** and **3**−**9** are summarized in Table 1. Introduction of nitrogen to the carbene carbon (C1′) attached to the cyclobutenyl ring causes the ^{13}C NMR signal of C1′ in **4** to shift upfield about 83 ppm as compared with that of the alkoxy−alkoxy biscarbene complex **1a**,[9] while the ^{13}C NMR signal of the carbene carbon (C1″) stabilized by the vinylogous nitrogen was shown at almost the same position ($\Delta\delta = 2$ ppm). In the newly formed compounds from **1a**, the ^{13}C NMR chemical shifts of O═C1′, S═C1′, and Se═C1′ are around 164, 203, and 211 ppm, and those of O═C1″, S═C1″, and Se═C1″ are about 169, 210, and 216 ppm, respectively. For those compounds generated from the alkoxy−amino biscarbene complex **4**, the ^{13}C NMR signals of O═C1′, S═C1′, and Se═C1′ are shown around 164, 188, and 190 ppm, while those of O═C1″, S═C1″, and Se═C1″ appear at 169−170, 210−211, and 216−218 ppm, respectively. The order of ^{13}C NMR chemical shifts of O═C, S═C, and Se═C in **5**−**9** is $\delta(O{=}C) < \delta(S{=}C) < \delta(Se{=}C)$. On the basis of a comparison of the ^{13}C NMR chemical shifts of carbene carbon C1′ in **5**−**9** it is concluded that the amino nitrogen obviously altered the electronic property of the carbene carbon attached by the cyclobutenyl moiety.

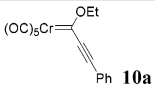
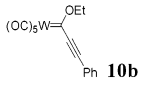
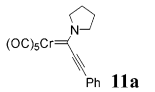
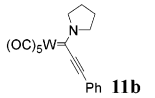
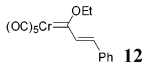
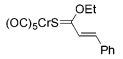
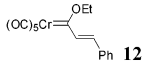
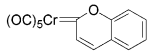
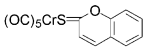
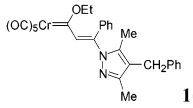
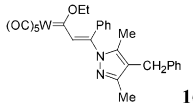
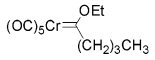
Table 2. Selenylative Demetalation of Fischer Carbene Complexes with Selenium in the Presence of CO[a]

entry	carbene	temp (°C)	time (h)	results (yield[b] (%))
1	 **10a**	55	5	complicated[c]
2	 **10b**	55	5	complicated[c]
3	 **11a**	55	14	no reaction
4	 **11b**	55	14	no reaction
5	 **12**	23	0.5	 **13** (76.5)
6	 **14**	23	14	 **15** (88.6)
7	 **16a**	23	14	complicated[c]
8	 **16b**	23	14	complicated[c]
9	 **17**	55	7	 **18**[13] (40.0)

[a] Reaction conditions: carbene, 0.3 mmol; selenium, 36 mg (0.45 mmol); Et_3N, 30 mg (0.3 mmol); CO, 0.1 MPa; THF, 8 mL. [b] Isolated yield. [c] 100% conversion for the carbene complex, but no produt could be isolated.

The same methodology was extended to the demetalation of other Fischer carbene complexes, i.e., alkynyl, alkenyl, and alkyl Fischer alkoxy or amino monocarbene complexes. The results are summarized in Tables 2 and 3. The mixture of a carbene complex, elemental selenium or sulfur powder, and triethylamine in THF was stirred under atmospheric pressure of CO at ambient temperature or 55 °C. Alkynyl carbene complexes **10a** and **10b** did not undergo demetalation with selenium at ambient temperature overnight, but they underwent complicated demetalation at 55 °C within 5 h without any success of isolating products from the reaction mixture (entries 1 and 2, Table 2). 1-Alkynyl Fischer aminocarbene complexes **11a** and **11b** stayed unchanged under the demetalation conditions. 1-Alkenyl carbene complex **12** underwent fast demetalation by means of selenium at ambient temperature, affording complex **13** as the product in 76.5% yield (entry 5 of Table 2). It should be noted that the reaction of **12** with selenium can also occur in the absence of CO, but the base Et_3N is necessary to promote the reaction. Complex **13** is a product formed by insertion of a selenium atom into the Cr═C bond of **12**, and it is not very stable, as further stirring of the

Table 3. Sulfurative Demetalation of Fischer Carbene Complexes with Sulfur in the Presence of CO[a]

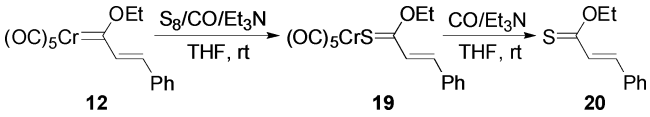
entry	carbene	temp (°C)	time (h)	results (yield[b] (%))
1	 **10a**	55	3	complicated[c]
2	 **10b**	23	14	complicated[c]
3	 **11a**	55	14	no reaction
4	 **11b**	55	14	no reaction
5	 **12**	23	0.5	 **19** (72.4)
6	 **12**	23	14	 **20**[14] (60.4)
7	 **14**	23	14	 **21** (76.8)
8	 **16a**	23	14	complicated[c]
9	 **16b**	23	14	complicated[c]
10	 **17**	55	14	no reaction

[a] Reaction conditions: carbene, 0.25 mmol; sulfur, 11 mg (0.33 mmol); catalytic amount of selenium, 2 mg (0.03 mmol); Et_3N, 25 mg (0.25 mmol); CO, 0.1 MPa; THF, 10 mL. [b] Isolated yield. [c] 100% conversion for the carbine complex, but no produt could be isolated.

reaction mixture under the reaction conditions or during storage at ambient temperature led to its decomposition. The decomposition products of **13** were not successfully isolated, and satisfactory elemental analyses were not achieved due to its decomposition during storage. The alkenyl carbene complex **14** easily underwent demetalation with selenium at ambient temperature to form a deep blue Se-insertion complex, **15**, in decent yield (88.6%) (entry 6, Table 2). Reactions of β-substituted alkenyl carbene complexes **16a** and **16b** generated only a complicated mixture from which no product was successfully isolated and identified. 1-Alkyl carbene complex **17** did not react with selenium at ambient temperature in the presence of CO, while it underwent selenylative demetalation at 55 °C, forming selenocarboxylate **18**[13] in 40.0% yield (entry 9, Table 2).

In a fashion similar to selenylative demetalation of **10a**,**b**, carbene complexes **10a** and **10b** were reacted with elemental sulfur in the presence of CO and a catalytic amount of selenium. Their reactions occurred at ambient temperature and proceeded faster at 55 °C, affording complicated mixtures (entries 1 and 2, Table 3). The aminocarbene analogues of **10a**,**b**, i.e., **11a** and **11b**, did not react under the stated conditions. Complex **12** reacted fast with sulfur, producing sulfur-insertion complex **19** in 72.4% yield (entry 5, Table 3). However, complex **19** is unstable in the solid state, as it was partially decomposed during dryness under reduced pressure at ambient temperature. A reaction mixture of **12** and sulfur was thus stirred overnight under the reaction conditions, from which thiocarboxylate **20**[14] was isolated in 60.4% yield (entry 6, Table 3). The sulfur-insertion complex **19** can be considered as the intermediate species for complete demetalation of the Fischer monocarbene complex **12** (Scheme 5). This phenomenon was also observed in the reactions of two Fischer iminocarbene complexes with selenium or sulfur in the presence of $NaBH_4$/EtOH.[15] Sulfuration of complex **14** gave a sulfur-insertion analogue of **15**, i.e., complex **21**, in 76.8% yield (entry 7, Table 3). The molecular structure of **21** was confirmed by X-ray crystallographic determination of its single crystal. The sulfuration reactions of carbene complexes **16a**,**b** were complicated as described above. The alkyl carbene complex **17** did not react with sulfur even at 55 °C overnight (entry 10, Table 3), although it underwent selenylative demetalation with selenium under similar conditions.

Scheme 5. Sulfurative Demetalation of 12



The NMR features of compounds **13**, **15**, and **18**−**21** are consistent with the structural assignments shown in Tables 2 and 3. The ^{13}C NMR chemical shift of C═Se in the free selenocarboxylate **18** is ca. 236 ppm,[13] while those of the C═Se in the Se-insertion complexes **13** and **15** are about 220 and 204 ppm, respectively. Coordination of the selenium atom to the metal center caused the NMR signals of C═Se in **13** and **15** to shift 16−32 ppm upfield as compared with that of **18**. The ^{13}C NMR chemical shift of C═S in the free thiocarboxylate **20** is 210.5 ppm (210.2 ppm[14]), and those of the C═S in the S-insertion complexes **19** and **21** are about 212 and 200 ppm, respectively. It is obvious that the variety of the ^{13}C NMR chemical shifts of C═Se and C═S in Se- or S-insertion complexes is attributed to the electronic and sterical properties of the moieties around the C═Se and C═S bonds. However, the ^{13}C NMR signals of the *trans*- and *cis*-CO in the $Cr(CO)_5$ moiety are always shown in a 1:4 ratio and appear at 223.94/216.32, 224.46/217.06, 223.19/215.30, and 223.79/215.95 ppm, respectively, for complexes **13**, **15**, **19**, and **21**, revealing no significant difference between the $M(CO)_5$ moieties in different Se- or S-insertion complexes.

The perspective views of **5b**, **6b**, **8a**, and **21** are shown in Figures 1−4. The crystal data and refinement details are summarized in Table 4, and selected bond lengths and angles are listed in Table 5. Selenocarboxylate monocarbene complex **5b** exhibits a molecular structure similar to its ester monocarbene analogue **2a** (M = Cr, Scheme 1)[9] with the C═Se bond being 1.770(7) Å and Cr−C bond being 2.103(7) Å (Figure 1). Diselenocarboxylate **6b** also exhibits a molecular structure similar to its diester analogue **3** with the two C═Se bonds (1.768(4) and 1.812(4) Å) *anti* to each other (Figure 2), while the two C═O bonds in **3** are positioned *syn*.[9] In the solid state,

(13) Cohen, V. I. *J. Org. Chem.* **1977**, *42*, 2645.

(14) Davrinche, C.; Jean-Daniel, B.; Pierre, R. *Synth. Commun.* **1984**, *14*, 1181.

(15) Zheng, Z. Y.; Chen, J. Z.; Yu, Z. K.; Han, X. W. *J. Organomet. Chem.* **2006**, *691*, 3679.

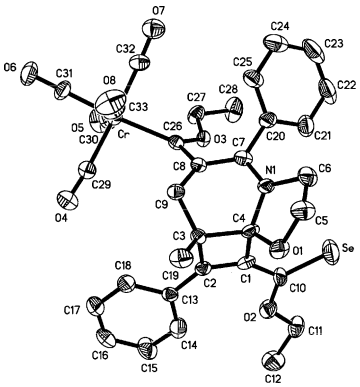


Figure 1. Perspective view of complex **5b**.

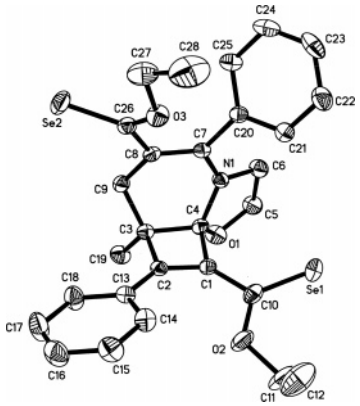


Figure 2. Perspective view of diselenocarboxylate **6b**.

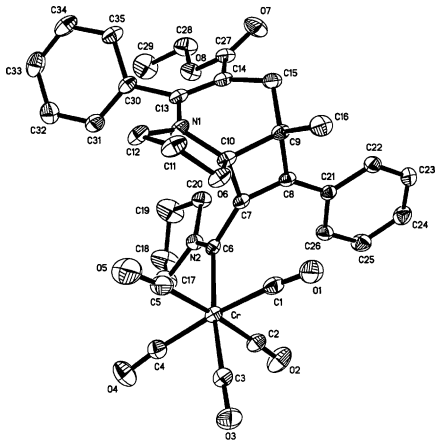


Figure 3. Perspective view of complex **8a**.

the molecular structure of *O*-carboxylate aminocarbene complex **8a** shows that the pyrrolidino-bonded Cr═C bond (2.114(2) Å) stays unchanged, as it is in **4**, but the other Cr═C bond in **4** was oxidatively demetalated to the C═O bond in **8a** with 1.0 equiv of PNO (Figure 3). Figure 4 reveals a sulfur-insertion complex, i.e., **21**, which was generated by insertion of a sulfur atom into the Cr═C bond of **14**. The C═S and coordinating Cr−S bond distances are 1.6601(19) and 2.3992(6) Å, respectively, and the Cr−S−C(6) bond angle is 115.53(7)°.

Conclusions

In conclusion, novel sulfuration with elemental sulfur and selenylation with elemental selenium of Fischer biscarbene complexes of chromium have been achieved by means of in-situ-generated SCO and SeCO for the first time, efficiently affording thio- and selenocarboxylates. The present CO-

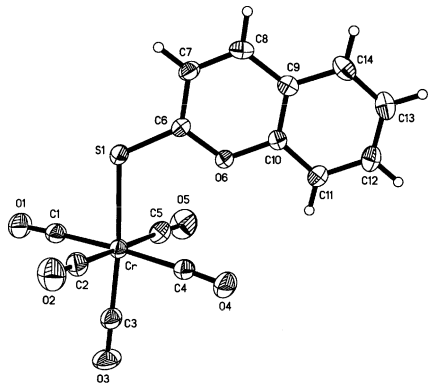
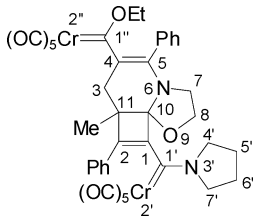


Figure 4. Perspective view of complex **21**.

promoted sulfuration and selenylation methodology provides a potential route to demetalate relatively unreactive Fischer aminocarbene complexes. Intramolecular reactivity inversion of the chromium carbene carbon bonds (Cr═C) in an alkoxy−alkoxy biscarbene complex can be realized by replacement of the alkoxy group bonded to the more reactive Cr═C carbon atom with an amino moiety. A strained cyclobutenyl ring remarkably activates the aminocarbene carbon bond, which thus undergoes oxidation, sulfuration, and selenylation under mild conditions. Selenium- and sulfur-insertion complexes can be obtained from the selenylative or sulfurative demetalation of 1-alkenyl Fischer monocarbene complexes.

Experimental Section

General Considerations. All operations were performed under nitrogen or CO atmosphere. Dried solvents were used in all experiments. Melting points are not corrected. Instrumentation: ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained with a Bruker DRX-400 spectrometer (chemical shifts refer to $\delta_{TMS} = 0.00$ ppm). IR spectra were obtained with a Bruker Tensor 27. Elemental analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. A typical procedure for oxidation of biscarbene complexes was described in our previous paper.[9] The monocarbene complexes **11a**,**b**, **12**, **14**, **16a**,**b**, and **17** were prepared as reported.[15]



Synthesis of biscarbene complex 1-(2,2,2,2,2-pentacarbonyl-2-chroma-1-pyrrolidin-1-yl-vinyl)-4-(2,2,2,2,2-pentacarbonyl-2-chroma-1-ethoxy-1-ylvinyl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene (4). To a solution of **1a** (203 mg, 0.25 mmol) in 10 mL of Et_2O precooled to −78 °C under nitrogen was added pyrroline (18 mg, 0.25 mmol) in 10 mL of Et_2O within 10 min. The mixture was stirred at −78 °C, and the reaction was monitored by TLC on silica gel. After **1a** was completely consumed over a period of 30 min, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (hexanes/dichloromethane, v/v = 1:1) to afford **4** as orange crystals (178 mg, 85%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 115 °C (dec); ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.41, 7.33, 7.27, and 7.04 (m each, 3:3:2:2 H, 2 Ph), 4.42 (m, 2 H, 1″-OCH_2), 4.32 and 4.27 (m

Table 4. Crystal Data and Refinement Details for 5b, 6b, 8a, and 21

	5b	6b	8a	21
empirical formula	$C_{33}H_{29}NO_8SeCr$	$C_{28}H_{29}NO_3Se_2$	$C_{35}H_{32}N_2O_8Cr$	$C_{14}H_6CrO_6S$
fw	698.53	585.44	660.63	354.25
temperature (K)	293(2)	293(2)	293(2)	293(2)
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.045(4)	9.8424(12)	9.9852(12)	6.9915(8)
b (Å)	23.888(10)	10.0858(13)	10.0883(12)	9.2960(10)
c (Å)	12.305(5)	14.5902(18)	16.4519(19)	11.6505(12)
α (deg)	90	107.768(2)	87.999(2)	95.864(2)
β (deg)	107.215(9)	103.307(2)	75.261(2)	100.443(2)
γ (deg)	90	100.490(2)	84.954(2)	101.288(2)
V (Å^3)	3101(2)	1291.5(3)	1596.4(3)	722.78(14)
Z	4	2	2	2
D_c (gcm^{-3})	1.496	1.505	1.374	1.628
μ (mm^{-1})	1.595	2.892	0.414	0.961
F(000)	1424	592	688	356
cryst size (mm^3)	0.18 × 0.15 × 0.05	0.52 × 0.46 × 0.35	0.51 × 0.47 × 0.35	0.49 × 0.46 × 0.30
θ limits (deg)	1.93−25.50	2.18−27.00	2.03−27.00	1.80−27.00
no. of data collected	15876	7635	9468	4272
no. of unique data	5774	5477	6765	3056
R(int)	0.1634	0.0652	0.0663	0.0483
no. of data obsd with $I > 2\sigma(I)$	1762	3226	5472	2602
no. of refined params	400	310	418	200
goodness-of-fit on F^2	0.844	0.862	1.012	1.073
R (all data/obsd data)	0.2042/0.0499	0.0824/0.0513	0.0607/0.0521	0.0392/0.0343
R_w^2 (all data/obsd data)	0.1129/0.0674	0.1285/0.1194	0.1480/0.1423	0.0970/0.0943
residual ρ_{max} (e Å^{-3})	0.264(−0.376)	0.789(−0.736)	0.622 (−0.685)	0.294 (−0.364)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5b, 6b, 8a, and 21

		Complex **5b**			
Cr−C(26)	2.103(7)	C(8)−C(26)	1.432(9)	C(7)−C(8)	1.393(9)
Se−C(10)	1.770(7)	C(1)−C(10)	1.468(9)	C(1)−C(2)	1.340(8)
C(8)−C(26)−O(3)	105.1(6)	C(1)−C(10)−O(2)	112.7(6)		
		Diselenocarboxylate **6b**			
Se(1)−C(10)	1.768(4)	Se(2)−C(26)	1.812(4)	C(1)−C(2)	1.348(5)
C(7)−C(8)	1.369(5)				
C(1)−C(10)−O(2)	110.8(4)	C(8)−C(26)−O(3)	113.5(3)		
		Complex **8a**			
Cr−C(6)	2.114(2)	C(6)−C(7)	1.476(3)	N(2)−C(6)	1.304(2)
C(7)−C(8)	1.350(3)	O(7)−C(27)	1.202(3)	C(13)−C(14)	1.351(3)
Cr−C(6)−C(7)	116.72(13)				
		Complex **21**			
Cr−S	2.3992(6)	C(6)−S	1.6601(19)	C(6)−O(6)	1.340(2)
C(10)−O(6)	1.387(2)	C(7)−C(8)	1.344(3)		
Cr−S−C(6)	115.53(7)	O(6)−C(6)−S	118.20(13)	C(3)−Cr−S	174.59(7)

each, 1:1 H, 7′-H), 3.92 and 3.29 (m each, 1:1 H, 4′-H), 3.87 (d, J = 14.0 Hz) and 3.53 (m) (1:1 H, 8-H), 3.84 (m, 2 H, 3-H), 3.11 (dd, J = 10.3, 5.28 Hz) and 2.86 (d, J = 13.8 Hz) (1:1 H, 7-H), 2.20 and 2.10 (m each, 1:1 H, 6′-H), 1.85 (m, 2H, 5′-H), 1.66 (s, 3 H, 11-C*H*$_3$), 0.45 (t, 3 H, 1″-OCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 315.26 and 261.89 (s each, Cq each, Cr═C, C1″ and C1′), 223.48 and 217.72 (s each, Cq, 1:4, *trans*- and *cis*-CO, C1″-Cr(CO)$_5$), 223.26 and 217.91 (s each, Cq, 1:4, *trans*- and *cis*-CO, C1′-Cr(CO)$_5$), 151.13 (s, Cq, C═*C*-N, C5), 140.58, 133.38 and 131.62 (s each, Cq each, C1, C2, and C4), 137.94 and 134.22 (s each, Cq, *i*-C of 2 Ph), 129.80, 129.21, and 127.50 (s each, 1:8:1 *C*H of 2 Ph), 96.39 (s, Cq, C10), 73.76 (s, C1″-O*C*H$_2$), 66.17 (s, C8), 62.42 (s, Cq, C11), 60.25, 57.06, 49.04, and 40.10 (s each, C7′, C4′, C7, and C3), 26.32 and 25.45 (s each, C6′ and C5′), 19.60 (s, C11-*C*H$_3$), 13.93 (s, C1″-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 2048 (60), 1919 (90) [ν(C≡O)], 1474 (40), 1463 (40), 1437 (30) [ν(C═C)]. Anal. Calcd for $C_{40}H_{32}Cr_2N_2O_{12}$: C, 57.42; H, 3.86; N, 3.35. Found: C, 57.43; H, 3.98; N, 3.18.

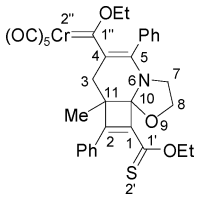
Typical Procedure for Sulfuration: Stepwise Sulfuration of 1a. (1) Partial Sulfuration. A mixture of powdered elemental sulfur (10 mg, 0.3 mmol), a catalytic amount of elemental selenium (2 mg, 0.03 mmol), and triethylamine (25 mg, 0.25 mmol) in THF (10 mL) was vigorously stirred under atmospheric pressure of carbon monoxide at ambient temperature for 5 h. Then the atmosphere was switched to nitrogen. Powdered sulfur (1 mg, 0.03 mmol) was added in one portion under a nitrogen atmosphere to precipitate selenium, and the mixture was stirred at 0 °C for 1 h. Complex **1a** (203 mg, 0.25 mmol) was then added and reacted at 0 °C under a nitrogen or CO atmosphere, and the reaction was monitored by TLC on silica gel. After **1a** was completely consumed over a period of 2 h, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (hexanes/dichloromethane, v/v = 1:1) to afford complex **5a** as brown crystals (135 mg, 83%).

(2) Complete Sulfuration. A mixture of powdered elemental sulfur (19 mg, 0.60 mmol), a catalytic amount of elemental selenium (5 mg, 0.06 mmol), and triethylamine (50 mg, 0.50 mmol) in THF (10 mL) was vigorously stirred under atmospheric pressure of carbon monoxide at ambient temperature for 5 h. Powdered sulfur (2 mg, 0.06 mmol) was added in one portion under a nitrogen atmosphere to precipitate selenium, and the mixture was further stirred for 1 h. Complex **1a** (203 mg, 0.25 mmol) was then added and reacted under a nitrogen or CO atmosphere. After **1a** was completely consumed over a period of 2 h, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (hexanes/dichloromethane, v/v = 1:1) to afford complex **6a** as orange crystals (96 mg, 78%).

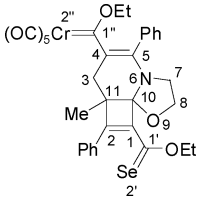
Typical Procedure for Selenylation: Stepwise Selenylation of 1a. (1) Partial Selenylation. A mixture of elemental selenium powder (24 mg, 0.3 mmol) and triethylamine (25 mg, 0.25 mmol) in THF (10 mL) was vigorously stirred under atmospheric pressure of carbon monoxide at ambient temperature for 0.5 h. Complex **1a** (203 mg, 0.25 mmol) was added under a nitrogen atmosphere. The mixture was stirred at ambient temperature under a nitrogen or CO atmosphere, and the reaction was monitored by TLC on silica gel. After **1a** was completely consumed, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (hexane/dichloromethane, v/v = 1:1) to afford complex **5b** as dark crystals (143 mg, 82%).

(2) Complete Selenylation. A mixture of elemental selenium powder (47 mg, 0.6 mmol) and triethylamine (50 mg, 0.5 mmol) in THF (10 mL) was vigorously stirred under atmospheric pressure of carbon monoxide at 55 °C for 0.5 h. Complex **1a** (203 mg, 0.25 mmol) was added under a nitrogen atmosphere. The mixture was stirred at 55 °C under a nitrogen or CO atmosphere, and the reaction was monitored by TLC on silica gel. After **1a** was completely consumed, all the volatiles were removed under reduced pressure and the resultant residue was subject to purification by flash silica gel column chromatography (hexane/dichloromethane, v/v = 1:1), affording complex **6b** as dark crystals (104 mg, 71%).

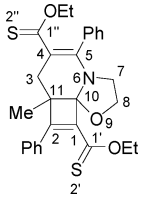
Typical Procedure for Synthesis of Hetero-dicarboxylates: Synthesis of *Se,S*-Carboxylate (7). A mixture of elemental selenium (24 mg, 0.3 mmol) and triethylamine (25 mg, 0.25 mmol) in THF (10 mL) was vigorously stirred under atmospheric pressure of carbon monoxide at 55 °C for 0.5 h. Complex **5a** (163 mg, 0.25 mmol) was added under a nitrogen atmosphere. The mixture was stirred at 55 °C under a CO atmosphere, and the reaction was monitored by TLC on silica gel. After **5a** was completely consumed over a period of 3 h, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (hexanes/dichloromethane, v/v = 1:1) to afford complex **7** as red crystals (133 mg, 99%).



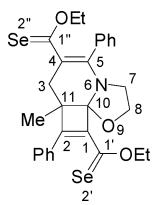
4-(2,2,2,2,2-Pentacarbonyl-2-chroma-1-ethoxy-1-ylvinyl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta-[*d*]indene-1-carbothioic acid *O*-ethyl ester (5a): brown crystals (135 mg, 83%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 117 °C (dec); ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.57, 7.36, and 7.34 (m each, 2:6:2 H, 2 Ph), 4.59 (q, 2 H, 1″-OCH_2), 4.42 (dt) and 4.23 (q) (1:1 H, 1′-OCH_2), 4.12 (m) and 4.02 (q) (1:1 H, 3-H), 3.81 (m) and 3.54 (d, J = 13.4 Hz) (1:1 H, 8-H), 3.26 (m) and 2.70 (d, J = 13.4 Hz) (1:1 H, 7-H), 1.61 (s, 3 H, 11-CH_3), 1.34 and 0.62 (t each, 3:3 H, 1′-OCH$_2$CH_3 and 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 313.08 (s, Cq, Cr═C, C1″), 223.96 and 218.20 (s each, Cq, 1:4, *trans*- and *cis*-CO, C1″-Cr(CO)$_5$), 202.95 (C═S, C1′), 158.31 (s, Cq, C═*C*-N, C5), 151.58, 131.78, and 131.22 (s each, Cq, C1, C2, and C4), 137.48 and 132.02 (s each, Cq, *i*-C of 2 Ph), 130.53, 129.78, 129.46, 129.45, 128.76, and 128.30 (s each, 1:2:1:2:2:2 *C*H, 2 Ph), 95.51 (s, Cq, C10), 73.69 and 67.38 (s each, C1″-O*C*H$_2$ and C1′-O*C*H$_2$), 67.03 (s, C8), 64.68 (s, Cq, C11), 48.90 and 38.42 (s each, C7 and C3), 19.55 (s, C11-*C*H$_3$), 14.44 and 13.63 (s each, C1″-OCH$_2$*C*H$_3$ and C1′-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 2046 (95), 1911 (100) [ν(C≡O)], 1585 (60), 1569 (60), 1468 (95), 1437 (90) [ν-(C═C)], 1231 (90) [ν(C═S)]. Anal. Calcd for $C_{33}H_{29}CrNO_8S$: C, 60.82; H, 4.49; N, 2.15. Found: C, 61.10; H, 4.70; N, 2.07.



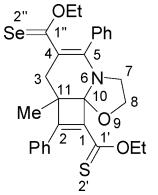
4-(2,2,2,2,2-Pentacarbonyl-2-chroma-1-ethoxy-1-ylvinyl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta-[*d*]indene-1-carboselenoic acid *O*-ethyl ester (5b): black crystals (143 mg, 82%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 125−128 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.58, 7.36, and 7.32 (m each, 2:4:4 H, 2 Ph), 4.67 (m, 2 H, 1″-OCH_2), 4.47 (t) and 4.32 9q) (1:1 H, 1′-OCH_2), 4.09 and 4.03 (m each, 1:1 H, 3-H), 3.83 (m) and 3.56 (d, J = 13.3 Hz) (1:1 H, 8-H), 3.29 (t) and 2.70 (d, J = 13.2 Hz) (1:1 H, 7-H), 1.62 (s, 3 H, 11-CH_3), 1.41 and 0.63 (t each, 3:3 H, 1′-OCH$_2$CH_3 and 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 312.60 (s, Cq, Cr═C, C1″), 223.94 and 218.15 (s each, Cq, 1:4, *trans*- and *cis*-CO, C1″-Cr(CO)$_5$), 210.86 (C═Se, C1′), 156.63 (s, Cq, C═*C*-N, C5), 152.03, 131.94, and 131.78 (s each, Cq, C1, C2, and C4), 137.41 and 136.31 (s each, Cq, *i*-C of 2 Ph), 130.46, 129.95, 129.56, 129.08, 128.73, and 128.33 (s each, 1:2:1:2:2:2 *C*H of 2 Ph), 95.69 (s, Cq, C10), 73.63 (s, C1″-O*C*H$_2$), 71.48 (s, C1′-O*C*H$_2$), 67.16 (s, C8), 65.49 (s, Cq, C11), 49.41 and 38.09 (s each, C7 and C3), 18.94 (s, C11-*C*H$_3$), 14.42 and 13.61 (s each, C1″-OCH$_2$*C*H$_3$ and C1′-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 2046 (80), 1925 (100) [ν(C≡O)], 1558 (40), 1466 (80), 1430 (60) [ν(C═C)], 1014 (65) [ν(C═Se)]. Anal. Calcd for $C_{33}H_{29}CrNO_8Se$: C, 56.74; H, 4.18; N, 2.01. Found: C, 56.53; H, 4.36; N, 1.86.



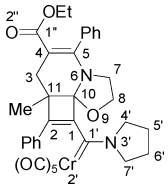
2a-Methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-1,4-dicarbothioic acid di-*O*-ethyl ester (6a): orange crystals (96 mg, 78%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 177 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.71 and 7.36 (m each, 2:8 H, 2 Ph), 4.61 and 4.51 (m each, 1:1 H, 1″-OCH_2), 4.40 and 4.08 (m each, 1:1 H, 1′-OCH_2), 4.05 and 3.88 (m each, 1:1 H, 3-H), 4.03 (m) and 3.86 (d, J = 14.4 Hz) (1:1 H, 8-H), 3.18 (m) and 2.37 (d, J = 14.4 Hz) (1:1 H, 7-H), 1.45 (s, 3 H, 11-CH_3), 1.38 and 0.47 (t each, 3:3 H, 1′-OCH$_2$CH_3 and 1″-OCH$_2$CH_3); ^{13}C-{^{1}H} NMR ($CDCl_3$, 23 °C) δ 210.11 and 203.00 (s each, Cq, C1″═S and C1′═S), 158.80 (s, Cq, C═*C*-N, C5), 153.33, 131.83, and 113.63 (s each, Cq, C4, C1 and C2), 138.07 and 131.70 (s each, Cq, *i*-C of 2 Ph), 130.16, 129.54, 128.90, 128.31, and 128.14 (s each, 1:2:4:1:2 *C*H of 2 Ph), 94.97 (s, Cq, C10), 67.39 and 66.74 (s each, C1′-O*C*H$_2$ and C1″-O*C*H$_2$), 66.31 (s, C8), 64.96 (s, Cq, C11), 48.86 and 37.22 (s each, C7 and C3), 19.39 (s, C11-*C*H$_3$), 13.66 and 12.79 (s each, C1″-OCH$_2$*C*H$_3$ and C1′-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1}, 1529 (50), 1492 (35), 1418 (30) [ν(C═C)], 1221 (55), 1196 (25) [ν(C═S)]. Anal. Calcd for $C_{28}H_{29}NO_3S_2$: C, 68.40; H, 5.95; N, 2.85. Found: C, 68.25; H, 5.90; N, 2.74.



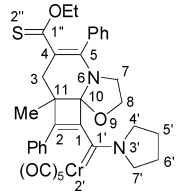
2a-Methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-1,4-dicarboselenoic acid di-*O*-ethyl ester (6b): dark crystals (104 mg, 71%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 183 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.74 and 7.32 (m each, 2:8 H, 2 Ph), 4.70 and 4.60 (m each, 1:1 H, 1″-OCH_2), 4.43 and 4.20 (m each, 1:1 H, 1′-OCH_2), 4.13 (d, J = 14.4 Hz) and 3.98 (m) (1:1 H, 8-H), 4.10 and 4.04 (m each, 1:1 H, 3-H), 3.18 (m) and 2.51 (d, J = 14.3 Hz) (1:1 H, 7-H), 1.46 (s, 3 H, 11-CH_3), 1.43 and 0.47 (t each, 3:3 H, 1′-OCH$_2$CH_3 and 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 216.35 and 210.97 (s each, Cq, C1″=Se and C1′=Se), 157.30 (s, Cq, C=*C*-N, C5), 153.48, 132.26, and 118.44 (s each, Cq, C1, C2 and C4), 138.10 and 136.21 (s each, Cq, *i*-C of 2 Ph), 130.24, 129.35, 129.20, 128.52, and 128.27 (s each, 1:2:2:1:4 *C*H of 2 Ph), 95.58 (s, Cq, C10), 71.62 and 70.45 (s each, C1′-O*C*H$_2$ and C1″-O*C*H$_2$), 66.88 (s, C8), 65.40 (s, Cq, C11), 49.84 and 38.45 (s each, C7 and C3), 18.71 (s, C11-*C*H$_3$), 13.68 and 12.80 (s each, C1″-OCH$_2$*C*H$_3$ and C1′-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 1518 (52), 1492 (50), 1445 (30) [ν(C=C)], 1190 (45), 1016 (45) [ν(C=Se)]. Anal. Calcd for $C_{28}H_{29}NO_3Se_2$: C, 57.44; H, 4.99; N, 2.39. Found: C, 57.59; H, 5.28; N, 2.29.



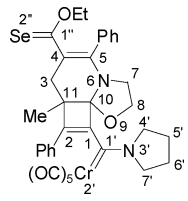
4-Ethoxyselenocarbonyl-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-1-carbothioic acid *O*-ethyl ester (7): red crystals (133 mg, 99%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 178−179 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.75 and 7.36 (m each, 2:8 H, 2 Ph), 4.62 and 4.51 (m each, 1:1 H, 1″-OCH_2), 4.40 and 4.19 (m each, 1:1 H, 1′-OCH_2), 4.12 (d, J = 14.4 Hz) and 4.03 (m) (1:1 H, 8-H), 4.01 and 3.95 (m each, 1:1 H, 3-H), 3.17 (m) and 2.51 (d, J = 14.4 Hz) (1:1 H, 7-H), 1.46 (s, 3 H, 11-CH_3), 1.39 and 0.48 (t each, 3:3 H, 1′-OCH$_2$CH_3 and 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 216.23 (s, Cq, C=Se, C1″), 202.91 (s, Cq, C=S, C1′), 158.82 (s, Cq, C=*C*-N, C5), 153.21, 138.07, and 118.22 (s each, Cq, C1, C2, and C4), 131.59 and 131.50 (s each, Cq, *i*-C of 2 Ph), 130.29, 129.72, 129.13, 128.84, 128.53, and 128.18 (s each, 1:2:1:1:2:2 *C*H of 2 Ph), 95.22 (s, Cq, C10), 70.42 and 67.48 (s each, C1′-O*C*H$_2$ and C1″-O*C*H$_2$), 66.66 (s, C8), 64.48 (s, Cq, C11), 49.26 and 38.77 (s each, C7 and C3), 19.26 (s, C11-*C*H$_3$), 13.65 and 12.76 (s each, C1″-OCH$_2$*C*H$_3$ and C1′-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 1518 (60), 1491 (60), 1369 (50) [ν (C=C)], 1221 (70) [ν (C=S)], 1016 (60) [ν (C=Se)]. Anal. Calcd for $C_{28}H_{29}NO_3SSe$: C, 62.44; H, 5.43; N, 2.60. Found: C, 62.52; H, 5.58; N, 2.27.



1-(2,2,2,2,2-Pentacarbonyl-2-chroma-1-pyrrolidin-1-ylvinyl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-4-carboxylic acid ethyl ester (8a): yellow crystals (137 mg, 83%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 168 °C (dec); ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.40, 7.34, and 7.27 (m each, 3:2:3:2 H, 2 Ph), 4.30 (q, 2 H, 1″-OCH_2), 4.25 and 4.07 (m each, 1:1 H, 7′-H), 3.83 and 3.14 (m each, 1:1 H, 4′-H), 3.71 (m, 2 H, 3-H), 3.44 (m) and 3.30 (d, J = 14.7 Hz) (1:1 H, 8-H), 3.02 (dd, J = 9.56, 4.00 Hz) and 2.26 (d, J = 14.6 Hz) (1:1 H, 7-H), 2.14 and 2.02 (m each, 1:1 H, 6′-H), 1.73 (m, 2H, 5′-H), 1.56 (s, 3 H, 11-CH_3), 0.64 (t, 3 H, 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 261.17 (s, Cq, Cr=C, C1′), 223.77 and 217.91 (s each, Cq, 1:4, *trans*- and *cis*-CO, C1′-Cr(CO)$_5$), 169.98 (s, Cq, C=O, C1″), 153.51 (s, Cq, C=*C*-N, C5), 141.01, 133.16, and 104.21 (s each, Cq, C1, C2, and C4), 136.84 and 132.49 (s each, Cq each, *i*-C of 2 Ph), 129.89, 129.19, 128.89, 128.72, 128.46, and 127.20 (s each, 1:2:1:2:2:2 *C*H of 2 Ph), 96.78 (s, Cq, C10), 66.33 (s, C8), 65.23 (s, Cq, C11), 60.11 (s, C1″-O*C*H$_2$), 59.38, 56.94, 47.87, and 35.28 (s each, C7′, C4′, C7, and C3), 25.79 and 25.38 (s each, C6′ and C5′), 19.02 (s, C11-*C*H$_3$), 13.72 (s, C1″-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 2052 (25), 1950 (40), 1890 (47), 1873 (44) [ν(C≡O)], 1668 (40) [ν(C=O)], 1556 (20), 1500 (15) [ν(C=C)]. Anal. Calcd for $C_{35}H_{32}CrN_2O_8$: C, 63.63; H, 4.88; N, 4.24. Found: C, 63.66; H, 4.99; N, 4.03.

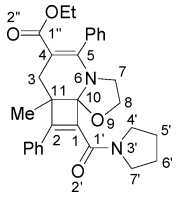


1-(2,2,2,2,2-Pentacarbonyl-2-chroma-1-pyrrolidin-1-ylvinyl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-4-carbothioic acid *O*-ethyl ester (8b): yellow crystals (130 mg, 77%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 160 °C (dec); ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.41, 7.33, 7.27, and 7.15 (m each, 3:2:3:2 H, 2Ph), 4.31 (q, 2 H, 1″-OCH_2), 4.25 and 3.78 (m each, 1:1 H, 7′-H), 4.07 (m, 2 H, 3-H), 3.89 (d, J = 14.7 Hz) and 3.50 (m) (1:1 H, 8-H), 3.72 and 3.14 (m each) (1:1 H, 4′-H), 3.08 (dd, J = 10.6, 5.00 Hz) and 2.44 (d, J = 14.6 Hz) (1:1 H, 7-H), 2.15 and 2.03 (m each, 1:1 H, 6′-H), 1.74 (m, 2H, 5′-H), 1.56 (s, 3 H, 11-CH_3), 0.45 (t, 3 H, 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 261.15 (s, Cq, Cr=C, C1′), 223.63 and 217.83 (s each, Cq, 1:4, *trans*- and *cis*-CO, C1′-Cr(CO)$_5$), 211.26 (Cq, C=S, C1″), 152.70 (s, Cq, C=*C*-N, C5), 140.13, 132.27 and 116.25 (s each, Cq, C1, C2, and C4), 137.43 and 133.83 (s each, Cq, *i*-C of 2 Ph), 129.90, 129.20, 128.88, 128.75, and 127.25 (s each, 1:2:1:4:2 *C*H of 2 Ph), 96.58 (s, Cq, C10), 66.49 (s, C8), 66.22, 56.92, 48.54, and 39.33 (s each, C7′, C4′, C7, and C3), 64.55 (s, Cq, C11), 60.05 (s, C1″-O*C*H$_2$), 25.94 and 25.37 (s each, C6′ and C5′), 18.88 (s, C11-*C*H$_3$), 12.98 (s, C1″-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 2052 (60), 1890 (90), 1873 (80) [ν(C≡O)], 1517 (40), 1487 (45), 1443 (30), 1406 (30) [ν(C=C)], 1063 (40) [ν(C=S)]. Anal. Calcd for $C_{35}H_{32}CrN_2O_7S$: C, 62.12; H, 4.77; N, 4.14. Found: C, 61.83; H, 4.91; N, 3.88.

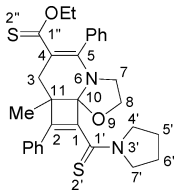


1-(2,2,2,2,2-Pentacarbonyl-2-chroma-1-pyrrolidin-1-ylvinyl)-2a-methyl-2,5-diphenyl-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-4-carboselenoic acid *O*-ethyl ester (8c): red crystals (174 mg, 95%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 168−170 °C (dec); ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ (all the proton resonance signals were broadened) 7.30 (m, 10 H, 2 Ph), 4.33 (m, 2 H, 1″-OCH_2), 4.23 and 3.99 (m each, 1:1 H, 7′-H), 4.23 and

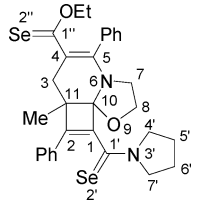
3.12 (m each, 1:1 H, 4′-H), 4.15 (d, J = 13.7 Hz) and 3.44 (m, 1:1 H, 8-H), 3.82 (m, 2 H, 3-H), 3.12 (m, J = 10.6, 5.00 Hz) and 2.58 (d, J = 13.8 Hz) (1:1 H, 7-H), 2.15 and 2.03 (m each, 1:1 H, 6′-H), 1.74 (m, 2H, 5′-H), 1.58 (s, 3 H, 11-CH_3), 0.47 (t, 3 H, 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 261.28 (s, Cq, Cr═C, C1′), 223.58 and 217.82 (s each, Cq, 1:4, *trans*- and *cis*-CO, C1′-Cr(CO)$_5$), 217.59 (s, Cq, C═Se, C1″), 152.41 (s, Cq, C═*C*-N, C5), 139.6, 132.18, and 121.035 (s each, Cq, C1, C2, and C4), 137.50 and 1334.23 (s each, Cq, *i*-C of 2 Ph), 130.11, 129.22, 129.02, 128.92, and 127.36 (s each, 1:2:1:4:2 *C*H of 2 Ph), 96.87 (s, Cq, C10), 70.48 (s, C1″-O*C*H$_2$), 66.18 (s, C8), 60.06, 56.89, 48.87, and 40.74 (s each, C7′, C4′, C7, and C3), 64.14 (s, Cq, C11), 25.98 and 25.36 (s each, C6′ and C5′), 18.76 (s, C11-*C*H$_3$), 12.96 (s, C1″-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 2052 (80), 1890 (100) [ν(C≡O)], 1507 (60), 1483 (80), 1445 (60) [ν(C═C)], 1045 (60) [ν(C═Se)]. Anal. Calcd for $C_{35}H_{32}CrN_2O_7Se$: C, 58.10; H, 4.46; N, 3.87. Found: C, 57.90; H, 4.60; N, 3.66.



2a-Methyl-2,5-diphenyl-1-(pyrrolidine-1-carbonyl)-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-4-carboxylic acid ethyl ester (9a): colorless crystals (91 mg, 75%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 148−149 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.55−7.12 (10 H, 2 Ph), 4.21 (m) and 3.98 (q) (1:1 H, 1″-OCH_2), 3.70, 3.64, and 3.60 (m each, 1:1:2 H, 7′-H and 4′-H), 3.58 and 3.26 (m each, 1:1 H, 3-H), 3.16 and 3.12 (m each, 1:1 H, 8-H), 3.08 (m) and 2.12 (d, J = 14.8 Hz) (1:1 H, 7-H), 1.86 and 1.71 (m each, 2:2 H, 6′-H and 5′-H), 1.57 (s, 3 H, 11-CH_3), 0.58 (t, 3 H, 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 169.19 and 163.56 (s each, Cq, C═O, C1″ and C1′), 153.50 (s, Cq, C═*C*-N, C5), 151.10 and 101.56 (s each, Cq, C1 and C4), 137.11 and 132.03 (s each, Cq, *i*-C of 2 Ph), 129.50, 129.07, 128.85, 128.64, 128.02, and 127.61 (s each, 1:2:2:1:2:2 *C*H of 2 Ph), 95.12 (s, Cq, C10), 65.99 (s, C8), 63.71 (s, Cq, C11), 58.84 (s, C1″-O*C*H$_2$), 47.05, 46.34, 45.65, and 32.45 (s each, C7′, C4′, C7 and C3), 25.90 and 24.42 (s each, C6′ and C5′), 20.11 (s, C11-*C*H$_3$), 13.65 (s, C1″-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 1668 (100), 1603 (100) [ν(C═O)], 1558 (90), 1412 (90) [ν(C═C)]. Anal. Calcd for $C_{30}H_{32}N_2O_4$: C, 74.36; H, 6.66; N, 5.78. Found: C, 74.06; H, 6.88; N, 5.53.

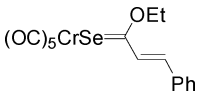


2a-Methyl-2,5-diphenyl-1-(pyrrolidine-1-carbothioyl)-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-4-carbothioic acid *O*-ethyl ester (9b): yellow crystals (97 mg, 75%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 147−148 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.55−7.13 (10 H, 2 Ph), 4.38 and 4.01 (m each, 1:1 H, 1″-OCH_2), 3.98, 3.93 and 3.88 (m each, 1:2:1 H, 7′-H and 4′-H), 3.77 (m, 2 H, 3-H), 3.53 and 3.38 (m each, 1:1 H, 8-H), 3.13 (m) and 2.41 (d, J = 14.5 Hz) (1:1 H, 7-H), 1.96 and 1.80 (m each, 2:2 H, 6′-H and 5′-H), 1.57 (s, 3 H, 11-CH_3), 0.42 (t, 3 H, 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 210.40 and 188.11 (s each, Cq, C═S, C1″ and C1′), 152.29 (s, Cq, C═*C*-N, C5), 145.70, 137.97, and 114.02 (s each, Cq, C1, C2, and C4), 133.02 and 132.05 (s each, Cq, *i*-C of 2 Ph), 129.47, 129.06, 128.89, 128.83, 128.32, and 127.59 (s each, 1:2:1:2:2:2 *C*H of 2 Ph), 96.12 (s, Cq, C10), 66.25 (s, C1″-O*C*H$_2$), 65.92 (s, C8), 62.26 (s, Cq, C11), 52.40, 51.95, 47.66, and 37.20 (s each, C7′, C4′, C7, and C3), 26.27 and 24.35 (s each, C6′ and C5′), 19.93 (s, C11-*C*H$_3$), 12.81 (s, C1″-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 1526 (40), 1448 (40) [ν(C═C)], 1198 (40), 1065 (40) [ν(C═S)]. Anal. Calcd for $C_{30}H_{32}N_2O_2S_2$: C, 69.73; H, 6.24; N, 5.42. Found: C, 69.55; H, 6.52; N, 5.41.



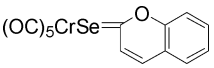
2a-Methyl-2,5-diphenyl-1-(pyrrolidine-1-carboselenoyl)-2a,3,6,7-tetrahydro-8-oxa-5a-aza-cyclobuta[*d*]indene-4-carboselenoic acid *O*-ethyl ester (9c): red crystals (140 mg, 92%). Single crystals were obtained by recrystallization from dichloromethane and pentane at −20 °C: mp 177−178 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.72−7.13 (10 H, 2 Ph), 4.40 and 4.16 (m each, 1:1 H, 1″-OCH_2), 4.12 (m), 4.00 (m), and 3.90 (q) (1:1:2 H, 7′-H and 4′-H), 3.87 and 3.74 (m each, 1:1 H, 3-H), 3.38 and 3.22 (m each, 1:1 H, 8-H), 3.11 (m) and 2.55 (d, J = 14.4 Hz) (1:1 H, 7-H), 2.00 and 1.86 (m each, 2:2 H, 6′-H and 5′-H), 1.58 (s, 3 H, 11-CH_3), 0.44 (t, 3 H, 1″-OCH$_2$CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 216.44 and 189.68 (s each, Cq, C═Se, C1″ and C1′), 152.22 (s, Cq, C═*C*-N, C5), 144.23, 137.97, and 118.42 (s each, Cq, C1, C2, and C4), 135.12 and 131.94 (s each, Cq, *i*-C of 2 Ph), 129.57, 129.13, 128.67, 128.44, and 127.68 (s each, 1:4:1:2:2 *C*H of 2 Ph), 95.98 (s, Cq, C10), 70.34 (s, C1″-O*C*H$_2$), 65.89 (s, C8), 61.76 (s, Cq, C11), 56.00, 53.25, 48.20 and 38.70 (s each, C7′, C4′, C7, and C3), 26.41 and 24.31 (s each, C6′ and C5′), 19.83 (s, C11-*C*H$_3$), 12.80 (s, C1″-OCH$_2$*C*H$_3$); IR (KBr) cm^{-1} 1483 (90), 1444 (80) [ν(C═C)], 1186 (80), 1047 (80) [ν(C═Se)]. Anal. Calcd for $C_{30}H_{32}N_2O_2Se_2$: C, 59.02; H, 5.28; N, 4.59. Found: C, 59.89; H, 5.48; N, 4.35.

Typical Procedure for Selenylation of Fischer Monocarbene Complexes. A mixture of a monocarbene complex (0.3 mmol), elemental selenium powder (36 mg, 0.45 mmol), and triethylamine (30 mg, 0.3 mmol) in THF (8 mL) was vigorously stirred under atmospheric pressure of CO at ambient temperature or 55 °C. The reaction was monitored by TLC on silica gel. After the carbene complex was completely consumed, the reaction mixture was diluted with CH_2Cl_2, filtered through a short pad of Celite, and then concentrated under reduced pressure. The resultant residue was subject to purification by flash silica gel column chromatography, affording the product.

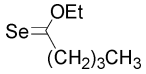


Synthesis of Pentacarbonyl(3-phenyl-selenoacrylic acid *O*-ethyl ester)chromium (13). A mixture of carbene complex **12** (106 mg, 0.3 mmol), Se (36 mg, 0.45 mmol), and Et_3N (30 mg, 0.3 mmol) in 8 mL of THF was vigorously stirred under CO (1 atm) at ambient temperature. **12** was completely consumed within 30 min by TLC analysis on silica gel. All the volatiles were removed under reduced pressure, and the resultant residue was purified by flash silica gel column chromatography with petroleum ether (30−60 °C) as the eluent, affording **13** as a dark purple solid (99 mg, 76.5%): mp 95−98 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.84−7.44 (m, 7 H, CH═CHPh), 4.75 (br, 2 H, OCH$_2$), 1.65 (br, 3 H, CH$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 223.94 and 216.32 (Cq each, 1:4, *trans*- and *cis*-CO, Cr(CO)$_5$), 219.64 (Cq, C═Se),

138.71 and 131.67 (2 CH, CH═CH), 134.60 (Cq, *i*-C of Ph), 129.76 and 129.21 (3:2 CH, Ph), 73.84 (OCH_2), 14.26 (CH_3); IR (KBr) cm^{-1} 2060 (25), 1928 and 1903 (65) [ν(C≡O)], 1273 (24) [ν(Se═C)]. Anal. Calcd for $C_{16}H_{12}CrO_6Se$: C, 44.56; H, 2.80. Found: C, 45.79; H, 3.11. Satisfactory elemental analyses were not achieved due to easy decomposition of **13** in the solid state.

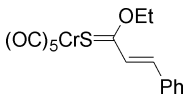


Synthesis of Pentacarbonyl(chromene-2-selone)chromium (15). A mixture of complex **14** (97 mg, 0.3 mmol), Se (36 mg, 0.45 mmol), and Et_3N (30 mg, 0.3 mmol) in 8 mL of THF was stirred under CO (1 atm) at ambient temperature overnight. The resultant mixture was concentrated and then subjected to purification by silica gel column chromatography (v/v, petroleum ether (30−60 °C)/CH_2Cl_2 = 9:1), affording complex **15** as a dark purple solid (107 mg, 88.6%): mp > 120 °C, dec; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.76−7.45 (m and br, 6 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 224.46 and 217.06 (Cq each, 1:4, *trans*- and *cis*-CO, Cr-$(CO)_5$), 203.97 (Cq, Se═C), 158.50 (Cq, C−O), 133.22, 132.13, 130.26, 128.42, 127.35, and 116.97 (6 CH), 122.43 (Cq); IR (KBr) cm^{-1} 2053 (32), 1920 (73) [ν(C≡O)], 1534 (24) [ν(CH═CH)], 1236 (15) [ν(Se═C)]. Anal. Calcd for $C_{14}H_6CrO_6Se$: C, 41.92; H, 1.51. Found: C, 41.95; H, 1.52.



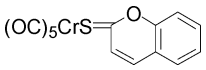
Selenylation of Alkyl Fischer Monocarbene Complex 17. A mixture of carbene complex **17** (92 mg, 0.3 mmol), selenium powder (36 mg, 0.45 mmol), and Et_3N (30 mg, 0.3 mmol) in 8 mL of THF was vigorously stirred under CO (1 atm) at 55 °C. After the starting complex was completely consumed within 7 h, the reaction mixture was diluted with CH_2Cl_2, filtered through 1 cm of Celite, and then concentrated under reduced pressure. The resultant residue was subjected to flash silica gel column chromatography with petroleum (30−60 °C) as the eluent, affording **18** as a yellow oil (22 mg, 40.0%). **18** was identified as pentaneselenoic acid *O*-ethyl ester by NMR measurements and comparison with its reported NMR data.[13]

Typical Procedure for Sulfuration of Fischer Monocarbene Complexes. A mixture of a monocarbene complex (0.25 mmol), elemental sulfur powder (11 mg, 0.33 mmol), a catalytic amount of elemental selenium (2 mg, 0.03 mmol), and triethylamine (25 mg, 0.25 mmol) in THF (10 mL) was vigorously stirred under atmospheric pressure of CO at ambient temperature or 55 °C. The reaction was monitored by TLC on silica gel. After the carbene complex was completely consumed, the reaction mixture was diluted with CH_2Cl_2, filtered through a short pad of Celite, and then concentrated under reduced pressure. The resultant residue was subjected to purification by flash silica gel column chromatography, affording the product.



Synthesis of Pentacarbonyl(3-phenyl-thioacrylic acid *O*-ethyl ester)chromium (19). A mixture of complex **12** (88 mg, 0.25 mmol), sulfur powder (11 mg, 0.33 mmol), selenium (2 mg, 0.03 mmol), and Et_3N (25 mg, 0.25 mmol) in 10 mL of THF was vigorously stirred under CO (1 atm) at ambient temperature. After the reaction was finished within 30 min, all the volatiles were removed under reduced pressure. The resultant residue was subjected to purification by flash silica gel chromatography with petroleum ether (30−60 °C) as the eluent, giving complex **19** as a dark purple solid (69 mg, 72.4%, mp 83−85 °C. Complex **19** was not stable enough upon dryness under reduced pressure and became partially decomposed, so that the solvent could not be completely removed from the product. 3-Phenyl-thioacrylic acid *O*-ethyl ester (**20**) was identified as the decomposition product of **19** on the basis of the NMR features of the isolated material from the reaction mixture. Complex **19**: ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.64 and 7.47 (br each, 7 H), 4.66 (br, OCH_2), 1.56 (br, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 223.19 and 215.30 (Cq each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 211.63 (Cq, S═C), 141.00 and 131.60 (CH═CH), 134.11 (Cq, *i*-C of Ph), 129.49 and 129.11 (2:3 CH, Ph), 70.21 (OCH_2), 14.12 (CH_3); IR (KBr) cm^{-1} 2063 (10), 1933 (30) [ν(C≡O)], 1643 (10) [ν(CH═CH)], 1275 (15) [ν(S═C)]. No satisfactory elemental analyses were achieved.

The same reaction of complex **12** (88 mg, 0.25 mmol) was continued overnight under the above stated conditions, affording a yellow, oily product (29 mg, 60.4%), which was identified as 3-phenylthioacrylic acid *O*-ethyl ester (**20**) by NMR measurements and comparison with its reported NMR data.[14]



Synthesis of Pentacarbonyl(chromene-2-thione)chromium (21). A mixture of carbene complex **14** (45 mg, 0.14 mmol), powdered sulfur (6 mg, o.18 mmol), selenium (1 mg, 0.017 mmol), and Et_3N (25 mg, 0.25 mmol) in 10 mL of THF was vigorously stirred under CO (1 atm) at ambient temperature overnight. After the starting complex **14** was completely consumed, all the volatiles were removed under reduced pressure. The resulting residue was subjected to flash silica gel column chromatography with petroleum ether (30−60 °C)/CH_2Cl_2 (v/v, 9:1), affording complex **21** as a dark purple solid (38 mg, 76.8%). Single crystals suitable for X-ray crystallographic studies were obtained by recrystallization from petroleum ether (30−60 °C)/CH_2Cl_2 (v/v, 5:1) at −20 °C: mp >150 °C, dec; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz) δ 7.69−7.39 (br and m, 6 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 223.80 and 215.95 (Cq each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 199.74 (Cq, S═C), 156.48 (Cq, C−O), 133.16, 132.26, 128.21, 127.76, 126.86, and 116.60 (6 CH), 121.05 (Cq); IR (KBr) cm^{-1} 2058 (12), 1925 (35) [ν(C≡O)], 1540 (10) [ν(CH═CH)], 1238 (10) [ν(S═C)]. Anal. Calcd for $C_{14}H_6CrO_6S$: C, 47.47; H, 1.71. Found: C, 47.48; H, 1.72.

X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for compounds **5b**, **6b**, **8a**, and **21** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and refinement details for these compounds are summarized in Table 2.

Acknowledgment. We are grateful to the "Hundred Talented Program" Funding of the Chinese Academy of Sciences.

Supporting Information Available: Copies of NMR spectra for new compounds and X-ray crystallographic files for **5b**, **6b**, **8a**, and **21**, also in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060288M