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Asymmetric Cleavage of Biscycloalka-1,4-diselena-2,5-cyclohexadienes and 1,4-Diselenafulvenes by Iron Nonacarbonyl Including the Isolation of Intermediate Metallapropellanes[1]

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Reactions of $Fe_2(CO)_9$ with various biscycloalka-1,4-diselena-2,5-cyclohexadienes lead to a variety of products: (diselenato)diiron hexacarbonyls, ferracyclohexadienones, ferracyclopentadienes, cycloalkenobenzenes, and unique diiron diselenametallapropellanes. These latter complexes are intermediates in the fragmentation of the starting heterocycles to the other observed products. The nature of the exact product distribution from the reactions depends upon the ring size of the starting heterocycle. An X-ray crystallographic analysis of a metallapropellane is reported. Reactions of 1,4-diselenafulvenes are also reported, leading to a related asymmetric cleavage to form (diselenato)diiron hexacarbonyl complexes but with no isolable or observable products from the remaining organic fragment. With a styryl-substituted diselenafulvene, an unusual triiron nonacarbonyl complex is isolated.

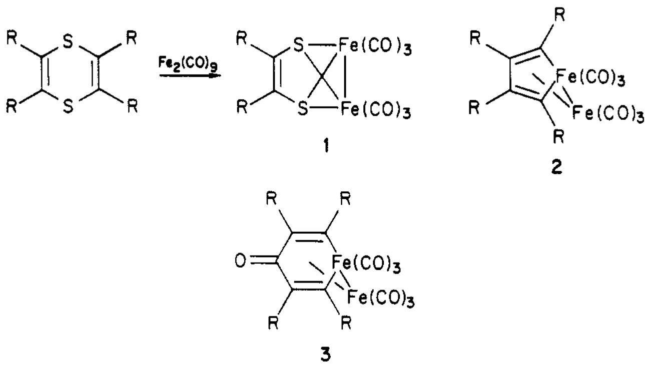
Introduction

We have recently been investigating the chemical reactions of various S (Se) heterocycles with transition-metal complexes, with special emphasis upon the thia(selena)diazole systems.[1-3] The Se heterocycles are of particular interest as organic synthons for the formation of alkynes, and the cycloalka-1,2,3-selenadiazole have been utilized for the formation of transient cycloalkynes with some success.[4] From our studies, a wide variety of new chemistry has resulted involving the formation of heterocycle derived fragments stabilized on transition-metal centers, e.g., thio(seleno)ketocarbenes, thio(seleno)ketoketenes, thio(seleno)ketoimines, etc. However, until recently, we were unable to observe the formation of cycloalkyne complexes.[5]

Bird and Hollins have reported that the reaction between $Fe_2(CO)_9$ and tetraphenyl-1,4-dithia-2,5-cyclohexadiene yields products derived from the asymmetric cleavage of the ligand.[6] Thus, the only sulfur-containing complex obtained was the (dithiolato)diiron hexacarbonyl while ferracycle complexes were isolated from the presumed expulsion of diphenylacetylene from the starting compound (Scheme I).

No information appears in the literature concerning the reactions of the related selenium compounds with transition-metal complexes. Indeed, this illustrates a more general absence of studies on organoselenium compounds when compared to their sulfur analogues. Given the progressively growing use of organoselenium compounds as organic synthons this is surprising. We undertook an investigation into the reactions of the selenium compounds with $Fe_2(CO)_9$ to determine the properties of such heterocycles and, also in the hope that, by analogy to the report of Bird and Hollins, we might be able to provide an alternative route to the systematic formation of (cycloalkyne)metal complexes and, in the case of the fulvenes, of vinylcarbene complexes.

Scheme I



Experimental Section

All manipulations were performed in an atmosphere of dry nitrogen, using dry oxygen-free solvents. The starting diselenacyclohexadienes and fulvenes were prepared by using the published procedures.[4,8] Spectroscopic and analytical data for the various new complexes are recorded in Tables I and II.

Reaction of Biscyclopenta-1,4-diselena-2,5-cyclohexadiene with $Fe_2(CO)_9$. A suspension of 0.3 g (1.03 mmol) of the diselenacyclohexadiene and 3.0 g (8.2 mmol) of the iron carbonyl in 50 mL of hexane was stirred at ambient temperature until all the iron carbonyl was consumed, approximately 24 h. The resulting dark brown solution was evaporated to dryness and the residue dissolved in the minimum volume of a 1:1 CH_2Cl_2/hexane solvent mixture, placed upon an alumina column, 50 × 2.5 cm, and eluted with hexane. This procedure resulted in the separation of **1a** (210

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Table I. IR and NMR Spectroscopic Data

complex	ν(CO),[a] cm^{-1}					
1a	2071 (m)	2032 (s)	1996 (s)	1979 (w)		
1b	2071 (m)	2034 (s)	1992 (s)	1980 (w)		
1c	2071 (m)	2035 (s)	1994 (s)	1980 (w)		
1d	2071 (m)	2034 (s)	1997 (s)	1979 (w)		
1e	2072 (m)	2036 (s)	1998 (s)	1982 (w)		
1f	2072 (m)	2032 (s)	2002 (s)	1993 (w)		
1g	2072 (m)	2037 (s)	1998 (s)			
1h	2072 (m)	2038 (s)	2000 (s)			
2d	2060 (m)	2020 (m)	2020 (s)	1984 (s)	1972 (m)	1938 (w)
3d	2070 (m)	2038 (s)	2001/1997 (s)	1988 (w)		
6b	2070 (m)	2031 (s)	2002 (s)	1989 (m)	1978 (w)	1709 (w)
6c	2069 (m)	2030 (s)	2002 (s)	1989 (m)	1977 (w)	1702 (w)
7c	2081 (m)	2062 (s)	2035 (w)	2022 (m)	2012 (s)	
	2002 (m)	1970 (w)	1640 (w)	1600 (w)		
8	2056 (s)	2037 (s)	2016 (s)	2000 (s)		
9	2074 (m)	2057 (w)	2033 (s)	2000 (w)	1992 (s)	

complex	δ (CDCl$_3$)[b]
1a	H$_\alpha$, 2.60 (m); H$_\beta$, 1.80 (m)
1b	H$_\alpha$, 2.30 (m); H$_\beta$, 1.50 (m)
1c	H$_\alpha$, 2.25 (m); H$_{\beta,\gamma}$, 1.50 (m)
1d	H$_\alpha$, 2.25 (m); H$_{\beta,\gamma}$, 1.50 (m)
1g	C$_6$H$_5$, CH=, 7.22 (s)
1h	C$_6$H$_5$, 7.40 (s); H(1), 7.26 (d, J = 9.6 Hz); H(2), 6.71 (d, J = 9.6 Hz); H(3), 6.44 (s)
9	C$_6$H$_5$, 7.20 (s); H(1), 6.16 (d, J = 9.6 Hz); H(2), 2.10 (d, J = 9.6 Hz); H(3), 2.52 (s)

[a] In hexane. [b] α, β, and γ refer to the positions of the methylene protons relative to the double bond.

Table II. Analytical Data[a]

complex	mol wt	C	H	mp, °C
1a, $C_{11}H_6Fe_2O_6Se_2$	504 (503.78)	26.78 (26.23)	1.51 (1.20)	oil
1b, $C_{12}H_8Fe_2O_6Se_2$	518 (517.81)	28.00 (27.84)	1.41 (1.56)	118–120
1c, $C_{13}H_{10}Fe_2O_6Se_2$	532 (531.84)	30.13 (29.36)	2.07 (1.90)	oil
1d, $C_{14}H_{12}Fe_2O_6Se_2$	546 (545.87)	30.92 (30.81)	2.40 (2.22)	120–121
1e, $C_9H_4Fe_2O_6Se_2$		21.63 (22.60)	1.13 (0.94)	142–143
1f, $C_{12}H_{10}Fe_2O_6Se_2$		29.80 (24.20)	1.28 (2.02)	128–129
1g, $C_{14}H_6Fe_2O_6Se_2$		31.28 (31.13)	1.29 (1.21)	108–110
1h, $C_{16}H_8Fe_2O_6Se_2$		34.44 (33.95)	1.67 (1.41)	133–134
2d, $C_{22}H_{24}Fe_2O_6$	496 (496.13)	53.21 (53.26)	5.02 (4.88)	160–162
3d, $C_{23}H_{24}Fe_2O_7$	524 (524.14)	52.67 (52.71)	4.71 (4.61)	184–186
6b, $C_{19}H_{16}Fe_2O_7Se_2$		36.25 (36.46)	2.53 (2.58)	184–186 dec
6c, $C_{21}H_{20}Fe_2O_7Se_2$		38.67 (38.57)	2.87 (3.08)	190–192 dec
7c, $C_{22}H_{20}Fe_2O_8Se_2$		38.89 (38.75)	2.80 (2.96)	dec
9, $C_{19}H_8Fe_3O_9Se_2$		32.60 (32.34)	1.23 (1.14)	162–163

[a] Analyses performed by Canadian Microanalytical Service, Vancouver, British Columbia, Canada, and the Galbraith Laboratories, Knoxville, TN. Figures in parentheses are theoretical values for both analysis and molecular weight determinations. The latter were performed by mass spectral analysis in the Department of Chemistry at the University of Texas at El Paso on a Du Pont 421 spectrometer.

mg, 44%) from small amounts of other unidentified iron carbonyl products.

Reaction of Biscyclohexa-1,4-diselena-2,5-cyclohexadiene with $Fe_2(CO)_9$. A mixture of the diselenacyclohexadiene (1.0 g, 2.7 mmol) and iron carbonyl (10 g, 27.5 mmol) was stirred in 100 mL of hexane for 15 h at ambient temperature. After removal of the solvent under reduced pressure, the residue was subjected to column chromatography as noted above. Elution with hexane and increasing amounts of CH_2Cl_2 yielded the following products in sequence: **1b** (620 mg, 38%, recrystallized from hexane); **5b** [30 mg, 12%, recrystallized from ethanol, mp 230–231 °C (lit.[9] mp 230–232 °C)]; **6b** (590 mg, 30%, recrystallized from hexane/CH_2Cl_2).

Reaction of Biscyclohepta-1,4-diselena-2,5-cyclohexadiene with $Fe_2(CO)_9$. A mixture of the bis diselenacyclohexadiene (1.6 g, 5.08 mmol) and $Fe_2(CO)_9$ (15 g, 41.2 mmol) was stirred at ambient temperature in hexane for 24 h. Workup as described above led to the following complexes sequentially: **1c** (860 mg, 32% recrystallized from hexane); **5c** [75 mg, 16%, recrystallized from ethanol, mp 182–184 °C (lit.[10] mp 184–185 °C)]; **7c** (625 mg, 18%, recrystallized from hexane/CH_2Cl_2); **6c** (660 mg, 20%, recrystallized from hexane/CH_2Cl_2).

Reaction of Biscycloocta-1,4-diselena-2,5-cyclohexadiene with $Fe_2(CO)_9$. A mixture of the diselenacyclohexadiene (2.0 g, 5.35 mmol) and $Fe_2(CO)_9$ (20 g, 54.9 mmol) in 100 mL of hexane was stirred at ambient temperature for 20 h, followed by workup as described above, which led to the sequential isolation of the following complexes: **1d** (1.2 g, 42%, recrystallized from hexane); **2d** (690 mg, 26%, recrystallized from hexane/CH_2Cl_2); **3d** (900 mg, 32%, recrystallized from hexane/CH_2Cl_2); **5d** [110 mg, 19%, recrystallized from ethanol, mp 196–198 °C (lit.[11] mp 197–198 °C)].

Reaction of the Metallapropellane 6b with $Fe_2(CO)_9$. A mixture of **6b** (200 mg, 0.32 mmol) and $Fe_2(CO)_9$ (5.0 g, 13.7 mmol) was stirred in 50 mL of hexane at ambient temperature for 4 days. Workup as described above produced the complex **1b** (35 mg, 22%) as the only isolated product.

Reaction of 2,ω-Dimethyl-1,4-diselenafulvene with $Fe_2(CO)_9$. A suspension of 1.0 g (4.2 mmol) of the 1,4-diselenafulvene and 6.0 g (16 mmol) of the iron carbonyl in 100 mL of hexane was stirred at room temperature until all the iron carbonyl was consumed, approximately 24 h. The resulting dark brown solution was evaporated to dryness, and the residue was dissolved in a minimum volume of CH_2Cl_2/hexane, placed upon an alumina column, 50 × 2.5 cm, and eluted with hexane. A red band was

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Table III. Crystal Data, Data Collection, and Least-Squares Parameters

empirical formula	$C_{19}H_{16}O_7Se_2Fe_2$
space group	$P\bar{1}$
M_r	626.0
a, Å	9.167 (1)
b, Å	11.630 (1)
c, Å	20.164 (2)
α, deg	92.56 (1)
β, deg	90.33 (1)
γ, deg	95.05 (1)
V, Å^3	2139.1 (7)
Z	4
D_{calcd}, g cm^{-3}	1.943
λ (Mo K$\bar{\alpha}$), Å	0.710 73
μ (Mo K$\bar{\alpha}$), cm^{-1}	47.6
2θ limits, deg	3–52
scan technique	θ–2θ
scan angle, deg	0.35 + 0.35 tan θ
max scan time, min	1.5
total no. of intensities collected	7503
no. of reflctns with zero intensity	729
range of Miller indices	
h	0 to +10
k	−13 to +13
l	−24 to +24
reflctns used in least-squares, NO	6251 ($F_o^2 \geq 2.0\sigma(F_o^2)$)
no. of variables, NV	542
R_o	0.036
R_w	0.046
R_{tot}	0.042
$(\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\mathrm{NO} - \mathrm{NV}))^{1/2}$	2.65
weights	$(\sigma^2(F_o) + 0.25(pF_o^2)^{-1}$, $p = 0.01$
empirical abs correctn (psi scan)	
max transmissn, %	99.9
min transmissn, %	47.7
max correctn	1.00
min correctn	0.69
crystal	thin brownish plates
approx cryst size, mm	0.02 × 0.08 × 0.15

collected and recrystallized from hexane to yield dark red crystals **1e** (0.2 g, 10%). A second red band was collected by eluting with hexane/CH_2Cl_2 (1:1) and recrystallized from hexane to yield a small amount of **8** (mp 138–140 °C).

Reaction of 2,ω-Di-*tert*-butyl-1,4-diselenafulvene with $Fe_2(CO)_9$. A mixture of 1.0 g (3.1 mmol) of the 1,4-diselenafulvene and 6.0 g (16 mmol) of the iron carbonyl in 100 mL of hexane was stirred at room temperature for 24 h, followed by workup as described above. Elution with hexane and increasing amounts of CH_2Cl_2 yielded the following products in sequence: **1f** (0.15 g, 9%, recrystallized from hexane); **8** (small amount, recrystallized from hexane).

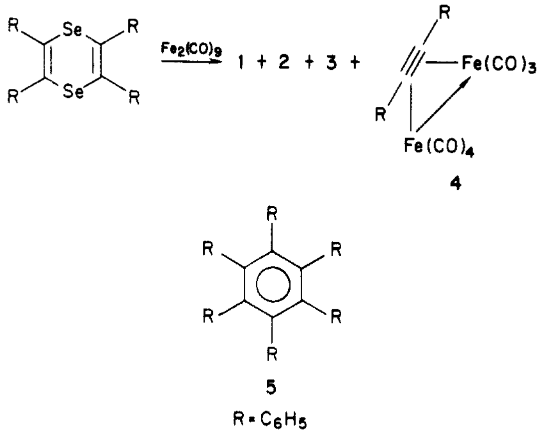
Reaction of 2,ω-Diphenyl-1,4-diselenafulvene with $Fe_2(CO)_9$. A mixture of 1.0 g (2.8 mmol) of the 1,4-diselenafulvene and 6.0 g (16 mmol) of the iron carbonyl in 100 mL of hexane was stirred at room temperature for 24 h. Workup as described above led to the following products in sequence: **1g** (0.4 g, 26%, recrystallized from hexane); **8** (small amount, recrystallized from hexane).

Reaction of 2,ω-Distyryl-1,4-diselenafulvene with $Fe_2(CO)_9$. A suspension of 1.0 g (2.4 mmol) of 1,4-diselenafulvene and 9.0 g (25 mmol) of the iron carbonyl in 100 mL of hexane was stirred at room temperature for 3 days. Workup as described above led to the following products in sequence: **1b** (0.14 g, 10%, recrystallized from hexane); **9** (0.13 g, 8%, recrystallized from hexane), **8** (small amount, recrystallized from hexane).

X-ray Crystallographic Analysis of 6b. Crystal data, data collection, and least-squares parameters are summarized in Table III.

The unit cell parameters were obtained by least squares from the setting angles of 25 reflections (18 < θ < 22°) carefully centered on an Enraf-Nonius computer controlled four-circle CAD4 diffractometer at room temperature. Graphite monochromated Mo Kα radiation was used both in unit cell determination and the collection of intensity data (CAD4 diffractometer, room temperature).

Scheme II



An empirical (psi scan) absorption correction[12] was applied (cf. Table III). The mean absorption curve was calculated from the recorded intensities of six reflections (200, 300, 400, 500, 201, 301) as rotated around the scattering vector.

The positions of the eight heavy atoms were determined by direct methods (MULTAN[13]). All other non-hydrogen atomic positions were obtained by successive structure factor and Fourier calculations.

Since the asymmetric unit contained two enantiomeric molecules, the choice of space group was reinvestigated. The transformation of the unit cell to a monoclinic one was successful only if angles α and β were set to 90° (i.e., allowance is made for errors greater than the accuracy of the diffractometer by two orders of magnitude). The transformation matrix is as follows:

$$\begin{matrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{matrix}$$

Applying the same transformation to atomic coordinates an approximate n glide plane between the two molecules can be established. The averaging of the reflections equivalent by the monoclinic symmetry gave, however, a poor agreement factor on intensities (0.45), and 4124 reflections were rejected on the $|I - I_{av}| \geq 5\sigma(I)$ basis. No systematic absences could be detected. Space group P_1 was then retained and further confirmed by successful least-squares refinement.

All hydrogen atomic coordinates were generated from assumed geometries (C–H = 0.95 Å) at the end of the full-matrix isotropic refinement. Hydrogen atoms were only included in structure factor calculations but were not refined. Their isotropic temperature factors were calculated from those of the carbon atoms to which they are bonded ($B_H = B_C + 1$, Å^2). Non-hydrogen atoms were then refined by anisotropic block-diagonal least squares.

Results and Discussion

Diselena-2,5-cyclohexadienes. Prior to our investigation into the properties of the selenium heterocycles we thought it prudent to reinvestigate the the reaction of tetraphenyl-1,4-dithia-2,5-cyclohexadiene with $Fe_2(CO)_9$. In addition to those complexes reported (Scheme I), we also obtained complex **4** and hexaphenylbenzene, **5**, as shown in Scheme II.

The two "extra" compounds **4** and **5** are obtained in sufficient yields to indicate the ready formation of a free acetylene liberated during the fragmentation process. Complex **4** was identified by comparison of its spectral and elution properties with those reported for the complex by

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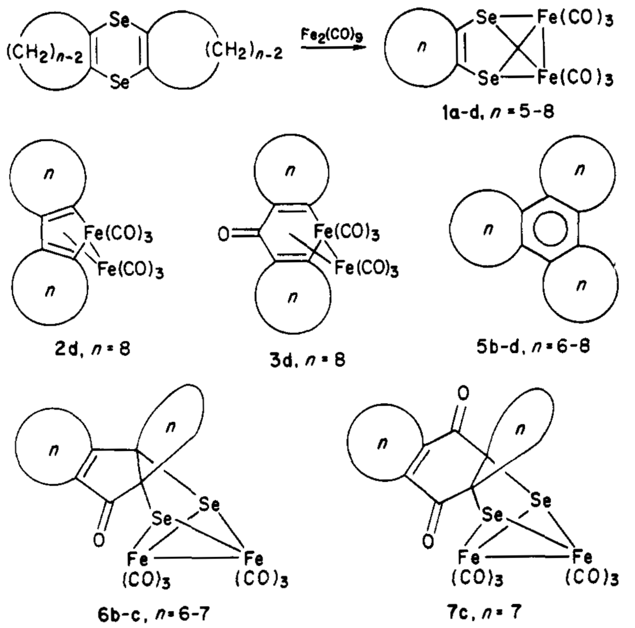
Scheme III



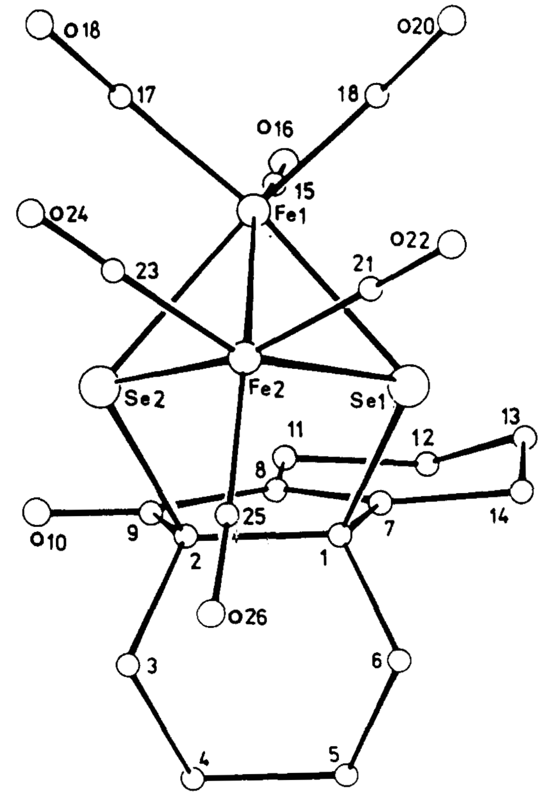


Figure 1. Crystal structure of **6b**, $C_{19}H_{16}Fe_2O_7Se_2$. Various bond lengths and angles are reported in Table IV.

Hübel and co-workers from the reaction of iron carbonyl with diphenylacetylene.[14]

The various reactions of the biscycloalka-1,4-diselena-2,5-cyclohexadienes with iron carbonyl give both expected and unexpected products, and the range of products are dependent upon the size of the alkene ring (Scheme III).

The general results from our studies, illustrated in Scheme III, are as follows.

(a) All the starting selenadiazoles produced the corresponding (cycloalkenediselenato)diiron hexacarbonyl complexes **1** in yields ranging from 20 to 40%, and all, except the biscyclopenta-1,4-diselena-2,5-cyclohexadiene, give moderate yields (10–20%) of the corresponding substituted benzene. This latter product is presumably formed from the metal-promoted trimerization of the cycloalkyne.[15]

(b) For the biscyclopenta-1,4-diselena-2,5-cyclohexadiene no further products can be isolated although trace amounts of metal carbonyl complexes are observed.

(c) For the biscycloocta-2,4-diselena-2,5-cyclohexadiene two ferracycle complexes are obtained, **2** and **3**. While these could be interpreted as being derived from the reaction between free cycloalkyne with iron carbonyl,[14] they are not the products reported from the reaction of cyclooctyne with iron carbonyl.[16]

This feature of the chemistry clearly suggests that the various products obtained do not originate from a "free" cycloalkyne but from some other intermediate species. Evidence for the nature of such a possible intermediate complex was provided from the products obtained from the reactions of the biscyclohexa- and biscyclohepta-1,4-diselena-2,5-cyclohexadiene with iron carbonyl.

In addition to the (diselenato)diiron complexes and the appropriately substituted benzenes, two further complexes **6** and **7** were obtained, neither of which are obtained from the reactions of the five- and eight-membered-ring heterocycles. We have performed an X-ray crystallographic structure determination on **6b**, and the the structure obtained is illustrated in Figure 1. The structure clearly indicates that the starting heterocycle has not been fragmented in the same manner as in the original study by Bird and Hollins. Partial cleavage is apparent, and an unprecedented metallapropellane structure has been formed. Two carbon atoms originally bound to the selenium atoms disengage and become bonded to two carbon atoms of the other cycloalkene ring. During this process either one (complex **6**) or two (complex **7**) carbonyl insertion reactions occur. The two selenium atoms become bonded to two iron atoms as in the various (diselenato)diiron hexacarbonyl complexes also obtained in this study.

For complex **6b**, the molecules of the asymmetric unit are enantiomers, with C(1) and C(2) being centers of symmetry. Bond lengths and angles of the two crystallographically independent molecules agree. The mean selenium–carbon lengths are somewhat shorter for the selenium atoms bonded to the –CO—C═C conjugated system (Se(2)–C(2)) = 1.997 (1) Å, cf. Se(1)–C(1) = 2.015 (2) Å). The mean Se–Fe and Fe–Fe bond distances are 2.361 (2) and 2.542 (3) Å, respectively. A full listing of bond lengths and angles is presented in Table IV.

The conformation of the saturated six-membered ring, C(1), C(2), C(3), C(4), C(5), and C(6), is $B_{3,6}$ and $^{3,6}B$ (boat related by inversion according to Boeyens≈ notation[17]). The puckering amplitudes are nearly identical, $Q = 0.722$ (6) and 0.732 (6) Å.[18] The other six-membered ring possesses a half-chair conformation, $^5H_4$, and the extent of the puckering is less equivalent in the two molecules, $Q = 0.493$ (6) and 0.276 (8) Å.

The intermediacy of the metallapropellanes in the decomposition of the parent heterocycle is suggested powerfully by their unusual structures, containing the (diselenato)diiron hexacarbonyl structural unit. The presence of a free alkene group within the structures provides a coordination site for further reactivity with metal complexes, and the various products obtained in the study can

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Table IV. Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses

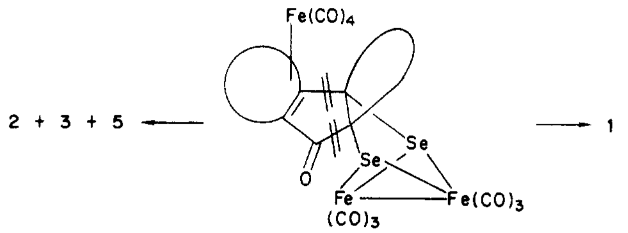
Bond Lengths

Se(1)–Se(2)	3.084 (0)	Fe(2)–C(25)	1.792 (5)	C(6)–H(5A)	0.948 (17)	C(12)–H(12A)	0.958 (19)
Se(1)–Fe(1)	2.358 (1)	C(1)–C(2)	1.533 (5)	C(5)–H(5B)	0.952 (11)	C(12)–H(128)	0.953 (12)
Se(1)–Fe(2)	2.355 (1)	C(1)–C(6)	1.533 (6)	C(6)–H(6A)	0.949 (12)	C(13)–C(14)	1.533 (10)
Se(1)–C(1)	2.019 (4)	C(1)–C(7)	1.493 (6)	C(6)–H(6B)	0.951 (16)	C(13)–H(13A)	0.944 (17)
Se(2)–Fe(1)	2.364 (1)	C(2)–C(3)	1.523 (6)	C(7)–C(8)	1.345 (6)	C(13)–H(13B)	0.956 (17)
Se(2)–Fe(2)	2.367 (1)	C(2)–C(9)	1.528 (6)	C(7)–C(14)	1.491 (6)	C(14)–H(14A)	0.955 (17)
Se(2)–C(2)	1.993 (4)	C(3)–C(4)	1.525 (7)	C(8)–C(9)	1.468 (6)	C(14)–H(14B)	0.952 (15)
Fe(1)–Fe(2)	2.539 (1)	C(3)–H(3A)	0.952 (12)	C(8)–C(11)	1.497 (7)	C(15)–O(16)	1.138 (6)
Fe(1)–C(15)	1.790 (4)	C(3)–H(3B)	0.941 (16)	C(9)–O(10)	1.209 (5)	C(17)–O(18)	1.129 (5)
Fe(1)–C(17)	1.799 (4)	C(4)–C(5)	1.535 (6)	C(11)–C(12)	1.484 (9)	C(19)–O(20)	1.139 (5)
Fe(1)–C(19)	1.788 (4)	C(4)–H(4A)	0.960 (16)	C(11)–H(11A)	0.951 (14)	C(21)–O(22)	1.136 (5)
Fe(2)–C(21)	1.786 (4)	C(4)–H(4B)	0.947 (11)	C(11)–H(11B)	0.947 (16)	C(23)–O(24)	1.138 (5)
Fe(2)–C(23)	1.783 (4)	C(5)–C(6)	1.517 (7)	C(12)–C(13)	1.350 (10)	C(25)–O(26)	1.142 (6)

Bond Angles

Se(2)–Se(1)–Fe(1)	49.3 (0)	C(21)–Fe(2)–C(23)	92.3 (3)	C(1)–C(7)–C(8)	113.3 (6)
Se(2)–Se(1)–Fe(2)	49.4 (0)	C(21)–Fe(2)–C(25)	97.3 (3)	C(1)–C(7)–C(14)	123.9 (6)
Se(2)–Se(1)–C(1)	67.1 (2)	C(23)–Fe(2)–C(25)	98.4 (3)	C(8)–C(7)–C(14)	122.8 (7)
Fe(1)–Se(1)–Fe(2)	65.2 (0)	Se(1)–C(1)–C(2)	112.4 (4)	C(7)–C(8)–C(9)	109.5 (6)
Fe(1)–Se(1)–C(1)	103.2 (2)	Se(1)–C(1)–C(6)	105.9 (4)	C(7)–C(8)–C(11)	125.3 (7)
Fe(2)–Se(1)–C(1)	104.4 (2)	Se(1)–C(1)–C(7)	107.5 (4)	C(9)–C(8)–C(11)	125.2 (7)
Se(1)–Se(2)–Fe(1)	49.1 (0)	C(2)–C(1)–C(6)	112.6 (5)	C(2)–C(9)–C(8)	107.8 (6)
Se(1)–Se(2)–Fe(2)	49.0 (0)	C(2)–C(1)–C(7)	104.4 (5)	C(2)–C(9)–O(10)	124.9 (7)
Se(1)–Se(2)–C(2)	67.5 (2)	C(6)–C(1)–C(7)	114.1 (6)	C(8)–C(9)–O(10)	127.2 (7)
Fe(1)–Se(2)–Fe(2)	64.9 (0)	Se(2)–C(2)–C(1)	113.0 (4)	C(8)–C(11)–C(12)	110.9 (8)
Fe(1)–Se(2)–C(2)	104.3 (2)	Se(2)–C(2)–C(3)	108.7 (4)	C(8)–C(11)–H(11A)	108.7 (17)
Fe(2)–Se(2)–C(2)	103.5 (2)	Se(2)–C(2)–C(9)	105.0 (4)	C(8)–C(11)–H(11B)	109.1 (17)
Se(1)–Fe(1)–Se(2)	81.6 (0)	C(1)–C(2)–C(3)	113.6 (5)	C(12)–C(11)–H(11B)	109.2 (17)
Se(1)–Fe(1)–Fe(2)	57.3 (0)	C(1)–C(2)–C(9)	104.9 (5)	C(12)–C(11)–H(11B)	109.0 (17)
Se(1)–Fe(1)–C(15)	101.9 (2)	C(3)–C(2)–C(9)	111.3 (5)	H(11A)–C(11)–H(11B)	109.8 (23)
Se(1)–Fe(1)–C(17)	157.6 (2)	C(2)–C(3)–C(4)	111.1 (6)	C(11)–C(12)–C(13)	119.2 (11)
Se(1)–Fe(1)–C(19′)	88.8 (2)	C(2)–C(3)–H(3A)	109.0 (16)	C(11)–C(12)–H(12A)	107.2 (18)
Se(2)–Fe(1)–Fe(2)	57.7 (0)	C(2)–C(3)–H(3B)	109.5 (16)	C(11)–C(12)–H(12B)	107.3 (18)
Se(2)–Fe(1)–C(15)	105.3 (2)	C(4)–C(3)–H(3A)	109.5 (16)	C(13)–C(12)–H(12A)	106.9 (19)
Se(2)–Fe(1)–C(17)	89.1 (2)	C(4)–C(3)–H(3B)	108.8 (16)	C(13)–C(12)–H(12B)	106.9 (19)
Se(2)–Fe(1)–C(19′)	155.5 (2)	H(3A)–C(3)–H(3B)	109.0 (22)	H(12A)–C(12)–H(12B)	109.2 (24)
Fe(2)–Fe(1)–C(15)	152.8 (2)	C(3)–C(4)–C(5)	112.9 (7)	C(12)–C(13)–C(14)	121.3 (11)
Fe(2)–Fe(1)–C(17)	100.6 (2)	C(3)–C(4)–H(4A)	108.8 (16)	C(12)–C(13)–H(13A)	106.3 (19)
Fe(2)–Fe(1)–C(19′)	98.2 (2)	C(3)–C(4)–H(4B)	108.9 (16)	C(12)–C(13)–H(13B)	106.6 (19)
C(15)–Fe(1)–C(17)	100.1 (3)	C(5)–C(4)–H(4A)	108.6 (16)	C(14)–C(13)–H(13A)	106.7 (18)
C(15)–Fe(1)–C(19′)	98.7 (3)	C(5)–C(4)–H(4B)	108.4 (16)	C(14)–C(13)–H(13B)	106.5 (18)
C(17)–Fe(1)–C(19′)	91.5 (3)	H(4A)–C(4)–H(4B)	109.1 (22)	H(13A)–C(13)–H(13B)	109.0 (24)
Se(1)–Fe(2)–Se(2)	81.5 (0)	C(4)–C(5)–C(6)	113.3 (7)	C(7)–C(14)–C(13)	109.6 (8)
Se(1)–Fe(2)–Fe(1)	57.5 (0)	C(4)–C(5)–H(5A)	108.3 (16)	C(7)–C(14)–H(14A)	109.1 (16)
Se(1)–Fe(2)–C(21)	88.5 (2)	C(4)–C(5)–H(5B)	108.7 (16)	C(7)–C(14)–H(14B)	109.3 (17)
Se(1)–Fe(2)–C(23)	154.2 (2)	C(6)–C(5)–H(5A)	108.3 (16)	C(13)–C(14)–H(14A)	109.6 (17)
Se(1)–Fe(2)–C(25)	107.2 (2)	C(6)–C(5)–H(5B)	108.4 (16)	C(13)–C(14)–H(14B)	109.3 (17)
Se(2)–Fe(2)–Fe(1)	57.4 (0)	H(5A)–C(5)–H(5B)	109.8 (22)	H(14A)–C(14)–H(14B)	110.0 (22)
Se(2)–Fe(2)–C(21)	160.6 (2)	C(1)–C(6)–C(5)	110.6 (6)	Fe(1)–C(15)–O(16)	178.1 (7)
Se(2)–Fe(2)–C(23)	89.7 (2)	C(1)–C(6)–H(6A)	109.0 (16)	Fe(1)–C(17)–O(18)	179.7 (7)
Se(2)–Fe(2)–C(25)	101.5 (2)	C(1)–C(6)–H(6B)	109.6 (16)	Fe(1)–C(19)–O(20)	178.8 (7)
Fe(1)–Fe(2)–C(21)	103.1 (2)	C(5)–C(6)–H(6A)	109.5 (16)	Fe(2)–C(21)–O(22)	178.7 (7)
Fe(1)–Fe(2)–C(23)	97.4 (2)	C(5)–C(6)–H(6B)	109.0 (16)	Fe(2)–C(23)–O(24)	179.1 (7)
Fe(1)–Fe(2)–C(25)	153.6 (2)	H(6A)–C(6)–H(6B)	109.2 (22)	Fe(2)–C(25)–O(26)	176.8 (7)

Scheme IV



be considered to form via such a reaction path (Scheme IV).

We have studied the reactions of the intermediate metallapropellanes with iron carbonyl. From such reactions the appropriate (diselenato)diiron complexes are obtained in moderate yield after relatively long reaction periods. We have been unable to observe or isolate the various ferroles related to **2d** and **3d** isolated from the reaction of biscycloocta-1,4-diselena-2,5-cyclohexadiene with iron carbonyl. This is not suprising since we have not observed them in the initial reactions of the *n* = 6 and 7 heterocycles. Clearly the ring size plays a large role in determining the stability of the metallapropellane, presumably by affecting the activation energy for the expulsion of the cycloalkyne/metal fragment.

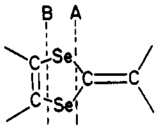
For the *n* = 8 system the activation energy is relatively low since the product cyclooctyne is a thermodynamically stable species. In the case of the *n* = 6 and 7 complexes this is no longer true; thus the activation parameters for alkyne expulsion are increased, permitting isolation of the new metallapropellanes.

The infrared and NMR data (Table I) of the various complexes are in total accord with their respective structures. The infrared stretching frequencies of the (diselenato)diiron hexacarbonyls are very similar to those reported for the previously known sulfur analogues.[6] In general the ^1H NMR data is not particularly informative. All the cycloalka complexes exhibit multiplets between δ

2.6 and 2.2 for the methylene protons adjacent to the sp^2 C atoms and between δ 1.5 and 1.8 for the remaining methylene protons.

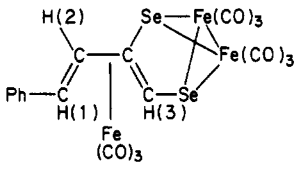
Diselenafulvenes. The reactions of the various diselenafulvenes lead to a related asymmetric cleavage of the organoselenium compound to form (diselenato)diiron complexes of the same general type as obtained with the diselenacyclohexadienes 1. In each case small amounts of $Se_2Fe_2(CO)_9$ (8) are also obtained. The spectral and analytical properties of the new (diselenato)diiron complexes are recorded in Tables I and II.

It is of interest that cleavage of the Se–C bonds occurs only in the direction A outlined below, and no evidence was obtained for cleavage as in mode B. It is conceivable that cleavage occurs via route B followed by a rapid isomerization involving Se–C and C–C migrations. The absence of any acetylenic derived products as noted for the diselenacyclohexadiene effectively rules out this rather improbable process.



Given the yields of the diselenato complexes it is also surprising, and disappointing, that we observe no iron complexes derived from the vinylcarbene fragment, nor its isomers and oligomers. The fate of this portion of the molecules is therefore unknown at this time.

The reaction of $Fe_2(CO)_9$ with the 2,ω-distyryldiselenafulvene leads to both of the above-mentioned complexes and also a third complex, 9. In this complex the conjugated diene system is able to form a bonding interaction with another $Fe(CO)_3$ fragment. The ^1H NMR data for this complex and for the styryl(diselenato)diiron hexacarbonyl are useful for structure corroboration. For the hexacarbonyl complex, the olefinic protons 1, 2, and 3 have resonances at δ 7.26, 6.71, and 6.44, respectively, with J_{12} of 9.6 Hz. Proton 3 is a singlet. Upon coordination of the third $Fe(CO)_3$ unit the expected shifts are observed due to the complexation of the diene unit, resulting in the resonances for protons 1, 2, and 3 being at δ 6.16, 2.10, and 5.52, respectively (J_{12} = 9.6 Hz).



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Registry No. **1a**, 97353-00-9; **1b**, 97353-01-0; **1c**, 97374-09-9; **1d**, 97353-02-1; **1e**, 97353-03-2; **1f**, 97353-04-3; **1g**, 97374-10-2; **1h**, 97353-05-4; **2d**, 97374-11-3; **3d**, 97390-81-3; **5b**, 1610-39-5; **5c**, 737-48-4; **5d**, 7099-19-6; **6b**, 97353-06-5; **6c**, 97353-07-6; **7c**, 97353-08-7; **9**, 97374-12-4; $Fe_2(CO)_9$, 15321-51-4; biscyclopenta-1,4-diselena-2,5-cyclohexadiene, 35676-33-6; biscyclohexa-1,4-diselena-2,5-cyclohexadiene, 35831-82-4; biscyclohepta-1,4-diselena-2,5-cyclohexadiene, 35831-83-5; biscycloocta-1,4-diselena-2,5-cyclohexadiene, 34631-75-9; 2,ω-dimethyl-1,4-diselenafulvene, 69773-65-5; 2,ω-di-*tert*-butyl-1,4-diselenafulvene, 97353-09-8; 2,ω-diphenyl-1,4-diselenafulvene, 15995-14-9; 2,ω-distyryl-1,4-diselenafulvene, 73214-45-6.

Supplementary Material Available: Tables of observed and calculated structure factors, atomic coordinates temperature factor expressions, and bond lengths and angles for the metallapropellane structure (51 pages). Ordering information is given on any current masthead.

Solvent Effects in the Luminescence Spectra of Terbium(III) Methylcyclopentadienyl Compounds

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The photoluminescence of monomeric and dimeric Tb(III) methylcyclopentadienyl (MeCp) derivatives has been obtained at cryogenic temperatures under conditions of high resolution. The spectra obtained for monomeric $Tb(MeCp)_3(THF)$, $Tb(MeCp)_2(Cl)(THF)$, and $Tb(MeCp)_2(CH_3)(THF)$ compounds were all found to be extremely similar, as were the Tb(III) luminescence lifetimes. The spectra of the analogous dimeric compounds $[Tb(MeCp)_2Cl]_2$ and $[Tb(MeCp)_2CH_3]_2$ were noted to differ significantly from those of the corresponding monomers, and the lifetime trends also were quite different. Since the monomer/dimer structure is largely an effect caused by solvent coordination, the Tb(III) luminescence is therefore a useful property for studies of complex solvation.

Introduction

Modern organolanthanide chemistry relies almost entirely upon X-ray crystallography for studies of solid-state chemistry and upon nuclear magnetic resonance for the examination of compounds in the solution phase. Far less work has concentrated on the use of optical spectroscopic techniques for the study of solution phase structures. Recently, luminescence within f–f transitions has been used to study cyclopentadienyl derivatives of Tb(III)[1] and Yb(III).[2,3]

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(1) Brittain, H. G.; Meadows, J. H.; Evans, W. J. *Organometallics* 1983, *2*, 1661.

(2) Schlesener, C. J.; Ellis, A. B. *Organometallics* 1983, *2*, 529.

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