trans-ClIr(CO)(PPh_3)$_2$, 15318-31-7; PhC(O)OMe, 93-58-3; $PhCH_2C(O)IrCl_2(CO)(PPh_3)_2$, 33395-39-0; $PhCH_2C(O)OMe$, 101-41-7; *trans*-*n*-PrOIr(CO)(PPh_3)$_2$, 94070-39-0; *trans*-*i*-PrOIr(CO)(PPh_3)$_2$, 99688-37-6; *trans*-*t*-BuOIr(CO)(PPh_3)$_2$, 98720-65-1; CH_3CHO, 75-07-0; $CH_3CH_2OC(O)Me$, 141-78-6; MeOIr(Me)(I)(CO)(PPh_3)$_2$, 107799-54-2; *trans*-IIr(CO)(PPh_3)$_2$, 19472-16-3; $MeOC(O)Ir(Me)(I)(PPh_3)_2$, 118515-37-0; $MeOC(O)Ir(Me)(I)(CO)(PPh_3)_2$, 118626-13-4; acetyl chloride, 75-36-5; methyl acetate, 79-20-9; benzoyl chloride, 7631-42-7; phenylacetyl chloride, 103-80-0; paraformaldehyde, 30525-89-4; methyl formate, 107-31-3; *n*-propyl formate, 110-74-7; *tert*-butyl formate, 762-75-4; *i*-propyl formate, 625-55-8; methanol, 67-56-1.

Reactions of $(\eta^5\text{-}C_5R_5)Co(C_2H_4)_2$ (R = H, Me) with Selected 1,2,3-Selenadiazoles

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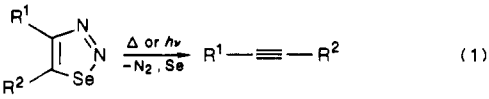
The reactions of $(\eta^5\text{-}C_5R_5)Co(C_2H_4)_2$ (R = H, Me) with cycloocta-1,2,3-selenadiazole and more saturated analogues have been studied. Products of three types have been isolated and characterized. The reactions of $(\eta^5\text{-}C_5H_5)Co(C_2H_4)_2$ yield binuclear complexes $[(\eta^5\text{-}C_5H_5)Co]_2$ $(\mu_2\text{-}\eta^3,\eta^2\text{-}C_8H_xSe)$ (x = 6, 10, 12) which are fluxional in solution. The reactions of $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ yield mononuclear complexes. Those derived from the less saturated 1,2,3-selenadiazoles are of the form $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-}C_8H_x(Se)CHCH_3)$ (x = 6, 8), in which a molecule of ethene has been incorporated into the organoselenium ligand. Those derived from the more saturated 1,2,3-selenadiazoles, $(\eta^5\text{-}C_5Me_5)Co(\eta^2\text{-}C_8H_xSe)(\eta^1\text{-}C_8H_xSeN_2)$ (x = 10, 12), contain an intact 1,2,3-selenadiazole ligand. ^1H and ^{13}C NMR spectroscopy in particular have been used to probe the structures of these compounds.

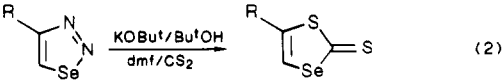
Introduction

Interest in 1,2,3-selenadiazoles over the last 20 years has centered on their utility in organic synthesis.[1] The chemistry of 1,2,3-selenadiazoles is dominated by the facility with which dinitrogen is eliminated: the fate of the residual organoselenium fragment determines the outcome of the reaction. When selenium is readily lost from this fragment, 1,2,3-selenadiazoles serve as intermediates in the preparation of alkynes (eq 1). A number of strained



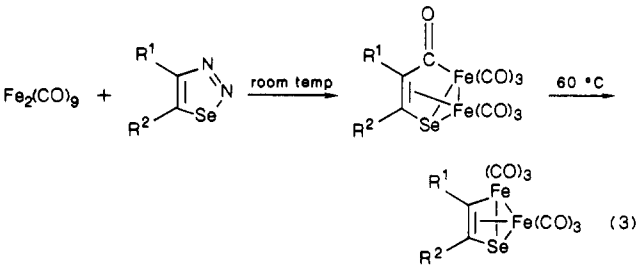
(1)

cycloalkynes, inaccessible by other routes, have been prepared in this way.[2-4] When selenium is retained, a variety of products may be formed (see Scheme I[5]). In the presence of external reagents the selenium-containing intermediates can be trapped to yield addition products (e.g. eq 2[6]).



(2)

We are interested in the ability of 1,2,3-selenadiazoles to function as ligands or ligand precursors in transition-metal complexes. Comparatively little work has been done in this area. A number of research groups have studied the reaction of nonacarbonyldiiron with 1,2,3-selenadiazoles (eq 3).[7] Interestingly, a different type of product was isolated from analogous reactions with 1,2,3-thiadiazoles (eq 4).[8] The preparation of 1,2,3-thiadiazole and



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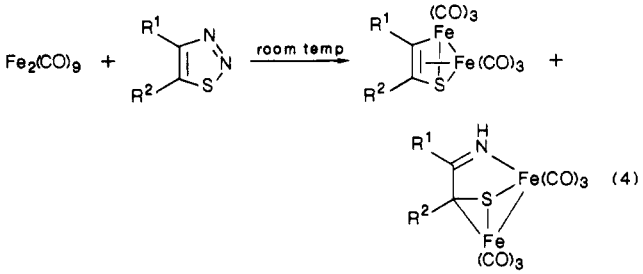

(4)

1,2,3-selenadiazole pentacarbonyl complexes of the ele-

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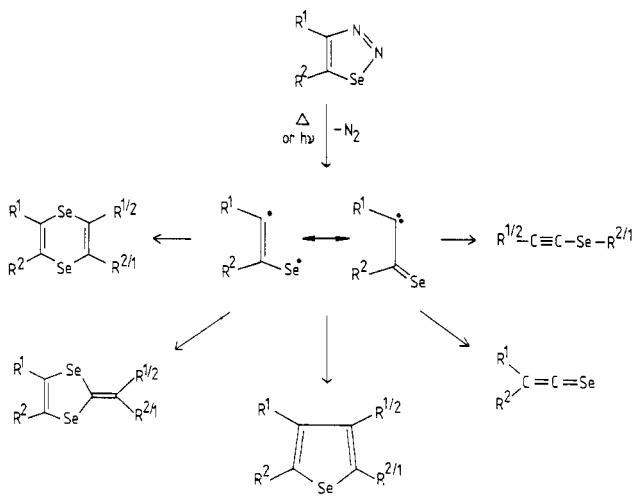
Table I. Microanalyses, Mass Spectra, and Melting Points

compd	color	mp, °C	mol wt (calcd)	microanalysis[a] C	H	Se	Co	mass spectra[b]
7	green-black	>300	429.15	50.26 (50.38)	3.74 (3.76)	18.31 (18.40)	27.36 (27.46)	430 (28%) M^+; 189 (100%) $(C_5H_5)_2Co^+$
9	green-black	109–111	433.18	49.82 (49.91)	4.93 (4.65)	18.20 (18.23)	27.01 (27.21)	434 (27%) M^+; 189 (100%) $(C_5H_5)_2Co^+$
10	green-black	113–114.5	435.20	49.84 (49.68)	5.14 (5.10)	17.93 (18.14)	26.98 (27.08)	436 (11%) M^+; 189 (100%) $(C_5H_5)_2Co^+$
11	dark red	160–162	403.31	58.69 (59.56)	5.86 (6.25)	20.36 (19.58)	15.04 (14.61)	404 (19%) M^+; 323 (100%) M – Se, H^+; 274 (15%) $C_5Me_5CoSe^+$
12	dark red	139–141	405.33	58.55 (59.27)	6.14 (6.71)	20.19 (19.48)	14.93 (14.54)	406 (42%) M^+; 274 (46%) $C_5Me_5CoSe^+$; 133 (100%) $C_{10}H_{13}^+$
13	dark green	195–197	592.43	53.10 (52.71)	6.21 (5.95)	26.49 (26.66)	9.58 (9.95)	594 (15%) M^+; 274 (17%) $C_5Me_5CoSe^+$; 119 (100%) $C_9H_{11}^+$
14	dark red	173–174	596.46	53.03 (52.36)	6.93 (6.59)	26.38 (26.48)	9.46 (9.88)	598 (38%) M^+; 274 (100%) $C_5Me_5CoSe^+$

[a] Calculated figures in parentheses. [b] Data presented as: m/e (relative abundance) assignment. m/e values are for isotopomers containing ^{80}Se; expected isotope distribution patterns are observed.

Scheme I



ments chromium, molybdenum, and tungsten has also been reported (eq 5).[9] In this paper we report the results of

$$M(CO)_5(thf) + \text{heterocycle} \xrightarrow{\text{room temp}} \text{heterocycle}\text{—}M(CO)_5 \qquad (5)$$

M = Cr, Mo, W; E = S, Se

investigations into the reactions of some 1,2,3-selenadiazoles with bis(ethene)(η^5-cyclopentadienyl)cobalt, $(\eta^5\text{-}C_5H_5)Co(C_2H_4)_2$ (**1**), and bis(ethene)(η^5-pentamethylcyclopentadienyl)cobalt, $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ (**2**). A preliminary report of part of this work has been published.[10]

Experimental Section

All operations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were predried by using $NaAlEt_4$ and then distilled from sodium/potassium alloy. $(\eta\text{-}C_5H_5)Co(C_2H_4)_2$ (**1**),[11] $(\eta\text{-}C_5Me_5)Co(C_2H_4)_2$ (**2**),[12] cycloocta-1,2,3-selenadiazole (**3**),[10] 8,9-dihydrocycloocta-1,2,3-selenadiazole (**4**),[3] 6,7,8,9-tetrahydrocycloocta-1,2,3-selenadiazole (**5**),[4] and 4,5,6,7,8,9-hexahydrocycloocta-1,2,3-selenadiazole (**6**)[13] were prepared according to literature methods.

^1H NMR spectra were recorded on a Bruker WH 400 or AM 200 instrument; ^{13}C NMR spectra were recorded on a Bruker WM 300 instrument. Infrared spectra were recorded of KBr disks prepared under an argon atmosphere by using a Nicolet 7199 infrared spectrophotometer. Mass spectra were measured with a Varian CH-5 spectrometer. Microanalysis was performed by Mssrs. Dornis and Kolbe, Mülheim-Ruhr, FRG. Melting points were measured on a Buchi SMP-20 apparatus using glass capillaries sealed under argon and are not corrected.

Alumina (Super 1 Grade) was treated with 1% water before use.

A general description of the synthetic methods employed is given below. Structural formula for the products **7–14** are shown in Charts II and III.

1. Reactions of $(\eta^5\text{-}C_5H_5)Co(C_2H_4)_2$ (1). Diethyl ether solutions (total volume 50 mL) of **1** (8 mmol) and 1,2,3-selenadiazole **3**, **4**, **5**, or **6** (4 mmol) were mixed at −30 °C, allowed slowly to warm to room temperature, and stirred overnight. The solvent was removed by distillation under reduced pressure to leave a dark brown residue. This was subjected to chromatography on an alumina column. A single dark green-black band was eluted with a 9:1 mixture of pentane and diethyl ether. The product obtained after removal of the solvent under reduced pressure was purified by low-temperature recrystallation from diethyl ether or pentane.

	7	**8**	**9**	**10**
yield (%, based on 1)	7	0	11	12

Analytical and spectroscopic data for compounds **7**, **9**, and **10** are summarized in Tables I–III. They are apparently air-stable over long periods both in the solid state and in solution and soluble in all common organic solvents.

2. Reactions of $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ (2). Toluene solutions (total volume 30 mL) of **2** (2 mmol) and 1,2,3-selenadiazole **3**, **4**, **5**, or **6** (2 mmol) were mixed at 0 °C, allowed slowly to warm to room temperature, and stirred overnight. The solvent was removed by distillation under reduced pressure.

The preparation of each of the compounds **11–14** was continued as follows.

(i) 11, 12, and 14. The red-black residue was chromatographed on an alumina column. After two small fractions, the largest band, which was dark red in color, was eluted with a 9:1 mixture of pentane and diethyl ether. The product obtained after removal of the solvent under reduced pressure was recrystallized from pentane at −78 °C.

(ii) 13. The dark green residue was chromatographed on an alumina column. After a number of small fractions, the largest band, which was dark green in color, was eluted with a 3:1 mixture

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Table II. ^{1}H NMR Spectra[a]

compd	solvent	chemical shift,[b] δ
7	C_4D_8O	4.85 (5, 10, $H^{7,8}$), 5.17 (d, 1, H^6), 5.35 (m, 1, H^4), 5.43 (m, 1, H^2), 5.50 (m, 1, H^5), 5.61 (m, 1, H^3), 6.89 (d, 1, H^1)
9	C_4D_8O	1.50 (m, 4, $H^{4,5}$), 2.06 (m, 2, H^6), 2.18 (m, 2, H^3), 4.81 (s, 10, $H^{7,8}$), 5.32 (m, 1, H^2), 6.72 (d, 1, H^1)
10	C_4D_8O	1.12–2.69 (m, 12, H^{1-6}), 4.82 (s, 10, $H^{7,8}$)
11	$C_6D_5CD_3$	1.14 (d, 3, H^8), 1.55 (s, 15, H^9), 2.30 (q, 1, H^7), 5.90 (m, 5, H^{2-6}), 6.63 (d, 1, H^1)
12	C_6D_6	1.23 (d, 3, H^8), 1.54 (s, 15, H^9), 1.95 (m, 2, $H^{3a,4a}$), 2.36 (q, 1, H^7), 2.64 (m, 2, $H^{3b,4b}$), 5.82 (m, 3, 2, $H^{5,6}$), 6.65 (d, 1, H^1)
13	C_6D_6	1.04–2.38 (m, 12, $H^{3-5,9-11}$), 1.28 (s, 15, H^{13}), 2.64 (m, 1, H^{12a}), 2.82 (m, 1, H^{6a}), 3.01 (m, 1, H^{12b}), 3.02 (m, 1, H^{6b}), 5.71 (m, 1, H^8), 5.86 (m, 1, H^2), 6.69 (d, 1, H^7), 7.02 (d, 1, H^1)
14[c]	C_6D_6	H^{1-12}: 0.83–1.72 (m, 12), 1.75 (m, 1), 1.86 (m, 1), 1.94 (m, 1), 2.04 (m, 1), 2.62 (m, 1), 2.82 (m, 1), 2.93 (m, 2), 3.04 (m, 2), 3.29 (m, 1), 3.38 (m, 1) H^{13}: 1.29 (s, 15)

[a] Recorded at room temperature. [b] In parentheses: multiplicity, integral, assignment. Abbreviations: s, singlet; d, doublet; q, quartet; m, multiplet. For assignment numbering, see Schemes III and IV. [c] Data presented as assignment: chemical shift (multiplicity, integral).

Table III. IR Spectral Data

compd	selected absorption maxima,[a] cm^{-1}
7	2990 (m), 2980 (m), 1632 (m, br), 1576 (m), 1449 (m), 1403 (m), 1105 (s), 813 (vs), 795 (s), 670 (vs)
9	3000 (m), 2915 (s), 2845 (m), 1440 (m), 1431 (m), 1412 (s), 1102 (s), 989 (s), 830 (s), 808 (vs), 800 (vs), 713 (s)
10	2920 (s), 2840 (m), 1451 (m), 1435 (m), 1417 (m), 1406 (m), 1103 (s), 989 (s), 816 (s), 794 (vs), 786 (s)
11	2990 (m), 2955 (m), 2900 (s), 2860 (m), 1603 (m), 1494 (m), 1453 (m, br), 1432 (m), 1373 (vs), 1022 (s), 820 (s), 669 (vs)
12	3015 (m), 2985 (m), 2970 (m), 2955 (m), 2925 (s), 2905 (s), 2885 (s), 1495 (m), 1451 (s), 1424 (m), 1375 (s), 1026 (s), 813 (s), 736 (s), 722 (s), 600 (s)
13	3015 (w), 2915 (s), 2845 (m), 1633 (w), 1535 (s), 1435 (s), 1371 (s), 1020 (s)
14	2920 (vs), 2845 (s), 1546 (m), 1465 (s), 1438 (s), 1358 (s), 1017 (s)

[a] Abbreviations in parentheses: m, medium; s, strong; vs, very strong; br, broad.

of toluene and pentane. The product obtained after removal of the solvent under reduced pressure was recrystallized from pentane at −78 °C.

	11	12	13	14
yield (%, based on 2)	50	17	8	17

Analytical and spectroscopic data for compounds 11–14 are summarized in Tables I–III. They are stable to air for short periods in the solid state but are rapidly decomposed when in solution. Compounds 11–14 are soluble in all common organic solvents.

Results and Discussion

$(\eta^5\text{-}C_5H_5)Co(C_2H_4)_2$ (1) and $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$ (2) have been shown to be convenient sources of the fragments

Chart I

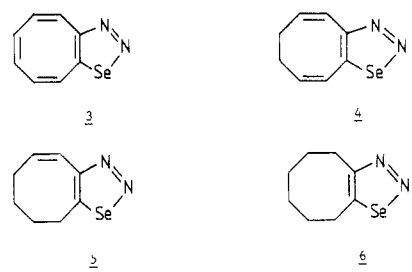
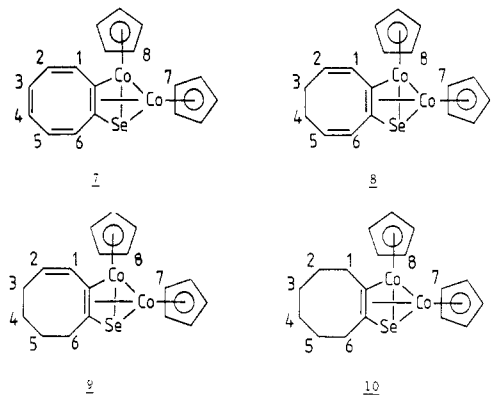


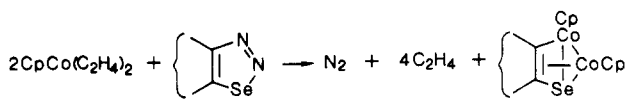
Chart II



$(\eta^5\text{-}C_5H_5)Co$ and $(\eta^5\text{-}C_5Me_5)Co$, respectively.[11,14] These 14-electron d^8 fragments are isolobal with $Fe(CO)_3$ and might therefore be expected to display similar behavior toward 1,2,3-selenadiazoles. The 1,2,3-selenadiazoles employed in this study are shown in Chart I.

Treatment of 1 with cycloocta-1,2,3-selenadiazole (3) in diethyl ether solution, at or slightly below room temperature, resulted in gas evolution, gradual darkening of the mixture, and precipitation of a black solid. Subsequent column chromatography led to isolation of the product 7 in low yield. The structure of 7 has been determined by standard spectroscopic means and confirmed by a single-crystal X-ray diffraction study.[10]

Reaction of 1 with the more saturated 1,2,3-selenadiazoles 5 and 6 yielded analogous products (9 and 10, respectively). However, although the reaction of 1 with 8,9-dihydrocycloocta-1,2,3-selenadiazole (4) appeared visually to take a similar course, only a trace of the expected product 8 was obtained. The reasons for this differing behavior are not clear. Structural formulas for the products 7–10 are shown in Chart II. The formation of 7–10 may be represented by eq 6 (Cp = η^5-C_5H_5). This equation



(6)

is obviously not a complete representation of the reactions, since the yields of 7–10 are low. Competing pathways lead to the major product of the reactions, which is a black intractable material; mass spectroscopy shows this to be a complex mixture of organocobalt/organoselenium derivatives. Altering the stoichiometry of the reactions has little effect on the yield of the desired product.

The molecular structure of 7 may be taken as typical for the series of compounds 7–10. As shown in Figure 1 it consists of a Co_2SeC_2 core in which the approximately coplanar atoms C1, C2, Se, and Co_2 are all bonded to Co_1. The structure is thus, as expected, similar to that of $[Fe(CO)_3]_2(\mu_2\text{-}\eta^2,\eta^3\text{-}C_8H_{12}Se)$.[15]

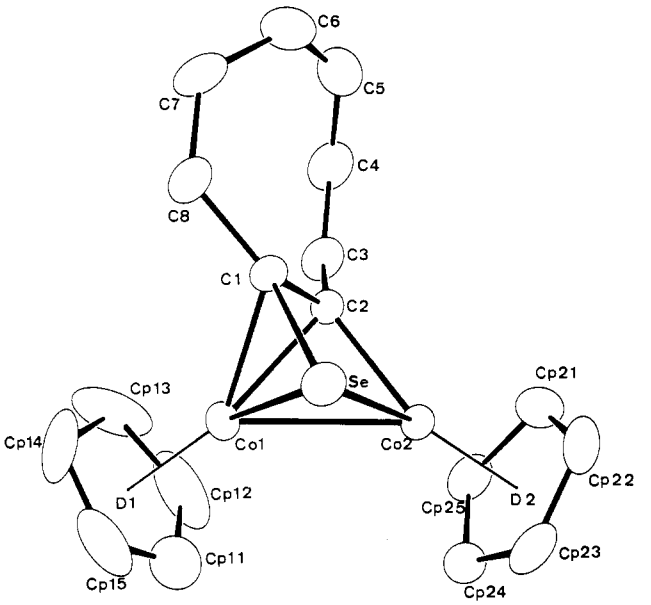
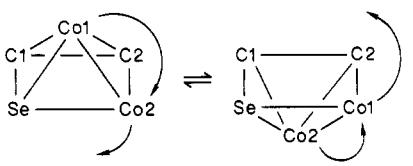


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)Co]_2(\mu_2\text{-}\eta^3,\eta^2\text{-}C_8H_6Se)$.

The two cobalt atoms are in chemically distinct environments, so that on the basis of the solid-state structure one would predict the observation of two resonances for the cyclopentadienyl hydrogens in the ^1H NMR spectra of compounds **7–10**. At room temperature, however, only one broad resonance is observed in each case (see Table II). On cooling to −30 °C the expected two signals are obtained: for example, for **7** the room-temperature resonance at δ 4.81 splits into one at δ 4.63 and one at δ 5.18. The same effect is observed in the ^{13}C NMR spectra: for example, in THF-d_8 solutions of **7** at 40 °C the cyclopentadienyl carbons give rise to a single broad resonance at δ 79.1; on cooling to −30 °C this splits into two, yielding one signal at δ 81.5 and one at δ 76.8. In all other respects the spectra remain unaffected by the change in temperature. The coalescence temperatures are approximately the same for the three compounds studied (**7**, **9**, and **10**). These data indicate that compounds **7–10** are fluxional and that the fluxional process equivalences the cyclopentadienyl groups without affecting the rest of the molecule. This process is most likely a rocking of the Co_2 unit as depicted below, such that first Co_1 is bonded and then Co_2 is bonded to C_1.



Replacing cyclopentadienyl (C_5H_5) by pentamethylcyclopentadienyl (C_5Me_5) is often much more than just a cosmetic change and has significant steric and electronic consequences.[16] In keeping with this there are major differences in the behavior of **1** and **2** toward 1,2,3-selenadiazoles.

2 was treated in toluene solution, at or slightly below room temperature, with one of the 1,2,3-selenadiazoles (**3–6**). In each case a gas was evolved and the mixture gradually darkened. Subsequent column chromatography revealed the presence of a number of products of which

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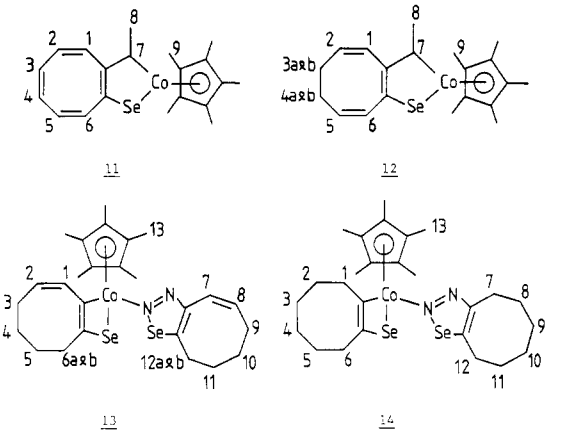
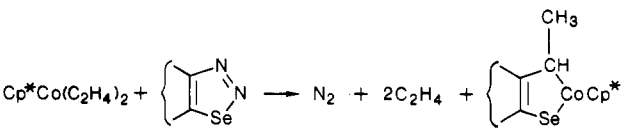
Chart III



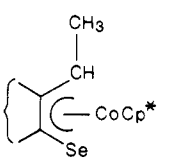
one was generally predominant. This was isolated, purified, and characterized by standard spectroscopic means. Structural formulas for the products **11–14** are shown in Chart III.

Two types of product are evident. Reaction of the less saturated 1,2,3-selenadiazoles (**3** and **4**) may be represented by eq 7 (Cp* = η-C_5Me_5).



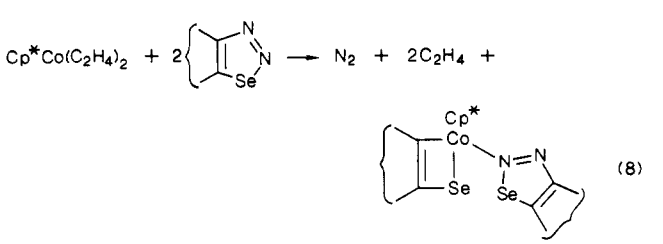
(7)

The presence of the ethylidene unit in compounds **11** and **12** was inferred from the ^1H NMR spectra (see Table II) and confirmed by examination of the ^{13}C NMR spectra: for example, in the ^{13}C NMR spectrum of **11**, a doublet at δ 60.7 and a quartet at δ 13.4 are readily assigned to the carbon atoms of the two-carbon unit. The position of the doublet resonance and its large C–H coupling constant ($^2J_{CH}$ = 162 Hz) imply considerable sp^2 character for this carbon atom. The carbon atoms of the adjacent double bond have ^{13}C resonances at δ 97.0 and 102.1, and it is reasonable to suppose that they are also bonded to the otherwise 16-electron cobalt atom. The bonding in these complexes is thus best described in terms of a (η^5-C_5Me_5)Co unit bonded to a delocalized four-electron donor ligand as shown below.



This situation resembles that in analogous 1,2-dithiolene complexes.

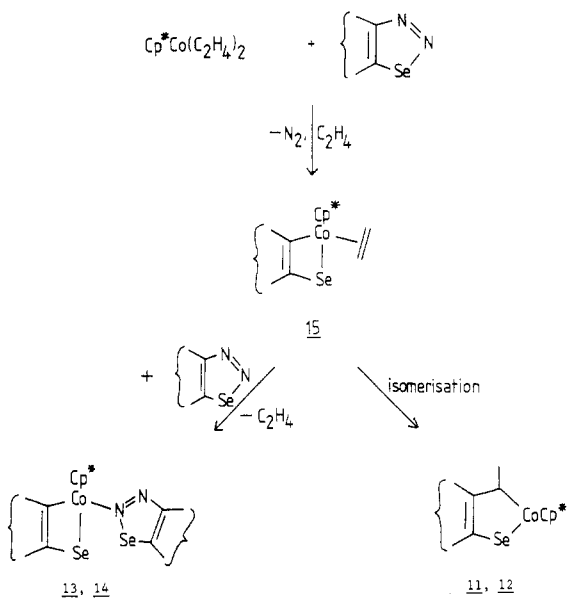
Reaction of the more saturated 1,2,3-selenadiazoles (**5** and **6**) with **2** may be represented by eq 8. ^1H NMR



(8)

spectroscopy is of little value in terms of structural characterization for these compounds since the spectra are in

Scheme II



general too complex to be interpreted (see Table II). ^{13}C NMR spectroscopy is more useful. For example, in the ^{13}C NMR spectrum of **14** the expected eighteen resonances are observed. Particularly informative are the peaks corresponding to the quaternary carbons in the eight-membered rings. In **14** these are found at δ 122.1, 159.2, 159.5, and 160.5; in **10** they are at δ 117.8 and 150.3 and in **6** are at δ 159.2 and 161.0. Peaks characteristic of both the $C_8H_{12}Se$ ligand and the $C_8H_{12}SeN_2$ molecule are therefore present in the ^{13}C NMR spectrum of **14**. The presence of an intact 1,2,3-selenadiazole ligand in these compounds was confirmed by infrared spectroscopy (see Table III)—there is a medium-to-strong band at ca. 1540 cm^{-1} which may be assigned to a N=N stretching mode (this band occurs at ca. 1515 cm^{-1} in free 1,2,3-selenadiazoles).

The two types of product resulting from reaction of 1,2,3-selenadiazoles with **2** may both be derived from the same hypothetical intermediate **15** (see Scheme II). Displacement of ethene by an intact 1,2,3-selenadiazole molecule leads to products like **13** and **14**; isomerization via a succession of olefin insertion and β-elimination steps leads to products like **11** and **12**. Which pathway is preferred appears to depend on the degree of unsaturation in the bicyclic 1,2,3-selenadiazole. That the preference is never strong is evidenced by the moderate yields obtained of any one particular product, and other reaction pathways probably also compete. No binuclear products analogous to **7–10** are formed presumably because of the steric effect of the pentamethylcyclopentadienyl ligand.

It is clear that a range of interesting and unusual complexes may be formed from 1,2,3-selenadiazoles. Work is now in progress to examine the reactivity of these novel compounds.

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Protodestannylation of Carbomethoxy-Substituted Vinylstannanes: Kinetics, Stereochemistry, and Mechanisms

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Five carbomethoxy- and four carboethoxy-substituted vinylstannanes have been prepared. Methyl 2-(trimethylstannyl)acrylate and ethyl 2-(trimethylstannyl)acrylate were prepared by hydrostannation of methyl and ethyl propiolate under polar conditions. The former compound was also prepared by Pd(0) catalyzed hydrostannation of methyl propiolate. The *E* and *Z* isomers of methyl and ethyl 3-(trimethylstannyl)acrylate were prepared by free radical hydrostannation of methyl and ethyl propiolate. Methyl and ethyl 2-(trimethylstannyl)fumarate were synthesized by hydrostannation of dimethyl and diethyl acetylenedicarboxylate under polar conditions. Methyl 2-(trimethylstannyl)maleate was prepared by Pd(0)-catalyzed hydrostannation of dimethyl acetylenedicarboxylate. Structures were confirmed by ^1H and ^{13}C NMR. The stereochemistry of stannyl cleavage was determined by deuteriodestannylation and ^1H NMR of the products. The methyl 3-(trimethylstannyl)acrylate isomers gave retention of configuration while the methyl 2-(trimethylstannyl)fumarate and -maleate resulted in approximately equal ratios of isomeric deuteriodestannylation products. In this latter case an allenol intermediate is proposed. Second-order rate constants for protodestannylation, in methanol–5% water, were determined at three temperatures for the carbomethoxy compounds. Activation parameters were calculated from the rate data. The carbomethoxy group was found to be deactivating for all compounds except methyl 2-(trimethylstannyl)maleate. In this case, interaction of the syn carbomethoxy groups may serve to provide a more reactive route to the allenol intermediate.

Introduction

In recent years there has been considerable interest in the synthesis and reactions of vinylstannanes. Methods have been developed which provide both regioselectivity and stereoselectivity in the preparation of vinylstannanes through additions to an alkyne. Early work by Neumann[1] and Leusink[2] showed that hydrostannation can take place either by a free radical mechanism or, in the presence of appropriate electron-withdrawing substituents, by a polar mechanism. The mechanism of addition can determine the regiospecificity, but the initial addition of tin and

(1) Neumann, W. P.; Sommer, R. *Leibigs Ann. Chem.* **1964**, *675*, 10.

(2) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295.

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