

Journal of Organometallic Chemistry, 405 (1991) 309–322
Elsevier Sequoia S.A., Lausanne
JOM 21344

Transition metal heterocyclic chemistry

XI *. Manganese cyclopentadienyldicarbonyl complexes of 1,2,3-selena- and thiadiazoles including structural comparison of free and complexed 1,2,3-benzothiadiazole and 4-phenyl-1,2,3-thiadiazole

Armin J. Mayr, Benjamin Carrasco-Flores, Francisco Cervantes-Lee,
Keith H. Pannell

Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968-0513 (USA)

László Párkányi

Central Research Institute Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest (Hungary)

and Krishan Raghuveer

Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403 (USA)

(Received May 30th, 1990; in revised form August 27th, 1990)

Abstract

Reactions of substituted 1,2,3-selena- and thia-diazoles with $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2\text{THF}$, R = H, Me, lead to isolable blue complexes in which THF is replaced by the diazole ligand. The X-ray structure of the benzothiadiazole complex is reported and shows the intact diazole bonded via N2 to manganese. *Ab initio* calculations on 1,2,3-thiadiazole generated a structure and protonation energies that confirm N2 as the site of coordination, and also predict significant structural variations upon coordination. However, the structure of the free benzo-1,2,3-thiadiazole was determined and shows no significant structural change upon coordination. Similarly, the structure of 4-phenyl-1,2,3-thiadiazole was determined and exhibits the same structural parameters as the $\text{W}(\text{CO})_5$ substituted ligand.

Introduction

1,2,3-Selena- and thia-diazoles have been shown to decompose thermally, and or photochemically, via α -selenoketo(thioketo)carbenes to yield acetylenic compounds [1,2]. Under mild conditions, in the presence of transition metal complexes, the diazoles react to form a series of complexes that involve coordination of decomposi-

* For part X see ref. 15.

tion fragments, including selenoketocarbenes and acetylenes, Scheme 1 [3–8]. A variety of other complexes are also obtained including those derived from α -selenoketoketenes and α -seleno(thio)ketoimines, and in general the nature of the isolated complex depends upon the starting transition metal complex and the substituents upon the diazole ligand [9–14].

It has been proposed that the initial interaction of the intact diazole with the various transition metal complexes is a σ -donation of one of the lone pairs of the heteroatoms. Complexes of this type have been isolated, and characterized spectroscopically and structurally for the system $M(\text{CO})_5\text{L}$, $M = \text{Cr, Mo, and W}$; $\text{L} = 1,2,3$ -thiadiazole [15,16]. The assumption is that such coordination facilitates the subsequent cleavage of the S(Se)–N bond. However, there is no example in the literature where the effect of coordination of a metal to the 1,2,3-thia(selena)diazole heterocycle has been evaluated in terms of structural modification of the ligand.

We wish to report the synthesis of such σ -bonded complexes that result from the reactions of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2\text{THF}$, $\text{R} = \text{H, Me}$, with 1,2,3-selena- and thia-diazoles, and present, for the first time, structural data for both a complexed and free 1,2,3-thiadiazole ligand, namely benzo-1,2,3-thiadiazole. The structure of 4-phenyl-1,2,3-thiadiazole has also been determined to permit comparison with the published structure of its $\text{Mo}(\text{CO})_5$ derivative [15].

Experimental

All manipulations were performed under inert atmospheres of N_2 or Ar, using dry, oxygen free solvents. The various selena- and thia-diazoles were prepared by literature procedures [1,2,14,23]. $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2\text{THF}$, $\text{R} = \text{H, Me}$, was prepared from $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_3$, (Strem Chemicals, Newburyport, MA.), via published procedures [17]. Infrared spectra were recorded on a Perkin Elmer 580B spectrophotometer, NMR spectra on an IBM/Bruker NR200 MHz multi-nuclear spectrometer, and elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. A typical reaction procedure is outlined below.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{THF}$ and 1,2,3-benzothiadiazole

In a 200 mL Schlenk flask, 1.30 g (9.5 mmol) of 1,2,3-benzothiadiazole was stirred with a solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{THF}$ in 80 mL THF (prepared from 2.0 g of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$) for 1 h at 20 °C. The solvent was removed and the residue purified by chromatography (2 × 25 cm silica gel), eluting the resultant royal blue band with a 2 : 1 CH_2Cl_2 /hexane solvent mixture at 0 °C. After removal of the solvent, crystallization from dichloromethane/cyclohexane at –40 °C yielded black–blue prisms of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(2\text{-}\{1,2,3\text{-benzothiadiazole}\})$, **3a**, 1.24 g (40%), m.p. 112–114 °C (dec). Spectroscopic and analytical data are recorded in Table 1 along with those of the other complexes synthesized by the same general procedure.

X-Ray structure determination

The structure determination of **3a** was performed using an Enraf–Nonius CAD-4 diffractometer at room temperature with graphite monochromated Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$). Crystal data, data collection, and least squares parameters are summarized in Table 2. The intensities of three check reflections were recorded

Table 1

Spectral and analytical data and melting points of complexes **3a** and **3'a**

	3a	3'a
IR ^a (ν CO cm ⁻¹)	1947, 1892	1943, 1888
¹ H NMR ^b (ppm)	8.0, 7.4, m (arom H) 4.7, m (Cp)	8.0, 7.3, m 4.5, m
¹³ C NMR ^b (ppm)	234.4 (CO) 129.0, 128.1, 126.8 123.1, 119.5, 116.1 (benzene ring) 84.7 (Cp)	233.9 129.1, 128.0, 126.8, 123.7, 119.4, 116.5, 84.6, 83.1, 81.5 13.1 (CH ₃)
Melting point	112–114 (d)	108–112 (d)
Analysis ^c	C ₁₃ H ₉ MnN ₂ O ₂ S	C ₁₄ H ₁₁ MnN ₂ O ₂ S
MW	312.23	326.26
C (%)	49.80 (50.01)	50.88 (51.54)
H (%)	3.06 (2.91)	3.40 (3.40)
N (%)	8.88 (8.97)	8.60 (8.59)

Due to the lability of complexes **3'b**, **3'd**, **3'e**, **4'b**, **4'c**, **4'd**. (these complexes are oils at R.T. and did not crystallize at lower temperatures) no satisfactory elemental or NMR data could be obtained. Their IR data are: **3'b**: 1941, 1887; **3'd**: 1924, 1853; **3'e**: 1022, 1851; **4'b**: 1936, 1870; **4'c**: 1938, 1879; **4'd**: 1928, 1861.

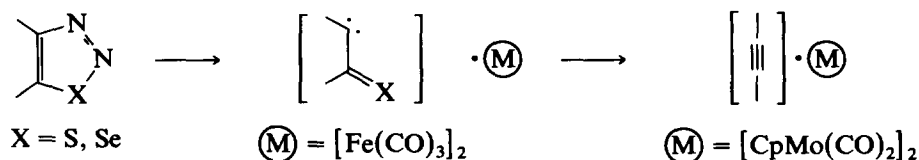
^a In hexane/CH₂Cl₂ 1:1. All reported IR-spectra show peaks with approximately 1:1 intensities. ^b In CDCl₃. ^c Performed by Galbraith Laboratories, Inc., Knoxville. TN. Theoretical values in parentheses.

every 1 h and they indicated crystal decay. An anisotropic decay correction was therefore applied. The structure was refined by anisotropic least-squares. After the isotropic refinement, an empirical spherical absorption correction [18] was applied (maximum, minimum, and average absorption corrections were 1.688, 0.747, and 0.96, respectively). Final positional parameters are listed in Table 3, and the bond lengths and angles are reported in Table 4. The structure is illustrated in Fig. 1a.

The data collection for 1,2,3-benzothiadiazole and 4-phenyl-1,2,3-thiadiazole were performed using a Nicolet *R3m/V* diffractometer using graphite monochromated Mo-*K_α* radiation ($\lambda = 0.71073 \text{ \AA}$). All pertinent data are recorded in Tables 2–4, and the structures are presented in Figs. 1b and 1c.

Calculations

Ab initio calculated structures of 1,2,3-thiadiazole, and the two isomeric protonated forms, i.e. protonation at N2 or N3, are presented in Fig. 2.



Scheme 1

Table 2

Crystal data, data collection, and least-square parameters of the 1,2,3-benzothiadiazole complex 3a, 1,2,3-benzothiadiazole, and 4-phenyl-1,2,3-thiadiazole

	1,2,3-Benzothiadiazole × Mn(CO) ₂ Cp	1,2,3-Benzothiadiazole	4-Phenyl-1,2,3-thiadiazole
<i>Crystal data</i>			
Empirical formula	C ₁₃ H ₉ O ₂ N ₂ SMn	C ₆ H ₄ N ₂ S	C ₈ H ₆ N ₂ S
Color, habit	Black-blue prisms	Colorless fragment	Colorless prisms
Crystal size (mm)	0.15 × 0.20 × 0.30	0.4 × 0.3 × 0.4	0.4 × 0.2 × 0.6
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>F</i> cab	<i>P</i> a
Unit cell dimensions	<i>a</i> = 17.673(4) Å <i>b</i> = 10.674(1) Å <i>c</i> = 14.532(2) Å β = 106.90(1)°	<i>a</i> = 7.279(2) Å <i>b</i> = 10.502(3) Å <i>c</i> = 15.784(4) Å	<i>a</i> = 7.4103(16) Å <i>b</i> = 5.6646(11) Å <i>c</i> = 9.133(2) Å β = 96.61(2)°
Volume (Å ³)	2623(1)	1206.6(5)	380.82(13)
<i>Z</i>	8	8	2
Formula weight	321.2	136.2	162.2
Density (calc.) g/cm ³	1.581	1.499	1.415
<i>F</i> (000)	1264	560	168
<i>Data collection</i>			
Diffractionmeter used	Enraf-Nonius CAD-4	Nicolet R3m/V	Nicolet R3m/V

Radiation	Cu-K α ($\lambda = 1.5418 \text{ \AA}$)	Mo-K α ($\lambda = 0.71073 \text{ \AA}$)	Mo-K α ($\lambda = 0.71073 \text{ \AA}$)
Temperature	298 K	298 K	298 K
Monochromator	Highly oriented graphite crystal	Highly oriented graphite crystal	Highly oriented graphite crystal
2 θ Range	3.0 to 150 $^\circ$	3.5 to 45.0 $^\circ$	3.5 to 45.0 $^\circ$
Index ranges	0 $\leq h \leq 22$, 0 $\leq k \leq 11$, -14 $\leq l \leq 13$	-2 $\leq h \leq 7$, -3 $\leq k \leq 11$, -4 $\leq l \leq 16$	0 $\leq h \leq 7$, -3 $\leq k \leq 6$, -9 $\leq l \leq 9$
Independent reflections	5399	781	648
Observed reflections	3253 ($F \geq 3.0\sigma(F)$)	627 ($F \geq 3.0\sigma(F)$)	537 ($F \geq 3.0\sigma(F)$)
<i>Solution and refinement</i>			
System used	SHELX 76	Nicolet SHELXTL PLUS (MicroVAX II)	Nicolet SHELXTL PLUS (MicroVAX II)
Solution	Heavy atom method	Direct methods	Direct methods
Refinement method	Full matrix least-squares	Full matrix least-squares	Full matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
Hydrogen atoms	Riding model, fixed isotropic U	Riding model, fixed isotropic U	Riding model, fixed isotropic U
Final R indices (obs. data)	R = 5.8%, wR = 6.7%	R = 3.41%, wR = 3.64%	R = 3.06%, wR = 4.33%
R indices (all data)	R = 8.2%	R = 4.55%	R = 3.12%
Goodness-of-Fit	3.65	1.87	1.17
Largest difference peak	0.43 e \AA^{-3}	0.14 e \AA^{-3}	0.19 e \AA^{-3}
Largest difference hole	-0.38 e \AA^{-3}	-0.14 e \AA^{-3}	-0.13 e \AA^{-3}

Table 3

Final positional parameters and B_{eq}^a (\AA^2) values (B for the hydrogen atoms)

Atom	x	y	z	B_{eq}/B
<i>A. 1,2,3-benzothioadiazole · Mn(CO)₂Cp</i>				
Mn	0.10686(4)	0.09420(8)	0.33908(6)	3.92(2)
S	0.12083(8)	−0.1990(1)	0.3090(1)	4.60(4)
O1	0.0354(2)	0.0833(5)	0.1317(3)	8.4(1)
O2	−0.0338(2)	−0.0227(4)	0.3703(3)	6.8(1)
N1	0.2423(2)	−0.0778(4)	0.3964(2)	3.9(1)
N2	0.1685(2)	−0.0620(3)	0.3531(2)	3.3(1)
C1	0.2650(3)	−0.2012(5)	0.4000(3)	3.8(1)
C2	0.3415(3)	−0.2468(6)	0.4448(4)	5.2(1)
C3	0.3535(3)	−0.3724(6)	0.4428(4)	5.6(2)
C4	0.2934(3)	−0.4549(6)	0.3985(4)	5.7(2)
C5	0.2193(3)	−0.4113(5)	0.3537(4)	5.8(2)
C6	0.2041(3)	−0.2863(5)	0.3544(3)	4.0(1)
C7	0.0649(3)	0.0823(5)	0.2142(4)	5.3(1)
C8	0.0230(3)	0.0219(5)	0.3583(4)	5.0(1)
C9	0.0867(4)	0.2790(6)	0.3795(6)	9.1(2)
C10	0.1247(4)	0.2144(6)	0.4624(5)	7.1(2)
C11	0.1972(3)	0.1789(6)	0.4539(4)	6.2(2)
C12	0.2059(3)	0.2188(6)	0.3675(4)	6.0(2)
C13	0.1354(5)	0.2809(6)	0.3203(5)	8.8(2)
Mn'	0.40753(4)	−0.62764(8)	0.73664(6)	4.10(2)
S'	0.23240(8)	−0.5501(1)	0.6216(1)	4.93(4)
O1'	0.4398(3)	−0.6573(6)	0.5525(3)	9.4(2)
O2'	0.3095(2)	−0.8532(4)	0.7021(3)	7.5(1)
N1'	0.3299(2)	−0.3822(4)	0.6950(3)	3.9(1)
N2'	0.3245(2)	−0.5010(4)	0.6879(2)	3.6(1)
C1'	0.2615(3)	−0.3202(5)	0.6475(3)	3.7(1)
C2'	0.2502(3)	−0.1919(5)	0.6432(4)	4.6(1)
C3'	0.1788(3)	−0.1437(6)	0.5939(4)	5.2(2)
C4'	0.1173(3)	−0.2234(6)	0.5486(4)	5.3(2)
C5'	0.1253(3)	−0.3511(6)	0.5500(4)	5.2(2)
C6'	0.1993(2)	−0.4014(5)	0.6014(3)	3.7(1)
C7'	0.4251(3)	−0.6434(6)	0.6240(4)	5.7(2)
C8'	0.3453(3)	−0.7585(5)	0.7141(4)	5.1(1)
C9'	0.4358(4)	−0.5971(8)	0.8873(4)	8.2(3)
C10'	0.4692(4)	−0.7066(8)	0.8698(5)	10.5(3)
C11'	0.5217(4)	−0.6772(7)	0.8175(5)	9.4(2)
C12'	0.5190(4)	−0.5448(8)	0.8078(5)	8.7(3)
C13'	0.4676(4)	−0.5009(7)	0.8502(4)	8.2(2)
H2	0.383(0)	−0.192(0)	0.476(0)	6.2(0)
H3	0.405(0)	−0.405(0)	0.473(0)	6.6(0)
H4	0.304(0)	−0.542(0)	0.399(0)	6.7(0)
H5	0.178(0)	−0.468(0)	0.322(0)	6.8(0)
H9	0.036(0)	0.316(0)	0.365(0)	10.1(0)
H10	0.105(0)	0.198(0)	0.515(0)	10.1(0)
H11	0.236(0)	0.133(0)	0.501(0)	10.1(0)
H12	0.251(0)	0.207(0)	0.345(0)	10.1(0)
H13	0.123(0)	0.318(0)	0.258(0)	10.1(0)
H2'	0.292(0)	−0.138(0)	0.675(0)	5.6(0)
H3'	0.171(0)	−0.056(0)	0.590(0)	6.2(0)
H4'	0.068(0)	−0.188(0)	0.515(0)	6.3(0)

Table 3 (continued)

Atom	x	y	z	B_{eq}/B
<i>A. 1,2,3-benzothiadiazole · Mn(CO)₂Cp</i>				
H5'	0.083(0)	-0.404(0)	0.517(0)	6.2(0)
H9'	0.397(0)	-0.590(0)	0.920(0)	9.2(0)
H10'	0.459(0)	-0.788(0)	0.890(0)	9.2(0)
H11'	0.553(0)	-0.734(0)	0.793(0)	9.2(0)
H12'	0.549(0)	-0.496(0)	0.776(0)	9.2(0)
H13'	0.455(0)	-0.415(0)	0.854(0)	9.2(0)
<i>B. 1,2,3-benzothiadiazole</i>				
S1	0.2499(1)	0.4739(1)	0.4637(1)	4.2(1)
N1	0.3887(4)	0.2642(2)	0.5016(1)	4.4(1)
N2	0.3447(4)	0.3310(2)	0.4369(1)	4.9(1)
C1	0.3498(3)	0.3233(2)	0.5778(2)	3.4(1)
C2	0.3860(4)	0.2720(3)	0.6579(2)	4.1(1)
C3	0.3393(4)	0.3424(3)	0.7273(2)	4.5(1)
C4	0.2575(5)	0.4625(3)	0.7187(2)	4.5(1)
C5	0.2242(4)	0.5146(2)	0.6409(2)	3.9(1)
C6	0.2696(4)	0.4435(2)	0.5696(2)	3.2(1)
<i>C. 4-phenyl-1,2,3-thiadiazole</i>				
S	0.15140(5)	0.2445(2)	0.72420(5)	5.4(1)
N2	0.1257(7)	-0.0297(8)	0.6590(4)	5.2(1)
N1	0.0618(6)	-0.0297(6)	0.5219(4)	4.4(1)
C3	0.0271(5)	0.1917(8)	0.4628(5)	3.2(1)
C4	0.0725(7)	0.3663(7)	0.5630(5)	4.1(1)
C5	-0.0482(5)	0.2195(6)	0.3078(5)	3.0(1)
C6	-0.0217(6)	0.0442(6)	0.2047(5)	3.2(1)
C7	-0.0884(6)	0.0710(7)	0.0599(5)	3.7(1)
C8	-0.1840(6)	0.2711(7)	0.0131(6)	3.7(1)
C9	-0.2118(6)	0.4474(7)	0.1136(5)	3.9(1)
C10	-0.1446(6)	0.4198(6)	0.2596(4)	3.4(1)

^a B_{eq} is defined as 4/3 trace (BG) where **B** is the thermal motion tensor and **G** is the direct metric tensor.

The structures obtained were optimized by gradient techniques at the HF/6-31 + G(d, p) level of theory, using the Gaussian 86 system of programs. Electron correlation and ZPE effects were calculated at the MP2 level using the basis set noted in Fig. 2. All calculations were performed using the facilities of the University of Texas Center for High Performance Computing, Austin, TX.

Discussion

The reactions of the various 1,2,3-selena- and/or thia-diazoles with (η^5 -C₅H₄R)Mn(CO)₂THF, R = H, Me, proceeded smoothly to produce deep blue solutions of the complexes (η^5 -C₅H₄R)Mn(CO)₂(2-thiadiazole), R = H (**3**), R = Me (**3'**), Scheme 2.

The new complexes are thermally and oxidatively unstable, especially in solution. Thus, whereas we have characterized all new complexes via infrared spectroscopy (Table 1), they exhibit the two expected ν (CO) absorptions in the regions 1920–1940 and 1850–1870 cm⁻¹, useful NMR analysis was possible only for **3a** and **3'b** due to extensive broadening of the resonances in all other cases. No infrared bands

Table 4

Bond lengths and bond angles of 1,2,3-benzothiadiazole·Mn(CO)₂Cp, **3a**, 1,2,3-benzothiadiazole, and 4-phenyl-1,2,3-thiadiazole

A. 1,2,3-benzothiadiazole·Mn(CO)₂Cp

Bond lengths (Å)

Mn–N2	1.970(4)	C2–C3	1.358(9)	Mn'–C13'	2.159(7)
Mn–C7	1.754(6)	C3–C4	1.386(8)	S'–N2'	1.715(4)
Mn–C8	1.763(5)	C4–C5	1.364(8)	S'–C6'	1.688(6)
Mn–C9	2.117(7)	C5–C6	1.362(8)	O1'–C7'	1.153(8)
Mn–C10	2.151(7)	C9–C10	1.381(11)	O2'–C8'	1.178(7)
Mn–C11	2.145(6)	C9–C13	1.382(10)	N1'–N2'	1.273(6)
Mn–C12	2.141(6)	C10–C11	1.375(7)	N1'–C1'	1.375(6)
Mn–C13	2.093(7)	C11–C12	1.376(9)	C1'–C2'	1.383(8)
S–N2	1.716(4)	C12–C13	1.402(9)	C1'–C6'	1.407(7)
S–C6	1.705(5)	Mn'–N2'	1.969(4)	C2'–C3'	1.358(7)
O1–C7	1.160(7)	Mn'–C7'	1.760(6)	C3'–C4'	1.388(8)
O2–C8	1.170(6)	Mn'–C8'	1.749(6)	C4'–C5'	1.371(10)
N1–N2	1.284(5)	Mn'–C9'	2.124(7)	C5'–C6'	1.410(7)
N1–C1	1.373(7)	Mn'–C10'	2.101(7)	C9'–C10'	1.366(12)
C1–C2	1.406(7)	Mn'–C11'	2.087(6)	C9'–C13'	1.355(11)
C1–C6	1.417(7)	Mn'–C12'	2.132(7)	C10'–C11'	1.396(9)
				C11'–C12'	1.419(12)
				C12'–C13'	1.323(9)

Bond angles (°)

N2–Mn–C7	95.8(4)	N2'–Mn'–C7'	92.6(4)
N2–Mn–C8	94.5(4)	N2'–Mn'–C8'	96.8(4)
N2–Mn–C9	153.2(4)	N2'–Mn'–C9'	101.1(4)
N2–Mn–C10	118.4(4)	N2'–Mn'–C10'	137.6(4)
N2–Mn–C11	90.7(3)	N2'–Mn'–C11'	150.9(4)
N2–Mn–C12	96.3(3)	N2'–Mn'–C12'	112.1(4)
N2–Mn–C13	132.3(4)	N2'–Mn'–C13'	89.7(4)
C7–Mn–C8	90.6(4)	C7'–Mn'–C8'	91.2(5)
C7–Mn–C9	107.4(5)	C7'–Mn'–C9'	157.0(5)
C7–Mn–C10	145.1(4)	C7'–Mn'–C10'	129.3(5)
C7–Mn–C11	146.1(4)	C7'–Mn'–C11'	95.5(5)
C7–Mn–C12	108.7(4)	C7'–Mn'–C12'	95.9(5)
C7–Mn–C13	88.8(5)	C7'–Mn'–C13'	126.1(5)
C8–Mn–C9	98.4(5)	C8'–Mn'–C9'	105.2(5)
C8–Mn–C10	93.2(4)	C8'–Mn'–C10'	89.0(5)
C8–Mn–C11	122.0(4)	C8'–Mn'–C11'	110.8(5)
C8–Mn–C12	156.7(4)	C8'–Mn'–C12'	149.8(5)
C8–Mn–C13	133.0(5)	C8'–Mn'–C13'	141.9(5)
C9–Mn–C10	37.7(4)	C9'–Mn'–C10'	37.7(5)
C9–Mn–C11	62.5(4)	C9'–Mn'–C11'	63.9(5)
C9–Mn–C12	64.0(4)	C9'–Mn'–C12'	61.9(5)
C9–Mn–C13	38.3(5)	C9'–Mn'–C13'	36.9(5)
C10–Mn–C11	37.3(4)	C10'–Mn'–C11'	38.9(5)
C10–Mn–C12	63.5(4)	C10'–Mn'–C12'	64.0(5)
C10–Mn–C13	63.8(5)	C10'–Mn'–C13'	62.6(5)
C11–Mn–C12	37.4(4)	C11'–Mn'–C12'	39.3(5)
C11–Mn–C13	63.1(4)	C11'–Mn'–C13'	63.1(5)
C12–Mn–C13	38.7(4)	C12'–Mn'–C13'	35.9(5)
N2–S–C6	92.7(4)	N2'–S'–C6'	92.0(4)

Table 4 (continued)

Bond angles (°)			
N2–N1–C1	112.8(7)	N2'–N1'–C1'	113.9(7)
Mn–N2–S	119.1(3)	Mn'–N2'–S'	118.6(4)
Mn–N2–N1	127.9(5)	Mn'–N2'–N1'	128.6(5)
S–N2–N1	112.9(5)	S'–N2'–N1'	112.7(5)
N1–C1–C2	125.5(8)	N1'–C1'–C2'	126.4(8)
N1–C1–C6	115.0(7)	N1'–C1'–C6'	113.2(7)
C2–C1–C6	119.5(8)	C2'–C1'–C6'	120.4(8)
C1–C2–C3	117.9(9)	C1'–C2'–C3'	119.9(9)
C2–C3–C4	122.2(10)	C2'–C3'–C4'	119.9(9)
C3–C4–C5	120.3(10)	C3'–C4'–C5'	122.7(9)
C4–C5–C6	119.6(9)	C4'–C5'–C6'	117.5(9)
S–C6–C1	106.5(6)	S'–C6'–C1'	108.2(6)
S–C6–C5	133.0(7)	S'–C6'–C5'	132.2(7)
C1–C6–C5	120.5(8)	C1'–C6'–C5'	119.6(8)
Mn–C7–O1	175.1(9)	Mn'–C7'–O1'	176.6(10)
Mn–C8–O2	177.9(8)	Mn'–C8'–O2'	173.8(9)
Mn–C9–C10	72.5(7)	Mn'–C9'–C10'	70.2(8)
Mn–C9–C13	69.9(7)	Mn'–C9'–C13'	72.9(7)
C10–C9–C13	108.5(11)	C10'–C9'–C13'	108.8(11)
Mn–C10–C9	69.8(7)	Mn'–C10'–C9'	72.0(8)
Mn–C10–C11	71.1(6)	Mn'–C10'–C11'	70.0(7)
C9–C10–C11	106.8(10)	C9'–C10'–C11'	107.5(11)
Mn–C11–C10	71.6(6)	Mn'–C11'–C10'	71.1(7)
Mn–C11–C12	71.1(6)	Mn'–C11'–C12'	72.1(7)
C10–C11–C12	110.5(10)	C10'–C11'–C12'	105.6(11)
Mn–C12–C11	71.4(6)	Mn'–C12'–C11'	68.6(7)
Mn–C12–C13	68.8(7)	Mn'–C12'–C13'	73.1(8)
C11–C12–C13	105.9(10)	C11'–C12'–C13'	108.4(11)
Mn–C13–C9	71.8(7)	Mn'–C13'–C9'	70.2(7)
Mn–C13–C12	72.5(7)	Mn'–C13'–C12'	71.0(8)
C9–C13–C12	108.3(11)	C9'–C13'–C12'	109.7(11)
B. 1,2,3-benzothiadiazole			
Bond lengths (Å)			
S1–N2	1.706(3)	S1–C6	1.708(3)
N1–N2	1.279(3)	N1–C1	1.384(3)
C1–C2	1.399(4)	C1–C6	1.397(3)
C2–C3	1.366(4)	C3–C4	1.402(4)
C4–C5	1.366(4)	C5–C6	1.390(4)
Bond angles (°)			
N2–S1–C6	92.6(1)	N2–N1–C1	113.4(2)
S1–N2–N1	112.7(2)	N1–C1–C2	125.1(2)
N1–C1–C6	114.2(2)	C2–C1–C6	120.7(2)
C1–C2–C3	118.0(3)	C2–C3–C4	121.0(3)
C3–C4–C5	121.5(3)	C4–C5–C6	118.1(2)
S1–C6–C1	107.1(2)	S1–C6–C5	132.2(2)
C1–C6–C5	120.6(2)		

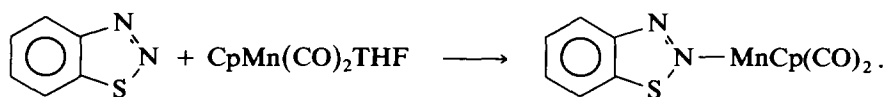
unambiguously assignable to Mn–N or N=N vibrations could be discerned. Thermal or photochemical decomposition of the complexes was readily observed, but no new isolable complexes could be obtained from such procedures. The conditions for such decompositions are mild, e.g. refluxing in THF, or even more slowly, at room

Table 4 (continued)

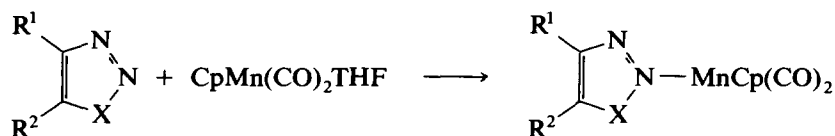
C. 4-phenyl-1,2,3-thiadiazole

Bond lengths (Å)			
S–N2	1.666(5)	S–C4	1.670(4)
N2–N1	1.286(5)	N1–C3	1.378(5)
C3–C4	1.363(6)	C3–C5	1.469(6)
C5–C6	1.397(5)	C5–C10	1.385(5)
C6–C7	1.366(6)	C7–C8	1.378(6)
C8–C9	1.388(6)	C9–C10	1.377(6)
Bond angles (°)			
N2–S–C4	93.2(2)	S–N2–N1	111.2(3)
N2–N1–C3	114.4(4)	N1–C3–C4	112.2(4)
N1–C3–C5	120.5(4)	C4–C3–C5	127.3(4)
S–C4–C3	109.0(3)	C3–C5–C6	120.4(3)
C3–C5–C10	121.3(4)	C6–C5–C10	118.4(4)
C5–C6–C7	120.6(3)	C6–C7–C8	120.5(4)
C7–C8–C9	119.8(4)	C8–C9–C10	119.6(4)
C5–C10–C9	121.1(4)		

temperature. Photochemical irradiation in non-polar solvents using a Hanovia 400 Watt medium pressure lamp, also led to rapid decomposition at room temperature. Monitoring these reactions via infrared spectroscopy did not indicate formation of any new metal carbonyl complexes. This chemistry contrasts the reactions of the



3a, 3'a

3a: Cp = C₅H₅3'a: Cp = CH₃C₅H₄

3': X = S

3'b: R¹ = tert-butyl, R² = HCp = CH₃C₅H₄ 3'd: R¹ = R² = (CH₂)₄3'e: R¹ = R² = (CH₂)₆

4': X = Se

4'b: R¹ = tert-butyl, R² = HCp = CH₃C₅H₄ 4'c: R¹ = C₆H₅, R² = H4'e: R¹ = R² = (CH₂)₄

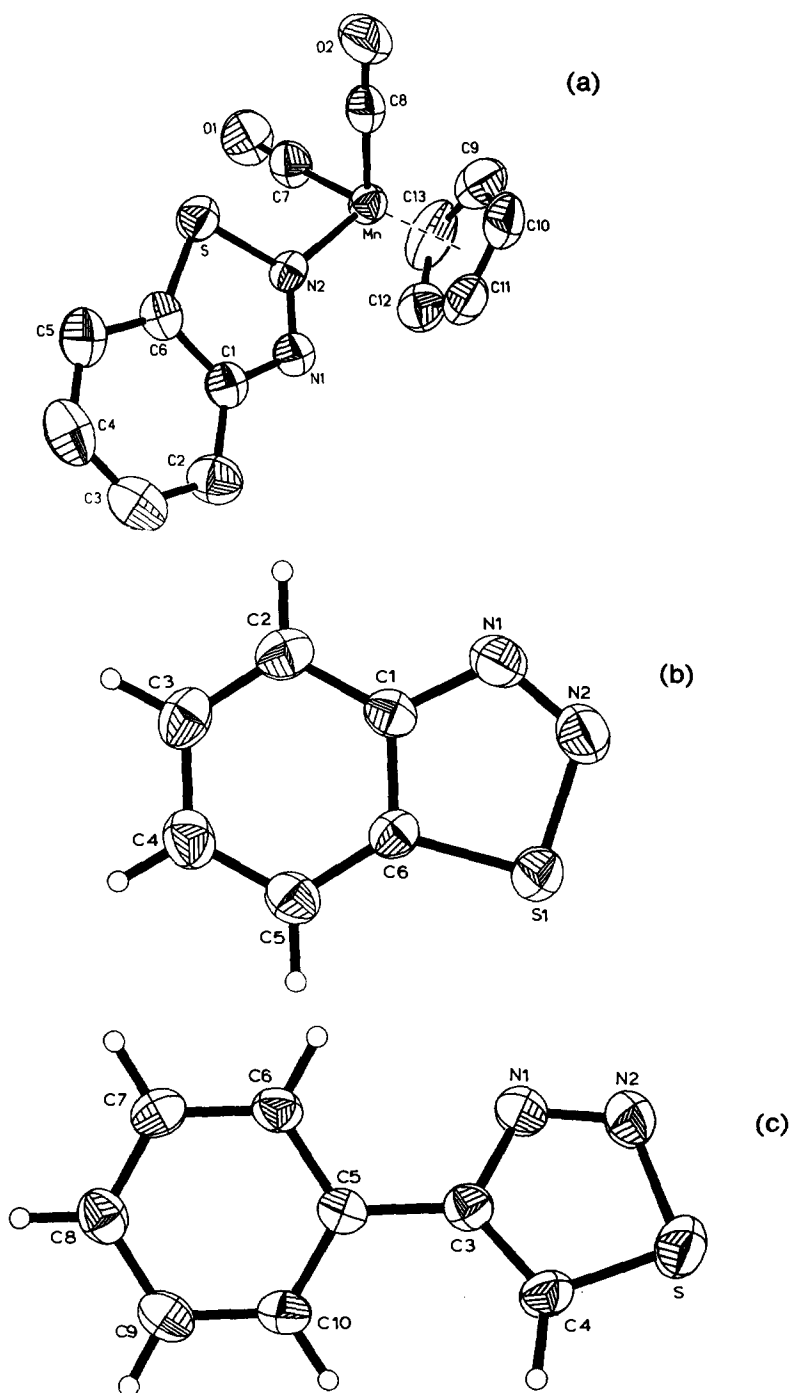
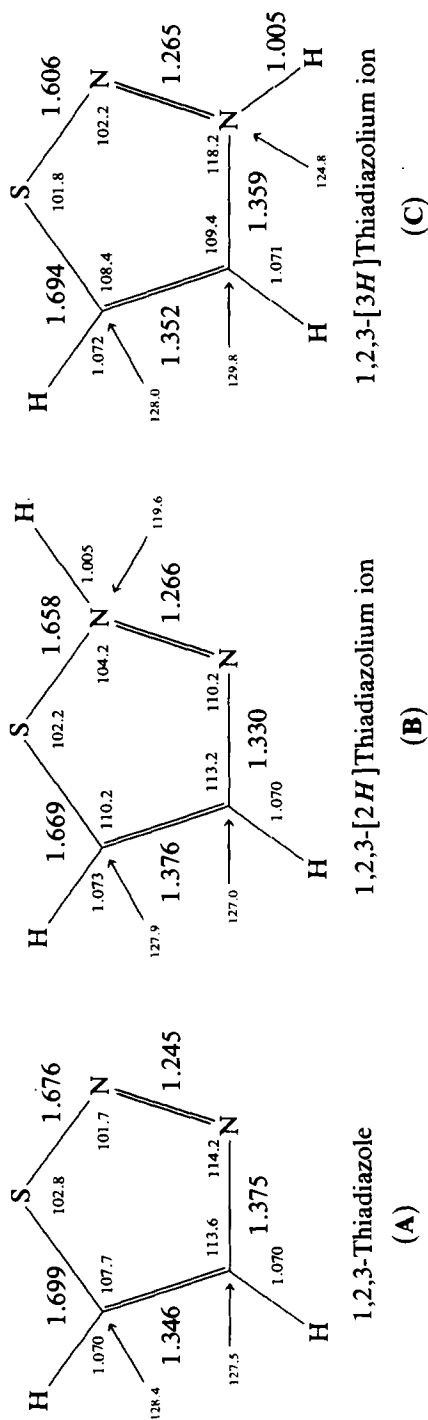


Fig. 1. X-Ray structures of 1,2,3-benzothiadiazole \times Mn(CO)₂Cp, 3a (a), 1,2,3-benzothiadiazole (b), and 4-phenyl-1,2,3-thiadiazole (c). Thermal ellipsoids are drawn at the 40% probability level.



Energies (hartrees)

	HF/6-31 + G(d, p)//	ZPE	HF/6-311 + G(2d, p)//	MP2/6-311 + G(2d, p)//
A	HF/6-31 + G(d, p)	0.046549	HF/6-31 + G(d, p)	HF/6-31 + G(d, p)
B	-583.25239	0.064310	-583.32319	-584.12513
C	-583.58880	0.061313	-583.65966	-584.45343
	-583.59568		-583.66810	-584.46432

Protonation is preferred at N2 over N1 by 8.75 kcal/mol (after ZPE correction)

Fig. 2. Calculated bond angles, lengths and the energies for 1,2,3-thiazole **A** and the related thiazolium ions **B**, protonated at N2 and **C** protonated at N3.

same manganese complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$, with α -diazocarbonyl compounds, the ring opened O analog of the Se and S diazoles, from which Herrmann reported complexes containing carbene, ketene, and imine fragments [20–22]. As noted in the introduction, stabilization of such fragments from Se and S diazoles with other transition metal complexes has been observed, however, apparently the nature of the metal is of key importance. The $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ system does not support such chemistry possibly due to the lower affinity of Mn for S or Se compared to O.

We have obtained crystals of **3a** suitable for X-ray analysis, and the structure of this complex is illustrated in Fig. 1a. The structure shows the diazole ligand to be intact and bonded to the manganese atom via the nitrogen atom adjacent to sulfur, N2. This parallels the results obtained by Bätzel and Boese, and ourselves, when the diazoles react with $\text{M}(\text{CO})_5\text{THF}$, M = Cr, Mo, and W [15,16]. The unit cell contains two molecules of the complex, and the geometry is identical for both. The main difference between the two enantiomeric molecules is the degree of rotation about the Mn–N bond. The torsion angles are S–N1–Mn–C7 = -56° (molecule 1) and 78° (molecule 2, -78° after inversion), and S–N1–Mn–C8 = 37° (molecule 1) and -13° (molecule 2; 13° after inversion). The structure of **3a** shows the manganese possesses a distorted trigonal pyramidal rather than a pseudo-tetrahedral geometry, a structural feature reported for similar manganese complexes [19].

We have suggested that coordination of a metal atom via the nitrogen, N2, lone pair of the 1,2,3-selena(thia)diazoles is the first step in the activation of the heterocyclic ring which leads to the ring opening observed from the reactions of other metal complexes. We have attempted to verify this suggestion by *ab initio* calculations performed on the parent 1,2,3-thiadiazole and its protonated forms, and also by determining the structural and energetic differences between the complexed and uncomplexed 1,2,3-thiadiazoles, complexed at both N2 and N3.

The results of the *ab initio* study are presented in Fig. 2. Calculation of the protonation energies for the 1,2,3-thiadiazole, show that N2 is the preferred site of protonation by almost 9 kcal/mol, a result that parallels the site of coordination of the metal center in the present study and those previous studies noted above [15,16]. The bond lengths calculated for the protonated forms of the 1,2,3-thiadiazole, are significantly different to those of the unprotonated species, exhibiting an elongated N=N bond length, but shortened S–N and C–N bond lengths. This result unfortunately contrasts with our suggestion that it is the initial coordination at N2 that begins the process of ring opening and decomposition of the heterocycle via elongation of the S–N bond.

The results of the single crystal X-ray analysis of the ligands benzo-1,2,3-thiadiazole and 4-phenyl-1,2,3-thiadiazole and comparison of their structures with the manganese complex reported here, and the $\text{Mo}(\text{CO})_5(2\text{-}\{4\text{-phenyl-1,2,3-thiadiazole}\})$ complex reported by Bätzel and Boese [15] also provide no support for the suggested activation. The data in Tables 2, 3, and 4 show that the structures of the free ligands are essentially unaltered upon complexation of either the $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ or $\text{W}(\text{CO})_5$ group. Whatever effect the metal may have upon the subsequent chemistry of the 1,2,3-thia(selena)diazoles is not reflected by any measureable structural changes upon coordination. The torsional angle between the phenyl and 1,2,3-thiadiazole units in 4-phenyl-1,2,3-thiadiazole and its $\text{W}(\text{CO})_5$ complex are 24.9° and 6.9° respectively. This rather large variation is probably due to crystal packing

effects since it is well established that barriers to rotation about the C–C bond in various biphenyls is low, and indeed biphenyl itself has a torsional angle of 0° in the solid state [24].

The cyclopentadienyl manganese dicarbonyl group appears to be an intermediate within the various metal complex systems that have been shown to react with the seleno- and thia-diazoles. It forms the relatively unstable, but isolable, complexes in which the ligand is intact. These complexes do not lead to stable fragmented product complexes. Such behaviour may be contrasted to the $\text{Fe}_2(\text{CO})_9$ system where no intact diazole ligands have been observed, but, probably due to the affinity of Fe for both S and Se, various fragmentation products are readily isolated. On the other hand, in the case of the group 6 metal carbonyl complexes, $\text{LM}(\text{CO})_5^-$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$, the intact ligand complexes are very stable.

Acknowledgements

Support of this research by the Robert A. Welch Foundation, Houston, TX, is gratefully acknowledged. Calculations were performed using the University of Texas System Center for High Performance Computing. Lists of observed and calculated structure factors and anisotropic thermal parameters are available from the authors.

References

- 1 H. Meier and K.P. Zeller, *Angew. Chem., Int. Ed. Engl.*, 14 (1975) 32.
- 2 (a) H. Meier and E. Voigt, *Tetrahedron*, 28 (1972) 187; (b) H. Buhl, B. Seitz and H. Meier, *Tetrahedron*, 33 (1977) 449.
- 3 T.L. Gilchrist, P.G. Mente and C.W. Rees, *J. Chem. Soc., Perkin Trans. I*, (1972) 2165.
- 4 G.N. Schrauzer and H.J. Kisch, *J. Am. Chem. Soc.*, 95 (1973) 2501.
- 5 R.C. Pettersen, K.H. Pannell and A.J. Mayr, *Cryst. Struct. Commun.*, 9 (1980) 643.
- 6 K.H. Pannell, A.J. Mayr, R. Hoggard and R. Pettersen, *Angew. Chem., Int. Ed. Engl.*, 19 (1980) 632.
- 7 R.C. Pettersen, K.H. Pannell, A.J. Mayr, *Acta Crystallogr.*, B36 (1980) 2434.
- 8 K.H. Pannell, A.J. Mayr, B. Carrasco-Flores, L. Parkanyi and F. Cervantes-Lee, manuscript in preparation.
- 9 K.H. Pannell, A.J. Mayr and D. VanDerveer, *Organometallics*, 2 (1983) 560.
- 10 K.H. Pannell, A.J. Mayr and D. VanDerveer, *J. Am. Chem. Soc.*, 105 (1983) 6186.
- 11 J. Knebel, C.P. Morley, G. Wilke, C. Krüger and J.M. Wallis, *J. Organomet. Chem.*, 334 (1987) C39.
- 12 C.P. Morley, R.R. Vaughan and B.J. Wheatley, *J. Organomet. Chem.*, 353 (1988) C39.
- 13 C.P. Morley, *Organometallics* 8 (1989) 800.
- 14 A.J. Mayr, K.H. Pannell, B. Carrasco-Flores and F. Cervantes-Lee, *Organometallics*, 8 (1989) 2961.
- 15 V. Bätzel, R. Boese, *Z. Naturforsch.*, 36B (1981) 172.
- 16 K.H. Pannell, A.J. Mayr, R. Hoggard, J.S. McKennis, J.C. Dawson, *Chem Ber.*, 116 (1983) 230.
- 17 E.O. Fischer and A.M. Herberhold, *Essays in Coordination Chemistry, Exper. Supp. IX*, p. 259 p.1964.
- 18 N. Walker, D. Stuart, *Acta Crystallogr.*, 39A (1983) 158.
- 19 U. Kirchgässner and U. Schubert, *Organometallics*, 7 (1988) 784.
- 20 W.A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 13 (1974) 599.
- 21 M.L. Ziegler, K. Weidenhammer and W.A. Herrmann, *Angew. Chem., Int. Ed., Engl.*, 16 (1977) 555.
- 22 W.A. Herrmann, *Chem. Ber.*, 108 (1974) 486.
- 23 S. Hünig and E. Fleckenstein, *Liebigs Ann. Chem.*, 738 (1970) 192.
- 24 C.P. Brock and R.P. Minton, *J. Am. Chem. Soc.*, 111 (1989) 4586.