Titanium–Sulfur–Nitrogen Heterocycles: Preparation and Molecular Structures of Titanocene Trisulfur Tetranitride $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and Titanocene Trisulfur Dinitride $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$

Clifford G. Marcellus,[1a] Richard T. Oakley,*[1a] William T. Pennington,[1b] and A. Wallace Cordes[1b]

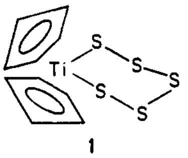
Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1 Canada, and Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received December 3, 1985

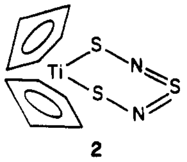
The reaction of bis(cyclopentadienyl)titanium dicarbonyl with tetrasulfur tetranitride produces two titanium–sulfur–nitrogen heterocycles, $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$, an eight-membered TiNSNSNSN ring system, and $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$, a six-membered ring structure based on a TiSSNSN sequence. The crystal structures of both compounds have been determined by single-crystal X-ray crystallography. Crystals of $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ are monoclinic of space group $P2_1/c$ with $a = 7.803(2)$ Å, $b = 20.012\ (4)$ Å, $c = 25.099\ (4)$ Å, $\beta = 92.75\ (2)°$, $V = 3914\ (2)$ Å^3, $Z = 12$, and $D_{calcd} = 1.693$ g cm^{-1}. Crystals of $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$ are orthorhombic of space group *Pbca* with $a = 7.874\ (1)$ Å, $b = 13.974\ (3)$ Å, $c = 21.312\ (3)$ Å, $V = 2345\ (1)$ Å^3, $Z = 8$, and $D_{calcd} = 1.71$ g cm^{-1}. Both structures were solved from Patterson maps and refined by Fourier and full-matrix least-squares techniques to final *R* values (observed reflections) of 0.040 (3609) for the former and 0.040 (1121) for the latter. The three crystallographically independent molecules in $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ all exhibit the same structural and conformational characteristics. The seven-atom NSNSNSN sequences are planar with the titanium atoms lying 0.619–0.824 (1) Å above these planes. The six-membered ring of $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$ adopts a half-chair conformation with a dihedral angle of 52.6° between the TiSS and TiNSNS fragments. The variations in the endocyclic bond lengths of $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ are related to the nature of the π-interactions between the NSNSNSN fragment and the titanium d orbitals.

Introduction

The study of the coordination properties of sulfur–nitrogen molecules and ions has a long history. In recent years rapid growth has occurred in this area; the ability of transition and main-group metals to stabilize the highly reactive S_2N_2 molecule as a coordinated ligand has attracted much attention,[2,3] as has the design of metallodithiatriazines, MS_2N_3.[4] Interest has also been generated in the use of simple metal MS_2N_2 complexes as "S_2N_2" transfer agents.[5] In this latter context we are currently pursuing the design and development of thiazyl transfer reagents based on the titanocene system, i.e., $(\eta^5\text{-}C_5H_5)_2TiS_xN_y$. Our hope in studying these systems stems from the success of compounds such as $(\eta^5\text{-}C_5H_5)_2TiS_5$ (1) as sulfur transfer agents in organosulfur chemistry.[6]

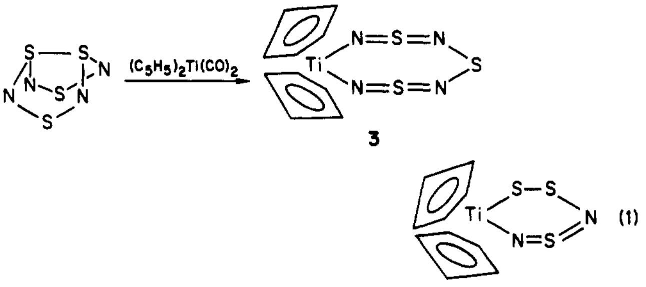


1



2

To this end we have investigated the reaction of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ with tetrasulfur tetranitride, S_4N_4, our intent being to prepare $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$ (**2**), the sulfur–nitrogen equivalent of **1**. We have isolated two products from this reaction (eq 1), with elemental compositions



3

4

(1)

corresponding to $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$. X-ray crystallographic analysis of these two compounds reveals an eight-membered ring structure **3** for the former and the six-membered ring system **4** for the latter. In this paper we provide a full account of the preparation and structures of these compounds.[7]

Experimental Section

Starting Materials and General Procedures. Tetrasulfur tetranitride was prepared according to literature methods.[8]

---

[1] (a) University of Guelph. (b) University of Arkansas.

[2] (a) Thewalt, U.; Holl, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 145. (b) Thewalt, U.; Muller, B. *Z. Anorg. Allg. Chem.* **1980**, *462*, 214. (c) Thewalt, U.; Burger, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 634.

[3] (a) Roesky, H. W.; Anhaus, J.; Sheldrick, W. S. *Inorg. Chem.* **1984**, *23*, 75. (b) Kynast, U.; Klingelhöfer, D.; Muller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *515*, 61.

[4] (a) Roesky, H. W.; Anhaus, J.; Schmidt, Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1207. (b) Anhaus, J.; Siddiqui, Z. A.; Roesky, H. W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1722. (c) Anhaus, J.; Jones, P. G.; Noltemeyer, M.; Pinkert, W.; Roesky, H. W.; Sheldrick, G. M. *Inorg. Chim. Acta* **1985**, *97*, L7.

[5] (a) Roesky, H. W.; Wiezer, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 258. (b) Roesky, H. W.; Holtschneider, G.; Wiezer, H.; Krebs, B. *Chem. Ber.* **1976**, *109*, 1358. (c) Wehner, E.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 498. (d) Heitmann, A.; Edelmann, F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 521.

[6] (a) Schmidt, R.; Wilhelm, E. *J. Chem. Soc., Chem. Commun.* **1970**, 111. (b) Schmidt, M.; Block, B.; Block, H. D.; Köpf, H.; Wilhelm, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 632. (c) Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149. (d) Steudel, R.; Strauss, R. *J. Chem. Soc. Dalton Trans.* **1984**, 1775. (e) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

[7] For a preliminary account of part of this work, see: Marcellus, C. G.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Chem. Soc., Chem. Commun.* **1983**, 1451.

[8] Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.

0276-7333/86/2305-1395$01.50/0

Solutions of (η^5-C_5H_5)$_2$Ti(CO)$_2$ were prepared by the reduction of (η^5-C_5H_5)$_2$TiCl$_2$ (Aldrich) with aluminum under an atmosphere of carbon monoxide[9] (Matheson) and used in situ. Tetrahydrofuran was dried by distillation from lithium aluminum hydride. All reactions were performed under an atmosphere of dry nitrogen. Infrared spectra were recorded (on Nujol mulls in CsI cells) using a Perkin-Elmer 1330 grating spectrophotometer. ^{1}H NMR spectra were obtained on a Varian XL-200 spectrometer. UV-visible spectra were recorded (in CH_2Cl_2) on a Cary 219 spectrophotometer. Low-resolution mass spectra (EI, 70 eV) were run on a VG 7070 EF spectrometer, samples being admitted through conventional inlet systems. Elemental analyses were performed by MHW laboratories, Phoenix, AZ.

Reaction of (η^5-C_5H_5)$_2$Ti(CO)$_2$ with S_4N_4. A solution of (η^5-C_5H_5)$_2$Ti(CO)$_2$ (prepared by the reduction of (η^5-C_5H_5)$_2$TiCl$_2$ (2.50 g, 10.0 mmol) with aluminum) in 50 mL of THF was added dropwise to a slurry of S_4N_4 (1.25 g, 6.8 mmol) in 50 mL of THF. The resulting mixture rapidly turned dark brown. After 16 h the mixture was filtered to remove some particulate matter and the filtrate reduced to dryness in vacuo. The tarry residue was extracted with 3 × 100 mL toluene, and the extracts were concentrated on a rotary evaporator to a volume of 25 mL. This solution was filtered through a glass plug and loaded onto a 25 × 700 mm Bio-Beads SX-8 gel permeation chromatography column which was eluted with toluene. Partial separation of two bands, a dark green leading component and a dark brown zone, was thus achieved. Residual S_4N_4 was removed as the final band. The two partially separated leading bands were individually chromatographed again, and complete resolution of the two components was then achieved. The two bands were evaporated to dryness. The green material was extracted into acetonitrile, and the extracts were concentrated to a volume of 50 mL and cooled to −25 °C, yielding green-black needles of (η^5-C_5H_5)$_2$TiS$_3$N$_4$ (**3**) (0.38 g, 1.15 mmol), mp 105–107 °C. Anal. Calcd for $C_{10}H_{10}N_4S_3Ti$: C, 36.36; H, 3.05; N, 16.96; S, 29.12. Found: C, 36.37; H, 3.23; N, 16.74; S, 28.87. ^{1}H NMR (CDCl$_3$): δ 5.84. Infrared (1600–250 cm^{-1} region): 1215 (s, br), 1130 (w), 1069 (w, br), 965 (m), 845 (sh), 830 (s), 815 (s), 480 (w), 425 (m), 405 (m). UV–vis: λ_{max} (ϵ) 584 (2 × 10^3), 458 (4 × 10^3), 324 (1 × 10^4) nm (M^{-1} cm^{-1}). The brown material was recrystallized from hot toluene as dark brown blocks of (η^5-C_5H_5)$_2$TiS$_3$N$_2$ (**4**) (0.40 g, 1.32 mmol), mp >260 °C. Anal. Calcd for $C_{10}H_{10}N_2S_3Ti$: C, 39.73; H, 3.33; N, 9.27; S, 31.82. Found: C, 39.61; H, 3.59; N, 9.06; S, 31.06. ^{1}H NMR (CDCl$_3$): δ 6.21. Infrared (1600–250 cm^{-1} region): 1129 (s), 1078 (vw), 1069 (vw), 1031 (w), 1019 (w), 1013 (w), 928 (w), 860 (m), 835 (sh), 829 (sh), 820 (vs), 620 (m), 603 (w), 542 (m), 480 (w), 430 (m, br), 370 (w), 352 (w), 330 330 (w), 278 (m). UV–vis: λ_{max} (ϵ) 488 (2 × 10^3), 378 (5 × 10^3), 324 (5 × 10^3) nm (M^{-1} cm^{-1}).

X-ray Measurements. Crystals of **3** and **4** were mounted on a glass fiber with epoxy glue. All data were collected by using an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Data for both crystals were collected with θ–2θ scans to a 2θ_{max} of 50°. Crystal data, data collection parameters, and refinement results are listed in Table I.

The structures were solved by Patterson methods and refined by full-matrix least-squares analyses based on $(|F_o| - |F_c|)^2$. Neutral atom scattering factors[10] were corrected for real and imaginary anomalous dispersion.[11] Hydrogen atoms were constrained to idealized positions (C–H = 0.95 Å) with isotropic temperature parameters of 1.2 times the thermal parameter of the carbon atom to which they are bonded. The weighting schemes gave no systematic variation of $\Delta F/\sigma$ as a function of F or sin θ. No secondary extinction corrections were made. The computer programs used were those of the Enraf-Nonius Structure Determination Package.[12] Atom coordinates for **3** and **4** are given in Tables II and III and bond distance and angle information for the heterocyclic rings are provided in Tables IV and V. Tables containing the anisotropic thermal parameters and the calculated vs. observed structure factor amplitudes have been deposited as supplementary material.

Table I. Data for the Structure Determinations of 3 and 4

	4	3
	A. Crystal Data	
formula	$TiC_{10}H_{10}S_3N_2$	$TiC_{10}H_{10}S_3N_4$
fw	302.3	330.3
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	*P*2$_1$/*c*
no. of refl in cell detn	25	25
a, Å	7.874 (1)	7.803 (2)
b, Å	13.974 (3)	20.012 (4)
c, Å	21.312 (3)	25.099 (4)
β, deg	90	92.75 (2)
V, Å^3	2345 (1)	3914 (2)
D_{calcd}, g cm^{-3}	1.71	1.69
μ(Mo Kα), cm^{-1}	12.0	11.0
Z	8	12
size, mm	0.22 × 0.22 × 0.10	0.16 × 0.18 × 0.30
total decay	1.2%	0.5%
abs correctn	0.87–1.00	0.95–1.00
	B. Data Collection and Refinement	
total unique refl	2393	4425
obsd data ($I < 3\sigma(I)$)	1121	3609
parameters refined	145	487
R	0.040	0.040
R_w	0.049	0.046
GOF	1.18	1.40
refl/parameter ratio	7.7/1	7.4/1
max shift/error	0.01	0.2
final diff map max, e Å^{-3}	+0.3, −0.4	+0.5, −0.3
p factor of counting statistics for weights	0.05	0.035

Results and Discussion

Reaction of (η^5-C_5H_5)$_2$Ti(CO)$_2$ with S_4N_4. The reaction of (η^5-C_5H_5)$_2$Ti(CO)$_2$ with sulfur yields exclusively the cyclopentasulfide **1** in high yield.[13] The same compound may be made by a variety of methods and is obtained free of contamination by other Ti_xS_y ring sizes.[6,14] These can be obtained by the reaction of **1** with thiophiles or by the use of the more sterically bulky pentamethylcyclopentadienyl ligand on titanium.[14-16] In the reaction of (η^5-C_5H_5)$_2$Ti(CO)$_2$ with S_4N_4 such specificity is not achieved. In addition, because of the availability of both sulfur and nitrogen, a variety of coordination modes can be anticipated. In the two products **3** and **4** nitrogen coordination seems to predominate, perhaps because it is the harder center. Both compounds are crystalline solids which are soluble in most organic solvents. In the solid state they are stable in air for several days but should be stored under an inert atmosphere. In solution they are more susceptible to hydrolysis and rapidly decompose in silica, alumina, and fluorosil columns. The purification thus requires gel permeation methods. We have tried to extend this type of synthesis to the preparation of (C_5H_5)$_2$VS$_x$N$_y$ rings by the reaction of (η^5-C_5H_5)$_2$V with S_4N_4. A vigorous reaction was observed, but the only isolated product was a black insoluble polymer. More tractable materials may be obtained if more sterically bulky organic ligands are employed.

---

(9) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *101*, C24.

(10) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(11) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(12) Enraf-Nonius (1982) Structure Determination Package, Enraf-Nonius, Delft.

(13) Muller, E. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91.

(14) Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823.

(15) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620.

(16) Giolando, D. M.; Rauchfuss, T. B. *Organometallics* **1984**, *3*, 487.

Table II. Positional Parameters for 3 and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
Ti(1)	0.1366 (1)	0.33240 (5)	0.11261 (4)	3.04 (2)
Ti(2)	0.3638 (1)	0.08078 (5)	0.29067 (4)	3.02 (2)
Ti(3)	0.1153 (1)	0.36681 (5)	0.40486 (4)	3.02 (2)
S(1)	−0.1238 (2)	0.29821 (9)	0.21086 (6)	4.22 (4)
S(2)	−0.2064 (2)	0.15727 (9)	0.17046 (8)	5.18 (4)
S(3)	0.0769 (2)	0.16794 (8)	0.09345 (7)	4.70 (4)
S(4)	0.7784 (2)	0.0871 (1)	0.32870 (8)	5.70 (5)
S(5)	0.7057 (3)	0.0930 (1)	0.44646 (8)	7.14 (5)
S(6)	0.3407 (2)	0.04747 (9)	0.42009 (6)	4.98 (4)
S(7)	0.2155 (2)	0.46439 (9)	0.50953 (7)	5.15 (4)
S(8)	0.5103 (2)	0.3774 (1)	0.54971 (7)	6.08 (5)
S(9)	0.3877 (2)	0.26698 (8)	0.47398 (7)	4.66 (4)
N(1)	0.1466 (6)	0.2360 (2)	0.1033 (2)	4.4 (1)
N(2)	−0.0835 (6)	0.1425 (3)	0.1227 (2)	5.0 (1)
N(3)	−0.2068 (6)	0.2280 (3)	0.2001 (2)	4.7 (1)
N(4)	0.0133 (6)	0.3276 (2)	0.1788 (2)	3.9 (1)
N(5)	0.6139 (6)	0.0713 (2)	0.2990 (2)	4.3 (1)
N(6)	0.7926 (7)	0.1003 (3)	0.3911 (2)	6.1 (1)
N(7)	0.506 (7)	0.0749 (3)	0.4501 (2)	5.8 (1)
N(8)	0.3201 (6)	0.0447 (2)	0.3610 (2)	3.8 (1)
N(9)	0.3855 (7)	0.4400 (3)	0.5380 (2)	5.6 (1)
N(10)	0.1251 (6)	0.4245 (2)	0.4661 (2)	4.3 (1)
N(11)	0.4969 (6)	0.3111 (3)	0.5156 (2)	5.2 (1)
N(12)	0.2371 (6)	0.2929 (2)	0.4414 (2)	4.0 (1)
C(1)	0.3775 (7)	0.3351 (3)	0.1764 (3)	4.9 (2)
C(2)	0.43248 (8)	0.3998 (3)	0.1667 (3)	5.2 (2)
C(3)	0.3544 (8)	0.4154 (3)	0.1148 (3)	5.9 (2)
C(4)	0.4208 (7)	0.3592 (4)	0.0908 (3)	5.5 (2)
C(5)	0.4367 (7)	0.3088 (3)	0.1301 (3)	5.2 (2)
C(6)	−0.1289 (7)	0.3217 (3)	0.0615 (3)	4.9 (2)
C(7)	0.0039 (8)	0.3247 (4)	0.0267 (2)	6.6 (2)
C(8)	0.0759 (8)	0.3868 (4)	0.0308 (2)	7.2 (2)
C(9)	−0.0101 (8)	0.4222 (3)	0.0694 (3)	5.6 (2)
C(10)	−0.1367 (7)	0.3817 (3)	0.0871 (3)	4.5 (1)
C(11)	0.3191 (8)	−0.0343 (3)	0.2674 (2)	4.3 (1)
C(12)	0.1623 (7)	−0.0023 (3)	0.2626 (2)	4.7 (1)
C(13)	0.1685 (9)	0.0426 (3)	0.2212 (3)	6.8 (2)
C(14)	0.332 (1)	0.0392 (4)	0.2020 (3)	6.6 (2)
C(15)	0.4208 (8)	−0.0089 (3)	0.2303 (3)	5.1 (2)
C(16)	0.2356 (8)	0.1742 (3)	0.3333 (3)	5.0 (2)
C(17)	0.1705 (8)	0.1718 (3)	0.2815 (3)	5.4 (2)
C(18)	0.303 (1)	0.1842 (3)	0.4292 (3)	6.1 (2)
C(19)	0.4532 (9)	0.1944 (3)	0.2813 (3)	5.5 (2)
C(20)	0.4071 (9)	0.1872 (3)	0.3335 (3)	5.0 (2)
C(21)	−0.1525 (8)	0.3663 (3)	0.3542 (3)	5.6 (2)
C(22)	−0.1063 (7)	0.3024 (3)	0.3600 (3)	4.9 (2)
C(23)	−0.1097 (9)	0.2841 (4)	0.4099 (3)	7.2 (2)
C(24)	−0.1543 (8)	0.3389 (6)	0.4404 (3)	11.0 (3)
C(25)	−0.1817 (7)	0.3901 (4)	0.4027 (3)	8.8 (2)
C(26)	0.1678 (9)	0.4256 (4)	0.3250 (3)	8.5 (2)
C(27)	0.2476 (9)	0.4611 (3)	0.3669 (3)	7.2 (2)
C(28)	0.3808 (7)	0.4225 (3)	0.3871 (3)	4.8 (2)
C(29)	0.3833 (7)	0.3645 (3)	0.3607 (3)	4.5 (1)
C(30)	0.2511 (8)	0.3656 (4)	0.3231 (3)	6.4 (2)

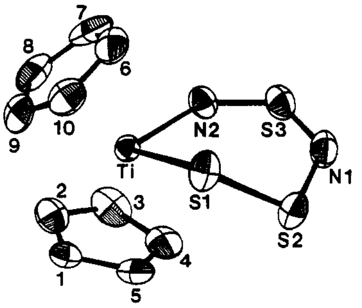


Figure 1. Ortep drawing (50% probability ellipsoids) of 4, showing atom numbering scheme.

Table III. Positional Parameters for 4 and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Ti	0.1595 (1)	0.07509 (7)	0.12459 (4)	2.03 (2)
S(2)	−0.1511 (2)	0.2587 (1)	0.12098 (9)	3.63 (4)
S(1)	0.0347 (2)	0.2041 (1)	0.06401 (8)	3.31 (3)
S(3)	0.0856 (2)	0.2467 (1)	0.22488 (8)	3.21 (3)
N(2)	0.1722 (6)	0.1587 (3)	0.1999 (2)	2.8 (1)
N(1)	−0.0590 (7)	0.2974 (4)	0.1870 (2)	3.3 (1)
C(1)	−0.0038 (8)	−0.0585 (4)	0.0926 (3)	3.4 (1)
C(2)	0.0926 (9)	−0.0874 (4)	0.1449 (3)	3.8 (2)
C(3)	0.041 (1)	−0.0357 (5)	0.1967 (3)	4.1 (2)
C(4)	−0.0925 (9)	0.0255 (5)	0.1777 (3)	4.3 (2)
C(5)	−0.1190 (8)	0.0115 (5)	0.1129 (3)	3.9 (2)
C(6)	0.4025 (9)	0.1531 (5)	0.0791 (3)	4.1 (2)
C(7)	0.4568 (8)	0.1010 (6)	0.1297 (3)	4.5 (2)
C(8)	0.4264 (9)	0.0034 (5)	0.1181 (4)	4.2 (2)
C(9)	0.3567 (8)	−0.0026 (5)	0.0584 (3)	4.0 (2)
C(10)	0.3412 (9)	0.0893 (5)	0.0348 (3)	3.8 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)$ $[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table IV. Bond Distance and Angle Data for 3

Bond Distances (Å)			
Ti(1)–N(1)	1.946 (4)	S(4)–N(6)	1.587 (5)
Ti(1)–N(4)	1.962 (4)	S(5)–N(6)	1.581 (5)
Ti(2)–N(5)	1.962 (4)	S(5)–N(7)	1.601 (5)
Ti(2)–N(8)	1.951 (4)	S(6)–N(7)	1.566 (5)
Ti(3)–N(10)	1.921 (4)	S(6)–N(8)	1.486 (4)
Ti(3)–N(12)	1.962 (4)	S(7)–N(9)	1.555 (5)
S(1)–N(3)	1.566 (4)	S(7)–N(10)	1.500 (4)
S(1)–N(4)	1.490 (4)	S(8)–N(9)	1.605 (5)
S(2)–N(2)	1.597 (4)	S(8)–N(11)	1.579 (5)
S(2)–N(3)	1.599 (4)	S(9)–N(11)	1.585 (5)
S(3)–N(1)	1.482 (4)	S(9)–N(12)	1.491 (4)
S(3)–N(2)	1.566 (4)	C–C(av)	1.372
S(4)–N(5)	1.488 (4)	C–C(range)	1.307–1.411
Bond Angles (deg)			
N(1)–Ti(1)–N(4)	94.4 (2)	S(2)–N(2)–S(3)	144.5 (3)
N(5)–Ti(2)–N(8)	94.8 (2)	S(1)–N(3)–S(2)	149.8 (3)
N(10)–Ti(3)–N(12)	94.6 (2)	Ti(1)–N(4)–S(1)	150.5 (3)
N(3)–S(1)–N(4)	124.3 (2)	Ti(2)–N(5)–S(4)	149.6 (3)
N(2)–S(2)–N(3)	121.8 (2)	S(4)–N(6)–S(5)	147.1 (3)
N(1)–S(3)–N(2)	121.0 (2)	S(5)–N(7)–S(6)	146.5 (3)
N(5)–S(4)–N(6)	123.2 (3)	Ti(2)–N(8)–S(6)	150.9 (3)
N(6)–S(5)–N(7)	121.9 (2)	S(7)–N(9)–S(8)	145.7 (3)
N(7)–S(6)–N(8)	122.7 (2)	Ti(3)–N(10)–S(7)	154.3 (3)
N(9)–S(7)–N(10)	121.9 (2)	S(8)–N(11)–S(9)	147.7 (3)
N(9)–S(8)–N(11)	122.1 (2)	Ti(3)–N(12)–S(9)	150.4 (3)
N(11)–S(9)–N(12)	123.5 (2)	C–C–C (range)	103.7–110.8
Ti(1)–N(1)–S(3)	156.1 (3)		

Table V. Bond Distance and Angle Data for 4

Bond Distances (Å)			
Ti–S(1)	2.426 (2)	S(3)–N(2)	1.504 (5)
Ti–N(2)	1.987 (4)	S(3)–N(1)	1.565 (5)
S(1)–S(2)	2.049 (2)	C–C(av)	1.395
S(2)–N(1)	1.673 (5)	C–C(range)	1.365–1.414
Bond Angles			
S(1)–Ti–N(2)	90.8 (1)	S(2)–N(1)–S(3)	127.1 (3)
Ti–S(1)–S(2)	104.51 (8)	Ti–N(2)–S(3)	138.1 (3)
S(1)–S(2)–N(1)	108.0 (2)	C–C–C(range)	106.7–108.9
N(1)–S(3)–N(2)	121.1 (3)		

Crystal and Molecular Structure of (η^5-C_5H_5)$_2$TiS$_3$N$_2$ (4). Molecules of (η^5-C_5H_5)$_2$TiS$_3$N$_2$ occupy general positions of an orthorhombic unit cell of space group *Pbca*. There are no intermolecular contacts shorter than the sum of the van der Waals' radii of the atoms involved. Although packing forces may well have some effect on the molecule (e.g., the conformation of the C_5H_5 rings), short intramolecular interactions appear to be more important. Molecules of (η^5-C_5H_5)$_2$TiS$_3$N$_2$ (Figure 1) consist of nonplanar six-membered heterocyclic rings as in 4. Each heterocyclic ring adopts a half-chair confor-

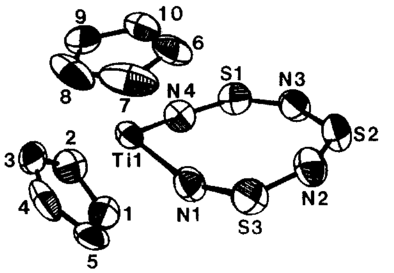


Figure 2. Ortep drawing (50% probability ellipsoids) of **3**, showing atom numbering scheme.

mation similar to that found in S_4N_2,[17] with the five-atom Ti–N(2)–S(3)–N(1)–S(2) sequence planar to within 0.053 (5) Å and the remaining atom S(1) lying 1.070 Å out of this plane. The corresponding half-chair dihedral angle in S_4N_2 is 52.6°. The Ti–S(1) distance of 2.426 (2) Å agrees with the values found in two separate determinations of $(\eta^5\text{-}C_5H_5)_2TiS_5$ (2.425 and 2.435 Å)[13,18] and in $[(\eta^5\text{-}C_5H_4CH_3)_2TiS_3]_2$ (2.425 Å).[15] The S(1)–S(2) distance of 2.049 (2) Å falls within the wide range of S–S distances in the above-mentioned structures and for the S–S bond length in orthorhombic sulfur itself (2.05 Å).[19] The sequence S(2)–N(1)–S(3)–N(2) is planar to within 0.031 Å and contains three significantly different S–N bonds, the variation in which indicates that the valence bond representation shown in **4** is not entirely adequate. The Ti–N(2) distance (1.987 (4) Å) is slightly longer than that found in for $(\eta^5\text{-}C_5H_5)_2Ti(NCO)_2$ (Ti–N(av) = 2.012 Å)[20] and $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$ (Ti–N(av) = 2.085 Å).[21]

The 104.51 (8)° angle at S(1) is over 4° smaller than the Ti–S–S angle found in $(\eta^5\text{-}C_5H_5)_2TiS_5$ (mean value = 108.8°),[13,18] the difference probably arising from ring strain in **4** occassioned by the shorter S–N linkages. Similarly the angle at S(3) (121.1 (3)°) differs from the N–S–N angles in $S_3N_3^-$ (116.6°)[22] and S_4N_2 (122.9°).[17] Here also the differences probably stem from the sizes of the ring bonds.

The geometry about titanium is similar to that observed for many $(\eta^5\text{-}C_5H_5)_2Ti$ complexes[23] and can be described as a distorted tetrahedron, with a N(2)–Ti–S(1) angle of 90.8 (1)° and the angle formed by the titanium to cyclopentadienyl–centroid vectors equal to 131.8°. The small range of Ti–C distances (2.333 (7)–2.406 (6) Å) verifies the η^5-coordination of the cyclopentadienyl rings. The C_5H_5 rings are both planar with d(C–C) ranging from 1.37 (1) to 1.41 (1) Å and average 1.395 Å, as in $(\eta^5\text{-}C_5H_5)_2TiS_5$.

In contrast to the conformational rigidity of $(\eta^5\text{-}C_5H_5)_2TiS_5$, whose C_5H_5 rings are distinguishable at room temperature by ^1H NMR spectroscopy[24] (ΔG^* for the chair inversion process is 76.3 kJ/mol),[25] the half-chair conformation of $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$ is remarkably flexible; its ^1H NMR resonances appear as a simple sharp singlet down to −90 °C at 200 MHz. We have no calculated estimate of the inversion barrier, but note that in S_4N_2,[17] which probably represents an upper limit, the predicted value is approximately 25 kJ/mol.

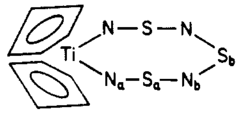
Table VI. Mean Bond Lengths (in Å) of Chemically Distinct Bonds in $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ (3) and $SO_2S_3N_4$ (6)[a]

compd	N_a–S_a	S_a–N_b	N_b–S_b
3	1.489	1.570	1.594
6	1.565	1.550	1.584

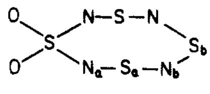
[a] Reference 27.

Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ (3). Molecules of this compound occupy general positions of a monoclinic cell. The asymmetric unit contains three crystallographically independent molecules—a very unusual occurrence; a brief survey of 150 $P2_1/c$ structures in the recent literature showed no precedent. Although there are some short contacts between molecules, intramolecular interactions seem to be much more important. Each of the three independent molecules of $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ consists of an eight-membered heterocycle **3** (Figure 2) in which the seven-atom NSNSNSN sequence is essentially planar. Each molecule possesses approximate C_s symmetry; for all three molecules the corresponding bonds on either side of the pseudo mirror plane are equal to within 3σ's.

There are several gross structural differences in the three molecules, the discussion of which is facilitated by reference to the general labeling scheme shown in **5**. The seven-atom NSNSNSN sequence of molecule 1 is planar to within 0.086 (5) Å, and the titanium is displaced by 0.619 (1) Å. For molecules 2 and 3 the corresponding deviations from planarity are 0.087 (4) and 0.086 (5) Å, respectively, and the titanium displacements 0.824 (1) and 0.703 (1) Å, respectively. The S–N bond distances vary considerably around the rings (see Table VI); the N_a–S_a type form a fairly tight cluster ranging from 1.482 (4) to 1.500 (4) Å, while the S_a–N_b (range 1.555 (5)–1.587 (6) Å) and N_b–S_b (range 1.579 (5)–1.605 (5) Å) are slightly more scattered. The endocyclic angles also show some spread from molecule to molecule and also across each molecule, but by and large the three molecules are remarkably similar; the different crystal environments induce relatively minor fluctuations.



5



6

The geometry about the titanium is similar to that found for $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$. The small range of Ti–C distances (2.354 (4)–2.420 (4) Å) verifies the η^5-coordination of the cyclopentadienyl rings. The length of the Ti to C_5H_5–centroid vector ranges from 2.065 (1) to 2.095 (1) Å with a mean value of 2.08 Å. The angle formed by the vectors is 131.9, 132.7, and 131.5° for molecules 1, 2, and 3, respectively. The N–Ti–N angle is equivalent for the three molecules with a mean of 94.6(2)°. The mean Ti–N distances (1.954 (4), 1.957 (4) Å in **1**, **2**, and **3**, respectively) are shorter than in $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$ (1.987 (4) Å) and $(\eta^5\text{-}C_5H_5)_2Ti(NCO)_2$ (2.012 Å)[20] with one (Ti(3)–N(10)) approaching that found in $[(Me_2N)_2Ti]_2(\mu\text{-}t\text{-Bu})_2$ (1.918 Å).[26] Evidently π-bonding between titanium and the NSNSNSN fragment is substantial (vide infra).

---

[17] Chivers, T.; Codding, P. W.; Laidlaw, W. G.; Liblong, S. W.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1983**, *105*, 1186.

[18] Epstein, E. F.; Bernal, I.; Kopf, H. *J. Organomet. Chem.* **1971**, *26*, 229.

[19] Coppens, P.; Yang, Y. Y.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1977**, *99*, 760.

[20] Anderson, S. J.; Brown, D. S.; Norbury, A. H. *J. Chem. Soc., Chem. Commun.* **1974**, 996.

[21] Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368.

[22] Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517.

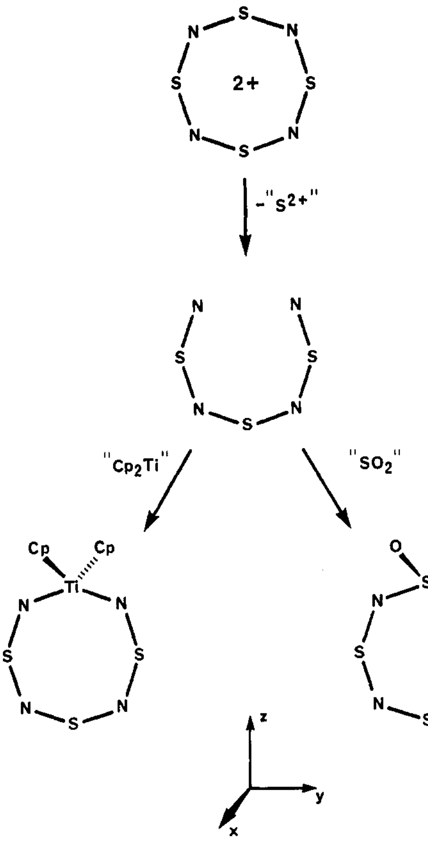
[23] Villa, A. C.; Manfredotti, A. G.; Guastini, C. *Acta Crystallogr., Sect. B: Struct. Crystallog. Cryst. Chem.* **1976**, *32B*, 909 and references therein.

[24] Kopf, H.; Block, B.; Schmidt, M. *Chem. Ber.* **1968**, *101*, 272.

[25] Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* **1978**, *160*, 75.

[26] Thorn, D. L.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 357.

Scheme I



The maximum deviation of a carbon atom from the cyclopentadiene plane is 0.018 (7) Å for C(26). The mean C–C distance is, as noted above, slightly shorter (1.37 Å) than normal. As in the case of $(\eta^5\text{-}C_5H_5)_2TiS_3N_2$, the ^{1}H NMR spectrum of $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ exhibits a single singlet down to −90 °C, indicative of a low barrier to ring inversion.

Electronic Structure of ES_3N_4 Molecules. The above structural account establishes the remarkable uniformity between the three crystallographically independent molecules of $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$. The short Ti–N distances indicate substantial π-bonding between the metal atom and the NSNSNSN ligand, but the variation in the N–S distances, all of which are substantially shorter than a pure N–S bond (1.76 Å), seems at odds with any simple valence bond description. The structural pattern seems even more unusual when compared with that observed in the formally isoelectronic $SO_2S_3N_4$ molecule[27] **6** (Table VI). The dichotomy between these two molecules, particularly with respect to the N_a–S_a linkages, suggests a fairly fundamental difference in their electronic structures. Because of the size of the $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ molecule we have not attempted an all-electron SCF molecular orbital study of its electronic structure. While such a study would undoubtedly be useful, we believe that the underlying electronic factors which dictate the structural trends in both $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and $SO_2S_3N_4$ can be understood by means of a simple Hückel molecular orbital analysis of their respective π-systems. To this end we consider both structures as one-atom perturbations of the 10π-electron $S_4N_4^{2+}$ cation (Scheme I).[28]

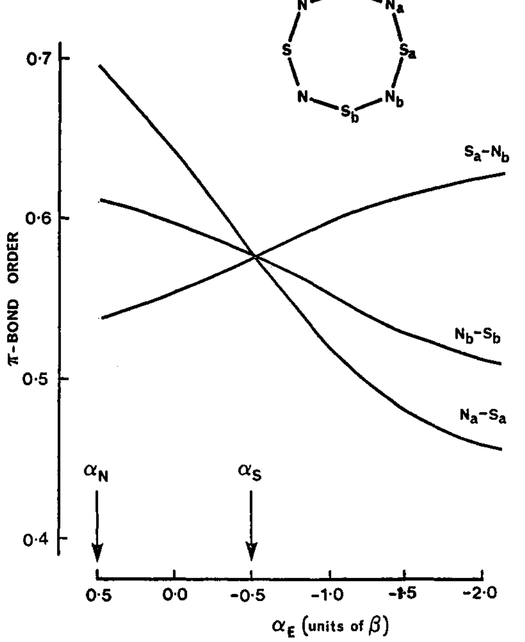


Figure 3. HMO π-bond orders for a planar 10π-electron ES_3N_4 ring, plotted as a function of α_E. All resonance parameters (β's) are assumed equal. Values of α_S and α_N are indicated. Symmetric interactions at E (i.e., the d_{xz} orbital) are assumed.

The question arises as to the nature of the perturbation; what orbitals of the heterogroup ($(\eta^5\text{-}C_5H_5)_2Ti$ or SO_2) are important, and how will they interact with the π-system of the NSNSNSN fragment? If we assume, as seems reasonable, the involvement of the $3d_{xy}$ and $3d_{xz}$ orbitals on the heteroatom, the problem becomes one of determining the relative importance of the two orbitals and also the energetic differences between the 3d orbitals of titanium(IV) and sulfur(VI). Qualitatively the second point is more easily resolved; the 3d orbitals of titanium[29] are much more low lying than those of sulfur.[30]

The structural ramifications of this latter difference are far-reaching and can be demonstrated by a series of HMO calculations on a model ES_3N_4 π-system in which symmetric interactions between the hetero orbital and the S_3N_4 unit are invoked. Figure 3 illustrates the variation in the π-bond orders for the three chemically distinct N–S bonds as a function of the electronegativity of the hetero orbital on E (expressed in terms of its Coulomb parameter α_E). The most notable feature of this plot is the way in which the relative magnitudes of the bond orders, particularly those of the N_a–S_a bond, reverse themselves for electropositive and electronegative perturbations of the $S_4N_4^{2+}$ structure (for which $\alpha_E = -0.5$).

We now have a basis for an understanding of the structural differences between $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and $SO_2S_3N_4$; they can be attributed to the differing energetic characteristics of transition metal and main-group element d orbitals and the consequent extent of mixing of the heterogroup E with the N_3S_4 π-system. However, several caveats must be introduced. We draw attention in particular to the use of a symmetric perturbation (i.e., the d_{xz} orbital) rather than an antisymmetric one (i.e., the d_{xy} orbital). Several consequences of this restriction are worth noting. (1) In the limit of an extremely electropositive

---

(27) (a) Roesky, H. W.; Schaper, W.; Petersen, O.; Muller, T. *Chem. Ber.* **1977**, *110*, 2695. (b) Jones, P. G.; Pinkert, W.; Sheldrick, G. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 827.

(28) (a) Sharma, R. D.; Aubke, F.; Paddock, N. L. *Can. J. Chem.* **1981**, *59*, 3157. (b) Trsic, M.; Laidlaw, W. G.; Oakley, R. T. *Can. J. Chem.* **1982**, *60*, 2281. (c) Gillespie, R. J.; Kent, J. D.; Sawyer, J. R.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1981**, *20*, 3799.

(29) (a) Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639. (b) Bruce, A. E.; Bruce, M. R. M.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 6660. (c) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(30) Coulson, C. A.; Gianturco, F. A. *J. Chem. Soc. A* **1968**, 1618.

perturbation (i.e., large positive α_E values) the π-bond orders calculated for either symmetric or antisymmetric interactions will merge; the model collapses to an open-chain NSNSNSN fragment. (2) For electronegative values of α_E the omission of antisymmetric interactions becomes more serious; their inclusion will tend to offset the trend observed for the symmetric perturbation. The lack of agreement between the lengths of the S_a–N_b and N_b–S_b bonds in $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and the bond orders predicted from the above "symmetric-only" calculations are manifestations of this deficiency.

The above comments notwithstanding, the molecular orbital issues developed here provide an appealing framework for understanding the structural dichotomy between $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and $SO_2S_3N_4$. The fundamental importance of the metal d orbitals in $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ in influencing the structural features of the NSNSNSN fragment are readily apparent. By contrast the structure of $SO_2S_3N_4$ suggests only limited involvement of sulfur d orbitals (on the sulfone moiety) with the delocalized π-system of the NSNSNSN chain. The implications of these conclusions on the interpretation of the electronic spectra of these derivatives is currently being investigated.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the National Science Foundation (EPSCOR Grant ISP 801147), and the State of Arkansas for fianancial support.

Supplementary Material Available: Tables of anisotropic thermal parameters for 3 and 4 and structure factor tables for each structure (53 pages). Ordering information is given on any current masthead page.

Synthesis of Triangular Rhodium–Silver Clusters by the Addition of Silver Electrophiles to an Electron-Rich Rhodium–Rhodium Bond. X-ray Crystal Structure of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}AgO_2CCH_3)]$

Sandra Lo Schiavo, Giuseppe Bruno, Pasquale Piraino, and Felice Faraone*

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Piazza S. Pugliatti, 98100 Messina, Italy

Received November 21, 1985

$[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (1) [dppm = bis(diphenylphosphino)methane] reacts with silver acetate, trifluoroacetate, and diethyldithiocarbamate, AgY, to give the triangular mixed clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgY)]$ (**2**, Y = CH_3CO_2; **3**, Y = CF_3CO_2; **4**, Y = $(C_2H_5)_2NCS_2$); the reactions occur by electrophilic attack of the silver salts on the electron-rich rhodium–rhodium bond of **1**. Compounds **2**–**4** have been spectroscopically characterized; compound **2** has been also characterized by X-ray analysis. Crystals of **2** are orthorombic of space group *Pnma* with $a = 14.426$ (1) Å, $b = 18.134$ (2) Å, $c = 12.614$ (1) Å, and $Z = 4$. The structure was solved and refined to R and R_w values of 0.035 and 0.034 for the 1629 reflections with $I \geq 3\sigma(I)$. In the triangular Rh_2Ag framework the two equivalent Rh–Ag distances are 2.730 (1) Å, and the Rh(1)–Rh(1′) bond distance is 2.751 (1) Å. The rhodium atoms are bridged by CO and dppm ligands and are symmetrically capped by η-cyclopentadienyl ligands. The cyclopentadienyl ligands are in cis position with an interplanar angle of 93.4 (3)° and are located in the less hindered side of the molecule. The acetate group is chelated to the silver atom [Ag–O(2) = 2.432 (7) Å; O(2)–Ag–O(2′) and O(2)–C(8)–O(2′) angles are respectively 51.0 (3)° and 123.7 (13)°]. The Ag, Rh(1), Rh(1′), O(2), and O(2′) atoms form a distorted square-planar pyramid with the silver atom in the apical position. The structural modification of **1** caused by the presence of the bridged AgO_2CCH_3 is discussed. Compound **1** reacts with silver malonate to give $[\{Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)\}_2\{\mu\text{-}Ag_2(CO_2)_2CH_2\}]$ (**5**) in which two triangular Rh_2Ag skeletons are joined by the bridged malonate group.

Introduction

In recent studies several mixed-metal clusters in which a group 11 element, Cu, Ag, or Au, is part of a cluster polyhedron have been reported; while general synthetic routes were developed for the synthesis of mixed-metal clusters containing gold atoms,[1] few systematic methods are available for the introduction of fragments containing silver or copper atoms into a bi- or polynuclear framework.[2] The interest in these studies arises from the isolobal relationship between the proton and the group 11 cations (especially Au(I) as Au(PPh$_3$)[2]) so that the latter react with anionic metal complexes or polynuclear clusters as the H^+ species does. (However, there are exceptions to this correlation, so caution must be exercised in its use.)

Among the mixed-metal complexes containing silver, some show a linear arrangement of metal atoms, as, for example, in $[\{(\eta\text{-}C_5H_5)Rh(CO)PPh_3\}_2Ag]PF_6$,[2a,b] while most of them are closed clusters in which the electrophile Ag^+ or $[AgPPh_3]^+$ bridges two metal atoms[2c,f,h,n] or caps a triangular face of a metal cluster.[2e]

We recently reported the synthesis of the trinuclear mixed-metal clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)]$,[3] $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AuPPh_3)]X$ (X = BF_4, PF_6),[4] and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$[5] by addition of an electrophile containing the metal to the electron-rich rhodium–rhodium bond of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$[6] (1) [dppm = bis(diphenylphosphino)methane]. During these studies we found that in contrast to the $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]X$[5] (X = BF_4, PF_6) complexes, the difluorophosphate derivative is very stable. Thus, the presence