Table I. Comparison of Bond Lengths (Å) and Valency Angles (Deg) in $H_3N{\cdot}BH_2CO_2H$ and Some Structurally Related Compounds

$XH_3YH_2C(O)O(H)$

	$H_3N{\cdot}BH_2$-CO_2H[a]	$\overset{+}{N}H_3CH_2$-COOH[b]	NH_3CH_2-COO^-[c]	CH_3CH_2-COOH[d]
		lengths		
X-Y	1.587 (3)	1.481 (1)	1.475 (1)	1.536
Y-C	1.601 (3)	1.504 (1)	1.525 (1)	1.502
C=O	1.246 (2)	1.202 (1)	1.251 (1)[e]	1.226
C-O	1.321 (2)	1.312 (1)	1.251 (1)[e]	1.324
O-H···O	2.668 (2)			2.644
		angles		
X-Y-C	108.8 (2)	110.3 (1)	111.8 (1)	113.0
Y-C=O	124.2 (2)	123.4 (1)	117.4 (1)[e]	124.0
Y-C-O	116.1 (2)	111.6 (1)	117.4 (1)[e]	113.7
O=C-O	119.7 (2)	125.0 (1)	125.5 (1)	122.2

[a] Present work. [b] Glycine hydrochloride, neutron diffraction: A. R. Al-Karaghouli, M. S. Lehmann, C. F. Miskell, J. J. Verbist, and T. F. Koetzle, *J. Chem. Phys.*., 63, 1360 (1975). [c] α-Glycine, neutron diffraction: L. F. Power, K. E. Turner, and F. H. Moore, *Acta Crystallogr., Sect. B*, **32B**, 11 (1976). [d] F. S. Strieter, D. H. Templeton, R. F. Scheuerman, and R. L. Sass, *Acta Crystallogr.*, 15, 1233 (1962). [e] Equal, owing to the presence of the $-COO^-$ group.

CAD-3 automated diffractometer (Ni-filtered Cu Kα radiation, $\lambda = 1.5418$ Å; θ–2θ scans). Although molecules of **1** exist in the solid state in a form typical of optically inactive or racemic carboxylic acids, i.e., as centrosymmetric dimers (see Figure 1), they have a slightly longer, and thus weaker, 0–H···O hydrogen-bonded distance [O···O = 2.668 (2) Å in **1** vs. ca. 2.64 Å in simple acids[5]]. Dimers of **1** are further associated via interdimer N–H···O hydrogen bonds (N···O = 2.981 and 3.157 Å) involving two of the amino hydrogen atoms, a class of relatively strong intermolecular interactions not available to simple carboxylic acids, and a feature which must be partly responsible for the elevated melting point of **1** compared to propionic acid (−20.8 °C). Bond lengths and valency angles for **1** are presented in Table I along with corresponding values for glycine, glycine hydrochloride, and propionic acid. Comparison of the valency angles at the carboxy groups reveals a significantly smaller difference between the B–C–O and O═C—O angles in **1**[6] (Δ 3.6°) and those in glycine hydrochloride (Δ 13.4°) and propionic acid (Δ 8.5°). In addition, the N–B–C angle in **1** is smaller than that of 114.4 (10)° in $Me_3N{\cdot}BH_2CO_2H$, presumably as a consequence of reduced steric factors in **1**.

Hydrolysis of **1** occurs very slowly as manifested by the observation that a 0.118 M solution of **1** in water underwent only trace decomposition in 3 h. Very slow decomposition of **1** also took place in alkali; e.g., a 0.126 M solution of **1** in 1 N NaOH underwent only 0.33% decomposition in 3 h, with tapering off after that time, only trace amounts of gas being evolved in the following 3 days. In contrast, **1** is readily hydrolyzed in acid; e.g., a 2.23:1 mole ratio of gas to **1** was evolved after 3.5 h from a 0.126 M solution of **1** in 1 N HCl, and this increased to 2.27 after 20.5 h, by which time gas evolution was complete. A total of 2 mol of H_2 per mol of **1** would be anticipated, assuming that only hydrolysis of the B–H bonds occurs. However, IR analysis of the evolved gas showed that it contained CO, a fact which may be indicative of the involvement of a carbonyl intermediate, $[H_3N{\cdot}BH_2CO]^+$, which could undergo subsequent hydrolysis to yield CO and H_2. That compound **1** is reasonably thermally stable was demonstrated by heating 0.778 mmol of **1** in an evacuated flask at 60 °C for 8 h when only 0.55 mol % was found to be decomposed.

Significant antitumor[7] and antihyperlipidemic[8] activities were found when dosages of 20 mg/kg per day of **1** were administered to CF_1 male mice; the LD_{50}[9] is >0.2 g/kg. In the Ehrlich ascites screen, inhibition of tumor growth was 76.5% for **1**, while lowering of the serum cholesterol level was 44% after 9 days and 60% after 16 days.

Acknowledgment. This research was supported in part by the Army Research Office. M.K.D. thanks the authorities of Jadavpur University, India, for a leave of absence.

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(5) I. Nahringbauer, *Acta Chem. Scand.*, **24**, 453 (1970); F. J. Strieter, D. H. Templeton, R. F. Scheuerman, and R. L. Sass, *Acta Crystallogr.*, **15**, 1233 (1962); F. J. Strieter and D. H. Templeton, *ibid.*, **15**, 1240 (1962); R. F. Scheuerman and R. L. Sass, *ibid.*, **15**, 1244 (1962).

(6) A like difference (Δ 5.6°) was found in $Me_3N{\cdot}BH_2CO_2H$.

(7) According to standard procedures, see: C. Piantadosi, C. S. Kim, and J. L. Irwin, *J. Pharm. Sci.*, **58**, 821 (1969). The control in this screen, 6-mercaptopurine, showed 99% inhibition.

(8) Serum cholesterol was assayed by means of the Lieberman–Burchard reaction. The control in this assay, clofibrate, which requires 300 mg/kg for significant antihyperlipidemic activity, showed 98% inhibition.

(9) The LD_{50} value was determined by use of the method of J. T. Litchfield and F. Wilcoxon, *J. Pharmacol. Exp. Ther.*, **96**, 99 (1949).

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Received December 10, 1979

Synthesis, Structure, and Equilibration of *s*-Cis- and *s*-Trans-η^4-conjugated Diene–Zirconocene Complexes

Sir:

For numerous cases, it has been demonstrated that acyclic conjugated dienes when η^4 bound to a transition-metal center favor the *s*-cis arrangement over the *s*-trans geometry,[1] independent of the preferred conformation adopted by the free ligand.[2] We have for the first time obtained conclusive evidence that a conjugated diene can bind very well to a single metal atom through both double bonds and still in principle retain its favored transoid geometry. We report several examples of η^4-diene–zirconocene complexes where the '*s*-trans isomer' has been found equal (or even higher) in thermodynamic stability to the corresponding '*s*-cis' form, depending on the substitution of the polyolefin.

We recently observed that photochemical activation of diarylzirconocene complexes yields biaryls formed strictly by intramolecular coupling.[3] This photoreaction can be very efficiently used to generate and transfer the elusive bis(η^5-cyclopentadienyl)zirconium(II) to a variety of substrates. If the photolysis of diphenylzirconocene (2% in toluene, −30 °C, HPK 125, Pyrex filter) is carried out in the presence of suitable conjugated dienes (10% excess), the corresponding monomeric η^4-diene–zirconocene complexes are formed.[4] After workup at ambient temperature and fractional crystallization from toluene, we isolated $Cp_2Zr(\eta^4\text{-diene})$ complexes [diene = 1,3-butadiene (**1**, **1a**), isoprene (**2**), 2,3-dimethylbutadiene (**3**), *trans,trans*-

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(1) Systems showing an *s*-trans-conjugated diene bridging a metal–metal bond have been reported: Sasse, H. E.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1972**, *392*, 167–172. Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 1976–1980.

(2) Tai, C. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *98*, 7928–7932. Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *Ibid.* **1979**, *101*, 3657–3659.

(3) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189–202. See also: Rausch, M. D.; Boon, W. H.; Alt, H. G. *Ibid.* **1977**, *141*, 299–312. Rausch, M. D.; Boon, W. H.; Mintz, E. A. *Ibid.* **1978**, *160*, 81–92.

(4) Instead of the formation of isolable complexes, with some substrates catalytic isomerizations and hydrogen-transfer reactions occur; e.g., benzene and cyclooctene are obtained from a 1:1 mixture of any of the cyclohexadiene plus cyclooctadiene isomers.

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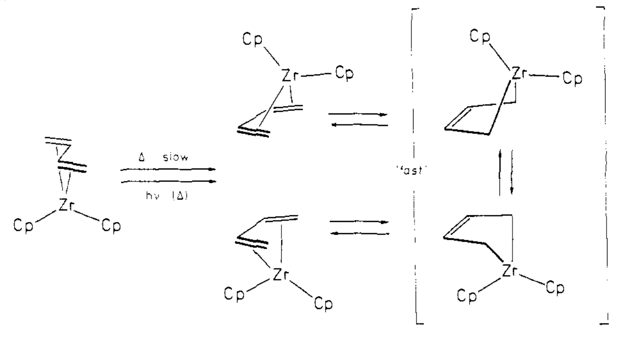
Table I. Equilibrium and Activation Parameters for Cp_2Zr–(*s-cis*- and *s-trans*-diene) Complexes

parameters	7	3	2	5	1	4	6
s-cis/*s*-trans[a]	100/–	100/–	100/–	100/–	55/45	40/60	5/95
$\Delta G^{\ddagger}$ rearrange (T, °C)[b]		18.2 (–25)	19.6 (–14)	21.0 (+5)	22.7 (+10.5)		
$\Delta G^{\ddagger}$ exchange (T, °C)[c]	10.8 (–58) [10.6 (–40)]	11.5 (–42) [11.1 (–30)]	12.2 (–29)	8.0 (–112) [7.9 (–100)]	12.6 (–19.5)		

[a] At 25 °C. [b] *s*-Trans → *s*-cis, kcal mol^{-1}. [c] Mutual exchange of diastereotopic Cp groups [CH_2 protons], kcal mol^{-1}.

Scheme I



1a 1 1b

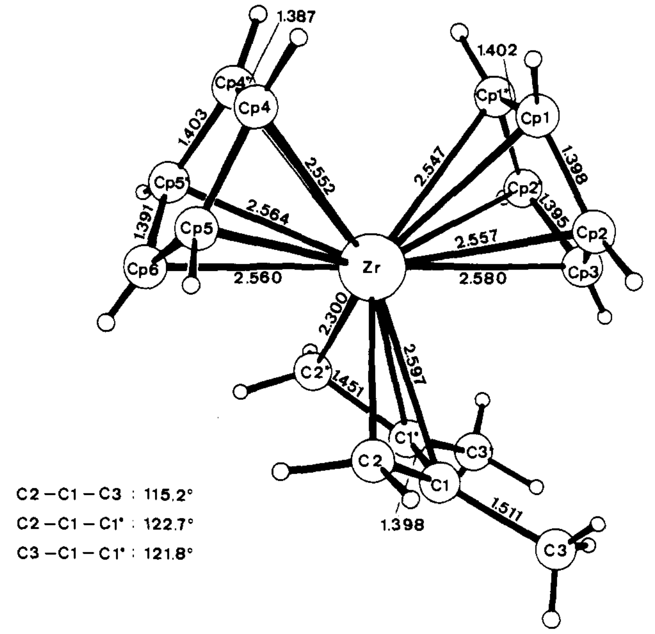


Figure 1. Molecular structure of Cp_2Zr(*s-cis*-C_6H_{10}) (**3**).

2,4-hexadiene (**4**, **4a**), 2,3-diphenylbutadiene (**5**), *trans,trans*-1,4-diphenylbutadiene (**6a**), 1,2-dimethylenecyclohexane (**7**), and 2,3-dimethylenenorbornane (**8**)] as red crystalline solids (30–60% yield). Complexes **1** and **4** were obtained as mixtures with the isomeric complexes **1a** (45%) and **4a** (60%). **1** can be completely isomerized to **1a** photochemically.[5] In this way, diene complexes **2**, **3**, and **5** also can be converted to isomeric complexes **2a**, **3a**, and **5a**. A similar photochemical isomerization of the zirconocene complexes **7** and **8** which contain conjugated dienes fixed in the *s*-cis geometry could not be observed. The relative thermodynamic stability of the isomers appears to be quite substituent dependent. Since the barrier of the thermal equilibration is relatively low (Table I), the photochemical isomerizations have to be performed at sufficiently low temperatures.[6]

By these procedures, we thus obtained two sets of monomeric bis(η^5-cyclopentadienyl)(diene)zirconium isomers whose structural relation is characteristically reflected by their spectroscopic data. From IR and NMR spectra, a η^4-bonding mode of the diene unit for both types of complexes in solution is implied.[7] The X-ray crystallographic analyses (see below) reveal that the isomeric forms differ only in the conformation adopted by the η^4-diene ligand and identify them as zirconocene-(*s-cis*- and *s-trans*-diene) complexes.

The isomers can readily be distinguished by NMR. J_{HH} coupling constants on the order of 10.5 (*s*-vicinal), 12.5 ('trans'-vicinal), and 10 Hz (geminal) have been found for the coordinated *s-cis*-diene.[8] The zirconocene–*s-cis*-diene complexes **1–5**, **7**, and **8** characteristically exhibit nonequivalency of the Cp ligands. At ambient temperature, however, for **1–3**, **5**, and **7**, this effect becomes obscured by a dynamic process, leading to a rapid pairwise equilibration of Cp groups as well as 'syn' and 'anti' hydrogens at the diene termini. From variable temperature ^1H and ^{13}C NMR spectra for a given complex, within experimental accuracy, identical activation barriers for both interconversions of diastereotopic groups are obtained (Table I), suggesting they occur by the same chemical process. This automerization observed only for Cp_2Zr(*s*-cis-diene) isomers can easily be explained by a rapid migration of the Cp_2Zr unit from one face of the diene ligand to the other via an intermediate metallacyclopentene (Scheme I).[9,10]

The solid-state structure of bis(η^5-cyclopentadienyl)(η^4-*s-cis*-2,3-dimethylbutadiene)zirconium (**3**)[11] indicates that the interconversion between the η^4-diene complex and the intermediate metallacyclopentene could well be a facile process requiring only relatively small changes in the molecular geometry. The metal atom in **3** (Figure 1) is pseudotetrahedrally coordinated to two η^5-Cp groups (Cp–Zr–Cp = 124°) and the double bonds of a planar *s-cis*-2,3-dimethylbutadiene ligand. From covalent radii, it appears that interaction of the metal with all four carbon atoms of the diene framework is given. However, the bond lengths indicate considerably stronger bonding to the diene termini than to C2–C3 (Zr–C1 = 2.300 Å, Zr–C2 = 2.597 Å). Comparison with other η^4-diene–metal complexes suggests that the structure of **3** is almost approaching the limiting metallacyclic σ^2,π-bonding situation. This interpretation is in accord with the observed bond lengths within the diene unit (C1–C2 = 1.451 Å, C2–C3 = 1.398 Å).[12]

The *s-trans*-diene complexes **1a–6a** show a spectroscopic behavior distinctly different from their *s-cis*-diene isomers. Except for **2a**, these compounds each possess equivalent Cp groups. In

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(5) HPK 125, Pyrex filter. **1**: UV (ether) λ_{max} 430 nm (ϵ 875). **1a**: λ_{max} 365 nm (sh).

(6) For all complexes isolable at ambient temperature, satisfactory analytical (C, H) or molecular weight data were obtained.

(7) (a) There is no evidence for the presence of uncomplexed C=C bonds in the solution IR spectra. (b) ^{13}C NMR data of the butadiene ligand (benzene, relative to Me_4Si, gated decoupled). **1**: δ 112.0 (d, J_{CH} = 156 Hz), 49.0 (t, J_{CH} = 144 Hz). **1a**: δ 96.0 (d, J_{CH} = 152 Hz), 59.0 (dd, J_{CH} = 149, 159 Hz). ^1H NMR (toluene-d_8, –53 °C), **1**: δ 4.85 (m, 2 H), 3.15 (br t, 2 H), –0.70 (br t, 2 H). **1a**: δ 3.2 (m, 2 H), 2.9 (m, 2 H), 1.2 (m, 2 H). See for a comparison: Preston, H. G., Jr.; Davis, J. C., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 1585–1586. Retcofsky, H. L.; Frankel, E. N.; Gutowsky, H. S. *Ibid.* **1966**, *88*, 2710–2712. Datta, S.; Wreford, S. S.; Beatty, R. P.; Mc Neese, T. J. *Ibid.* **1979**, *101*, 1053–1054. Beatty, R. P.; Datta, S.; Wreford, S. S. *Inorg. Chem.* **1979**, *18*, 3139–3145. (c) Coinciding with our work, the syntheses of (*s-cis*-diene) complexes **1**, **2**, and **3** by an independent route have been reported: Yasuda, H.; Kajihara, Y.; Nakamura, A. IX International Conference on Organometallic Chemistry, Dijon, 1979; Abstr. C 47.

(8) Obtained from complexes of substituted dienes.

(9) An analogous process has been observed for (a) cationic CpMo-$(CO)_2(\eta^4$-diene) (Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858–4859) and (b) $(C_8H_8)M(\eta^4$-diene), M = Zr, Hf (Wilke, G., personal communication).

(10) The Gibbs activation energies obtained (Table I) are approaching the limiting value expected for a rate-determining dynamic process whose barrier is primarily determined by the torsional potentials of two Cp_2Zr–C σ bonds: Jefferey, J.; Lappert, M. F.; Tuyet Luong-Thi, N.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081–1083. Jordan, R. F.; Tsang, E.; Norton, J. R. *J. Organomet. Chem.* **1978**, *149*, C53–56.

(11) **3** crystallizes in the orthorhombic space group *Pnma*. Cell dimensions: a = 8.0077 (9), b = 11.725 (1), c = 14.4515 (8) Å; Z = 4; Zr at position c (International Tables) (symmetry m). R = 0.029 (R_w = 0.044) for 2266 reflections, of which 652 were considered unobserved (2σ).

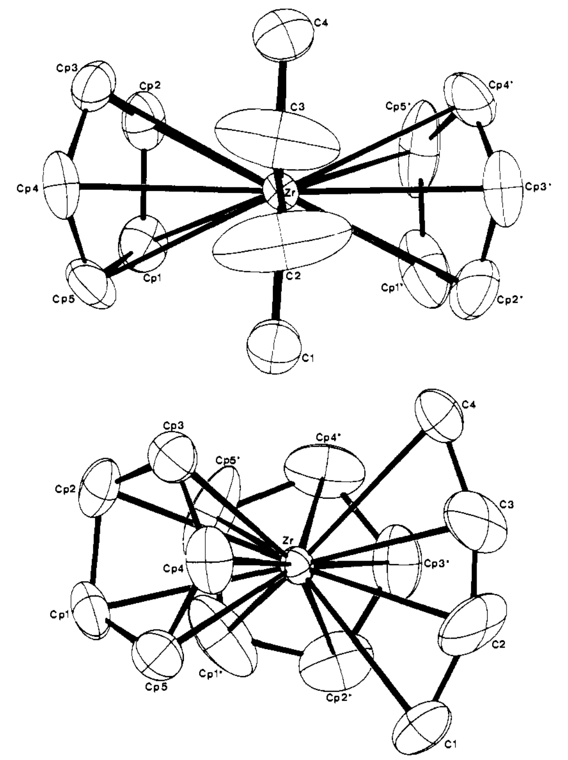

Figure 2. Views of the molecular geometry of $Cp_2Zr(s\text{-}trans\text{-}C_4H_6)$ (**1a**).

the NMR spectra for the diene unit, a substantial deshielding of terminal carbon atoms C1–C4 and the adjacent anti hydrogens, a negligible influence on the syn H absorption, and a considerable upfield shift for internal carbon atoms C2–C3 and the accompanying protons are observed in comparison to the *s*-cis isomers.[7b,13] A characteristic set of proton coupling constants is observed, showing decreased J_{HH}(geminal) (4.5–5.5 Hz) and increased J_{HH}(vicinal) values (*s*-vicinal ~ 14, trans ~ 16 Hz).[8]

The crystal structure of **1a** is somewhat obscured by relatively high thermal motion of the central two carbon atoms of the diene ligand. The conformation of the ligand, however, can be assigned as *s*-trans (Figure 2). Again, pseudotetrahedral coordination of zirconium prevails. The molecule has, in contrast to **3**, only approximate C_2 symmetry; the diene ligand is located in a plane bisecting the Cp–Zr–Cp (126°) group. Whereas geometrical features of the Cp_2Zr unit are similar to those given for **3**, the Zr–C(diene) distances are longer (2.48 Å) for the terminal sites than for the central carbon atoms (2.33 Å). C–C distances within the ligand are artificially shortened.

Our results demonstrate that coordination of a conjugated diene in the *s*-trans geometry does not necessarily require two metal centers as has been stressed in the literature[1b,13] but can be observed in a monometal system as well. However, in view of the number of diene complexes studied in the past, it appears surprising that a mononuclear *s-trans*-diene complex has, to our knowledge, never been isolated before. Therefore, one is tempted to speculate that the unusual ability of the zirconocene unit to bind a diene *s*-trans conformer might be a special feature of this system. Bent metallocenes differ from other coordinatively unsaturated complexes by an arrangement of orbitals available for bonding to additional ligands exclusively in one plane (bisecting the Cp–M–Cp angle).[15] It is conceivable that such an orientation could create a slightly less favorable bonding situation for a *s-cis*-diene than usual and favor the coordination of the more 'linearly' arranged *s*-trans rotamer. The pronounced substituent effect on the ratio of the *s*-cis/*s*-trans equilibrium (Table I) demonstrates how severely the Cp_2Zr–diene system is affected by energetically small variations in the diene ligand.

The observation of stable isolable *s-trans*-diene complexes makes it a fascinating alternative to postulate analogous short-lived intermediates being responsible for the observed stereochemical course of catalytic conversions of conjugated dienes.[16] Therefore, we are currently studying the differences of the chemistry of η^4-*s*-cis- and *s*-trans-conjugated diene–metallocene complexes.

Acknowledgment. We thank Professor G. Wilke for very helpful and stimulating discussions.

Supplementary Material Available: Atomic coordinates and thermal parameters for **3** and **1a** (3 pages). Ordering information is given on any current masthead page.

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[13] Similar ^{1}H NMR chemical shift differences for a $(s\text{-}cis\text{-}C_4H_6)Os$ unit and a bridging $(s\text{-}trans\text{-}C_4H_6)Os\text{–}Os$ unit have been reported for isomeric osmium–diene complexes: Tachikawa, M.; Shapley, J. R.; Haltiwanger, R. C.; Pierpont, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 4651–4652.

[14] **1a** crystallizes in the monoclinic space group $P2_1/n$. Cell dimensions: $a = 7.687$ (1), $b = 11.503$ (1), $c = 13.4553$ (8) Å; $\beta = 92.553$ (7)°; $Z = 4$. $R = 0.038$ ($R_w = 0.046$) for 3421 reflections, of which 785 were considered unobserved (2σ).

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Received August 20, 1979

Synthesis and Reactivity of Several Trithiocarbamate Complexes of Osmium(III) and the Crystal and Molecular Structures of $[Os_2(S_3CNMe_2)_2(S_2CNMe_2)_3]PF_6$ and $Os_2(S_5)(S_3CNEt_2)(S_2CNEt_2)_3$

Sir:

The existence of trithiocarbamate ligand, $S_3CNR_2^-$, has been in question for some time.[1,2] This ligand is important since it has been proposed to be a key intermediate in rubber vulcanization accelerated by zinc dithiocarbamates and related compounds.[2,3] In addition, such "sulfur-rich" species are important with respect to sulfur transport between organic and metallo compounds.[4,5] Until recently,[6] there were no examples of trithiocarbamate ligands although one attempted synthesis has been published.[7] This is surprising since metal complexes of trithiocarboxylates, S_3CR^-, have been known for some time.[1,4,8,9] Our recent success[6] at isolating the first trithiocarbamate complex of osmium(III), $[Os_2\text{-}\mu\text{-}(S_3CNEt_2)_2(S_2CNEt_2)_3]BPh_4$, in very low yield (<3% as a byproduct of the reaction of $(NH_4)_2[OsCl_6]$ with NaS_2CNEt_2 in $MeOH/H_2O$ solution) has prompted us to react $Os(S_2CNR_2)_3$, R = Me or Et,[10] with elemental sulfur. This reaction has led to the synthesis of a new and novel mixed trithiocarbamate–S_5–dithiocarbamate complex, $Os_2\text{-}\mu\text{-}(S_5)\text{-}\mu\text{-}(S_3CNR_2)(S_2CNR_2)_3$ (I)

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