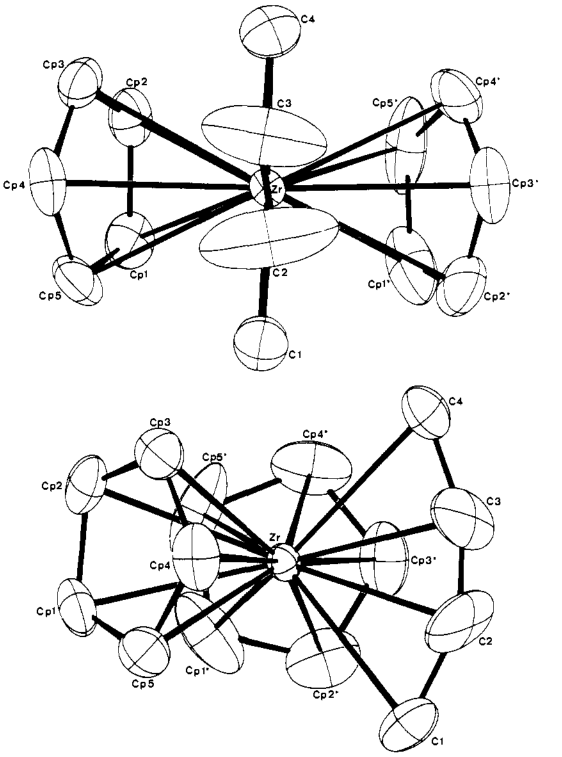

Figure 2. Views of the molecular geometry of $Cp_2Zr(s\text{-}trans\text{-}C_4H_6)$ (**1a**).

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–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.

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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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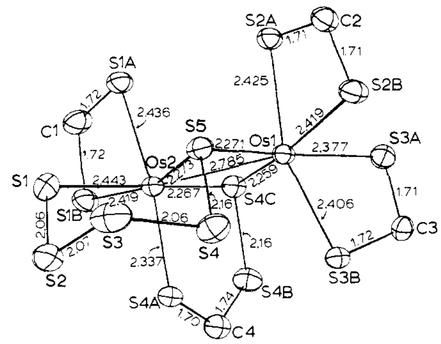

Figure 1. ORTEP drawing (ellipsoids at 30% probability surfaces) and labeling scheme for complex I with selected distances. Esd in distances (Å): Os–Os, 0.001; Os–S, 0.003; S–S, 0.005; S–C, 0.01 Å. Important angles are the following: S1A–Os2–S1B, 71.7 (1); S2A–Os1–S2B, 71.8 (1); S3A–Os1–S3B, 72.8 (1); S4A–Os2–S4C, 90.8 (1); S1–Os2–S5, 86.0 (1); Os2–S4C–S4B, 106.4 (2); Os2–S5–S4, 113.0 (2); Os1–S5–Os2, 75.6 (1); Os1–S4C–Os2, 75.9 (1); S5–Os2–S4C, 104.0 (1); S5–Os1–S4C, 104.3 (1)°.

(60% yield), in addition to $[Os_2\text{-}\mu\text{-}(S_3CNR_2)_2(S_2CNR_2)_3]PF_6$ (II) (10% yield), where R = Me and Et. These complexes (I, R = Et; II, R = Me) have been characterized by single-crystal X-ray diffraction. Importantly, compound I is converted into II in good yield by reaction with tetraalkylthiuram disulfide, R_4tds, and compound II is partially converted into its dithiocarbamate analogue $[Os_2\text{-}\mu\text{-}(S_2CNR_2)_2(S_2CNR_2)_3]PF_6$[6] by reaction with nucleophiles such as $P(n\text{-}C_4H_9)_3$ and $P(OMe)_3$. These complexes and their reactions have important implications in the mechanism of sulfur exchange between metal–dithiocarbamate complexes and sulfur.

Complexes I and II were prepared and isolated as follows. $Os(S_2CNR_2)_3$ (0.5 mmol) and elemental sulfur (2.4 mmol as S) were heated together to reflux in DMF solution and immediately cooled. The residue which remained upon vacuum distillation of the DMF was extracted into CH_2Cl_2, followed by column chromatography with alumina (Alcoa F-20). Complex I was isolated as a brown band by using acetone/CH_2Cl_2 (10:90 v/v) as eluent while II was eluted as a brown band by using MeOH. The PF_6^- salt of II was formed by the addition of $NaPF_6$ in MeOH to the collected fraction. Crystallization of I and II was acheived by using CH_2Cl_2/EtOH and CH_3CN/toluene solvents, respectively. Both compounds were found to be pure by elemental analysis and ^{1}H NMR spectroscopy.[11]

The structures of I (R = Et) and II (R = Me) were determined by single-crystal X-ray diffraction.[12] The coordination core

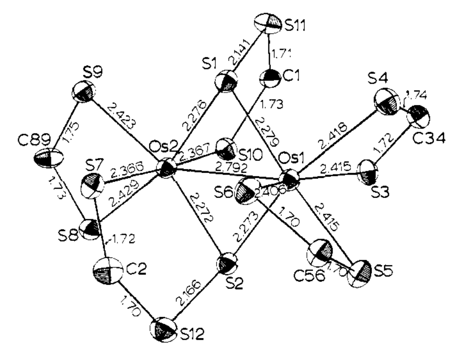

Figure 2. ORTEP drawing (ellipsoids at 30% probability surfaces) and labeling scheme for complex II with selected distances. Esd in distances (Å): Os–Os, 0.001; Os–S, 0.003; S–S, 0.005; S–C, 0.02 Å. Important angles are the following: S3–Os1–S4, 72.3 (1); S5–Os1–S6, 71.9 (1); S8–Os2–S9, 71.9 (1); S1–Os2–S10, 90.9 (1); S2–Os2–S7, 91.2 (1); Os2–S1–S11, 106.8 (2); Os2–S2–S12, 106.6 (2); Os1–S1–Os2, 75.6 (1); Os1–S2–Os2, 75.8 (1); S1–Os1–S2, 104.2 (1); S1–Os2–S2, 104.3 (1)°.

geometries for I and II are shown in Figures 1 and 2, respectively. Both structures contain similar binuclear $S_4Os(\mu\text{-}S)_2OsS_4$ cores[14] which possess Os(III)–Os(III) metal–metal bonds. This interaction accounts for the observed diamagnetism of both complexes. The Os–Os distances are essentially the same in both compounds [average 2.789 (1) Å]. Complex I contains a novel S_5^{2-} half-bridging bidentate ligand and one half-bridging bidentate $S_3CNEt_2^-$ ligand similar to that observed in $[Os_2\text{-}\mu\text{-}(S_3CNEt_2)_2(S_2CNEt_2)_3]BPh_4$.[6] The three $S_2CNEt_2^-$ ligands in I have normal bidentate geometries. This structure contains the first example of a S_5^{2-} ligand chelated in a bridging mode although there are several examples of nonbridged chelated S_5^{2-} ligands.[15–17] The Os–S(SCNR$_2$) distances and the $S_2CNR_2^-$ ligand geometries are essentially identical in the two structures [Os–S, average 2.413 (3) and 2.417 (3) Å; S–Os–S intraligand "bite" angle, average 72.1 (1) and 72.0 (1)°, in I and II, respectively]. The nonbridging Os–S(S_2CNR_2) distances are similar in both structures [average 2.357 (4) Å] and are shorter than the Os–S(SCNR$_2$) distances. The bridging Os–S(S_2CNR_2) distances and Os–S–Os angles are also similar in the two structures [average 2.268 (3) and 2.275 (3) Å; 75.76 (1) and 75.70 (1)°, in I and II, respectively], and therefore this Os_2S_2 bridge arrangement represents a very favorable bonding configuration. Additionally, the Os–S(bridging) distances are considerably shorter than the Os–S(nonbridging) distances. The S–C distances in I and II are all nearly identical, whether in a $S_3CNR_2^-$ ligand or in a $S_2CNR_2^-$ ligand, and range from 1.70 (1) to 1.75 (1) Å with an average value of 1.72 Å. The S–S bond distances in the $S_3CNR_2^-$ ligands in both complexes are identical within experimental error [average 2.156 (5) Å] and are the same as the S–S(bridging) bond distances in the S_5^{2-} ligand. The remaining distances and angles within the S_5^{2-} ligand and the overall chair conformation of the six-membered ring are similar to those in known metal complexes with chelating S_5^{2-} ligands.[15–17]

The $S_2C\text{–}NR_2$ distances in I and II are the same within experimental error [average 1.34 (1) and 1.32 (2) Å for I and II, respectively] and are similar to values observed in other complexes.[6] The $S_3C\text{–}NR_2$ distances are not significantly different from the $S_2C\text{–}NR_2$ distances and have values of 1.36 (1) Å in I and average 1.34 (2) Å in II. The ^{1}H NMR spectra of I and II (R = Me, 25 °C; $CDCl_3$ and CD_3CN solvents, respectively)

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(11) Anal. Calcd for I, R = Et ($Os_2C_{20}H_{40}N_4S_{14}$): C, 20.60; H, 3.46; S, 38.61. Found: C, 20.80; H, 3.57; S, 38.50. Calcd for II, R = Me ($Os_2C_{15}H_{30}N_5S_{12}PF_6\cdot C_7H_8$): C, 20.60; H, 2.99; N, 5.46; S, 30.00. Found: C, 20.52; H, 2.99; N, 5.45; S, 30.26. ^{1}H NMR (80 MHz, Varian CFT-20), I ($CDCl_3$, 25 °C, R = Me): δ 3.514 (s, 2), 3.353 (s, 1), 3.284 (s, 1), 3.215 (s, 1), 3.078 (s, 2), 3.037 (s, 1). II (CD_3CN, 25 °C, R = Me): δ 3.601 (s, 1), 3.364 (s, 1), 3.295 (s, 1), 3.271 (s, 1), 3.014 (s, 1). Excellent analyses were also obtained for the R = Me or Et analogues.

(12) Compound I, R = Et, crystallizes in the monoclinic space group $P2_1/c$ with lattice constants a = 11.769 (2), b = 10.771 (2), c = 30.882 (4) Å; β = 100.24 (1)°; ρ_{calcd} = 2.010 g cm^{-3} ($\rho_{measured}$ = 1.93 g cm^{-3}) for Z = 4. 6037 unique reflections were collected over one quadrant in the scan range 2θ = 0–48° by using a variable-rate ω scan technique. Least-squares refinement based on 3447 observed [$F_o^2 \geq 3.0\sigma(F_o^2)$] reflections (359 variables) led to a final R value of 0.038. Compound II, R = Me, crystallizes as a toluene solvate in the triclinic space group $P\bar{1}$ with lattice constants a = 6.294 (2), b = 15.820 (5), c = 21.065 (7) Å; α = 96.17 (3), β 93.76 (3), γ = 91.10 (2)°; ρ_{calcd} = 2.048 g cm^{-3} ($\rho_{measured}$ = 2.14 g cm^{-3}) for Z = 2. 6276 unique reflections were collected over one hemisphere in the scan range 2θ = 0–48° by using a variable-rate ω–2θ scan technique. Least-squares refinement based on 4032 observed [$F_o^2 \geq 3.0\sigma(F_o^2)$] reflections (398 variables) led to a final R value of 0.055. For both structures, the data were collected on a CAD4 automatic diffractometer with graphite monochromatized Mo Kα (λ = 0.71069 Å) radiation and was corrected for absorption effects (μ = 77.5 and 71.6 cm^{-1} for I and II, respectively).[13] All nonhydrogen atoms were refined with anisotropic thermal parameters except for two disordered terminal methyl carbon atoms in I and the toluene solvate carbon atoms in II. At this stage of refinement, H atom positions have not been included.

(13) The details of data collection, reduction, and refinement, including references of the crystallographic computer programs used, may be found in the reference: Wang, H. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 1470.

(14) The binuclear coordination cores of I and II are identical in composition, $S_4Os(\mu\text{-}S)_2OsS_4$; however, they have different diastereomeric configurations. In I, the two Os centers have opposing chiralities (Δ and Λ, assuming tris-chelate coordination) whereas in II they are the same.

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show signals which are consistent with slow S_xC-NMe_2 bond rotation.[11]

The conversion of I into II by reaction with R_4tds demonstrates that the half-bridging S_5 ligand is a likely intermediate in the formation of the half-bridging S_3CNR_2 ligand. Presumably, the μ-S atom of the S_5 ligand is incorporated into the S_3CNR_2 group. This is reasonable since the $Os_2(\mu\text{-}S)_2$ bonding arrangement is very favorable and probably quite stable (vide supra). It is likely that the formation of the half-bridging S_3CNR_2 ligand in these complexes results from initial activation of S_8 by $Os(S_2CNR_2)_3$, subsequent loss of a S_2CNR_2 radical, and dimerization into species which contain a $Os(\mu\text{-}S_5)Os$ arrangement such as found in I. The formation of the half-bridging S_3CNR_2 ligand could then proceed by the attack of a S_2CNR_2 radical on the μ-S followed by displacement of anionic sulfur radical species. R_4tds is well-known to produce S_2CNR_2 radicals thermally,[18] and therefore the conversion of I into II by reaction with R_4tds is consistent with this mechanism. It is also noteworthy that reaction of I with $S_2CNR_2^-$ does *not* lead to the formation of II. The recently discovered ability of $Os(S_2CNR_2)_3$ to dimerize by expanding its coordination core[19] may be important in these reactions with S_8, and consequently in the formation of S_3CNR_2 ligands. Once formed, the trithiocarbamate half-bridging ligand is very stable since 20% conversion of II into its "nonsulfur rich" analogue by reaction with nucleophiles such as $P(n\text{-}C_4H_9)_3$ requires 4 h in refluxing CH_2Cl_2 solutions. Work in progress is directed toward synthesizing trithiocarbamate complexes of different metals and coordination modes.

Acknowledgment. This research was supported by the National Science Foundation (NSF Grant CHE-78-21840). We also thank the NSF for partial support of our X-ray diffraction and structure-solving equipment (NSF Grant CHE-77-28505) and Engelhard Industries for a generous loan of OsO_4.

Supplementary Material Available: Atom-labeling scheme, positional coordinates, and thermal parameters for $Os_2(S_5)(S_3CNEt_2)(S_2CNEt_2)_3$ and $[Os_2(S_3CNMe_2)_2(S_2CNMe_2)_3]PF_6\cdot C_7H_8$ (6 pages). Ordering information is given on any current masthead page.

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Dimolybdenum: Nature of the Sextuple Bond

Sir:

Flash photolysis of $Mo(CO)_6$ has been shown to generate gaseous dimolybdenum, Mo_2,[1] a species which has also been trapped in inert gas matrixes.[2] Spectroscopic studies on the gas-phase species, which was presumed to have a $^1\Sigma_g^+$ ground state, have led to the following molecular parameters: R_e = 1.929 Å, ω_e = 477 cm^{-1}, $\omega_e x_e$ = 1.51 cm^{-1}, and $D_0°$ = 95 ± 15 kcal mol^{-1}. The reported molybdenum–molybdenum bond length in this molecule, if correct, is more than 0.1 Å shorter than that of any known Mo–Mo quadruple bond,[3] indicative of a bond order in Mo_2 that is probably greater than four. An SCF-Xα-SW calculation[4] on Mo_2, prior to its experimental detection, predicted a bond order of six, corresponding to a ...$9\sigma_g^2 5\pi_u^4 2\delta_g^4 10\sigma_g^2$ valence configuration, in which one δ bond and one σ bond have been "added to" the well-known $\sigma_g^2\pi_u^4\delta_g^2$ quadruple bond. On the basis of overlap population distributions derived from a projected Xα (PXα)[5] calculation on Mo_2, we have recently proposed[6] that the second σ bond in the molecule contributes significantly to the bond shortening whereas neither of the δ bonds contributes very much.

Table I. Calculated Molecular and Spectroscopic Parameters for Mo_2

calcn	no. of config	R_e, Å	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
A	64	2.09	414	−1.5
B	151	1.94	588	1.1
C	3212	2.06	392	0.5
D	3212	1.97	475	2.3
expt[a]		1.93	477	1.5

[a] Reference 1.

The only previous ab initio calculation on Mo_2 predicts a long bond length of 2.1 Å,[7] a value similar to that found for Mo–Mo quadruple bonds.[8] The authors neglect to explain the discrepancy between their result and the experimental one, leaving one to guess which value is in error. Furthermore, no attempt was made to discuss the relative importance of the different metal–metal bonding interactions. We now report the results of a calculation of the potential energy curve of $^1\Sigma_g^+$ Mo_2 by a multiconfiguration self-consistent-field method with configuration interaction (CI). This technique provides an accurate determination of the potential curve near the equilibrium internuclear distance but is not appropriate at the dissociation limit. Our predicted spectroscopic constants, R_e = 1.97 Å, ω_e = 475 cm^{-1}, and $\omega_e x_e$ = 2.3 cm^{-1}, provide excellent support for the experimental values. In addition, a natural orbital analysis confirms our previous proposal concerning the relative strengths of the various bonding interactions.

Four different calculations (A–D) are reported here. Linear combinations of Gaussian-type orbitals (GTOs) were obtained from a least-squares fit of near Hartree–Fock limit Slater atomic orbitals.[9] Three GTOs per atomic orbital were used, except for the Mo 3d and 4d orbitals for which four GTOs were used. The two most diffuse components of the 4d orbital were split off to form a triple-ζ representation. The most diffuse component of the 4p orbital was also split off, and an additional p GTO with an exponent of 0.10 was added to the basis, resulting in a set of (23s10p8d) primitive GTOs contracted to [9s5p4d] on each atom. This basis set has considerable flexibility in the valence region, but it is a poorer representation of the core regions. Calculations A–C used this basis while calculation D also had additional single s, p, and d GTOs, with exponents of 0.7, 0.4, and 0.4, respectively, at the midpoint of the bond (bond-centered functions). The generalized molecular orbital (GMO) method[10–12] was used to obtain an optimized set of strongly and weakly occupied valence orbitals. The metal–metal bonding $9\sigma_g$, $5\pi_u$, $2\delta_g$, and $10\sigma_g$ orbitals (strongly occupied) and their corresponding antibonding orbitals (weakly occupied) were used to define a configuration space for the CI calculation.

A full CI calculation on $^1\Sigma_g^+$ Mo_2 within this space of 12 orbitals would require more than 35 000 spin-adapted configurations and is computationally infeasible. Calculation A used all configurations involving paired excitations from the bonding orbitals to their corresponding antibonding orbitals. This set of 64

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