reported here clearly demonstrate that this observation does not necessarily imply that rapid thermally activated exchange processes are operative. A large coupling between two or more hydrides caused by a coherent exchange process can give spectra that are easily mistaken for the fast-limit spectra of a highly fluxional molecule. Such a situation is readily revealed by deuterium substitution, which quenches the quantum-mechanical process and allows the thermal exchange process to be clearly observed and quantified. We are continuing to investigate additional examples of this phenomenon.

Stannadesulfurization of a Bis(diethyldithiocarbamato)tungsten(II) Complex: Formation of an (Aminocarbyne)tungsten Complex

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Summary: The crystalline, blue, diamagnetic complex [(W(η^2-S$_2$CNEt$_2$))$_2$(μ-CNEt$_2$)(μ-S)(μ-S$_2$CNEt$_2$)(μ-S$_2$SnR$_2$)]-(*W,W*) (**3**) was obtained by heating [W(CO)$_2$(η^2-S$_2$CNEt$_2$)$_2$(SnR$_2$)] (R = CH(SiMe$_3$)$_2$) under reflux in benzene: single-crystal X-ray data on **3** confirm its structure and show that (i) the carbyne ligand CNEt$_2$ symmetrically bridges the two W atoms, (ii) the W$_2$(μ-CNEt$_2$)-containing fragment W$_2$CN(C$_\alpha$)$_2$ is planar, (iii) the W–S distances range from 2.30 to 2.61 Å, and (iv) the W–W distance is short, 2.614 (2) Å.

Reactions that form or break a C–C[1] or C–S[2] bond are important in organometallic chemistry. We recently reported that such processes are involved in the thermal stannadesulfurization of the new stannylenetungsten(II) complex [W(CO)$_2$(η^2-S$_2$CNR'$_2$)$_2$(SnR$_2$)] (R = CH(SiMe$_3$)$_2$, R' = Me; **1a**), yielding [SnR$_2$(μ-S)]$_n$ and the ditungsten-tin


1a, R' = Me
1b, R' = Et
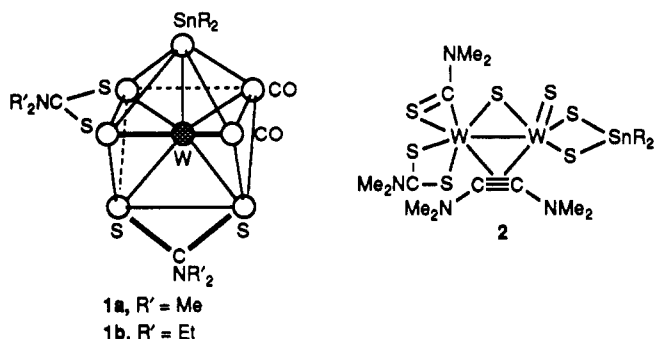
cluster **2**, featuring the diaminoalkyne ligand Me$_2$NCCNMe$_2$ (eq 1).[3] We suggested that the latter had

$$2\ \mathbf{1a}\ \xrightarrow[\substack{-(1/n)[SnR(\mu\text{-S})]_n \\ -4CO}]{}\ \mathbf{2} \tag{1}$$
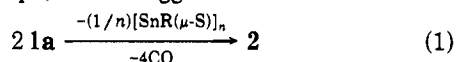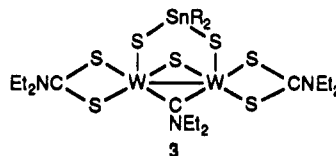
been formed by the coupling of coordinated aminocarbyne ligands C(NMe$_2$) of an intermediate along the reaction pathway (eq 2c, R' = Me).[3]

Although the internal oxidative addition of one dithiocarbamato C–S bond to tungsten is well-known (eq 2a),[3,4] cleavage of the remaining C–S bond, the carbyne-forming step (eq 2b), had not previously been unambiguously demonstrated.[5]

We now report the spectroscopic characterization and a single-crystal X-ray diffraction study of the product obtained from thermolysis of [W(CO)$_2$(η^2-S$_2$CNEt$_2$)$_2$-(SnR$_2$)] (**1b**). These results unequivocally establish the postulated double desulfurization of a coordinated dithiocarbamate (eq 2a,b).

$$L_xM(S)(\mu\text{-CNR'}_2)ML_y\ \xrightarrow{c}\ L_pM(S)(\mu\text{-R'}_2NCCNR'_2)ML_q \tag{2}$$
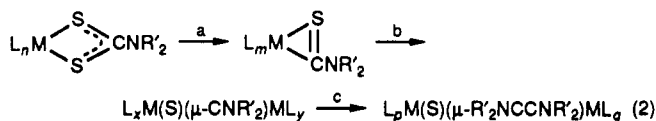
When a benzene solution of [W(CO)$_2$(η^2-S$_2$CNEt$_2$)$_2$-(SnR$_2$)] (**1b**)[6] was heated under reflux, a color change from yellow to dark blue occurred. From the reaction mixture, a blue crystalline solid (**3**) of empirical formula C$_{34}$H$_{78}$-N$_4$S$_9$Si$_4$SnW$_2$ was isolated after chromatography on Florisil.[7] The ¹H NMR spectrum showed (i) resonances
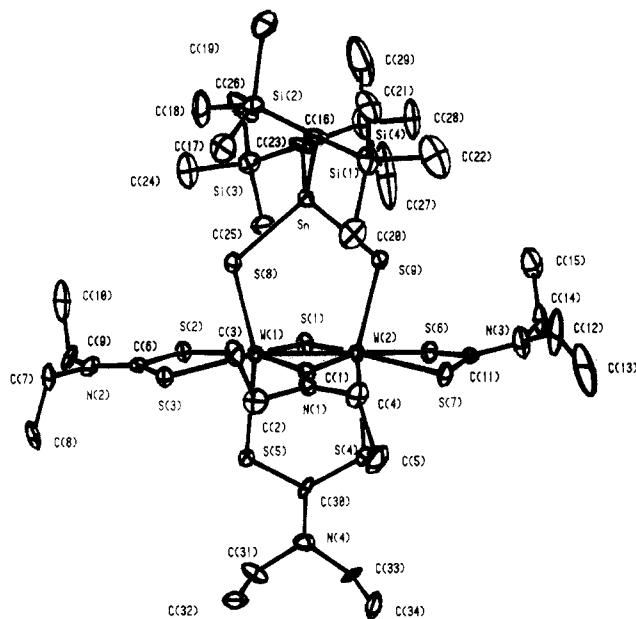

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(1) (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 8. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(2) Heterogeneous hydrodesulfurization is a dominant industrial reaction; see for example: (a) Angelici, R. J. *Acc. Chem. Res.* 1988, *21*, 387. (b) Massoth, F. E. *Adv. Catal.* 1978, *27*, 265.
(3) Hitchcock, P. B.; Lappert, M. F.; McGeary, M. J. *J. Am. Chem. Soc.* 1990, *112*, 5658.

(4) (a) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* 1973, *12*, 2182. (b) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* 1983, *105*, 2599. (c) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* 1986, *108*, 310.
(5) Such a transformation has been proposed to account for the photochemical reaction of [W(η^2-PhCCH)$_2$(η^2-S$_2$CNMe$_2$)$_2$] with PhCCH to yield a complex containing the [η^5-C$_5$H$_2$Ph$_2$(NMe$_2$)]⁻ ligand: Morrow, J. R.; Templeton, J. L.; Bandy, J. A.; Bannister, C.; Prout, C. K. *Inorg. Chem.* 1986, *25*, 1923.
(6) [W(CO)$_2$(η^2-S$_2$CNEt$_2$)$_2$(SnR$_2$)] (**1b**) was prepared by the 1:1 reaction of SnR$_2$ with [W(CO)$_3$(η^2-S$_2$CNEt$_2$)$_2$] (75%, after column chromatography on a Florisil support and elution with *n*-C$_6$H$_{14}$). IR (Nujol): ν(CO) 1981 (s) and 1894 (s), ν(CN) 1510 (m) and 1500 (m), ρ(SiCSi) 840 (s) cm⁻¹. ¹H NMR (C$_6$D$_6$, 303 K): δ 3.49 (q, $^3J_{HH}$ = 6.8 Hz, 2 H, NC*H$_2$*CH$_3$), 3.34 (q, $^3J_{HH}$ = 7.4 Hz, 2 H, NC*H$_2$*CH$_3$), 3.02 (q, $^3J_{HH}$ = 6.8 Hz, 4 H, NC*H$_2$*CH$_3$), 0.76 (complex m, 14 H, NCH$_2$C*H$_3$* and C(*H*)Si$_2$), 0.45 (br s, 36 H, Si(CH$_3$)$_3$). ¹³C NMR (C$_6$D$_6$, 303 K): δ 223.0 ($^1J_{WC}$ = 135 Hz, CO), 209.7 and 203.5 (S$_2$CN<), 52.3, 50.2, and 44.0 (NCH$_2$CH$_3$), 17.7 (C(H)Si$_2$), 12.3, 12.1, and 11.9 (NCH$_2$CH$_3$), 5.2 and 4.9 (Si(CH$_3$)$_3$). ¹¹⁹Sn NMR (C$_6$D$_6$, 303 K): δ 174.1. Mass spectrum (FAB; *m/z* (assignment)): 946 ((M – CO)⁺), 931 ((M – CO – CH$_3$)⁺), 918 ((M – 2CO)⁺). Anal. Calcd for C$_{26}$H$_{58}$N$_2$O$_2$S$_4$Si$_4$SnW: C, 32.1; H, 6.01; N, 2.88. Found: C, 31.7; H, 5.55; N, 3.06.

Figure 1. Ball and stick drawing of [(W(η^2-S$_2$CNEt$_2$))$_2$(μ-CNEt$_2$)(μ-S)(μ-S$_2$CNEt$_2$)(μ-S$_2$SnR$_2$)]-(*W*,*W*) (3), showing the atomic numbering scheme. Selected bond distances (Å) and angles (deg) are as follows: W(1)-W(2) = 2.614 (2), W(1)-S(1) = 2.299 (7), W(1)-S(2) = 2.543 (9), W(1)-S(3) = 2.605 (8), W(1)-S(5) = 2.482 (8), W(1)-S(8) = 2.376 (8), W(1)-C(1) = 2.07 (2), W(2)-S(1) = 2.302 (8), W(2)-S(4) = 2.497 (8), W(2)-S(6) = 2.536 (8), W-(2)-S(7) = 2.570 (9), W(2)-S(9) = 2.338 (10), W(2)-C(1) = 2.10 (2), C(1)-N(1) = 1.25 (3); S(1)-W(1)-C(1) = 106.8 (6), S(1)-W-(2)-C(1) = 105.7 (7), W(1)-C(1)-W(2) = 77.5 (6), W(1)-S(1)-W(2) = 69.3 (2).

assignable to four types of "NEt" groups, each of which contained diastereotopic methylene hydrogens, (ii) two singlets for the SnR$_2$ methine hydrogens, and (iii) two singlets for the SnR$_2$ methyl hydrogens; these data pointed to a structural formulation based on a ditungsten-tin cluster containing an average plane of molecular symmetry. The ^{13}C NMR spectrum was consistent with this interpretation and additionally showed low-field resonances at δ 312.0, 217.0, and 215.0; the signal at δ 312.0 suggested the presence of a carbyne ligand.

Definitive structural identification was provided by a single-crystal X-ray diffraction study,[8] which indeed re-

vealed a W$_2$Sn cluster with a (diethylamino)carbyne ligand bridging the tungsten atoms (Figure 1), the W-W axis being bridged by one [S$_2$CNEt$_2$]$^-$, one [S]$^{2-}$, and the unusual dithiostannate(IV) ligand [S$_2$SnR$_2$]$^{2-}$. A normal, chelating dithiocarbamato ligand completes the roughly octahedral coordination environment around each tungsten. The molecule has an approximate mirror plane. Noteworthy structural features include (i) the strong and symmetrical carbyne attachment to the W$_2$ core (W(1)-C(1) = 2.07 (2) Å, W(2)-C(1) = 2.10 (2) Å^3), (ii) a planar carbyneditungsten moiety (W(1), W(2), C(1), N(1), C(2), and C(4) are coplanar), (iii) substantial carbyne CN π-bonding (C(1)-N(1) = 1.25 (3) Å), (iv) a systematic progression in average tungsten-sulfur distances such that W$_2$(μ-S) (2.30 Å) < W(Sn)(μ-S) (2.36 Å) < W$_2$(μ-S$_2$CNEt$_2$) (2.49 Å) < W(η^2-S$_2$CNEt$_2$) trans to C(1) (2.54 Å) < W-(η^2-S$_2$CNEt$_2$) trans to S(1) (2.59 Å), and (v) an attractive tungsten-tungsten interaction as indicated by the short W-W separation, 2.614 (2) Å, and acute W(1)-S(1)-W(2) (69.3 (2)°) and W(1)-C(1)-W(2) (77.5 (6)°) angles. If the μ-CNEt$_2$ unit is considered as a trinegative ligand, a tungsten-tungsten single bond[10] would rationalize the apparent diamagnetism of this W^V d^1-W^V d^1 assembly. Aminocarbyne ligands have recently been featured in osmium cluster compounds, e.g., in [Os$_3$(CO)$_8$(μ-CNMe$_2$)(μ_3-CH$_2$C(CO$_2$Me)C(CO$_2$Me)CH)].[11]

Explicit mechanistic steps by which the complicated transformation **1b** → **3** proceeds are not known. However, since [(W(η^2-S$_2$CNEt$_2$))$_2$(μ-CNEt$_2$)(μ-S)(μ-S$_2$CNEt$_2$)(μ-S$_2$SnR$_2$)] (3) contains one extra sulfur than is available from the condensation of 2 equiv of [W(CO)$_2$(η^2-S$_2$CNEt$_2$)$_2$(SnR$_2$)] (**1b**), sulfur atom (or sulfide) transfer between intermediates must have occurred along the reaction coordinate. We have not yet succeeded in isolating or identifying the coproduct(s) from the thermolysis of **1b**.

The present results may be compared with those obtained for the thermolysis of [W(CO)$_2$(η^2-S$_2$CNMe$_2$)$_2$-(SnR$_2$)] (**1a** → **2**).[3] The stannylene ligand on **1b** was likewise oxidized to [S$_2$SnR$_2$]$^{2-}$ in **3**. However, in **3** the latter has a bridging role (contrasting with its terminal chelating mode in **2**), demonstrating the coordination flexibility of this new ligand. Formation of coordinated [S$_2$SnR$_2$]$^{2-}$ in **3** further illustrates the powerful thiophilicity of tin and reinforces our previous suggestion[3] that the Sn^{II}R$_2$ ligand can be an effective "internal reductant" capable of promoting C-S bond cleavage by shunting electrons to tungsten with its concomitant oxidation to tin(IV). The nature of the dithiocarbamato alkyl group R′ in the substrate 1 profoundly influences product identity in the stannadesulfurization reaction. For R′ = Et, formation of an alkyne adduct analogous to **2** via aminocarbyne coupling (eq 2c) may be inhibited by the increase in the steric bulk.

Supplementary Material Available: Tables of all bond angles and distances, anisotropic and isotropic thermal parameters, fractional atomic coordinates, and least-squares planes (12 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

(7) [(W(η^2-S$_2$CNEt$_2$))$_2$(μ-CNEt$_2$)(μ-S)(μ-S$_2$CNEt$_2$)(μ-S$_2$SnR$_2$)]-(*W*,*W*) (3; 35%, based on **1b**). IR (Nujol): ν(CN) 1495 (s), 1482 (sh), and 1436 (m), ρ(SiCSi) 842 (s) cm^{-1}. ^{1}H NMR (C$_7$D$_8$, 281 K): δ 4.70 (dq, ^2J = 13.9, ^3J = 7.2 Hz, 2 H, NCH$_2$), 4.48 (dq, ^2J = 13.9, ^3J = 7.2 Hz, 2 H, NCH$_2$), 3.58 (dq, ^2J = 13.9, ^3J = 7.2 Hz, 2 H, NCH$_2$), 3.53 (dq, ^2J = 13.9, ^3J = 7.2 Hz, 2 H, NCH$_2$), 3.40 (dq, ^2J = 13.9, ^3J = 7.2 Hz, 2 H, NCH$_2$), 3.27 (dq, ^2J = 13.9, ^3J = 7.2 Hz, 2 H, NCH$_2$), 2.91 (br, ^2J = 13.9 Hz, ^3J not resolved, 2 H, NCH$_2$), 2.78 (br, ^2J = 13.9 Hz, ^3J not resolved, 2 H, NCH$_2$), 1.59 (t, ^3J = 7.2 Hz, 6 H, NCCH$_3$), 1.06 (t, ^3J = 7.2 Hz, 6 H, NCCH$_3$), 0.91 (t, ^3J = 7.2 Hz, 6 H, NCCH$_3$), 0.43 (t, ^3J = 7.2 Hz, 6 H, NCCH$_3$), 0.36 (s, 18 H, SiMe$_3$), 0.24 (s, 18 H, SiMe$_3$), 0.07 (s, 1 H, CHSi$_2$), -0.20 (s, 1 H, CHSi$_2$). ^{13}C NMR (C$_7$D$_8$, 303 K): δ 312.0 (μ-CN<), 217.0 (η^2-S$_2$CN<), 215.0 (μ-S$_2$CN<), 58.6, 46.2, 45.4, and 44.8 (NCH$_2$), 15.4 and 13.0 (CHSi$_2$), 15.8, 12.7, 12.6, and 11.7 (NCCH$_3$), 4.5 (br, (SiMe$_3$)$_2$). ^{119}Sn NMR (C$_7$D$_8$, 303 K): δ 452.6. Mass spectrum (FAB; m/z (assignment)): 1430 ((P)$^+$). UV-vis (C$_4$H$_8$O; λ_{max}, nm (ϵ, mol^{-1} cm^{-1})): 223 (4.8 × 10^{-4}), 265.7 (4.5 × 10^4), 520.1 (4.9 × 10^3).

(8) Crystal data for [(W(η^2-S$_2$CNEt$_2$))$_2$(μ-CNEt$_2$)(μ-S)(μ-S$_2$CNEt$_2$)(μ-S$_2$SnR$_2$)]: triclinic, space group $P\bar{1}$, a = 12.092 (5) Å, b = 12.725 (5) Å, c = 21.888 (15) Å, α = 81.59 (4)°, β = 76.79 (5)°, γ = 72.88 (3)°, V = 3122.1 Å^3, Z = 2, D_c = 1.52 g cm^{-3}, F(000) = 1416, monochromated Mo Kα radiation, λ = 0.71069 Å, μ = 45.4 cm^{-1}. A total of 7635 unique reflections was measured for 2 < θ < 22° and +h,±k,±l, and 4406 reflections with |F^2| > σ(F^2) were used in the refinement (where σ(F^2) = (σ^2(*I*) + 0.041^2)$^{1/2}$*Lp*). There was no crystal decay. A correction (maximum 1.78, minimum 0.50) was made for absorption with use of DIFABS[9] after isotropic refinement. The structure was solved by routine heavy-atom methods, and non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions. The weighting scheme was w = 1/σ^2(*F*), and the final residuals were R = 0.079 and R' = 0.101.

(9) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(10) For a related structure with comments on metal-metal bonding, see: Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946. For general comments on metal-metal bonding, see: Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(11) Adams, R. D.; Babin, J. E.; Wolfe, T. A. *Organometallics* **1990**, *9*, 440 and references therein.