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Contribution from the Department of Chemistry, Memorial University
of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7

Stereochemical Nonrigidity in Thioether Complexes

Huikang Wu and C. Robert Lucas*

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Preparations of 1,6-bis(2-thienyl)-2,5-dithiahexane (L1), 1,9-bis(2-thienyl)-2,5,8-trithianonane (L2), and the complexes Mo(CO)$_4$·L (L = L1, L2) and W(CO)$_4$·L (L = L1, L3) (L3 = 2,5,8,11-tetrathia[12](2,5)thiophenophane) are described. At room temperature, all the complexes undergo rapid inversion of configuration at their metal-bound sulfurs by a solvent-independent mechanism, but no evidence of any 1,4-heteroatom fluxionality was found even at elevated temperatures. The presence of pendant thiophene groups in the acyclic ligands has no significant effect on metal–ligand interactions. The molecular structure of W(CO)$_4$·L3 has been determined by X-ray methods. Crystal data: monoclinic, space group *Cc*; *a* = 9.672 (4) Å, *b* = 14.777 (2) Å, *c* = 15.123 (2) Å, *β* = 99.56 (2)°; *Z* = 4; *R* = 0.036, R_w = 0.027.

Introduction

We have recently described 1,4-thioether binding site fluxionality in a thiophenophane–palladium complex.[1] That fluxional process may be the consequence of ligand rigidity, the presence of a Pd–S(thiophene) bond about which the ligand pivots, appropriate Pd–S(thioether) bond strengths, all three acting concertedly, or some other factor such as an unsuspected solvent effect. In an attempt to clarify which factors are important, we have examined the variable-temperature NMR spectra of the complexes M(CO)$_4$·L (M = Mo or W) in which L is one of the ligands shown in Figure 1. The interaction of metals with both thiophene and thioether sulfurs is currently of considerable interest in mechanistic studies of catalytic hydrodesulfurization[2,3] and in biological systems[4–6] and this report is a continuation of our earlier efforts in this area.[7]

Experimental Section

Commercially available reagents were obtained from the Aldrich Chemical Co. Inc. or from Morton Thiokol Alfa Products Inc. and were used without further purification. We have previously described the preparation of ligand L3.[7] Spectroscopic data were obtained by using the following instruments: IR, Mattson Polaris FT or Perkin-Elmer Model 283; NMR, General Electric 300-NB; mass spectra, V. G. Micromass 7070HS. X-ray data were collected by using a Rigaku AFC6S diffractometer. Analyses were performed by Canadian Microanalytical Services, Ltd.

Preparative Details. $C_{12}H_{14}S_4$, Ligand L1. Sodium (1.15 g, 50.0 mmol) was dissolved in commercial absolute ethanol (150 mL) under a nitrogen atmosphere, and 1,2-ethanedithiol (2.10 mL, 25.0 mmol) in ethanol (50 mL) was added dropwise. The resulting mixture was refluxed under nitrogen for 20 min, and then 2-chloromethylthiophene[8] (6.63 g, 50.0 mmol) in ethanol (50 mL) was added dropwise with stirring. Refluxing was continued for another hour during which time a white precipitate appeared. Water (100 mL) was added, and the mixture was extracted with chloroform (3 × 200 mL) and the extracts dried over calcium chloride. Volatiles were removed in vacuo, and the resulting oil was dissolved in a minimum amount of dichloromethane, filtered and methanol added until cloudiness appeared. After this was cooled to −5 °C, formation of a colourless oil occurred: yield 6.44 g (90%). MS: calcd for $[C_{12}H_{14}S_4]^+$, *m/e* = 285.9982; found, *m/e* = 285.9978. NMR ($CDCl_3$, in ppm from TMS internal standard, position identification from Figure 1): ^{1}H, 7.14 (m, 2 H, H1), 6.85 (m, 4 H, H2–H3), 3.84 (s, 4 H, H5), 2.60 (s, 4 H, H6); ^{13}C, 141.3 (C4), 126.3 (C3), 125.8 (C2), 124.7 (C1), 30.7 (C5), 30.2 (C6).

$C_{14}H_{18}S_5$, Ligand L2. This ligand was prepared in a manner analogous to L1 except that the final product precipitates as a white solid: yield 6.07 g (70%); mp 10 °C. Anal. Calcd for $C_{14}H_{18}S_5$: C, 48.51; H, 5.23; S, 46.26. Found: C, 48.72; H, 5.14; S, 46.24. NMR ($CDCl_3$, in ppm from TMS internal standard, position identification from Figure 1): ^{1}H, 7.21 (m, 2 H, H1), 6.91 (m, 4 H, H2–H3), 3.93 (s, 4 H, H5), 2.63 (s, 8 H, H6–H7); ^{13}C, 141.4 (C4), 126.5 (C3), 125.9 (C2), 124.9 (C1), 31.5 (C7), 31.2 (C5), 30.4 (C6).

Table I. Crystallographic Data for W(CO)$_4$·L3

chem formula: $C_{16}H_{18}O_4S_5W$	fw = 618.47
a = 9.672 (4) Å	space group: *Cc*
b = 14.777 (2) Å	*T* = 26 °C
c = 15.123 (2) Å	λ = 0.71069 Å
β = 99.56 (2)°	*μ* = 60.24 cm^{-1}
ρ_{calcd} = 1.927 g cm^{-3}	*R* = 3.6%[a]
V = 2131.4 Å^3	R_w = 2.7%[b]
Z = 4	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

Mo(CO)$_4$·L1. Molybdenum hexacarbonyl (130 mg, 0.492 mmol) and L1 (140 mg, 0.489 mmol) were added to commercial absolute ethanol (15 mL) and the mixture was refluxed under nitrogen for 4 h. The yellow precipitate that formed was separated, washed with ethanol and then diethyl ether, and dried in air: yield 205 mg (85%); mp 129–130 °C. Anal. Calcd for $C_{16}H_{14}MoO_4S_4$: C, 38.86; H, 2.85. Found: C, 38.75; H, 3.13.

Mo(CO)$_4$·L2. This preparation is similar to that for its L1 analog except that the product does not precipitate from the reaction mixture. Instead, the mixture is filtered and the filtrate is added to an equal volume of hexane. This solution is allowed to evaporate slowly giving yellow crystals: yield 177 mg (65%); mp 72–73 °C. Anal. Calcd for $C_{18}H_{18}MoO_4S_5$: C, 38.98; H, 3.27. Found: C, 39.08; H, 2.96.

W(CO)$_4$·L1. Tungsten hexacarbonyl (350 mg, 1.00 mmol) and L1 (140 mg, 0.489 mmol) were dissolved in commercial absolute ethanol (150 mL). The solution was irradiated with a 100-W Hanovia UV lamp and refluxed for 8 h under nitrogen. A yellow precipitate was separated from the cooled solution and washed with ethanol and then diethyl ether. The solid was placed in a sublimer and unreacted W(CO)$_6$ removed in vacuo. The remaining solid was chromatographed on SiO$_2$ using CH_2Cl_2 as eluant: yield 146 mg (50%); mp 148 °C dec. Anal. Calcd for $C_{16}H_{14}O_4S_4W$: C, 33.00; H, 2.42. Found: C, 33.10; H, 2.70.

W(CO)$_4$·L3. This preparation was similar to that of the L1 analog except that irradiation and refluxing were continued for 36 h: yield 247 mg (80%); mp 155 °C dec. Anal. Calcd for $C_{16}H_{18}O_4S_5W$: C, 31.07; H, 2.93; S, 25.92. Found: C, 32.11; H, 3.11; S, 27.03.

X-ray Studies. A summary of crystal data for W(CO)$_4$·L3 is given in Table I. Diffraction intensities were collected at 299 K by using the *ω*–2*θ* scan technique to a maximum 2*θ* value of 50.0°. Three standards measured after every 150 reflections showed no indication of significant crystal decay. The space group was determined by systematic absences. Unit cell parameters (Table I) were determined by a least-squares refinement of the setting angles of 25 reflections (40.03° < 2*θ* < 44.94°). Lorentz and polarization factors were applied and corrections were made for absorption. The structure was solved by direct methods[9] and refined by full-matrix least-squares techniques[10] with counting statistics weights. Non-hydrogen atoms were refined anisotropically while H atom positions were calculated but their parameters were not refined. The final cycle

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(10) Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/(Lp)^2$, *S* = scan rate, *C* = total integrated peak count, *R* = ratio of scan time to background counting time, *B* = total background count; *Lp* = Lorentz–polarization factor, and *p* = *p* factor.

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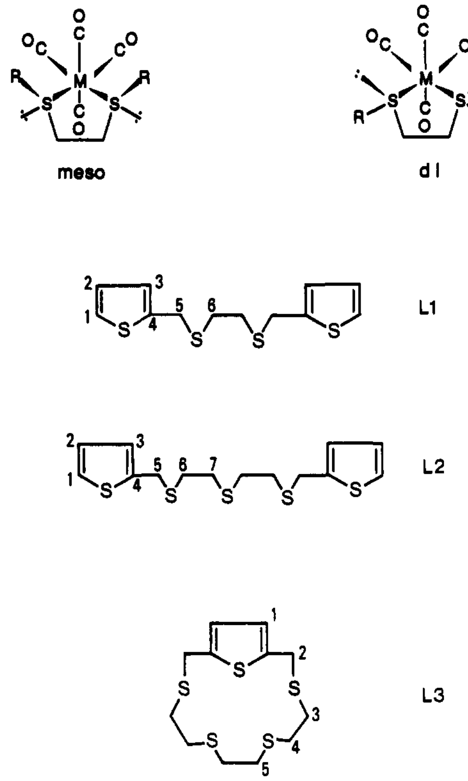

Figure 1. Isomers of $M(CO)_4{\cdot}L$ and ligands, L, with position identifiers mentioned in text.

Table II. Carbonyl Stretching Frequencies in CH_2Cl_2 Solution

ν, cm^{-1}				
$Mo(CO)_4{\cdot}L1$	$Mo(CO)_4{\cdot}L2$	$W(CO)_4{\cdot}L1$	$W(CO)_4{\cdot}L3$	assignt
2025 (m)	2025 (m)	2020 (m)	2019 (m)	A_1
1912 (s, br)	1907 (s, br)	1894 (s, br)	1896 (s, br)	$A_1 + B_2$
1869 (s)	1868 (s)	1865 (s)	1860 (s)	B_1

of refinement was based on 1603 observed reflections ($I > 3.00\sigma(I)$) and 233 variables and converged. All calculations were performed with the TEXSAN[11] crystallographic software from Molecular Structure Corp., and scattering factors were taken from the usual source.[12]

Results

Preparations are described for L1 and L2, the two open-chain thioether ligands having pendant thiophene units shown in Figure 1, and for $M(CO)_4{\cdot}L$ (M = Mo or W), (L = L1, L2, L3). The compounds have been characterized by elemental analysis, by mass, IR, and variable-temperature NMR spectroscopy, and by X-ray crystallography in the case of $W(CO)_4{\cdot}L3$. The results of these investigations are given in Figures 1–6 and in Tables I–IV and will be introduced at appropriate places in the discussion that follows.

Discussion

Preparations of the ligands and complexes are unremarkable. The processes shown in eqs 1 and 2 give disubstituted Group 6 carbonyls as the only product even when the ligand has more than two suitable donor sites.

$$Mo(CO)_6 + L \xrightarrow[\Delta]{EtOH} cis\text{-}Mo(CO)_4{\cdot}L + 2CO \qquad (1)$$

$$W(CO)_6 + L \xrightarrow[\Delta,h\nu]{EtOH} cis\text{-}W(CO)_4{\cdot}L + 2CO \qquad (2)$$

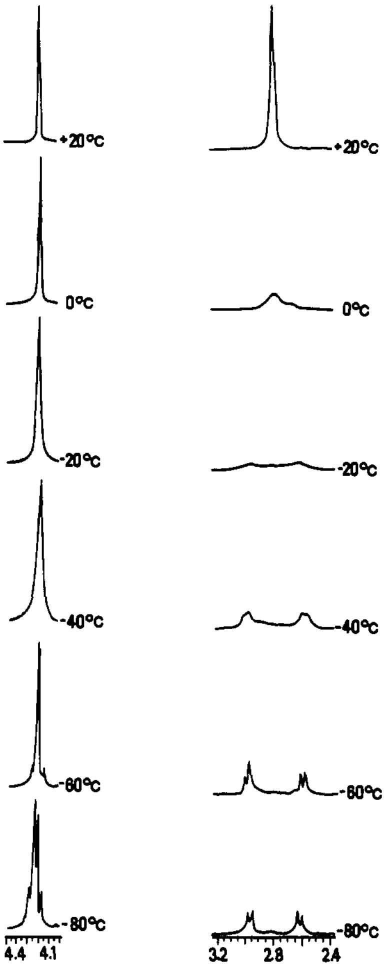

Figure 2. ^1H NMR spectra of methylene hydrogens of $Mo(CO)_4{\cdot}L1$ in THF-d_8.

The pale yellow complexes all exhibit IR spectra (Table II) in CH_2Cl_2 in the carbonyl stretching region that are typical of cis-disubstituted six-coordinate species with four carbonyls bound to a metal.[13] These results augment a surprising shortage of vibrational data for compounds of this type when compared to analogous phosphine or amine complexes. All isomers shown in Figure 1 may be formed and may undergo inversion at coordinated sulfurs resulting in conversions of $d \rightleftharpoons l$, meso $\rightleftharpoons$ meso or $dl \rightleftharpoons$ meso. In addition, conformational isomerism ($\delta \rightleftharpoons \lambda$) in the five-membered chelate rings may also occur. Studies of these processes are documented,[14–19] and in general, conformational isomerism is fast while inversion may be fast or slow.

Since interactions between thiophenes and metals are of importance in catalytic hydrodesulfurization of petroleum crude and in the 1,4-fluxional processes mentioned in the introduction, we began by comparing our L1 complexes with those reported previously[15] for bis(benzylthio)ethane. This comparison was to establish whether changing a phenyl group in bis(benzylthio)ethane into a thiophene unit (to give L1) causes any significant differences in the properties of the respective complexes. It also provides a convenient point of departure from the existing body of data concerning stereochemically nonrigid thioether complexes.

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Figure 3. ${}^1H$ NMR spectra of methylene hydrogens of $Mo(CO)_4{\cdot}L2$ in THF-d_8.

The behavior of $M(CO)_4{\cdot}L1$ (M = Mo, W) is not significantly different from that of the bis(benzylthio)ethane analogs. As seen in Figure 2, $Mo(CO)_4{\cdot}L1$ has a ${}^1H$ NMR spectrum that varies with temperature, and at temperatures below −60 °C, the spectrum shows two overlapping AB quartets near 4 ppm from TMS, only one of which is clearly resolved. These quartets, centered at 4.25 and 4.28 ppm from TMS, are due to nonequivalent hydrogens on each carbon atom adjacent to a thiophene ring and, by analogy with the bis(benzylthio)ethane system, indicate the presence of two isomers, *dl* and meso, in a ~5:1 ratio. Raising the temperature of the sample permits inversion at thioether sulfur causing exchange of the A and B sites to give a high-temperature limiting spectrum consisting of a singlet near 4.2 ppm. At low temperatures, the chelate ring methylenes, which are an AA′BB′ system, appear as two apparent doublets at 2.61 and 2.96 ppm from TMS. Since two isomers are present, two pairs of apparent doublets would be expected, as seen in spectra of a related thiophenophane complex of $PdBr_2$.[20] The appearance of only one pair is probably due to the fact that the signals from the two isomers overlap slightly, and one of the isomers is present in such a small relative amount that its signals are lost under those of the other isomer. By analogy with spectra of related systems,[14,15,20] the isomer present in greater amount is probably the *dl* form. Finally, addition of free ligand to the NMR tube containing the complex causes appearance of a singlet at 2.60 ppm from TMS which remains unchanged over the range of temperatures investigated. It is unlikely, therefore, that the inversion processes described here are occurring by a dissociative mechanism as observed in some other cases.[1]

When the structure of the ligand is changed by adding an extra nonbonded thioether, the possibility of the metal engaging in 1,4-fluxional "hopping" between thioether sites in addition to the inversion process is introduced. From Figure 3, it can be seen that, at room temperature, $Mo(CO)_4{\cdot}L2$ is undergoing a rapid inversion process similar to that observed for the L1 complexes. Thus, both thiophene-bound methylenes appear as singlets near 4 ppm from TMS at room temperature, but as the temperature is lowered, the signal due to the methylene closer to the metal collapses to an AB quartet superimposed on the singlet from the more remote methylene. The chelate ring signals indicate the presence of predominantly one isomer (*dl*) and vary with temperature in the same way as those of the $Mo(CO)_4{\cdot}L1$ complex described above except that superimposed upon them are the signals from the unchelated $-CH_2CH_2-$.

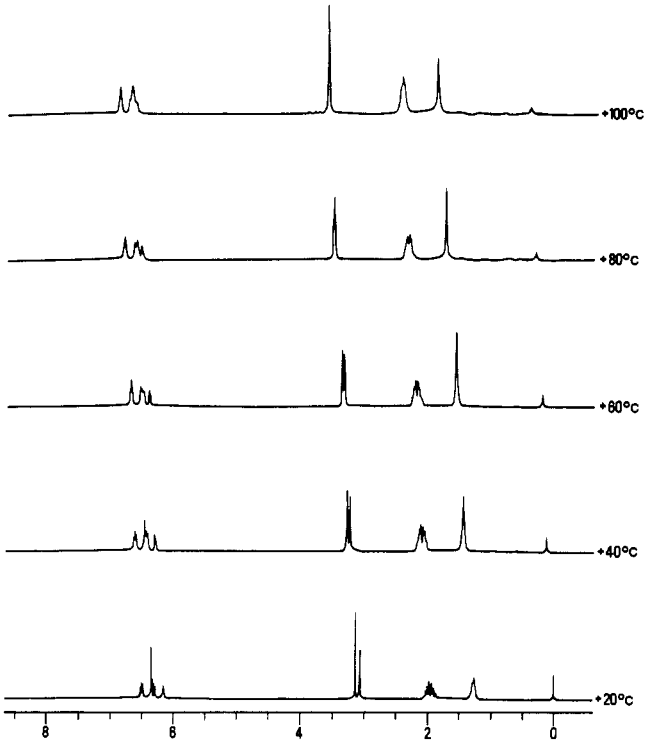

Figure 4. ${}^1H$ NMR spectra of $Mo(CO)_4{\cdot}L2$ in toluene-d_8.

At low temperatures, hydrogens in the unchelated portion of the chain give an ABC_2 signal consisting of two multiplets (the AB part) and a separate multiplet (the C_2 part) overlapping the high-field components of the other signals. The low-temperature spectrum appears thus as two multiplets near 2.8 ppm from TMS integrating for three and five hydrogens, the lower field of which is due to half of the signal from hydrogens on chelated carbons plus half of the signal from hydrogens on the adjacent unchelated carbon. The higher field multiplet arises from the other half of these signals plus that from hydrogens on the other unchelated carbon. The high-temperature spectrum consists of a shoulder at about 2.8 ppm due to hydrogens on the adjacent unchelated carbon, a narrow relatively more intense multiplet at slightly higher field due to hydrogens in the chelate ring, and, at still higher field, an envelope due to the two hydrogens on the more remote unchelated carbon. Addition of ligand to solutions in the NMR tube produces extra peaks in the spectra that do not change over the temperature range investigated and as noted for the L1 complexes, this is consistent with an intramolecular inversion process. All these spectral changes are consistent with inversions at the coordinated sulfurs, and there is no evidence for a fluxional process involving exchange of thioether binding sites. Such a process would also exchange thiophene-bound methylenes leading to one singlet at ~4 ppm from TMS instead of the two singlets actually observed at room temperature.

Fluxional metal binding by 1,4-heteroatoms is known[1,18,19] in cyclic systems but is unknown in acyclic ones although reports of 1,2-, 1,3- and 1,5-processes are available.[18,19,21,22] There seems

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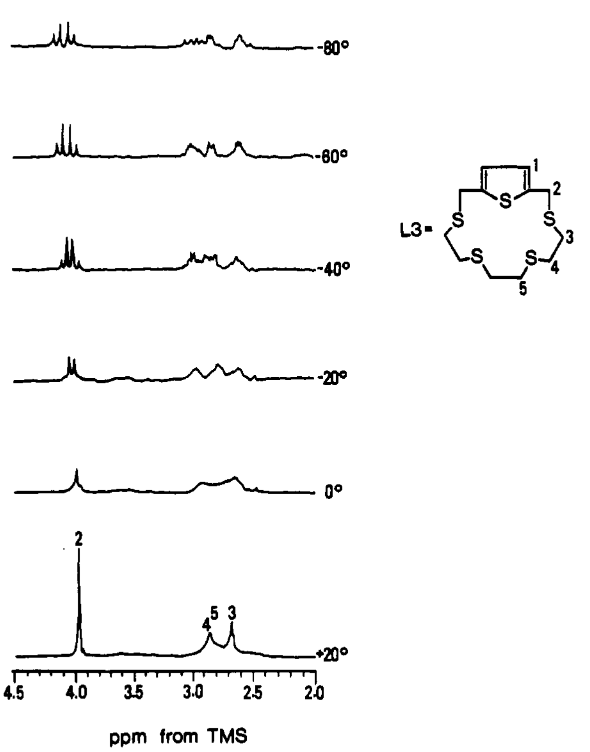

Figure 5. ^{1}H NMR spectra of methylene hydrogens of W(CO)$_4$·L3.

no reason why fluxionality in acyclic systems analogous to that in cyclic ones should not occur, providing the complexes do not decompose at the higher temperatures likely to be required. Therefore, we heated in toluene-d_8 the apparently robust Mo(CO)$_4$·L2, which should have a reasonably low activation energy for fluxionality,[18] in order to see whether a 1,4-fluxional process could be induced before thermal decomposition began. The NMR results are shown in Figure 4.

With rising temperature, the two singlets near 3 ppm from TMS, due to thiophene-bound methylenes, merge at about 80 °C. Simultaneously, multiplets near 2 ppm, due to the $-CH_2CH_2-$ that is not part of the chelate ring, begin to merge and the signal near 1.5 ppm, due to the $-CH_2CH_2-$ of the chelate ring, moves to lower field while the complex series of multiplets near 6.5 ppm, due to the two different thiophenes, begin to simplify as well. These changes may be caused by a 1,4-fluxional process or by a temperature-dependent change in chemical shifts that leads fortuitously to simultaneous merging of the signals in three different parts of the spectrum. Unfortunately, it is not possible to distinguish between these interpretations simply by raising the temperature further because decomposition begins at $T > 100$ °C and plots of chemical shift versus temperature for the various peaks suggest that at least 140 °C would be required to separate the peaks again if the merging is due to temperature-dependent chemical shifts. However, examination of peak shapes and chemical shifts over the range of temperatures investigated reveals that in both the ^{1}H (Figure 4) and ^{13}C NMR spectra the signals do not collapse and then grow again as expected for a 1,4-fluxional process. It is therefore our conclusion that the spectral changes are due to temperature-dependent chemical shifts and that the molecule is nonfluxional, at least within the temperature range investigated.

The variable-temperature NMR spectra of W(CO)$_4$·L3 have also been obtained (Figure 5). Although indicating inversion at metal-bound sulfur similar to that observed for the other complexes described in this study, these spectra also show no evidence for 1,4-fluxional behavior by W(CO)$_4$·L3 even when the temperature is raised to 100 °C. By analogy with the complexes discussed earlier, peak assignments between 2 and 4 ppm from TMS in the spectra of W(CO)$_4$·L3 are as shown in Figure 5. In the free ligand, the order in which signals from hydrogens at positions 3, 4, and 5 appear in reversed from that seen in Figure 5. This indicates that the complex's structure in solution is nonfluxional and similar to that in its solid state shown in Figure 6.

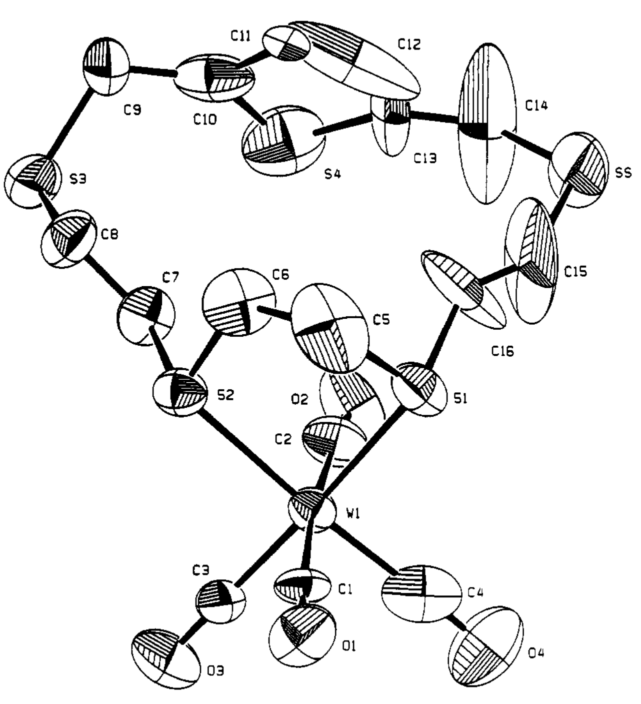

Figure 6. Molecular structure of W(CO)$_4$·L3.

In our earlier studies of MX$_2$·L (M = Pd, Pt; X = Cl, Br, I, SCN) and [Pd(η^3-allyl)(L)]$^+$ (L = $C_{10}H_{14}S_4$, 2,5,8-trithia[9]-(2,5)thiophenophane),[1,20] we observed 1,4-fluxional behavior when an allyl group is bound to the metal but not when it is replaced by a pair of chloro, bromo, iodo, or thiocyanato ligands. We also detected a metal-sulfur bond not involved in the fluxional movement that could be a pivot about which the fluxion occurs and we noted differences between the metal-sulfur bond lengths in the fluxional and nonfluxional species. Which, if any, of these factors influence the fluxional process is of interest.

Absence of 1,4-fluxional activity by either Mo(CO)$_4$·L2 or W(CO)$_4$·L3, even though both are expected to be more susceptible to it than related palladium species,[18] suggests that a pivot like the Pd–S(thiophene) bond noted above, about which the Pd(allyl) fragment swings during the fluxional process of [Pd(η^3-allyl)(L)]$^+$, may be necessary for 1,4-fluxional behavior. This conclusion supports earlier indications of the need for such a bond in fluxional molecules of this type.[23-25] Metal-sulfur bond strengths may also have a role in regulating fluxional behavior, and we have examined these bonds by X-ray methods in W(CO)$_4$·L3 which is nonfluxional in solution up to 100 °C. Details of the solid state structure are presented in Figure 6 and Tables III and IV. Because of conformational constraints in the ligand,[7] only the meso isomer is formed and only the two thioether sulfurs remote from thiophene coordinate to the metal. In the present context, the significant features of this structure are the two W–S distances of 2.586 (5) and 2.540 (5) Å. These bonds may be compared with W(0)–S distances in species such as [W(CO)$_5$(μ-SC$_6$Cl$_5$)W(CO)$_5$]$^-$ (2.586 (4) Å), [(η-C$_5$H$_5$)$_2$W^{IV}(μ-SC$_6$H$_5$)$_2$W^0(CO)$_4$] (2.58 (1) Å), [W(CO)$_5$SH]$^-$ (2.567 (5) Å), and [W$_2$(CO)$_{10}$(μ-SH)]$^-$ (2.587 (2), 2.596 (2) Å) or in [W(CO)$_5$(1,1,1-trifluoro-4-(2-thienyl)-4-thioxobutan-2-onato-S)]$^-$ (2.543 (2) Å) which is believed to have considerable W–S back-bonding.[26,27] Thus, the W–S distances

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Table III. Positional and Thermal Parameters and Equivalent Temperature Factors for $W(CO)_4{\cdot}L3$

atom	x	y	z	B_{eq},[a] Å^2
W(1)	1.0000	0.02167 (4)	1.0000	3.25 (2)
S(1)	1.2260 (5)	−0.0451 (3)	0.9557 (3)	4.7 (2)
S(2)	0.9449 (5)	−0.1459 (3)	1.0085 (3)	3.9 (2)
S(3)	0.9499 (6)	−0.2928 (4)	1.2658 (4)	5.8 (3)
S(4)	1.2737 (8)	−0.1711 (4)	1.3172 (4)	8.7 (4)
S(5)	1.5939 (7)	−0.0561 (5)	1.1672 (5)	10.1 (4)
O(1)	0.886 (2)	0.035 (1)	0.798 (1)	6 (1)
O(2)	1.131 (2)	0.048 (2)	1.210 (1)	6 (1)
O(3)	0.705 (1)	0.084 (1)	1.026 (1)	7.7 (8)
O(4)	1.087 (2)	0.228 (1)	0.994 (1)	8.2 (9)
C(1)	0.926 (3)	0.025 (2)	0.871 (2)	4 (1)
C(2)	1.083 (4)	0.036 (2)	1.137 (2)	5 (2)
C(3)	0.816 (2)	0.061 (1)	1.019 (1)	4.2 (8)
C(4)	1.057 (2)	0.149 (1)	0.994 (2)	6 (1)
C(5)	1.174 (3)	−0.160 (2)	0.922 (2)	9 (2)
C(6)	1.089 (2)	−0.206 (1)	0.978 (1)	6 (1)
C(7)	0.968 (2)	−0.177 (1)	1.128 (1)	5 (1)
C(8)	0.944 (2)	−0.277 (1)	1.147 (1)	5 (1)
C(9)	1.130 (2)	−0.337 (1)	1.301 (2)	6 (1)
C(10)	1.246 (2)	−0.279 (1)	1.281 (1)	6 (1)
C(11)	1.359 (2)	−0.293 (1)	1.228 (2)	2.2 (6)
C(12)	1.421 (4)	−0.246 (3)	1.221 (2)	14 (3)
C(13)	1.422 (3)	−0.163 (2)	1.264 (2)	11 (2)
C(14)	1.525 (4)	−0.106 (4)	1.254 (3)	42 (6)
C(15)	1.463 (3)	−0.048 (3)	1.066 (3)	31 (4)
C(16)	1.360 (2)	−0.062 (2)	1.057 (2)	13 (2)
H(1)	1.1213	−0.1575	0.8633	11.1
H(2)	1.2562	−0.1945	0.9220	11.1
H(3)	1.1492	−0.2222	1.0323	7.5
H(4)	1.0532	−0.2593	0.9477	7.5
H(5)	1.0611	−0.1624	1.1543	5.7
H(6)	0.9039	−0.1423	1.1550	5.7
H(7)	1.0141	−0.3122	1.1268	6.3
H(8)	0.8541	−0.2945	1.1156	6.3
H(9)	1.1435	−0.3465	1.3638	6.7
H(10)	1.1363	−0.3932	1.2713	6.7
H(11)	1.3712	−0.3504	1.1990	2.7
H(12)	1.4876	−0.2535	1.1837	15.0
H(13)	1.5043	−0.0550	1.2865	50.3
H(14)	1.6054	−0.1363	1.2850	50.3
H(15)	1.4989	−0.0857	1.0240	37.8
H(16)	1.4673	0.0133	1.0482	37.8
H(17)	1.3261	−0.0293	1.1028	15.3
H(18)	1.3563	−0.1253	1.0693	15.3

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table IV. Selected Bond Lengths and Angles in $W(CO)_4{\cdot}L3$

Distances (Å)			
W–S(1)	2.586 (5)	S(5)–C(14)	1.72 (4)
W–S(2)	2.540 (5)	S(5)–C(15)	1.82 (3)
W–C(1)	1.96 (3)	C(1)–O(1)	1.12 (3)
W–C(2)	2.11 (3)	C(2)–O(2)	1.13 (4)
W–C(3)	1.93 (2)	C(3)–O(3)	1.15 (2)
W–C(4)	1.97 (2)	C(4)–O(4)	1.20 (2)
S(1)–C(5)	1.82 (2)	C(5)–C(6)	1.44 (3)
S(1)–C(16)	1.86 (2)	C(7)–C(8)	1.52 (2)
S(2)–C(6)	1.78 (2)	C(9)–C(10)	1.48 (3)
S(2)–C(7)	1.84 (2)	C(10)–C(11)	1.48 (3)
S(3)–C(8)	1.81 (2)	C(11)–C(12)	0.93 (5)
S(3)–C(9)	1.85 (2)	C(12)–C(13)	1.38 (5)
S(4)–C(10)	1.69 (2)	C(13)–C(14)	1.34 (3)
S(4)–C(13)	1.77 (3)	C(15)–C(16)	1.01 (3)
Angles (deg)			
S(1)–W–S(2)	80.5 (2)	C(10)–S(4)–C(13)	91 (2)
S(1)–W–C(1)	86.4 (9)	C(14)–S(5)–C(15)	111 (1)
S(1)–W–C(2)	95.5 (9)	W–C(1)–O(1)	174 (2)
S(1)–W–C(3)	171.5 (5)	W–C(2)–O(2)	176 (3)
S(1)–W–C(4)	95.5 (6)	W–C(3)–O(3)	177 (2)
S(2)–W–C(1)	91.7 (7)	W–C(4)–O(4)	176 (2)
S(2)–W–C(2)	95.6 (8)	S(1)–C(5)–C(6)	116 (2)
S(2)–W–C(3)	94.4 (5)	S(2)–C(6)–C(5)	117 (2)
S(2)–W–C(4)	175.9 (7)	S(2)–C(7)–C(8)	115 (1)
C(1)–W–C(2)	172.7 (7)	S(3)–C(8)–C(9)	109 (1)
C(1)–W–C(3)	87 (1)	S(3)–C(9)–C(10)	116 (1)
C(1)–W–C(4)	89 (1)	S(4)–C(9)–C(10)	124 (2)
C(2)–W–C(3)	92 (1)	S(4)–C(10)–C(11)	103 (1)
C(2)–W–C(4)	84 (1)	C(9)–C(10)–C(11)	133 (2)
C(3)–W–C(4)	89.6 (8)	C(10)–C(11)–C(12)	119 (3)
W–S(1)–C(5)	102.6 (7)	C(11)–C(12)–C(13)	125 (4)
W–S(1)–C(16)	110.1 (8)	S(4)–C(13)–C(12)	102 (2)
C(5)–S(1)–C(16)	103 (1)	S(4)–C(13)–C(14)	141 (5)
W–S(2)–C(6)	107.1 (7)	C(12)–C(13)–C(14)	118 (5)
W–S(2)–C(7)	107.6 (6)	S(5)–C(14)–C(13)	138 (4)
C(6)–S(2)–C(7)	98.8 (9)	S(5)–C(15)–C(16)	129 (4)
C(8)–S(3)–C(9)	102.0 (9)	S(1)–C(16)–C(15)	129 (3)

in $W(CO)_4{\cdot}L3$ appear to be consistent with normal to strong W–S bonds.

Mechanistic details are limited for processes involving heteroatom binding site fluxionality of multidentate ligands although a transition state involving partial binding of both old and new donor atoms has been proposed.[18,19] Orientation of the nonbonding pairs on potential donor sites in conformationally nonrigid ligands seems unimportant in determining the activation energy for fluxionality[1,20,28] although in more rigid ligands it is of significance,[23] and as we have just shown, the presence of some form of pivot bond can be important. Since the activation energy for a particular process is controlled by attributes of the ground state or the transition state or both, our earlier observations of different metal–sulfur bond lengths in otherwise similar fluxional and nonfluxional palladium complexes[1,20] suggest that a ground-state effect may be important in certain circumstances. This conclusion is similar to one reached by Dixon, who has discussed factors influencing the dynamic stereochemistry of $[PtCl(PEt_3)(CH(PPh_2S)_2)]$[21] and $[PtCl(PEt_3)\{C(PPh_2S)_3\}]$.[25] Thus, in our palladium systems,[1,20] a pivot bond was present in both the fluxional and nonfluxional systems but in the nonfluxional case the metal–sulfur bonds were shorter. In the present molybdenum and tungsten examples, short metal–sulfur bonds and the absence of a pivot bond in either the ground state or an easily accessible transition state accompany nonfluxionality. Earlier suggestions[23,29,30] that the transition state may involve species of higher coordination number arising from partial coordination of the new binding site before full release of the old one are consistent with our results. Thus, in all our complexes where there is no possibility, for conformational or other reasons, of forming easily a species of higher coordination number and where there is no metal–sulfur pivot bond, no binding site fluxionality is detected.

In our previous studies,[1] solvent effects were sometimes important and as a conclusion to this report we note that solvent appears unimportant for the more coordinatively saturated compounds described herein. Spectra collected in CD_2Cl_2, $CDCl_3$, toluene-d_8 or tetrahydrofuran-d_8 showed no differences that are significant with respect to the mechanisms or activation energies of the processes described.

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Supplementary Material Available: Text giving a detailed description of the X-ray procedure and tables of anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and complete bond lengths and angles for $W(CO)_4{\cdot}L3$ (16 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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