carbonyls on molybdenum but considerably downfield from the CO resonance in $Cp_2Mo_2(CO)_4$, **3**, viz., δ 196.[1b]

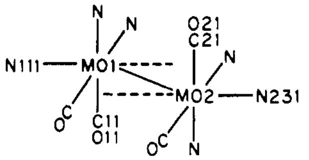
The formation of triply bonded **1** from the radical, **2**, parallels the formation of **3** from $Cp_2Mo_2(CO)_6$. The latter transformation has been shown to proceed via the radical pathway shown in eq 3.[18,19]

$$Cp_2Mo_2(CO)_6 \xrightarrow[h\nu]{\Delta\ \text{or}} 2CpMo(CO)_3\cdot \overset{-CO}{\rightleftharpoons} 2CpMo(CO)_2 \rightarrow \mathbf{3} \quad (3)$$

The structure[20] of **1** is shown in Figure 2. Unlike the Cp analogue $Cp_2Mo_2(CO)_4$ (**3**) which has a linear Cp–Mo–Mo–Cp axis,[21] the Tp–Mo–Mo–Tp axis is bent (ω = 153 ± 1°) and thus resembles $Cp_2Cr_2(CO)_4$ (ω = 162°)[22] and $Cp^*_2Mo(CO)_4$ (**4**, Cp* = C_5Me_5) (ω = 168°).[23] The Mo≡Mo distance in **1**, 2.507 (1) Å, may be compared to the Mo≡Mo distances of 2.448 (1) and 2.488 (3) Å in **3** and **4**, respectively.[21,23] Although the increased Mo≡Mo distances in **1** and **4** relative to **3** may be ascribed to the increased steric bulk of the Cp* and Tp ligands, increased electron donation from these liquids (vis-à-vis Cp) would be expected to populate M–M antibonding molecular orbitals and lead to increased Mo≡Mo distances.[22]

The overall symmetry of **1** approximates C_2, with the C_2 axis bisecting the Mo≡Mo bond and the N211–Mo2–Mol–N121 dihedral angle. The N donor atoms may be arranged into two sets. One set, consisting of N111 and N231, have their N–Mo bonds nearly parallel and approximately *trans* to the Mo≡Mo bond and are called "axial" (averge Mo–N_{ax} = 2.21 + 0.01, average Mo–Mo–N_{ax} = 154 + 2°). The other four N donors are essentially trans to the carbonyls and are called "equatorial" (average Mo–N_{eq} = 2.23 ± 0.01, average N_{eq}–Mo–CO = 166.6 ± 0.7).

A Mo–CO bond lies opposite to each axial nitrogen as shown



These carbonyls have shorter Mo–C distances (average = 1.93 ± 0.01 Å) and more acute Mo–Mo–CO angles (average = 70.5 ± 1.5°) than the other two carbonyls (average Mo–CO = 1.96 ± 0.01 Å, average Mo–Mo–CO = 83.4 (4)°). Thus it appears that one carbonyl on each molybdenum interacts across the Mo≡Mo bond with the residual "octahedral hydrid" on the remote Mo.

The reactivity of the radical, **2**, and the triply bonded dimer, **1**, are currently under investigation and will be reported in due course.

Acknowledgment. M.D.C. and K.-B.S. thank the National Science Foundation (Grant No. CHE-8206153) and the AMAX Foundation for support of this work. K.-B.S. also thanks the donors and the Department of Chemistry (UM) for a James E. Harris Fellowship. We also are grateful to the bloomington Academic Computing Service and the University of Michigan Computing Center for computing time. We also express our appreciation to Professor L. F. Dahl for a preprint of the structural characterization of complex **4**.

Registry No. 1, 85803-20-9; 2, 85803-21-0; $TpMo(CO)_3^-$, 47314-50-1.

Supplementary Material Available: Table I, fractional coordinates for $TpMo(CO)_3\cdot$ (**2**), Table II, fractional coordinates for $Tp_2Mo_2(CO)_4\cdot CHCl_3$ (**1**), Tables III and IV, listing of F_o vs. F_c for **2** and **1**, respectively (17 pages). Ordering information is given on any current masthead page.

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(19) Ginley, D. A.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85.

(20) a = 12.995 (2) Å, b = 16.974 (4) Å, c = 29.396 (6) Å, V = 6484 (2) $Å^3$, Z = 8; ρ(obsd) = 1.72 g cm^{-3} ρ(calcd) = 1.74 g cm^{-3}; space group *Pbca* (No. 61).

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(22) Curtis, M. D.; Butler, W. M. *J. Organomet. Chem.* **1978**, *155*, 131.

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Catenated Sulfur Ligands: The Synthesis of Metal Disulfanes and the Structures of *cis*-$(PPh_3)_2Pt(C_8H_4NO_2)SSCH(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)W(CO)_3SS\text{-}p\text{-}C_6H_4CH_3$

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Summary: Treatment of $(\eta^5\text{-}C_5H_5)W(CO)_3SH$ with RSNpht, RSSNpht and RS(O)Npht gave complexes which contain novel catenated sulfur ligands, namely, $(\eta^5\text{-}C_5H_5)W(CO)_3S_xR$, where x = 2 and 3, and $(\eta^5\text{-}C_5H_5)W(CO)_3SS(O)R$, respectively, where R = $CH_2C_6H_5$ and $p\text{-}C_6H_4CH_3$ and Npht = *N*-phthalimido. The complexes $(\eta^5\text{-}C_5H_5)W(CO)_3S_xR$, where x = 2 and 3, tend to desulfurize spontaneously in solution. The complexes *cis*-$(PPh_3)_2Pt(Npht)(S_xR')$, where x = 1 and 2 and R′ = $CH_2CH_2CH_3$, $CH(CH_3)_2$, $CH_2C_6H_5$, $p\text{-}C_6H_4CH_3$, and Npht, were prepared by oxidative addition of $R'S_xNpht$ to $(PPh_3)_2PtC_2H_4$. The complexes where x = 2 do not lose sulfur in solution. The X-ray structure of the complexes *cis*-$(PPh_3)_2Pt(Npht)SSCH(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)W(CO)_3SS\text{-}p\text{-}C_6H_4CH_3$ confirm the presence of the disulfide linkage with S–S distances and M–S–S–C torsional angles of 2.037 (4) Å and 89.5° and 2.053 (4) Å and 63.1°, respectively.

There is strong interest in complexes containing catenated polysulfur ligands. Several new cyclic compounds such as Cp_2MS_5, where M = Zr and Hf,[2] $[C_5(CH_3)_5]_2MS_3$, where M = Ti and Zr,[2] $(Et_4N)_2MoS(S_4)_2$,[3] and others[4] have recently been reported. Metal complexes containing the linear arrangement MS_xR which are analogues of organic polysulfides are rare.[5] In view of sulfur's pronounced

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(1) McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37–C39.

(2) Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, U. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 384–385.

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(4) (a) 1,5-$(Cp_2Ti)_2S_6$: Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620–5621. (b) $(PPh_4)_2[S_5FeS_2MoS_2]$: Coucouvanis, D.; Baenziger, N. C.; Simhon, E. D.; Stremple, P.; Swenson, D. *Ibid.* **1980**, *102*, 1730–1732. (c) $(PPh_4)_2[S_5FeS_2FeS_5]$: Coucouvanis, D.; Swenson, D.; Stremple, P.; Baenziger, N. C. *Ibid.* **1979**, *101*, 3392–3394.

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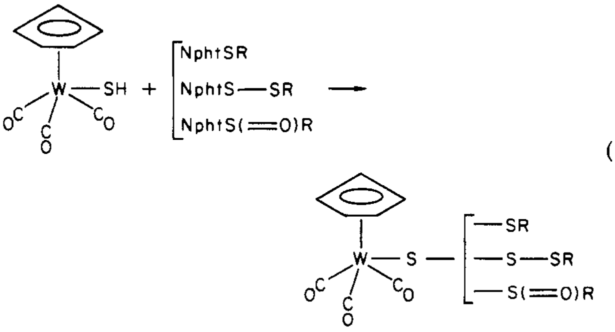
tendency to form catenated compounds, it is reasonable to assume the existence of a large class of complexes containing simple linear catenated polysulfur ligands.

Sulfur-transfer reagents of the type RS_xNpht,[6] where Npht = *N*-phthalimido, $x = 1$ and 2, and R is an organic group, provide an efficient route to unsymmetrical organic polysulfanes via reaction with thiols (eq 1). The reaction

$$R^1SH + RS_xNpht \rightarrow R^1SS_xR + HNpht \qquad (1)$$

of these reagents with the tungsten thiolo complex $CpW(CO)_3SH$,[7] where Cp = η^5-C_5H_5, has led to the novel tungsten disulfanes[8] $CpW(CO)_3SSR$ (eq 2). The complexes were characterized satisfactorily by IR, NMR, and mass spectroscopy and elemental analysis. The spectra of the disulfanes are similar but not identical with those of authentic samples of the corresponding thiolato complexes $CpW(CO)_3SR$,[9] which are low yield byproducts of the above reaction. The disulfanes tend to lose sulfur slowly to give the thiolato complexes upon standing in solution, and they could not be isolated by chromatography; however, they are stable in the solid state. To prepare the trisulfane analogues, $CpW(CO)_3SH$ was treated with RSSNpht[10] in a similar manner. New complexes, which we have identified as the trisulfanes $CpW(CO)_3SSSR$, were characterized in solution, but they decomposed to complicated mixtures upon workup. The disulfane complexes were identified in the NMR spectra of the crude reaction products in 25% concentration relative to the trisulfanes. Use of the transfer reagent RS(0)Npht[11] gave cleanly the oxidized disulfanes $CpW(CO)_3SS(O)R$, which were isolated and characterized satisfactorily. We conclude that these tungsten polysulfanes are less stable than organic di- and trisulfanes; however, the oxidized tungsten disulfanes are more stable than the organic analogues RSS(O)R.[12]



(2)

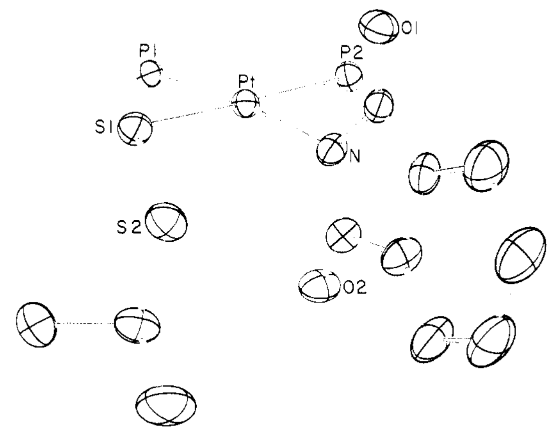


Figure 1. Perspective drawing of the solid-state structure of *cis*-$(PPh_3)_2Pt(Npht)SSCH(CH_3)_2$ with the phenyl rings not shown for clarity. The atoms are represented by thermal vibration ellipsoids drawn to encompass 30% of their electron density.

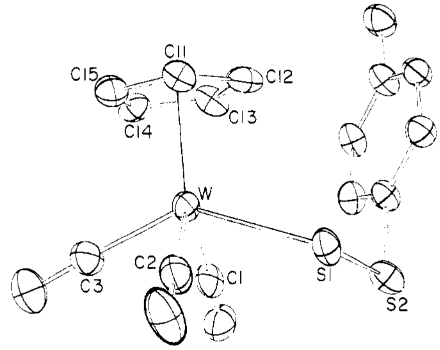
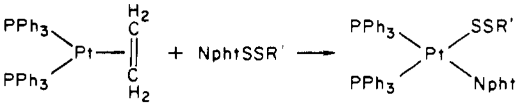


Figure 2. Perspective drawing of the solid-state structure of $(\eta^5$-$C_5H_5)W(CO)_3SS$-*p*-$C_6H_4CH_3$. The atoms are represented by thermal vibration ellipsoids drawn to encompass 30% of their electron density.

The sulfur–nitrogen bond in the reagent NphtSSNpht[13] oxidatively adds to $(PPh_3)_2PtC_2H_4$ to give the catenated species *cis*-$(PPh_3)_2Pt(Npht)(SSNpht)$ directly (eq 3). The reaction is general; thus use of $R'S_xNpht$, where R′ = Npht, $CH_2C_6H_5$, *p*-$C_6H_4CH_3$, $CH_2CH_2CH_3$, and $CH(CH_3)_2$ and $x = 1$ and 2, led to appropriate complexes which were isolated and fully characterized.[14] The platinum disulfanes do not spontaneously desulfurize in solution, in contrast to the tungsten complexes. In contrast to organic disulfides,[15] the complexes $CpW(CO)_3SSR$ and *cis*-$(PPh_{32}Pt(Npht)(SSCH_2C_6H_5)$ are desulfurized by triphenylphosphine to give the simple monosulfur thiolato compounds.



(3)

The structures of the complexes *cis*-$(PPh_3)_2Pt(Npht)SSCH(CH_3)_2$[16] and $CpW(CO)_3SS$-*p*-$C_6H_4CH_3$[17] have been determined and are shown in Figures 1 and 2, respectively. The platinum-to-sulfur distance of 2.353 (3) Å is similar

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(5) Bhattacharyya, S. N.; Senoff, C. V.; Walker, F. S *Inorg. Chim. Acta* **1980**, *44*, L273–L274.

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(14) All the complexes were assigned cis geometry on the basis of their ^{31}P NMR spectra.

(15) Harpp, D. N.; Gleason, J. G. *J. Am. Chem. Soc.* **1971**, *93*, 2437–2445.

(16) Crystal data: $C_{47}H_{41}NO_2P_2PtS_2$, $M_r = 3726.7$, yellow, thick plates, monoclinic, space group $P2_1/c$, $Z = 4$, $D_{calcd} = 1.494$ g cm^{-3}, $a = 11.963$ (4) Å, $b = 17.382$ (5) Å, $c = 22.030$ (8) Å, $\beta = 115.28$ (3)°, $U = 4141.9$ Å^3. The structure was solved by using 4347 reflections with $I > 3\sigma(I)$ collected in the range $3.5° < 2\theta < 45.0°$. The final residuals are $R_F = 5.5\%$ and $R_{wF} = 9.2\%$. The bond lengths (Å) in the coordination sphere are Pt–Pl = 2.265 (3), Pt–P2 = 2.295 (3), Pt–N = 2.044 (9), and Pt–S1 = 2.353 (3).

to that for simple thiolate ligands.[18] The novel Pt–S–S–$CH(CH_3)_2$ grouping features a sulfur–sulfur distance of 2.037 (4) Å and a torsion angle of 89.5°. In the tungsten complex[19,20] the W–S–S–$C_6H_4CH_3$ fragment has a sulfur–sulfur distance of 2.053 (4) Å and a torsion angle of 63.1°. The sulfur–sulfur bond distances in these two complexes are in the range found for most organic and inorganic disulfides.[21] However, while the PtSSC torsion angle is close to that found for open-chain organic disulfides (85 ± 20°)[22] the WSSC angle is much smaller[23] and outside this range.

These compounds are among the first linear representatives of a potentially large new class of complexes containing catenated-sulfur ligands. The preparative routes reported here are suitable for general application.

Acknowledgment. This research was supported by grants from the Natural Sciences and Engineering Research Council of Canada (NSERCC) the Quebec Department of Education and Imperial Oil Co of Canada. Predoctoral fellowships awarded to R.D.L. by McGill University and to J.H. by NSERCC are gratefully acknowledged. We thank Professor D.N. Harpp for helpful discussions.

Registry No. $CpW(CO)_3SH$, 51187-51-0; $NphtSCH_2C_6H_5$, 14204-26-3; NphtS-*p*-$C_6H_4CH_3$, 15199-26-5; $NphtSSCH_2C_6H_5$, 33704-38-0; NphtSS-*p*-$C_6H_4CH_3$, 33704-37-9; NphtS(=O)-$CH_2C_6H_5$, 40167-14-4; NphtS(=O)-*p*-$C_6H_4CH_3$, 42300-58-3; $CpW(CO)_3SCH_2C_6H_5$, 85882-86-6; $CpW(CO)_3S$-*p*-$C_6H_4CH_3$, 58057-63-9; $CpW(CO)_3SSCH_2C_6H_5$, 85882-87-7; $CpW(CO)_3SS$-*p*-$C_6H_4CH_3$, 85882-88-8; $CpW(CO)_3S(=O)CH_2C_6H_5$, 85893-30-7; $CpW(CO)_3S(=O)$-*p*-$C_6H_4CH_3$, 85893-31-8; NphtSNpht, 7764-29-6; $CH_3CH_2CH_2SNpht$, 17796-71-3; $(CH_3)_2CHSNpht$, 17796-72-4; $NphtS_2Npht$, 7764-30-9; $CH_3CH_2CH_2S_2Npht$, 30912-77-7; $(CH_3)_2CHS_2Npht$, 33704-40-4; *cis*-$(PPh_3)_2Pt(Npht)(SCH_2CH_2CH_3)$, 85882-89-9; *cis*-$(PPh_3)_2Pt(Npht)(S_2CH_2CH_2CH_3)$, 85882-90-2; *cis*-$(PPh_3)_2Pt(Npht)(SCH(CH_3)_2)$, 85882-91-3; *cis*-$(PPh_3)_2Pt(Npht)(S_2CH(CH_3)_2)$, 85882-92-4; *cis*-$(PPh_3)_2Pt(Npht)(SCH_2C_6H_5)$, 85882-93-5; *cis*-$(PPh_3)_2Pt(Npht)(S_2CH_2C_6H_5)$, 85882-94-6; *cis*-$(PPh_3)_2Pt(Npht)(S$-*p*-$C_6H_4CH_3)$, 85882-95-7; *cis*-$(PPh_3)_2Pt(Npht)(S_2$-*p*-$C_6H_4CH_3)$, 85882-96-8; *cis*-$(PPh_3)_2Pt(Npht)(SNpht)$, 85882-97-9; *cis*-$(PPh_3)_2Pt(Npht)(S_2Npht)$, 85882-98-0; $(PPh_3)_2PtC_2H_4$, 85882-99-1; PPh_3, 603-35-0.

Supplementary Material Available: Positional and thermal parameters, bond distances and bond angles with their estimated standard deviations, and listings of structure factor amplitudes for the complexes *cis*-$(PPh_3)_2Pt(Npht)SSCH(CH_3)_2$ and $CpW(CO)_3$-SS-*p*-$C_6H_4CH_3$ (29 pages). Ordering information is given on any current masthead page.

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(17) Crystal Data: $C_{15}H_{12}O_3S_2W$, M_r = 1904.53, red, brick-shaped, monoclinic, space group $P2_1/c$, $Z = 4$, D_{calcd} = 2.032 g cm^{-3}, a = 10.640 (3) Å, b = 11.400 (3) Å, c = 12.872 (3) Å, β = 94.58 (2)°, U = 1556.3 Å^3. The structure was solved by using 1672 reflections with $I > 3\sigma(I)$ collected in the range $3.5° < 2\theta < 45.0°$. The final residuals are R_F = 4.0% and R_{wF} = 5.5%.

(18) Bird, P. H.; Lai, R. D.; Shaver, A.; Siriwardane, U. *Can. J. Chem.* **1982**, *60*, 2075–2081.

(19) The W–S1 distance is 2.506 (2) Å. The Cp ring is titled slightly: C12 is farthest from W (2.397 (9) Å), while C14 and C15 are nearest (2.304 (9) and 2.313 (9) Å, respectively). Similar tilting has been observed for the complexes $CpM(CO)_3Cl$, M = Mo and W: Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197–2202 and is predicted on the basis of molecular orbital calculations.[20]

(20) The conformation of the S1–S2 bond with respect to the $CpW(CO)_3$ fragment is as predicted: Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180–188.

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(23) No significant intermolecular contacts were observed.

Book Reviews

Multiple Bonds Between Metal Atoms. By F. A. Cotton and R. A. Walton. Wiley-Interscience, New York. 1982. xiv + 466 pages. $47.50.

This book, with a foreword by R. Hoffmann, is the first to be published dealing only with compounds containing multiple bonds between metal atoms and is written by two accomplished practitioners in the field. The authors have covered the literature through 1980, and some of the early literature of 1981 is also included. Spot checks against this reviewer's files indicate that the coverage is exceptionally complete.

The book covers all aspects of the chemistry of compounds with metal–metal multiple bonds as indicated by the chapter headings: Chapter 1, Introduction and Survey (35 pp); Chapter 2, Quadruple Bonds Between Rhenium and Technetium (48 pp); Chapter 3, Quadruple Bonds between Molybdenum and Tungsten (66 pp); Chapter 4, Quadruple Bonds between Chromium Atoms (33 pp); Chapter 5, Triple Bonds between Metal Atoms (82 pp); Chapter 6, Double Bonds between Metal Atoms (46 pp); Chapter 7, Dirhodium and Isoelectronic Compounds (28 pp); Chapter 8, Physical, Spectroscopic, and Theoretical Results (114 pp). Within each of the chapters, 2–7, the synthesis, structures, and reactivity of the various compounds are presented and discussed. Where possible, reactivity–structure correlations are made and tied in with the theoretical results.

The organization of the material is built primarily around structural classes, which is understandable given the importance (indeed, necessity) of structural results to the field and the paucity of *systematic* reactivity studies. The text is clearly written, although in places the sheer rapidity with which the reader is bombarded with information makes casual reading difficult. Much of the first chapter is an interesting history of "How It All Began" and a polemic on "non-Wernerian" chemistry.

The book is remarkably free of error (only two minor ones were noted). Material is readily accessible via the adequate index or the detailed Table of Contents. This book is highly recommended to anyone who would like to see what the field of metal–metal multiple bonds entails, to teachers and students of inorganic chemistry, and to researchers in the field. For the latter, a perspicacious reading will reveal many areas of potentially rewarding research.

M. David Curtis, *The University of Michigan*

Chemically Modified Surfaces in Catalysis and Electrocatalysis. Edited by J. S. Miller. ACS Symposium Series No. 192. American Chemical Society, Washington, D.C. 1982. ix + 301 pp. $36.95.

This volume contains 17 articles containing material that was presented at the American Chemical Society Meeting in New York