Tris[(alkylthio)methyl]silanes: Syntheses and Structures of Chromium, Molybdenum, and Tungsten Complexes with a Tripodal Thioether Ligand

Hing W. Yim, Linh M. Tran, Ebern D. Dobbin, and Daniel Rabinovich*

Department of Chemistry, The University of North Carolina at Charlotte, 9201 University City Boulevard, Charlotte, North Carolina 28223

Louise M. Liable-Sands, Christopher D. Incarvito, Kin-Chung Lam, and Arnold L. Rheingold*

Department of Chemistry and Biochemistry, The University of Delaware, Newark, Delaware 19716

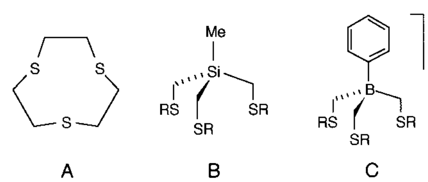
Received August 19, 1998

The first member of a new family of tripodal thioether ligands, the methyltris[(alkylthio)methyl]silanes MeSi(CH_2SR)$_3$ (R = Me), has been synthesized and characterized. Reactivity studies lead to the isolation of the complete series of group 6 metal carbonyl derivatives {η^3-MeSi(CH_2SMe)$_3$}M(CO)$_3$ (M = Cr, Mo, W), whose structures have been determined by single-crystal X-ray diffraction. The three complexes are isomorphous and display distorted octahedral structures with face-capping tridentate thioether ligands. {η^3-MeSi(CH_2SMe)$_3$}Cr(CO)$_3$ is monoclinic, $P2_1/c$, a = 8.1658(2) Å, b = 15.0563(2) Å, c = 26.5791(3) Å, β = 90.3653(6)°, V = 3267.74(8) Å^3, Z = 8. {η^3-MeSi(CH_2SMe)$_3$}Mo(CO)$_3$ is monoclinic, $P2_1/c$, a = 8.34630(6) Å, b = 15.2747(2) Å, c = 27.1865(4) Å, β = 90.8987(9)°, V = 3465.44(10) Å^3, Z = 8. {η^3-MeSi(CH_2SMe)$_3$}W(CO)$_3$ is monoclinic, $P2_1/c$, a = 8.1582(2) Å, b = 14.9903(2) Å, c = 26.7268(4) Å, β = 90.6568(8)°, V = 3268.30(9) Å^3, Z = 8.

Introduction

The coordination chemistry of simple monodentate (RSR′) and bidentate [RS(CH_2)$_n$SR′] thioethers is well-established.[1] Interest in polythioethers, the best known of which are macrocyclic species such as 1,4,7-trithiacyclononane (Chart 1A),[2] has increased substantially in recent years in view of their unique structural and electronic properties. Although a number of tridentate sulfide ligands other than crown thioethers are known, including MeC(CH_2SEt)$_3$,[3] RS(CH_2)$_2$S(CH_2)$_2$SR (R = Me,[4] Et[5]), 1,3,5-(MeS)$_3C_6H_9$,[6] and $C_6H_6S_3$,[7] reactivity studies with them are scant. With the aim of embarking on a systematic study of new trithioether ligands, we envisioned the syntheses of the methyltris[(alkylthio)methyl]silanes MeSi(CH_2SR)$_3$ (Chart 1B), expecting that distinctive steric and electronic effects could be attained by varying the terminal substituents (R) in the thioether arms. In support of this belief, the proposed ligands share this structural feature with and could be considered neutral isosteric analogues of Riordan's anionic poly[(alkylthio)methyl)]borates (Chart 1C).[8] In addition, the ease with which the Si−Cl bonds in chlorosilanes (e.g., $MeSiCl_3$) undergo nucleophilic substitution may be advantageously used to produce the silanes in good yields. We have recently applied this strategy to prepare the methyltris(pyrazolyl)silane nitrogen donors MeSi(3,5-RR′pz)$_3$ (R = R′ = Me; R = Bu^t, R′ = H) almost quantitatively from $MeSiCl_3$ and the corresponding lithium pyrazolates.[9] The synthesis and characterization of the (methylthio)methyl derivative MeSi(CH_2SMe)$_3$ and the preparation of its first transition metal complexes are described in this paper.

Chart 1. Tridentate Thioether Ligands



Results and Discussion

Synthesis and Characterization of MeSi(CH_2SMe)$_3$. The tripodal thioether methyltris[(methylthio)methyl]silane was readily synthesized by allowing a pentane solution of methyltrichlorosilane to react with 3 equiv of $LiCH_2SMe$ (eq 1).[10] The latter was generated in situ by deprotonation of dimethyl sulfide with

(1) (a) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365−414. (b) Müller, A.; Diemann, E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, Chapter 16.2, pp 551−558.
(2) (a) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1−72. (b) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1−80.
(3) Chatt, J.; Leigh, G. J.; Storace, A. P. *J. Chem. Soc. A* **1971**, 1380−1389.
(4) (a) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L.; Ortega, R. B. *Inorg. Chem.* **1986**, *25*, 3154−3157. (b) Baker, P. K.; Harris, S. D.; Durrant, M. C.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1994**, 1401−1407.
(5) Mannerskantz, H. C. E.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4454−4458.
(6) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730−6739.
(7) Grant, G. J.; Grant, C. D.; Setzer, W. N. *Inorg. Chem.* **1991**, *30*, 353−355.
(8) (a) Ge, P.; Haggerty, B. S.; Rheingold, A. L.; Riordan, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 8406−8407. (b) Ohrenberg, C.; Ge, P.; Schebler, P.; Riordan, C. G.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 749−754. (c) Schebler, P. J.; Riordan, C. G.; Guzei, I. A.; Rheingold, A. L. *Inorg. Chem.* **1998**, *37*, 4754−4755.
(9) Pullen, E. E.; Rheingold, A. L.; Rabinovich, D. *Inorg. Chem. Commun.*, in press.

10.1021/ic981001j CCC: $18.00
Published on Web 04/15/1999

$$\mathrm{MeSiCl_3 + 3LiCH_2SMe \xrightarrow[-3LiCl]{pentane} MeSi(CH_2SMe)_3} \quad (1)$$

n-butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA).[11] $MeSi(CH_2SMe)_3$ was isolated as a colorless (or more often pale yellow, but still spectroscopically pure) liquid in 60−75% yield after purification by fractional distillation (bp = 88−90 °C/(0.32 Torr)). It is quite thermally robust (no decomposition was observed upon heating to 250 °C), soluble in aliphatic and aromatic hydrocarbons, ethers, dichloromethane, and acetonitrile, and stable for months in dry air but susceptible to decomposition in the presence of water or alcohols.

Group 6 Metal Carbonyl Complexes. The molybdenum tricarbonyl complex $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}Mo(CO)_3$ was readily prepared by allowing $Mo(CO)_6$ to react with a slight excess of $MeSi(CH_2SMe)_3$ in refluxing methylcyclohexane (eq 2), conditions under which the product precipitated and was isolated by filtration in ca. 90% yield.

$$\mathrm{Mo(CO)_6 + MeSi(CH_2SMe)_3 \xrightarrow[-3CO]{methylcyclohexane} \{\eta^3\text{-}MeSi(CH_2SMe)_3\}Mo(CO)_3} \quad (2)$$

It is interesting to note that if aromatic hydrocarbons (e.g., benzene, toluene) are used as solvents for the above reaction, the known arene derivatives $(\eta^6\text{-}ArH)Mo(CO)_3$ form preferentially.[12] The corresponding reactions of the chromium or tungsten hexacarbonyls $M(CO)_6$ (M = Cr, W) with $MeSi(CH_2SMe)_3$ only produced dark mixtures of unidentified products. However, the complexes $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}M(CO)_3$ (M = Cr, W) were conveniently obtained (65−75% yield) by treating the labile nitrile derivatives $Cr(CO)_3(NCMe)_3$[13] or $W(CO)_3(NCEt)_3$[14] with the ligand in benzene/THF, reactions that proceeded to completion within minutes at room temperature. The three new thioether complexes are yellow, diamagnetic, moderately air-sensitive solids, only slightly soluble in benzene or toluene but more so in THF, solvents in which their solubilities decrease in the order Cr > Mo > W. Furthermore, dissolution of $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}M(CO)_3$ (M = Cr, Mo, W) in polar coordinating solvents such as acetonitrile resulted in the immediate generation of, inter alia, the adducts $M(CO)_3(NCMe)_3$ and the free thioether ligand, as determined by ^{1}H NMR spectroscopy. Interestingly, this observation is in contrast to the syntheses of the related trithiacyclononane derivatives $(\eta^3\text{-}ttcn)M(CO)_3$ (M = Cr,[15] Mo,[16,17] W[15]), which have been prepared from $M(CO)_6$ and the crown thioether *in* acetonitrile.

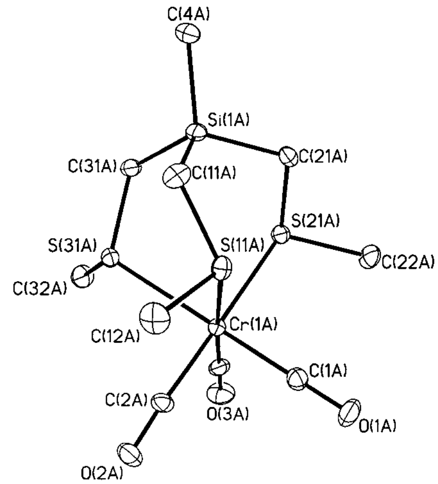


Figure 1. Molecular structure of $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}Cr(CO)_3$.

Spectroscopic Studies. Spectroscopic data in solution are consistent with the presence of tridentate facially coordinated thioether ligands in the octahedral $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}M(CO)_3$ (M = Cr, Mo, W) complexes. For example, their ^{1}H NMR spectra consist of three sharp singlet resonances in the ratio 3:2:1, corresponding to the methylthio, methylene, and methylsilyl protons, respectively. In their $^{13}C\{^1H\}$ NMR spectra (in tetrahydrofuran-d_8 (THF-d_8)), the chemical shifts for the three equivalent CO groups in each compound (231.7, 222.8, and 215.6 ppm for M = Cr, Mo, and W, respectively) are virtually identical to those observed for the crown thioether compounds $(\eta^3\text{-}ttcn)M(CO)_3$.[15] Likewise, the carbonyl region of their IR spectra (KBr pellets) shows two intense absorptions, centered near 1915 (A_1 mode) and 1780 cm^{-1} (E mode), as predicted for the facial isomer of a rigorously octahedral tricarbonyl complex.[18] However, a distortion from C_{3v} symmetry in the solid-state structures of $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}M(CO)_3$ (vide infra) is manifested by the presence of a third, weaker band (at ca. 1820 cm^{-1}), observed as a shoulder of the lower frequency ν(CO) stretch (see Experimental Section).[19] Albeit not common, this feature is precedented for other complexes of the type $L_3M(CO)_3$.[20]

Structures of $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}M(CO)_3$. The molecular structures of all three $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}M(CO)_3$ complexes (M = Cr, Mo, W) were determined by single-crystal X-ray diffraction. The complexes are isomorphous, with each asymmetric unit containing two crystallographically independent but chemically identical molecules differing only in the handedness of the thioether ligands. Representative molecules from each compound are depicted in Figures 1−3, with selected bond lengths and angles shown in Table 1. It is worth noting that while thioether complexes of Cr, Mo, and W are not rare, this appears to be the first complete series of group 6 metal thioether derivatives to be structurally characterized. The six-coordinate

(10) Similarly, using $MeSiCl_3$ and 3 equiv of the lithiated thioanisole reagent $LiCH_2SPh\cdot TMEDA$,[10a,b] we have prepared the (phenylthio)methyl derivative $MeSi(CH_2SPh)_3$, isolated as an off-white solid in 78% yield.[10c] (a) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097−4099. (b) Amstutz, R.; Laube, T.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1984**, *67*, 224−236. (c) Bunich, D.; Rabinovich, D. Unpublished results.

(11) Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717−1720.

(12) (a) Pidcock, A.; Smith, J. D.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 872−876. (b) Nesmeyanov, A. N.; Krivykh, V. V.; Kaganovich, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1975**, *102*, 185−193. (c) Strohmeier, W. *Chem. Ber.* **1961**, *94*, 3337−3341. (d) Angelici, R. J. *J. Chem. Educ.* **1968**, *45*, 119−120.

(13) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *2*, 433−434.

(14) Kubas, G. J.; Van der Sluys, L. S. *Inorg. Synth.* **1990**, *28*, 29−33.

(15) Kim, H.-J.; Do, Y.; Lee, H. W.; Jeong, J. H.; Sohn, Y. S. *Bull. Korean Chem. Soc.* **1991**, *12*, 257−259.

(16) Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636−638.

(17) (a) Sellmann, D.; Zapf, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 807−808. (b) Sellmann, D.; Zapf, L. *J. Organomet. Chem.* **1985**, *289*, 57−69.

(18) (a) Braterman, P. S. *Struct. Bonding* **1976**, *26*, 1−42. (b) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975.

(19) Solution IR spectra (in THF) exhibit only the two expected bands in the carbonyl region: for M = Cr, ν(CO) = 1924 and 1811 cm^{-1}, for M = Mo, ν(CO) = 1931 and 1819 cm^{-1}, and for M = W, ν(CO) = 1923 and 1811 cm^{-1}.

(20) (a) Cotton, F. A.; Zingales, F. *Inorg. Chem.* **1962**, *1*, 145−147. (b) Werner, H.; Deckelmann, K.; Schönenberger, U. *Helv. Chim. Acta* **1970**, *53*, 2002−2009. (c) Armanasco, N. L.; Baker, M. V.; North, M. R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1145−1149. (d) Haselhorst, G.; Stoetzel, S.; Strassburger, A.; Walz, W.; Wieghardt, K.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1993**, 83−90. (e) Siclovan, O. P.; Angelici, R. J. *Inorg. Chem.* **1998**, *37*, 432−444.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $\{\eta^3\text{-MeSi(CH}_2\text{SMe)}_3\}\text{M(CO)}_3$ Complexes

	M = Cr		M = Mo		M = W	
	molecule A	molecule B	molecule A	molecule B	molecule A	molecule B
M−S(11)	2.456(1)	2.459(1)	2.620(1)	2.625(1)	2.563(2)	2.568(2)
M−S(21)	2.438(1)	2.464(1)	2.623(1)	2.615(1)	2.569(2)	2.559(2)
M−S(31)	2.463(1)	2.469(1)	2.625(1)	2.600(1)	2.568(2)	2.544(2)
M−C(1)	1.833(5)	1.834(5)	1.974(2)	1.978(2)	1.942(8)	1.949(7)
M−C(2)	1.830(4)	1.834(5)	1.978(2)	1.971(2)	1.935(8)	1.948(8)
M−C(3)	1.822(5)	1.836(5)	1.977(2)	1.966(2)	1.935(7)	1.948(7)
S(11)−M−S(21)	92.3(1)	88.4(1)	88.2(1)	84.1(1)	88.0(1)	83.9(1)
S(11)−M−S(31)	86.2(1)	89.8(1)	86.8(1)	85.3(1)	86.8(1)	85.3(1)
S(21)−M−S(31)	86.6(1)	86.3(1)	84.6(1)	90.9(1)	84.5(1)	90.8(1)
C(1)−M−C(2)	86.6(2)	88.6(2)	88.1(1)	88.0 (1)	88.8(3)	88.7(3)
C(1)−M−C(3)	87.9(2)	85.5(2)	86.6(1)	87.0(1)	86.5(3)	88.1(3)
C(2)−M−C(3)	88.0(2)	86.3(2)	86.1(1)	87.5(1)	87.0(3)	87.8(3)
S(11)−M−C(1)	88.8(2)	93.6(1)	93.2(1)	93.2(1)	92.8(2)	92.5(2)
S(11)−M−C(2)	93.0(2)	93.0(2)	94.8(1)	98.1(1)	94.4(2)	98.2(2)
S(11)−M−C(3)	176.5(2)	178.9(2)	179.1(1)	174.3(1)	178.4(2)	173.9(2)
S(21)−M−C(1)	95.3(1)	94.7(1)	91.5(1)	92.7(1)	91.4(2)	92.1(2)
S(21)−M−C(2)	174.5(2)	176.3(2)	176.9(1)	177.7(1)	177.5(2)	177.6(2)
S(21)−M−C(3)	86.9(1)	92.4(2)	90.9(1)	90.3(1)	90.6(2)	90.0(2)
S(31)−M−C(1)	174.7(2)	176.5(2)	176.1(1)	176.0(1)	175.9(2)	176.1(2)
S(31)−M−C(2)	91.9(2)	90.3(2)	95.8(1)	88.6(1)	95.3(2)	88.5(2)
S(31)−M−C(3)	97.1(2)	91.1(2)	93.4(1)	94.9(1)	93.7(2)	94.5(2)

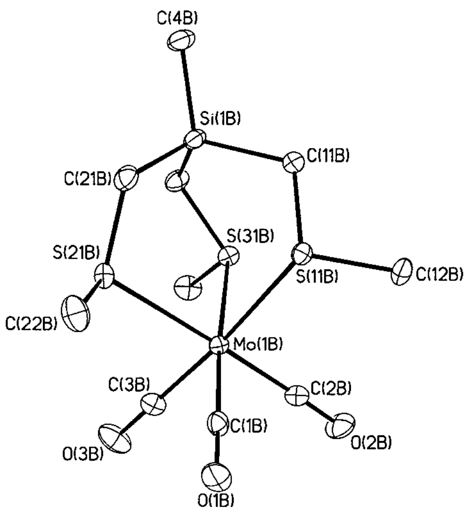


Figure 2. Molecular structure of $\{\eta^3\text{-MeSi(CH}_2\text{SMe)}_3\}\text{Mo(CO)}_3$.

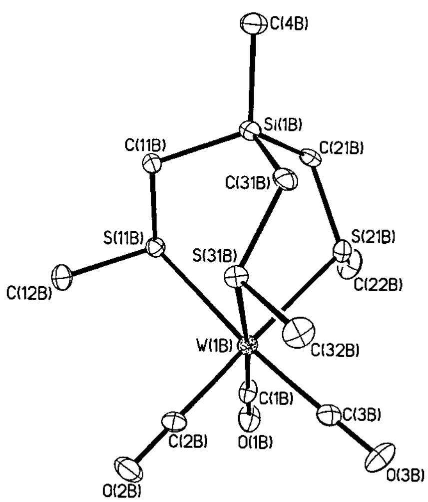


Figure 3. Molecular structure of $\{\eta^3\text{-MeSi(CH}_2\text{SMe)}_3\}\text{W(CO)}_3$.

complexes present distorted octahedral geometries in the solid state, with tridentate face-capping thioether ligands. The three M−CO groups are roughly opposite to the three M−S bonds, with the S−M−CO_{trans} angles being ca. 177°. In this regard, the structures resemble those of the trithiacyclononane derivatives $\{\eta^3$-ttcn$\}$M(CO)$_3$ (M = Mo,[16] W[15]) as well as several other known tricarbonyl complexes of general formula $L_3M(CO)_3$. Furthermore, the thioether arms of each ligand display a propeller-like arrangement about the metal, being canted relative to the C_3 axis containing the metal and the Si−C(4) group in each complex. Although the observed C−S−C angles (average 99.9°) suggest little distortion of the thioether groups upon coordination,[21] the flexibility of the ligands is indicated by the considerable range of M−S−C angles (between 99 and 115°).

The average Cr−S and Mo−S bond distances in $\{\eta^3\text{-MeSi(CH}_2\text{SMe)}_3\}\text{M(CO)}_3$, 2.458 and 2.618 Å, respectively, are among the longest observed for thioether complexes of zero valent chromium[22] and molybdenum.[23] While this observation

(21) For comparison, a C−S−C angle of 99.1° was found by electron diffraction for gaseous dimethyl sulfide: Iijima, T.; Tsuchiya, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2564−2567.

(22) Cr(0)−S(thioether) bond distances have been observed in the approximate range 2.34−2.46 Å: (a) Baker, E. N.; Larsen, N. G. *J. Chem. Soc., Dalton Trans.* **1976**, 1769−1773. (b) Lappert, M. F.; Shaw, D. B.; McLaughlin, G. M. *J. Chem. Soc., Dalton Trans.* **1979**, 427−433. (c) Lotz, S.; Schindehutte, M.; van Dyk, M. M.; Dillen, J. L. M.; van Rooyen, P. H. *J. Organomet. Chem.* **1985**, *295*, 51−61. (d) Raubenheimer, H. G.; Kruger, G. J.; Viljoen, H. W. *J. Organomet. Chem.* **1987**, *319*, 361−377. (e) van Rooyen, P. H.; Dillen, J. L. M.; Lotz, S.; Schindehutte, M. *J. Organomet. Chem.* **1984**, *273*, 61−68. (f) Raubenheimer, H. G.; Boeyens, J. C. A.; Lotz, S. *J. Organomet. Chem.* **1976**, *112*, 145−153. (g) Abel, E. W.; Cooley, N. A.; Kite, K.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Dawes, H. M. *Polyhedron* **1989**, *8*, 887−891. (h) Liu, S.-T.; Tsao, C.-L.; Cheng, M.-C.; Peng, S.-M. *Polyhedron* **1990**, *9*, 2579−2584. (i) Peach, M. E.; Burschka, C. *Can. J. Chem.* **1982**, *60*, 2029−2037. (j) Jogun, K. H.; Stezowski, J. J. *Acta Crystallogr.* **1979**, *B35*, 2310−2313. (k) Reisner, G. M.; Bernal, I.; Dobson, G. R. *Inorg. Chim. Acta* **1981**, *50*, 227−233. (l) Fischer, H.; Gerbing, U.; Treier, K.; Hofmann, J. *Chem. Ber.* **1990**, *123*, 725−732. (m) Fischer, H.; Treier, K.; Gerbing, U.; Hofmann, J. *J. Chem. Soc., Chem. Commun.* **1989**, 667−668. (n) Raubenheimer, H. G.; Viljoen, J. C.; Lotz, S.; Lombard, A. *J. Chem. Soc., Chem. Commun.* **1981**, 749−750. (o) Weber, L.; Boese, R. *Chem. Ber.* **1983**, *116*, 514−521. (p) Kruger, G. J.; Gafner, G.; de Villiers, J. P. R.; Raubenheimer, H. G.; Swanepoel, H. *J. Organomet. Chem.* **1980**, *187*, 333−340. (q) Kruger, G. J.; Coetzer, J.; Raubenheimer, H. G.; Lotz, S. *J. Organomet. Chem.* **1977**, *142*, 249−263. (r) Aumann, R.; Schröder, J.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1989**, *378*, 185−197. (s) Dötz, K. H.; Erben, H.-G.; Staudacher, W.; Harms, K.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1988**, *355*, 177−191. (t) Halverson, D. E.; Reisner, G. M.; Dobson, G. R.; Bernal, I.; Mulcahy, T. L. *Inorg. Chem.* **1982**, *21*, 4285−4290.

does not imply the absence of metal−thioether π bonding interactions, it is consistent with the presence of weakly bound, labile thioether ligands in $\{\eta^3\text{-MeSi(CH}_2\text{SMe)}_3\}\text{M(CO)}_3$. We also note that, assuming a covalent radius of 1.04 Å for sulfur[24a] and using the values proposed by Cotton for the radii of octahedral Cr(0) and Mo(0),[24b] the estimated lengths for Cr−S and Mo−S single bonds are 2.52 and 2.66 Å, respectively. In the case of the tungsten compound, the W−S bond lengths (average 2.562 Å) are within the range of reported W(0)−SR_2 distances (2.51−2.59 Å).[25] Furthermore, the observed W−S bond lengths are also slightly shorter than the corresponding values found in the Mo analogue, a phenomenom that is not uncommon and is considered to be an effect of the lanthanide contraction.[26] With regard to the metal−CO fragments, we observe fairly typical W−C bond lengths (mean = 1.943 Å), values which are also marginally shorter than the corresponding Mo−C distances (mean = 1.974 Å). All the other interatomic bond lengths (i.e., C−O, Si−C, and S−C) also seem to be normal.[27]

Conclusions

In summary, the new tripodal thioether ligand $\text{MeSi(CH}_2\text{SMe)}_3$ was synthesized, and its first transition metal derivatives, the group 6 metal carbonyl complexes $\{\eta^3\text{-MeSi(CH}_2\text{SMe)}_3\}\text{M(CO)}_3$ (M = Cr, Mo, W), were prepared and structurally characterized. Spectroscopic studies indicate that, electronically, $\text{MeSi(CH}_2\text{SMe)}_3$ is fairly similar to tridentate crown thioethers such as 1,4,7-trithiacyclononane. However, the new silane ligand has several practical advantages over the latter, including its ease of preparation, lower cost, and, more importantly, the potential to accommodate different coordination environments by modifying its steric requirements.

Experimental Section

General Considerations. All reactions were performed under dry oxygen-free nitrogen in an Innovative Technology System One-M-DC glovebox or under argon using a combination of high-vacuum and Schlenk techniques.[28] Solvents were purified and degassed by standard procedures, and all commercially available reagents were used as received. Whereas $\text{Cr(CO)}_3\text{(NCMe)}_3$[13] and $\text{W(CO)}_3\text{(NCEt)}_3$[14] were prepared as reported, LiCH_2SMe was synthesized by a modified literature procedure,[11] as described below. ^{1}H and ^{13}C NMR spectra were obtained on General Electric QE 300 or Varian Gemini (300 MHz) FT spectrometers. Chemical shifts are reported in parts per million relative to SiMe_4 (δ = 0 ppm) and were referenced internally with respect to the residual protio solvent resonances; coupling constants are given in hertz. IR spectra for solid and liquid samples were recorded as KBr pellets or neat in a cell with NaCl windows, respectively, on a Midac Collegian FT spectrophotometer and are reported in cm^{-1}; relative intensities of the absorptions are indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak, sh = shoulder). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

Synthesis of $\text{MeSi(CH}_2\text{SMe)}_3$. In a 1000 mL round-bottomed flask, under a constant flow of argon, a solution of LiBu^n in hexanes (2.5 M, 100 mL, 250 mmol) was added using a syringe to a cold (0 °C) stirred solution of Me_2S (28 mL, 381 mmol) and TMEDA (40 mL, 265 mmol) in pentane (60 mL), resulting in the formation of a yellow, slightly cloudy solution. The solution was allowed to warm to room temperature and refluxed for 2 h to complete the deprotonation reaction, producing a suspension of the LiCH_2SMe reagent. A solution of MeSiCl_3 (9.7 mL, 82.6 mmol) in pentane (80 mL) was then added in small portions via cannula over a 30 min period to the above reaction mixture cooled to −60 °C, resulting in the gradual formation of a white precipitate (LiCl) and a yellow solution. The suspension was allowed to warm to room temperature and refluxed for 18 h. After cooling to room

(23) Mo(0)−S(thioether) bond lengths have been observed in the range 2.41−2.59 Å. See refs 4a, 8a, 16, and the following: (a) Adams, R. D.; Shiralian, M. *Organometallics* **1982**, *1*, 883−884. (b) Adams, R. D.; Blankenship, C.; Segmüller, B. E.; Shiralian, M. *J. Am. Chem. Soc.* **1983**, *105*, 4319−4326. (c) Morris, R. H.; Ressner, J. M.; Sawyer, J. F.; Shiralian, M. *J. Am. Chem. Soc.* **1984**, *106*, 3683−3684. (d) Balbach, B. K.; Koray, A. R.; Okur, A.; Wülknitz, P.; Ziegler, M. L. *J. Organomet. Chem.* **1981**, *212*, 77−94. (e) Yoshida, T.; Adachi, T.; Ueda, T.; Watanabe, M.; Kaminaka, M.; Higuchi, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1171−1172. (f) Yoshida, T.; Adachi, T.; Kaminaka, M.; Ueda, T.; Higuchi, T. *J. Am. Chem. Soc.* **1988**, *110*, 4872−4873. (g) Adachi, T.; Sasaki, N.; Ueda, T.; Kaminaka, M.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1320−1322. (h) Yoshida, T.; Adachi, T.; Kawazu, K.; Yamamoto, A.; Sasaki, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 982−984. (i) Gelling, A.; Jeffery, J. C.; Povey, D. C.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 349−351. (j) Gelling, A.; Went, M. J.; Povey, D. C. *J. Organomet. Chem.* **1993**, *455*, 203-210. (k) Blower, P. J.; Jeffery, J. C.; Miller, J. R.; Salek, S. N.; Schmaljohann, D.; Smith, R. J.; Went, M. J. *Inorg. Chem.* **1997**, *36*, 1578−1582. (l) Jacobi, A.; Huttner, G.; Winterhalter, U. *Chem. Ber./Recueil* **1997**, *130*, 1279−1294. (m) Grant, G. J.; Carpenter, J. P.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1989**, *28*, 4128−4131. (n) de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1990**, *29*, 4084−4090. (o) Hoffmann, P.; Steinhoff, A.; Mattes, R. *Z. Naturforsch.* **1987**, *42B*, 867−873. (p) Sünkel, K.; Blum, A.; Polborn, K.; Lippmann, E. *Chem. Ber.* **1990**, *123*, 1227−1231. (q) Yoshida, T.; Adachi, T.; Sato, K.; Baba, K.; Kanokogi, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 1511−1513. (r) Alvarez, M.; Lugan, N.; Mathieu, R. *Inorg. Chem.* **1993**, *32*, 5652−5657. (s) Sellmann, D.; Binker, G.; Schwartz, J.; Knoch, F.; Böse, R.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1987**, *323*, 323−338. (t) Soltek, R.; Huttner, G.; Zsolnai, L.; Driess, A. *Inorg. Chim. Acta* **1998**, *269*, 143−156.

(24) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224. (b) Cotton, F. A.; Richardson, D. C. *Inorg. Chem.* **1966**, *5*, 1851−1854.

(25) See refs 15, 22h, and 23d,p, and the following: (a) Fischer, H.; Kalbas, C.; Stumpf, R. *Chem. Ber.* **1996**, *129*, 1169−1175. (b) Abel, E. W.; King, G. D.; Orrell, K. G.; Pring, G. M.; Sik, V.; Cameron, T. S. *Polyhedron* **1983**, *2*, 1117−1124. (c) Wu, H.; Lucas, C. R. *Inorg. Chem.* **1992**, *31*, 2354−2358. (d) Adams, R. D.; Falloon, S. B.; Perrin, J. L.; Queisser, J. A.; Yamamoto, J. H. *Chem. Ber.* **1996**, *129*, 313−318. (e) Reisner, G. M.; Bernal, I.; Dobson, G. R. *J. Organomet. Chem.* **1978**, *157*, 23−39. (f) Cannas, M.; Carta, G.; De Filippo, D.; Marongiu, G.; Trogu, E. F. *Inorg. Chim. Acta* **1974**, *10*, 145−149. (g) Raubenheimer, H. G.; Kruger, G. J.; Marais, C. F.; Otte, R.; Scott, F. *South Afr. J. Chem.* **1987**, *40*, 207−208. (h) Abel, E. W.; Orrell, K. G.; Rahoo, H.; Sik, V.; Mazid, M. A.; Hursthouse, M. B. *J. Organomet. Chem.* **1992**, *437*, 191−199. (i) Faller, J. W.; Zhang, N.; Chase, K. J.; Musker, W. K.; Amaro, A. R.; Semko, C. M. *J. Organomet. Chem.* **1994**, *468*, 175−182. (j) Pickering, R. A.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 817−821. (k) Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Sik, V.; Bates, P. A.; Hursthouse, M. B. *J. Organomet. Chem.* **1990**, *394*, 455−468. (l) Wang, H.-E.; Cheng, M.-C.; Peng, S.-M.; Liu, S.-T. *Acta Crystallogr.* **1995**, *C51*, 198−200. (m) Long, N. J.; Martin, J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 3083−3085. (n) Adams, R. D.; Yamamoto, J. H.; Holmes, A.; Baker, B. J. *Organometallics* **1997**, *16*, 1430−1439. (o) Al-Dulaymmi, M. F. M.; Hitchcock, P. B.; Richards, R. L. *Polyhedron* **1991**, *10*, 1549−1557. (p) Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1989**, *28*, 1751−1754. (q) Ros, R.; Vidali, M.; Graziani, R. *Gazz. Chim. Ital.* **1970**, *100*, 407−413.

(26) It is interesting to note that while the magnitude of the change in atomic radii for the elements La through Lu has historically been overrated, leading to deserving criticism,[26a] its relevance to the size of the elements following the lanthanides in the periodic table cannot be exaggerated. At least qualitatively, the fact that the metals in the third transition series are often smaller than their group congeners of the second transition series is more meaningful than the lanthanide contraction per se. In addition, a more modern view of the size variations among and between the 5d and f-block elements invokes the significant contribution of relativistic effects.[26b] (a) Lloyd, D. R. *J. Chem. Educ.* **1986**, *63*, 502−503. (b) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563−594.

(27) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(28) (a) Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie Academic & Professional: London, 1997. (b) *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, D.C., 1987. (c) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

temperature, the yellow supernatant solution was separated by filtration and the white residue extracted into pentane (50 mL). The volatile components from the combined filtrate and extract were removed under reduced pressure to give a viscous orange liquid. Fractional vacuum distillation of the oil yielded the desired product as a pale yellow, spectroscopically pure liquid with bp 88−90 °C at 0.32 Torr (13.5 g, 72%). ^{1}H NMR data (in C_6D_6): δ 0.31 (s, 3 H, C*H*$_3$Si), 1.85 (s, 6 H, C*H*$_2$), 1.86 (s, 9 H, SC*H*$_3$). ^{13}C NMR data (in C_6D_6): δ −5.2 (q, $^1J_{C-H}$ = 120, 1 C, *C*H$_3$Si), 18.0 (t, $^1J_{C-H}$ = 131, 3 C, *C*H$_2$), 20.0 (q, $^1J_{C-H}$ = 138, 3 C, S*C*H$_3$). IR data: 2966 (s), 2911 (vs), 2879 (s), 2829 (m), 1435 (s), 1423 (s), 1386 (s), 1314 (s), 1252 (s), 1136 (m), 1075 (m), 960 (s), 816 (vs), 714 (w). Anal. Calcd for $C_7H_{18}S_3Si$: C, 37.1; H, 8.0; S, 42.5. Found: C, 37.9; H, 8.4; S, 42.1.

Synthesis of {η^3-MeSi(CH$_2$SMe)$_3$}Cr(CO)$_3$. In a 250 mL Schlenk flask under argon, a dark brown stirred suspension of Cr(CO)$_3$(NCMe)$_3$ (1.40 g, 5.40 mmol) in benzene (50 mL) was treated with MeSi(CH$_2$SMe)$_3$ (1.20 mL, 6.04 mmol), added dropwise using a syringe. The resulting yellow-brown solution was stirred for 15 min at room temperature and filtered. Concentration of the filtrate to ca. 5 mL under reduced pressure and addition of diethyl ether (30 mL) led to the separation of a yellow microcrystalline solid, which was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo for 1 h (1.45 g, 74%). ^{1}H NMR data (in C_6D_6): δ −0.52 (s, 3 H, C*H*$_3$Si), 1.08 (s, 6 H, C*H*$_2$), 2.28 (s, 9 H, SC*H*$_3$). ^{13}C{^{1}H} NMR data (in THF-*d*$_8$): δ −3.1 (s, 1 C, *C*H$_3$Si), 16.3 (s, 3 C, *C*H$_2$), 28.7 (s, 3 C, S*C*H$_3$), 231.7 (s, 3 C, *C*O). IR data: 2916 (m), 1913 (vs), 1818 (sh), 1778 (vs), 1417 (s), 1395 (m), 1371 (m), 1318 (w), 1308 (w), 1251 (m), 1135 (s), 1081 (m), 974 (m), 963 (vs), 824 (vs), 772 (vs), 732 (m), 693 (s), 641 (vs), 616 (w), 540 (s). Anal. Calcd for $C_{10}H_{18}CrO_3S_3Si$: C, 33.1; H, 5.0. Found: C, 33.4; H, 5.0.

Synthesis of {η^3-MeSi(CH$_2$SMe)$_3$}Mo(CO)$_3$. A stirred suspension of Mo(CO)$_6$ (3.00 g, 11.36 mmol) and MeSi(CH$_2$SMe)$_3$ (2.50 mL, 12.58 mmol) in methycyclohexane (60 mL) was heated gently under argon, resulting in the formation, within 30 min, of a bright yellow solution. The solution was then heated to reflux, and a pale yellow solid started to precipitate after about 1 h. Heating was continued for an additional 4 h, after which the solution was allowed to cool to room temperature. The pale yellow microcrystalline product was isolated by filtration, washed with pentane (20 mL), and dried in vacuo for 1 h (4.09 g, 89%). ^{1}H NMR data: (in C_6D_6): δ −0.56 (s, 3 H, C*H*$_3$Si), 1.16 (s, 6 H, C*H*$_2$), 2.21 (s, 9 H, SC*H*$_3$). ^{13}C{^{1}H} NMR data (in THF-*d*$_8$): δ −2.4 (s, 1 C, *C*H$_3$Si), 18.7 (s, 3 C, *C*H$_2$), 29.4 (s, 3 C, S*C*H$_3$), 222.8 (s, 3 C, *C*O). IR data: 2924 (w), 1918 (vs), 1823 (sh), 1785 (vs), 1420 (m), 1417 (m), 1380 (m), 1318 (w), 1251 (w), 1140 (m), 1085 (w), 976 (w), 964 (m), 825 (s), 774 (s), 732 (w), 643 (m), 619 (m), 511 (m). Anal. Calcd for $C_{10}H_{18}MoO_3S_3Si$: C, 29.6; H, 4.5. Found: C, 29.6; H, 4.4.

Synthesis of {η^3-MeSi(CH$_2$SMe)$_3$}W(CO)$_3$. In a 250 mL Schlenk flask under argon, a dark brown stirred suspension of W(CO)$_3$(NCEt)$_3$ (1.00 g, 2.31 mmol) in a mixture of benzene (20 mL) and THF (100 mL) was treated with MeSi(CH$_2$SMe)$_3$ (0.50 mL, 2.52 mmol), added dropwise using a syringe. The resulting yellow-brown solution was stirred for 1 h at room temperature and filtered. Concentration of the filtrate to ca. 5 mL under reduced pressure and addition of diethyl ether (30 mL) led to the separation of a pale yellow microcrystalline solid, which was isolated by filtration, washed with diethyl ether (20 mL) and then with pentane (20 mL), and dried in vacuo for 30 min (0.49 g, 68%). ^{1}H NMR data: (in C_6D_6): δ −0.60 (s, 3 H, C*H*$_3$Si), 1.21 (s, 6 H, C*H*$_2$), 2.35 (s, 9 H, SC*H*$_3$). ^{13}C{^{1}H} NMR data (in THF-*d*$_8$): δ −2.5 (s, 1 C, *C*H$_3$Si), 18.7 (s, 3 C, *C*H$_2$), 31.1 (s, 3 C, S*C*H$_3$), 215.6 (s, 3 C, *C*O). IR data: 2918 (w), 1910 (vs), 1816 (sh), 1770 (vs), 1415 (m), 1374 (m), 1304 (w), 1250 (w), 1139 (m), 1084 (w), 978 (m), 964 (s), 826 (vs), 773 (s), 732 (w), 625 (w), 614 (w). Anal. Calcd for $C_{10}H_{18}O_3S_3SiW$: C, 24.3; H, 3.7. Found: C, 24.6; H, 3.6.

Table 2. Crystallographic Data for {η^3-MeSi(CH$_2$SMe)$_3$}M(CO)$_3$ Complexes

	M = Cr	M = Mo	M = W
formula	$C_{10}H_{18}CrO_3S_3Si$	$C_{10}H_{18}MoO_3S_3Si$	$C_{10}H_{18}O_3S_3SiW$
fw	362.51	406.45	494.36
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
T, K	173(2)	198(2)	198(2)
a, Å	8.1658(2)	8.34630(6)	8.1582(2)
b, Å	15.0563(2)	15.2747(2)	14.9903(2)
c, Å	26.5791(3)	27.1865(4)	26.7268(4)
β, deg	90.3653(6)	90.8987(9)	90.6568(8)
V, Å^3	3267.74(8)	3465.44(10)	3268.30(9)
Z	8	8	8
D_c, g cm^{-3}	1.474	1.558	2.009
μ(Mo Kα), cm^{-1}	11.53	11.84	75.22
color, habit	yellow block	orange rod	yellow plate
R_1/R_{w2} [$I > 2\sigma(I)$][a]	0.0474/0.1503	0.0260/0.0603	0.0404/0.0762
R_1/R_{w2} (all data)[a]	0.0654/0.1702	0.0338/0.0634	0.0756/0.0902

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_{w2} = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w^{-1} = \sigma^2(F_o) + (aP)^2 + bP$; $P = [2F_c^2 + \max(F_o^2,0)]/3$.

X-ray Structure Determinations. Crystallographic data for the complexes {η^3-MeSi(CH$_2$SMe)$_3$}M(CO)$_3$ (M = Cr, Mo, W) are collected in Table 2. Data were collected on a Siemens P4/CCD system using Mo Kα radiation (λ = 0.710 73 Å). Systematic absences in the diffraction data determined that the space group was $P2_1/c$ (No. 14). The three structures are isomorphous. The asymmetric unit contains two crystallographically independent but chemically identical molecules differing only in the handedness of the tripodal ligands. The Mo structure was solved by direct methods, completed from difference Fourier maps, and refined with anisotropic thermal parameters for all non-hydrogen atoms. The Cr and W structures were solved by isomorphic replacement of the metal atom and similarly refined. Empirical corrections for absorption were applied to the data. Hydrogen atoms were treated as idealized contributions. All computations used SHELXTL NT 5.10 and SADABS sotware (G. Sheldrick, Bruker AXS, Madison, WI).

Acknowledgment. We thank the Camille and Henry Dreyfus Foundation Faculty Start-Up Grant Program for Undergraduate Institutions, Research Corporation for a Cottrell College Science Award, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and The University of North Carolina at Charlotte for support of this research. We also thank Professor Ged Parkin (Columbia University) for helpful discussions.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structures of {η^3-MeSi(CH$_2$SMe)$_3$}M(CO)$_3$ (M = Cr, Mo, W) is available free of charge via the Internet at http://pubs.acs.org.

IC981001J