a filter solution of aqueous $Na_2Cr_2O_7$. The solution was stirred under N_2 while being irradiated for 18 h at room temperature. THF was then removed in vacuo to provide nearly pure compound **3e** (ratio of **3e**:**4e** > 10:1) in essentially quantitative yield. Compound **3e**: ^{13}C NMR (200 MHz) δ 153.6, 142.4, 133.8, 121.9, 109.7, 35.0, 30.1, 29.6, 28.9, 25.1, 21.1; IR ($CHCl_3$) 3083, 2995, 2960, 2871, 1460, 1390, 1386, 1363, 1359, 1300, 1261, 1227, 1102, 1020, 923, 796 cm^{-1}; High-resolution mass spectrum (*m/e*): calculated for $C_{26}H_{40}{}^{35}Cl_2{}^{48}Ti$, 470.198$_6$; found (EI), 470.197$_4$.

Preparation of Binaphtholate Complex 10. Sodium metal (50 mg, 2.2 mmol) was heated to reflux, with vigorous stirring, in 20 mL of dry toluene under argon until the sodium melted. The resulting suspension was cooled to 80 °C with stirring, and titanocene **3e** (100 mg, 0.21 mmol) and (±)-binaphthol (63.0 mg, 0.22 mmoil) were added in one portion. The mixture was heated at 80 °C for 80 min and then cooled and diluted with petroleum ether. The mixture was filtered through dry Celite, washing with dry ether. The filtrate was concentrated in vacuo, and the crude product obtained was purified by flash chromatography on silanized silica gel with toluene–petroleum ether (1:3) as eluent. A single, dark purple-red band eluted under these conditions, which was collected, and the solvents were removed in vacuo to provide spectroscopically pure compound **10** (50 mg, 34% yield) as a purple-red, microcrystalline solid. ^1H NMR (200 MHz): δ 7.77 and 7.71 (overlapping, broad doublets, J = 8.6 Hz, total 4 H), 7.25 (d, J = 8.6 Hz, 2 H), 7.12 (br t, J = 8.6 Hz, 2 H), 6.94 (br t, J = 8.6 Hz, 2 H), 6.81 (d, J = 8.6 Hz, 2 H), 5.76 (d, J = 2.4 Hz, 2 H), 5.20 (d, J = 2.4 Hz, 2 H), 3.58 (AA′ portion of AA′BB′ multiplet, 2 H), 3.24 (heptet, J = 7.0 Hz, 2 H), 3.13 (BB′ portion of AA′BB′ multiplet, 2 H), 1.39 (overlapping doublets, J = 7.0 Hz, total 12 H), 1.17 (s, 18 H). ^{13}C NMR (200 MHz): δ 165.8, 154.2, 137.6, 135.3, 132.6, 128.5, 128.1, 127.2$_4$, 127.1$_8$, 124.9, 121.7, 120.8, 117.6, 112.4, 105.9, 33.7, 29.8, 29.2, 29.1, 24.7, 23.3. IR ($CHCl_3$): 3060, 2998, 2957, 2925, 2868, 1611, 1589, 1498, 1457, 1421, 1389, 1385, 1363, 1361, 1357, 1328, 1272, 1244, 1140, 1125, 1071, 1047, 994, 952, 877, 849, 839, 818 cm^{-1}. High-resolution mass spectrum (*m/e*): calculated for $C_{46}H_{52}O_2{}^{48}Ti$, 684.344$_7$; found (EI), 684.344$_3$.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supplementary Material Available: Tables of H atom coordinates and isotropic thermal parameters for modification 2, anisotropic thermal parameters, and all bond angles, packing diagrams, and a list of nonbonded contacts for both modifications (11 pages); tables of structure factors for both modifications (22 pages). Ordering information is given on any current masthead page.

Cyclopentadienylniobium and -molybdenum Phosphorodithioate Complexes. X-ray Crystal Structures of $CpNbCl_3(S_2P(OPr^i)_2)$, $CpNbCl(\mu\text{-}Cl)_2Nb(S_2P(OPr^i)_2)Cp$, and *cis*-$Cp'Mo(CO)_2(S_2P(OPr^i)_2)$

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Reaction of $CpNbCl_4$ (Cp = η-C_5H_5) with $(Pr^iO)_2P(S)(SH)$ in the presence of NEt_3 yields $CpNbCl_3(S_2P(S_2Pr^i)_2)$ (**1**). Reduction of **1** with Na/Hg affords the Nb–Nb-bonded complex $CpNbCl(\mu\text{-}Cl)_2Nb(S_2P(OR)_2)Cp$ (**2**). In refluxing toluene, $(Pr^iO)_2P(S)(SH)$ with $[Cp'Mo(CO)_3]_2$ (Cp′ = η-C_5H_4Me) gives *cis*-$Cp'Mo(CO)_2(S_2P(OPr^i)_2)$ (**3**). Oxidation of **3** with I_2 affords $Cp'MoI_2(CO)(S_2P(OPr^i)_2)$ (**4**). The crystal structures of **1**–**3** are compared. For **1**, triclinic, $P\bar{1}$, a = 7.122 (3) Å, b = 11.365 (4) Å, c = 12.532 (4) Å, α = 77.38 (3)°, β = 89.08 (3)°, γ = 72.87 (3)°, V = 944.5 (8) Å^3, Z = 2, and $R(F)$ = 7.85%. For **2**, triclinic, $P\bar{1}$, a = 7.251 (3) Å, b = 12.386 (5) Å, c = 13.988 (5) Å, α = 102.66 (3)°, β = 103.56 (3)°, γ = 94.66 (3)°, V = 1180.0 (8) Å^3, Z = 2 and $R(F)$ = 2.70%. For **3**, orthorhombic, *Pbca*, a = 12.703 (3) Å, b = 16.706 (4) Å, c = 18.398 (4) Å, V = 3904.4 (17) Å^3, Z = 8, and $R(F)$ = 3.49%.

Introduction

Increasingly, phosphorodithioates, $S_2P(OR)_2$ (R = alkyl), are becoming recognized as ligands of synthetic utility.[1,2] These ligands are of interest, in part, due to their use as catalyst additives[3-5] and sequestering agents.[6,7] Phosphorodithioate complexes are generally very soluble. Additionally, the RO groups within the ligand may be varied to engender desirable properties, such as crystallinity or oil solubility.

Although many simple $M(S_2P(OR)_2)_n$ species have been prepared,[1,2] fewer organometallic phosphorodithioate complexes have been characterized[8-25] and only rarely

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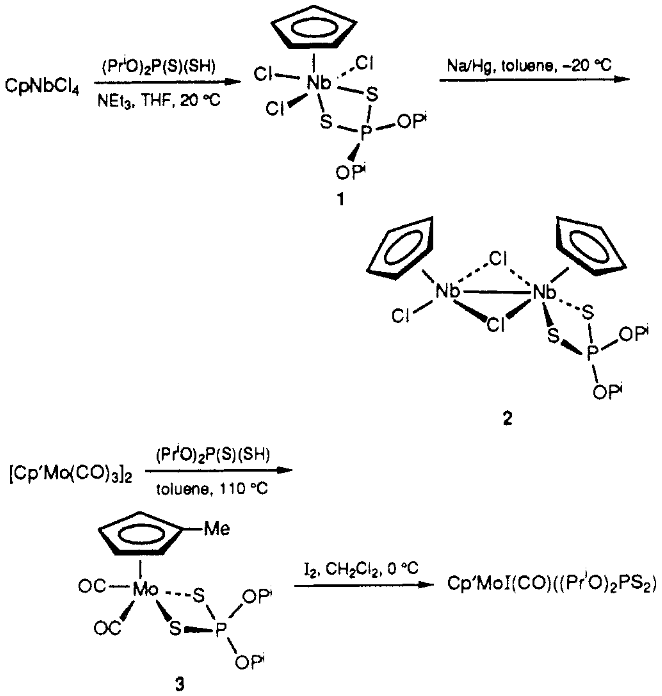
Scheme I



subjected to crystallographic study.[8-10] This paper describes the synthesis, reactivity, and X-ray crystal structures of cyclopentadienyl complexes of niobium and molybdenum containing $S_2P(OPr^i)_2$ moities. We are interested in these complexes as possible precursors to dinuclear and cluster complexes.

Results and Discussion

Synthesis and Characterization. Addition of $(Pr^iO)_2P(S)(SH)$ to a tetrahydrofuran (THF) solution of $CpNbCl_4$ in the presence of NEt_3 results in the formation of $CpNbCl_3(S_2P(OPr^i)_2)$ (1) in moderate yield (Scheme I). Careful crystallization is required to separate the complex as orange plates from an uncharacterized yellow material containing no cyclopentadiene ligand. Under similar conditions, reactions with 2 equiv of $(Pr^iO)_2P(S)(SH)$ yield only 1. The infrared spectrum (KBr disk) of 1 shows two PS stretches at 641 and 550 cm^{-1}, consistent with the presence of a bidentate dithioate group.[12,26] One $S_2P(OPr^i)_2$ group and a high-frequency signal at δ 6.31 assigned to the C_5H_5 ring are detected by ^{1}H NMR spectroscopy.

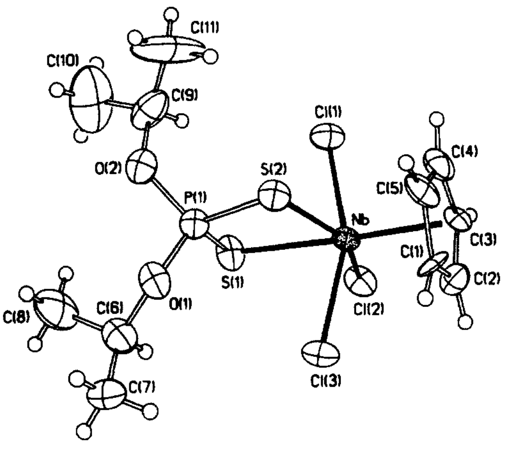
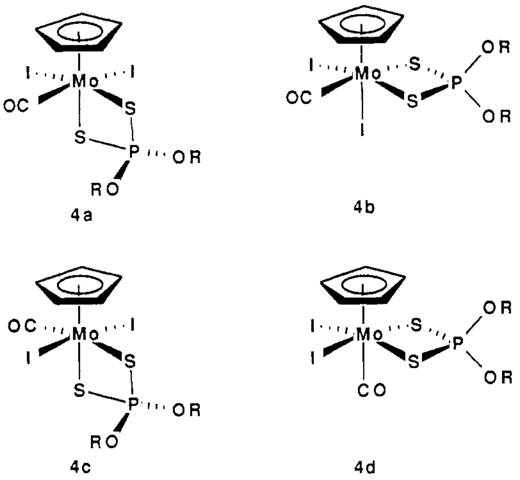


Figure 1. ORTEP plot (50% thermal ellipsoids) of $CpNbCl_3(S_2P(OPr^i)_2)$ (1).

Chart I



The high frequency of the ^{1}H signal may be due to a combination of the electron-withdrawing group on Nb and the magnetic anisotropy of the Nb–Cl bonds. The ^{13}C NMR chemical shift of the C_5H_5 ligand at δ 126.8 is, however, fairly typical for a niobium complex. No molecular ion is detected in the FAB mass spectrum (sulfolane matrix) of 1, the highest observed peak at m/z 619 corresponding to $[CpNbCl(S_2P(OPr^i)_2)_2]^+$. To confirm the degree of dithioic acid substitution, the structure of 1 was determined. A single bidentate dithioate ligand (Figure 1) is seen, while the overall geometry is very similar to that of $CpMo(dppe)Cl_3$.[27] The formation of $[CpNbCl(S_2P(OPr^i)_2)_2]^+$ cations in the mass spectrum of 1 is probably a probe effect.

Reduction of 1 with sodium amalgam results in low yields of a dark green crystalline material. Two PS stretches are observed (ν_{PS}(KBr) 655 and 555 cm^{-1}), suggesting a bidentate dithioate ligand.[12,26] The NMR data are consistent with the presence of a single dithioate ligand and two inequivalent C_5H_5 rings. Mass spectra of the crystals (EI and FAB modes) are uninformative. To unambiguously assign the structure, a crystallographic study was undertaken, revealing the molecule to be the Nb–Nb-bonded species $CpNbCl(\mu\text{-}Cl)_2Nb(S_2P(OPr^i)_2)Cp$ (2; Scheme I), isolated in 20% yield. Compound 2 probably arises from coupling of $[CpNbCl_2]$ and $[CpNbCl(S_2P(OPr^i)_2)]$ fragments produced by the reduction of 1. Despite being electron deficient, 2 shows no reactivity toward CO, presumably due to the unavailability of sufficient

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Table I. Selected Bond Distances and Angles for 1

(a) Bond Distances (Å)

Nb–Cl(1)	2.441 (4)	Nb–S(1)	2.651 (3)
Nb–Cl(2)	2.412 (4)	Nb–S(2)	2.532 (4)
Nb–Cl(3)	2.460 (4)	P(1)–S(1)	1.986 (6)
P(1)–O(1)	1.569 (9)	P(1)–S(2)	2.017 (4)
P(1)–O(2)	1.570 (10)	Nb–CNT[a]	2.108 (1)

(b) Bond Angles (deg)

S(1)–Nb–S(2)	76.1 (1)	S(2)–Nb–CNT	100.5 (4)
Cl(1)–Nb–Cl(2)	87.2 (1)	Cl(3)–Nb–S(1)	78.1 (1)
Cl(2)–Nb–Cl(3)	87.4 (1)	Cl(2)–Nb–S(2)	153.9 (1)
Cl(1)–Nb–Cl(3)	156.5 (1)	Cl(1)–Nb–S(2)	87.6 (1)
Cl(1)–Nb–S(1)	78.4 (1)	Cl(3)–Nb–S(2)	87.1 (1)
O(1)–P(1)–O(2)	101.5 (5)	O(1)–P(1)–S(1)	115.8 (4)
O(2)–P(1)–S(1)	114.9 (4)	O(1)–P(1)–S(1)	106.2 (3)
S(1)–P(1)–S(2)	105.9 (2)	O(2)–P(1)–S(2)	112.4 (4)
Nb–S(1)–P(1)	87.4 (1)	Nb–S(2)–P(1)	90.1 (2)
Cl(1)–Nb–CNT	100.7 (4)	Cl(2)–Nb–CNT	105.6 (4)
Cl(3)–Nb–CNT	102.9 (4)	S(1)–Nb–CNT	176.5 (4)

[a] CNT = centroid of Cp ring system.

metal electron density for back-donation to CO.

Reaction of $(Pr^iO)_2P(S)(SH)$ with $[Cp'Mo(CO)_3]_2$ in refluxing toluene affords a very high yield of purple *cis*-$Cp'Mo(CO)_2(S_2P(OPr^i)_2)$ (**3**; Scheme I). A cis dicarbonyl is clearly indicated by solution IR spectroscopy (ν_{CO}(CH_2Cl_2) 1954 s and 1860 s cm^{-1}),[28] while the presence of two low-frequency stretches (ν_{PS}(KBr) 542 m and 439 m cm^{-1}) indicates a bidentate phosphorodithioate ligand.[12,26] A closely related C_5H_5 analogue of **3** is known,[12] but its structure has not been determined crystallographically.

The action of I_2 on **3** in CH_2Cl_2 at 0 °C leads to a new monocarbonyl (ν_{CO}(CH_2Cl_2) 2006 s cm^{-1}), isolable as black crystals in reasonable yield (56%). This compound is assigned the structure $Cp'MoI_2(CO)(S_2P(OPr^i)_2)$ (**4**; Scheme I). The ^1H NMR spectrum of **4** shows four diastereotopic isopropyl methyl signals (δ($CDCl_3$) 1.36, 1.37, 1.42, and 1.44). Thus, it is clear that the complex **4** exists as a lower symmetry structure, either **4a** or **4b** rather than **4c** or **4d** (Chart I). The hypothetical **4c,d** have symmetry planes that would result in only two isopropyl methyl signals being observed. Although we prefer structure **4a** over **4b**, further discussion is unprofitable in the absence of crystallographic data.

Reactions of **3** with other oxidizing agents are less successful. Stirring **3** under an O_2 atmosphere results in slow decomposition to molybdenum oxide with no detectable intermediate, while reaction with S_8 in refluxing toluene results only in the isolation of $Cp'_2Mo_2S_4$.[29] Bubbling NO gas through toluene solutions of **3** results in the slow formation of a new nitrosyl species (ν_{NO}(toluene) 1670 s cm^{-1}), which we are currently unable to isolate.

The ^1H NMR spectra of all the phosphorodithioate complexes show characteristic pseudoseptets for their isopropyl CH hydrogens. However, homonuclear decoupling experiments reveal that these signals are in fact more complex multiplets due to phosphorus coupling. Related phosphorus–carbon couplings to both the OCH and methyl carbons are seen in the ^{13}C NMR spectra of these complexes.

Crystallographic Studies. Only mono dithioic acid substitution is observed for $CpNbCl_3(S_2P(OPr^i)_2)$ (**1**) in the solid state. An ORTEP plot is shown in Figure 1. Relevant atomic coordinates, bond distances, and angles are given in Table I. If the cyclopentadienyl ligand is assumed to accommodate a single coordination site (rather than the normal three), the geometry at the metal may be described as approximately octahedral, similar to that in Cp'Mo(dppe)Cl_3[27] and $Cp^*TaCl_4(CH_2PMePh_2)$[30] (Cp^* = η-C_5Me_5). Direct comparison of related niobium geometries is difficult; apparently no other mononuclear monocyclopentadienylniobium(V) species has been structurally characterized.[31] However, the average Nb–Cl (2.438 (15) Å) and Nb–C distances (2.429 (15) Å) in **1**, while similar to those in $[Cp'NbCl_3(H_2O)]_2O$, seem to be somewhat shorter. The ranges observed for the Nb–Cl distances in **1** and $[Cp'NbCl_3(H_2O)]_2O$ are 2.41–2.460 and 2.463–2.481 Å, respectively, and the corresponding values for the Nb–C distances are 2.397–2.456 and 2.402–2.481 Å. The two Nb–S distances are considerably different, 2.651 (3) and 2.532 (4) Å; the longer bond is to the "axial" sulfur atom trans to the Cp group. A similar difference between axial and equatorial Mo–P distances is observed in CpMo(dppe)Cl_3.[27] For comparison Nb–S distances of 2.665 (3) and 2.626 (3) Å are found in $Nb(S_2P(OPr^i)_2)_4$;[35] these longer

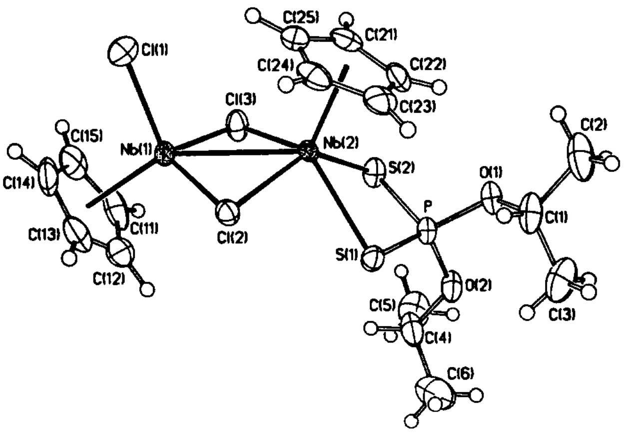

Figure 2. ORTEP plot (50% thermal ellipsoids) of $CpNb(Cl)(\mu$-$Cl)_2Nb(S_2P(OPr^i)_2)Cp$ (**2**).

Table II. Selected Bond Distances and Angles for 2

(a) Bond Distances (Å)

Nb(1)–Nb(2)	2.979 (1)	Nb(1)–Cl(1)	2.366 (1)
Nb(1)–Cl(2)	2.287 (1)	Nb(1)–Cl(3)	2.301 (1)
Nb(2)–Cl(3)	2.408 (1)	Nb(2)–Cl(2)	2.426 (1)
Nb(2)–S(2)	2.605 (1)	Nb(2)–S(1)	2.576 (1)
S(1)–P	2.000 (1)	S(2)–P	1.985 (1)
P–O(1)	1.575 (3)	P–O(2)	1.575 (3)
Nb(1)–CNT(1)	2.118 (4)	Nb(2)–CNT(2)	2.082 (4)

(b) Bond Angles (deg)

Nb(2)–Nb(1)–Cl(1)	105.9 (1)	Nb(2)–Nb(1)–Cl(2)	52.9 (1)
Cl(1)–Nb(1)–Cl(2)	107.8 (1)	Nb(2)–Nb(1)–Cl(3)	52.4 (1)
Cl(1)–Nb(1)–Cl(3)	108.3 (1)	Cl(2)–Nb(1)–Cl(3)	102.6 (1)
Nb(1)–Nb(2)–Cl(2)	48.7 (1)	Nb(1)–Nb(2)–Cl(3)	49.2 (1)
Cl(2)–Nb(2)–Cl(3)	95.6 (1)	Nb(1)–Nb(2)–S(1)	119.5 (1)
Cl(2)–Nb(2)–S(1)	78.6 (1)	Cl(3)–Nb(2)–S(1)	131.8 (1)
Cl(3)–Nb(2)–S(2)	78.7 (1)	Cl(2)–Nb(2)–S(2)	137.5 (1)
Nb(1)–Cl(3)–Nb(2)	78.5 (1)	S(1)–Nb(2)–S(2)	75.0 (1)
Nb(2)–S(2)–P	86.5 (1)	Nb(1)–Cl(2)–Nb(2)	78.4 (1)
Nb(2)–Nb(1)–CNT(1)	144.9 (1)	Nb(2)–S(1)–P	87.0 (1)
Cl(1)–Nb(1)–CNT(1)	109.3 (1)	S(1)–P–S(2)	104.6 (1)
Cl(2)–Nb(1)–CNT(1)	113.7 (1)	Nb(1)–Nb(2)–CNT(2)	113.4 (1)
Cl(3)–Nb(1)–CNT(1)	114.7 (1)	Cl(3)–Nb(2)–CNT(2)	114.8 (1)
S(2)–Nb(2)–CNT(2)	109.2 (1)	Cl(2)–Nb(2)–CNT(2)	111.2 (1)
S(1)–Nb(2)–CNT(2)	111.8 (1)		

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Table III. Selected Bond Distances and Angles for 3

	(a) Bond Distances (Å)		
Mo-CNT	2.017 (5)	Mo-S(2)	2.559 (1)
Mo-S(1)	2.550 (1)	S(1)-P	1.992 (1)
S(2)-P	1.994 (1)	Mo-C(1)	1.971 (5)
Mo-C(2)	1.942 (5)		
	(b) Bond Angles (deg)		
S(2)-Mo-CNT	116.5 (1)	P-S(1)-Mo	89.1 (1)
S(1)-Mo-CNT	114.3 (1)	P-S(2)-Mo	88.8 (1)
C(1)-Mo-CNT	118.7 (1)	S(1)-P-S(2)	105.0 (1)
C(2)-Mo-CNT	119.9 (1)	S(1)-Mo-S(2)	76.5 (1)
S(1)-Mo-C(1)	127.1 (1)	S(2)-Mo-C(1)	80.5 (1)
S(1)-Mo-C(2)	79.5 (1)	S(2)-Mo-C(2)	123.6 (1)

bonds probably reflect the high coordination number. A somewhat shorter Nb-S bond (2.602 (4) Å) is observed for the η^1-$S_2P(OEt)_2$ ligand of $Cp_2Nb(\eta^1$-$S_2P(OEt)_2)(S_2)$.[10] Due to the different coordination numbers and geometries, no generalizations concerning the change in Nb-S distances with the Nb oxidation state may be drawn from these data.

A crystallographic investigation of **2** reveals it to be a rather unusual diniobium species. An ORTEP plot and relevant structural features are given in Figure 2 and Table II, respectively. A three-legged piano-stool coordination geometry about Nb(1) is observed, while that about Nb(2) is four-legged. Both metals have a formal 16-electron count that may be arrived at in two ways: assigning the oxidation state of +3 to each Nb requires a dative bond from Nb(2) to Nb(1), whereas a "normal" metal–metal bond is required if Nb(1) is assigned a +2 oxidation state and Nb(2) is assigned as +4. The Nb-Nb bond distance of 2.979 Å is shorter than the Nb-Nb single bonds found in $Cp'_2Nb_2(CO)_4(\mu$-$Cl)_2$ (3.056 (1) Å) and $Cp'_2Nb_2(ArCCAr)_2(\mu$-$Cl)_2$ (Ar = *p*-tolyl; 3.072 (1) Å)[36] but longer than those found in some niobium clusters (ca. 2.85 Å)[37] The Nb-S distances in **2** are 2.576 (1) and 2.605 (1) Å. These distances are bracketed by the short and long Nb-S distances found in **1**. There is no obvious reason the Nb-S bond lengths in **2** should differ by nearly 0.03 Å (21σ).

In order to compare the geometries of our niobium complexes with that of a representative molybdenum species, we solved the structure of *cis*-$Cp'Mo(CO)_2(S_2P(OPr^i)_2)$ (**3**). The Mo-S distances are 2.550 (1) and 2.559 (1) Å (average 2.555 Å), which are shorter than the Nb-S distances, except for the one Nb-S(2) distance (2.532 (4) Å) in **1**. The ligand bite angle (S(1)-Mo-S(2)) is 76.5 (1)°. The two Nb compounds **1** and **2** have similar ligand bite angles of S(1)-Nb-S(2) = 76.1 (1)° and S(1)-Nb(2)-S(2) = 75.0 (1)°, respectively. The S-Pd-S angle in $Pd(Ph_2PS_2)_2(PPh_3)$ (one bidentate and one monodentate R_2PS_2 ligand) is 82°, and the Pd-S bond lengths are 2.36 Å (S trans to S) and 2.47 Å (S trans to P).[9] The bite angles seem to be determined by the preferred S-P-S angle, ca. 106° in bidentate R_2PS_2 complexes, and the M-S bond length. If the S-P-S angle is fixed, then simple geometry demands a larger bite angle as the M-S bond distance decreases. The S-P-S angle in monodentate R_2PS_2 complexes (112–119°) is much larger than in the bidentate ones (ca. 106°).[8-10]

Experimental Section

General Comments. Infrared spectra were recorded on a Nicolet 5DXB spectrometer. Mass spectra were measured on either a Finnigan Model 4021 GC-MS or a VG 70-250s spectrometer using EI or FAB ionization modes. Proton NMR (300.1 MHz) and ^{13}C NMR (75.5 MHz) spectra were obtained on a Bruker AM-300 spectrometer. Elemental analyses were performed by the University of Michigan microanalytical service.

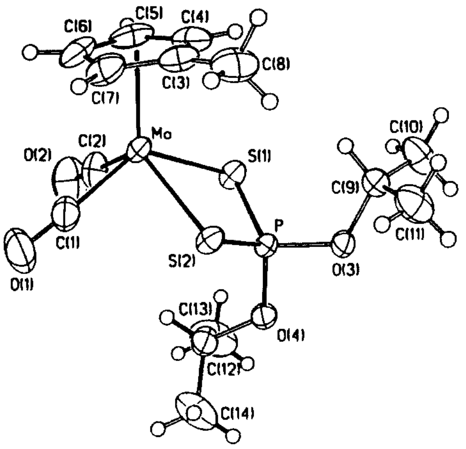

Figure 3. ORTEP plot (50% thermal ellipsoids) of $Cp'Mo(CO)_2(S_2P(OPr^i)_2)$ (**3**).

The compounds $CpNbCl_4$[34] and $[Cp'Mo(CO)_3]_2$[38] are available by literature methods. The phosphorodithioic acid $(Pr^iO)_2P(S)(SH)$ was prepared in a manner analogous to that for $Bu(^nO)_2P(S)(SH)$[39]. (^1H NMR ($CDCl_3$, 20 °C): δ 1.35 (d, 12 H, J_{HH} = 6 Hz, CH*Me*), 3.03 (s, 1 H, br, SH), 4.87 (m, 2 H, J_{HH} = 6 Hz, J_{PH} = 12.5 Hz, OCH). ^{13}C NMR ($CDCl_3$, 20 °C): δ 23.5 (d, J_{PC} = 5 Hz, CH*Me*), 73.8 (d, J_{PC} = 6 Hz, OCH).) The acid is conveniently purified by preparation of $(Pr^iO)_2P(S)(SNa)$, extraction into water, reacidification, and flash distillation. All manipulations were performed under nitrogen atmospheres with use of deoxygenated solvents dried by an appropriate agent.

Preparation of $CpNbCl_3(S_2P(OPr^i)_2)$ (1). Neat $(Pr^iO)_2P(S)(SH)$ (1.46 g, 6.81 mmol) was added to a suspension of $CpNbCl_4$ (2.00 g, 6.66 mmol) in THF (250 mL) containing NEt_3 (1.00 mL, 0.73 g, 7.17 mmol). The mixture was stirred (1 h), during which time the $CpNbCl_4$ dissolved and the color changed from red to orange-brown. The solvent was removed and the residue repeatedly extracted with toluene. The combined extracts were filtered through Celite and concentrated in vacuo until crystallization was apparent (ca. 30 mL). The solution was filtered and hexane (8 mL) added. Cooling (−15 °C) afforded $CpNbCl_3((Pr^iO)_2PS_2)$ (**1**) as deep orange plates (1.49 g). Concentration of the mother liquors afforded a second crop (0.20 g); total yield 1.69 g (53%). Anal. Calcd $C_{11}H_{19}Cl_3NbOPS_2$: C, 26.77; H, 3.88. Found: C, 26.75; H, 3.83. IR (KBr disk) ν_{PS} 641 m, 550 m cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 1.29 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 1.40 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 5.03 (m, 2 H, J_{HH} = 6 Hz, J_{PH} = 12.5 Hz, OCH), 7.19 (s, 5 H, Cp). ^{13}C NMR ($CDCl_3$, 20 °C): δ 23.7 (d, J_{PC} = 5 Hz, CH*Me*), 23.9 (d, J_{PC} = 4 Hz, CH*Me*), 75.3 (d, J_{PC} = 5 Hz, OCH), 126.8 (Cp). Mass spectrum (FAB, sulfolane matrix): *m/z* 619 ($[CpNbCl(S_2P(OPr^i)_2)_2]^+$) 584 ($[CpNb(S_2P(OPr^i)_2)]^+$).

Preparation of $CpNbCl(\mu$-$Cl)_2Nb(S_2P(OPr^i)_2)Cp$ (2). A solution of $CpNbCl_3(S_2P(OPr^i)_2)$ (**1**; 0.75 g, 1.56 mmol) in toluene (40 mL) was added to Na amalgam (0.071 g, 3.09 mmol, 1% in Hg) cooled to −20 °C. The mixture was stirred (40 min), during which time the mixture became gray. The supernatant solution was filtered through Celite with a toluene wash and the solvent removed under vacuum to give a brown oil. Extraction with toluene/hexane (1:3), filtration through Celite, and removal of the solvent gave a yellow/green oil. This oil was extracted with the minimum amount of toluene/hexane (1:5), and the extracts were filtered. Cooling (−15 °C) afforded $CpNbCl(\mu$-$Cl)_2Nb(S_2P(OPr^i)_2)Cp$ (**2**) as green plates (0.10 g, 20%). Anal. Calcd for $C_{16}H_{24}Cl_3Nb_2O_2PS_2$: C, 30.23; H, 3.81. Found, C, 30.49; H, 3.74. IR (KBr disk): ν_{PS} 655 m, 555 m cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 1.09 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 1.57 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 3.95 (m, 1 H, J_{HH} = 6 Hz, J_{PH} = 12 Hz, OCH), 4.91 (m,

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Table IV. Crystallographic Data for 1-3

	1	2	3
(a) Crystal Parameters			
formula	$C_{11}H_{19}O_2PS_2Cl_3Nb$	$C_{16}H_{24}O_2PS_2Cl_3Nb_2$	$C_{14}H_{21}O_4PS_2Mo$
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
cryst syst	triclinic	triclinic	orthorhombic
a, Å	7.122 (3)	7.251 (3)	12.703 (3)
b, Å	11.365 (4)	12.386 (5)	16.706 (4)
c, Å	12.532 (4)	13.988 (5)	18.398 (4)
α, deg	77.38 (3)	102.66 (3)	
β, deg	89.08 (3)	103.56 (3)	
γ, deg	72.87 (3)	94.66 (3)	
V, Å^3	944.5 (8)	1180.0 (8)	3904.4 (1.7)
Z	2	2	8
cryst dimens, mm	0.08 × 0.22 × 0.42	0.30 × 0.38 × 0.50	0.31 × 0.31 × 0.38
cryst color	red	brown	deep red
D(calc), g/cm^3	1.679	1.788	1.511
μ(Mo Kα), cm^{-1}	13.37	15.27	9.53
temp, °C	23	23	23
T(max)/*T*(min)	1.578	1.239	
(b) Data Collection			
diffractometer		Nicolet R3m	
monochromator		graphite	
scan technique		Wyckoff	
radiation		Mo Kα (λ = 0.71073 Å)	
2θ scan range, deg	4-48	4-52	4-52
data collected	±9,±14,±15	±9,±16,±18	+15,+20,+22
scan speed, deg/min	var, 5-20	var, 6-20	var, 6-20
no. of rflns collected	3156	4906	4381
no. of indpt rflns	2906	4625	3842
R(merg), %	4.78	1.34	
no. of indpt rfln obsd, $F_o > 5\sigma(F_o)$	2109	3980	2675
std rflns		3 stds/197 rflns	
var in stds, %	~7	~1	~2
(c) Refinement			
R(*F*), %	7.85	2.70	3.49
R(w*F*), %	7.86	3.17	3.90
Δ/σ(max)	0.066	0.120	0.041
Δ(ρ), e/Å^3	2.224	0.419	0.515
N_o/N_v	11.46	16.9	13.4
GOF	1.940	1.035	1.042

Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 1

	x	*y*	*z*	*U*[a]
Nb	8844.8 (14)	785.3 (10)	7324.2 (9)	39.1 (4)
Cl(1)	9436 (5)	2164 (4)	5650 (3)	65 (1)
Cl(2)	6830 (5)	104 (4)	6204 (3)	63 (1)
Cl(3)	6985 (5)	106 (4)	8888 (3)	63 (2)
P(1)	6713 (4)	3420 (3)	8032 (3)	48 (1)
O(1)	5757 (12)	3444 (8)	9167 (7)	60 (4)
O(2)	6576 (13)	4849 (8)	7594 (7)	63 (4)
S(1)	5528 (4)	2677 (3)	7025 (3)	59 (1)
S(2)	9516 (4)	2307 (3)	8365 (3)	51 (1)
C(1)	11322 (25)	−842 (17)	8566 (9)	46 (9)
C(2)	10670	−1413	7802	61 (12)
C(3)	11258	−924	6752	39 (9)
C(4)	12274	−51	6867	65 (12)
C(5)	12313	−1	7988	65 (12)
C(6)	3661 (21)	3553 (15)	9331 (12)	73 (7)
C(7)	3467 (26)	3120 (15)	10501 (15)	99 (9)
C(8)	2458 (23)	4907 (18)	8945 (15)	108 (10)
C(9)	7013 (31)	5388 (15)	6465 (13	92 (9)
C(10)	5561 (38)	6605 (21)	6092 (18)	183 (16)
C(11)	9004 (37)	5534 (26)	6472 (20)	190 (18)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 2

	x	*y*	*z*	*U*[a]
Nb(1)	2660.8 (4)	1466.0 (2)	2089.0 (2)	34.5 (1)
Nb(2)	2135.0 (3)	3854.5 (2)	2723.6 (2)	28.1 (1)
Cl(1)	762 (2)	476 (1)	2868 (1)	73 (1)
Cl(2)	4710 (1)	2843 (1)	3336 (1)	38 (1)
Cl(3)	734 (1)	2463 (1)	1161 (1)	48 (1)
S(1)	5059 (1)	5386 (1)	3251 (1)	40 (1)
S(2)	1381 (1)	5098 (1)	1439 (1)	46 (1)
P	3414 (1)	6246 (1)	2423 (1)	38 (1)
O(1)	2520 (4)	7164 (2)	3073 (2)	47 (1)
O(2)	4558 (4)	7000 (2)	1924 (2)	52 (1)
C(1)	3466 (6)	7747 (3)	4138 (3)	60 (2)
C(2)	1940 (8)	8290 (4)	4541 (3)	88 (2)
C(3)	5144 (8)	8542 (4)	4219 (4)	92 (2)
C(4)	5638 (7)	6547 (3)	1186 (4)	67 (2)
C(5)	4489 (9)	6595 (5)	156 (4)	91 (3)
C(6)	7548 (7)	7242 (5)	1516 (5)	105 (3)
C(21)	−943 (5)	4002 (3)	2982 (3)	55 (1)
C(22)	198 (5)	5019 (3)	3544 (3)	56 (2)
C(23)	1584 (6)	4790 (4)	4337 (3)	59 (2)
C(24)	1308 (5)	3661 (4)	4261 (3)	54 (1)
C(25)	−240 (5)	3172 (3)	3439 (3)	54 (1)
C(11)	3527 (8)	719 (4)	546 (3)	78 (2)
C(12)	5201 (6)	1093 (4)	1307 (4)	68 (2)
C(13)	5323 (6)	414 (4)	1972 (3)	68 (2)
C(14)	3708 (7)	−371 (3)	1636 (4)	75 (2)
C(15)	2576 (6)	−194 (3)	748 (4)	73 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orghogonalized U_{ij} tensor.

1 H, J_{HH} = 6 Hz, J_{PH} = 12 Hz, OCH), 5.33 (s, 5 H, Cp), 6.20 (s, 5 H, Cp). ^{13}C NMR ($CDCl_3$, 20 °C): δ 23.3 (d, J_{PC} = 3 Hz, CH*Me*), 23.8 (d, J_{PC} = 4 Hz, CH*Me*), 73.4 (d, J_{PC} = 6 Hz, OCH), 74.4 (d, J_{PC} = 9 Hz, OCH), 102.7 (Cp), 106.8 (Cp). No reaction was observed by ^1H NMR spectroscopy when solutions of **2** were stirred under CO atmospheres for 24 h.

Preparation of *cis*-Cp′Mo(CO)$_2$(S$_2$P(OPr^i)$_2$) (3). A mixture of $(Pr^iO)_2P(S)(SH)$ (1.50 g, 7.01 mmol) and $[Cp'Mo(CO)_3]_2$ (1.00 g, 1.93 mmol) in toluene (100 mL) was refluxed (16 h) until the color became purple. The toluene was removed and the residue

Table VII. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 3

	x	*y*	*z*	U^a
Mo	1751.9 (3)	8177.0 (2)	2716.6 (2)	39.1 (1)
S(1)	80.0 (8)	7341.1 (6)	2607.3 (6)	45.3 (3)
S(2)	2444.5 (8)	6756.8 (6)	2507.6 (6)	41.4 (3)
P	966.6 (8)	6358.7 (6)	2559.9 (5)	34.8 (3)
O(1)	3416 (3)	8125 (3)	3963 (3)	99 (2)
O(2)	571 (4)	8708 (3)	4111 (2)	107 (2)
O(3)	656 (2)	5755 (2)	1936 (1)	46 (1)
O(4)	770 (2)	5754 (2)	3213 (1)	46 (1)
C(1)	2811 (4)	8127 (3)	3498 (3)	62 (2)
C(2)	1013 (4)	8506 (3)	3591 (3)	64 (2)
C(3)	2318 (4)	8487 (3)	1476 (3)	60 (2)
C(4)	−1261 (4)	8700 (3)	1547 (3)	68 (2)
C(5)	1167 (5)	9285 (3)	2096 (3)	78 (2)
C(6)	2191 (5)	9435 (3)	2373 (3)	77 (2)
C(7)	2895 (4)	8916 (3)	2003 (3)	68 (2)
C(8)	2781 (4)	7919 (4)	920 (3)	83 (2)
C(9)	685 (3)	6027 (3)	1169 (2)	49 (1)
C(10)	−427 (4)	5955 (4)	878 (3)	78 (2)
C(11)	1474 (4)	5521 (4)	779 (3)	76 (2)
C(12)	890 (4)	6017 (3)	3966 (2)	60 (2)
C(13)	−209 (5)	6015 (4)	4294 (3)	115 (3)
C(14)	1615 (4)	5428 (4)	4334 (3)	96 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orghogonalized U_{ij} tensor.

extracted with CH_2Cl_2. The extracts were filtered through a short plug of Al_2O_3, and the solvent was removed to yield a maroon solid. Recrystallization from CH_2Cl_2/hexane afforded *cis*-Cp′Mo$(CO)_2(S_2P(OPr^i)_2)$ (**3**) as maroon crystals (1.52 g, 89%). Anal. Calcd for $C_{14}H_{21}MoO_4PS_2$: C, 37.84; H, 4.76; S, 14.43. Found: C, 38.04; H, 4.72; S, 14.91. IR (KBr disk) ν_{CO} 1951 s, 1847 s cm^{-1}; ν_{PS} 542 m, 439 m cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 1.29 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 1.36 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 1.98 (s, 3 H, Cp′), 4.40 (m, 1 H, J_{HH} = 6 Hz, J_{PH} = 12 Hz, OCH), 4.59 (m, 1 H, J_{HH} = 6 Hz, J_{PH} = 12 Hz, OCH), 5.20 (m, 2 H, Cp′), 5.24 (m, 2 H, Cp′). ^{13}C NMR ($CDCl_3$, 20 °C): δ 13.9 (Cp′), 23.5 (d, J_{PC} = 3 Hz, CH*Me*), 23.7 (d, J_{PC} = 4 Hz, CH*Me*), 72.2 (d, J_{PC} = 6 Hz, OCH), 74.0 (d, J_{PC} = 9 Hz, OCH), 88.8 (Cp′), 96.4 (Cp′), 117.1 (Cp′), 255.4 (d, J_{PC} = 6 Hz, CO). Mass spectrum (EI): 446 (M^+), 418 ($(M - CO)^+$), 390 ($(M - 2CO)^+$).

Preparation of Cp′$MoI_2(CO)(S_2P(OPr^i)_2)$ (4). Solid I_2 (0.36 g, 1.41 mmol) was added to a solution of *cis*-Cp′$Mo(CO)_2(S_2P(OPr^i)_2)$ (0.60 g, 1.40 mmol) in CH_2Cl_2 (60 mL) at 0 °C. The mixture became orange-brown (2 h), and an IR spectrum indicated the reaction to be complete. The solvent was removed and the residue extracted with CH_2Cl_2, and the extracts were filtered through Celite. The filtrate was concentrated and hexane added to yield black microcrystals. Recrystallization from CH_2Cl_2/hexane afforded Cp′$MoI_2(CO)(S_2P(OPr^i)_2)$ (**4**) as black crystals (0.51 g, 56%). Anal. Calcd for $C_{13}H_{21}I_2MoO_3PS_2$: C, 23.30; H, 3.16. Found: C, 23.12; H, 2.90. IR (KBr disk): ν_{CO} 1996s cm^{-1}; ν_{PS} 553 m, 493 m cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 1.36 (d, 6 H, J_{HH} = 6 Hz, CH*Me*) 1.37 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 1.42 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 1.44 (d, 6 H, J_{HH} = 6 Hz, CH*Me*), 2.38 (s, 3 H, Cp′), 4.83 (m, 1 H, J_{HH} = 6 Hz, J_{PH} = 11.5 Hz, OCH), 5.30 (m, 1 H, Cp′), 5.33 (m, 1 H, Cp′), 5.39 (m, 1 H, J_{HH} = 6 Hz, J_{PH} = 12 Hz, OCH), 5.88 (m, 2 H, Cp′). ^{13}C NMR ($CDCl_3$, 20 °C): δ 16.5 (Cp′), 23.7 (m, CH*Me*), 74.3 (d, J_{PC} = 6 Hz, OCH), 74.6 (d, J_{PC} = 9 Hz, OCH), 95.6 (Cp′), 97.4 (Cp′), 98.3 (Cp′), 99.4 (Cp′), 110.0 (Cp′), 219.8 (d, J_{PC} = 2 Hz, CO). Mass spectrum (EI): 628 ($(M - 1 - Pr^i)^+$), 501 ($(M - 1 - Pr^i - I)^+$).

X-ray Structure Determinations for $CpNbCl_3(S_2P(OPr^i)_2)$ (1), $CpNbCl(\mu\text{-}Cl)_2Nb(S_2P(OPr^i)_2)Cp$ (2), and *cis*-Cp′$Mo(CO)_2(S_2P(OPr^i)_2)$ (3). X-ray Data Collection for 1–3. Crystal, data collection, and refinement parameters are given in Table IV. Crystals of **1** and **2** were grown by slow cooling of toluene-/hexane mixtures to 0 °C. Crystals of **3** were obtained from a CH_2Cl_2/hexane mixture at 0 °C. Data were collected at ambient temperatures on crystals mounted on glass fibers with epoxy cement. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterization showed $\bar{1}$ Laue symmetry for **1** and **2** and *mmm* symmetry for **3**. For **1** and **2**, the centrosymmetric alternative, $P\bar{1}$, was suggested by *E* statistics and confirmed by the chemically sensible results of refinement. Systematic absences in the diffraction data uniquely established the space group for **3**. Three standard reflections monitored every 197 reflections showed insignificant variations in **2** and **3** but approximately 7% linear variation in **1**, for which a correction was made. Empirical absorption corrections were applied to the data sets of **1** and **2** (216 ψ-scan reflections, pseudoellipsoid model); none were required for **3**.

Structural Solution and Refinement for 1–3. Both **1** and **3** were solved by direct methods to locate the metal atoms. **2** was solved with use of heavy-atom methods. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.96 Å; $U = 1.2U$ for attached C). For **2** and **3**, all non-hydrogen atoms were refined anisotropically. For **1**, the Cp ring was disordered over two sites in a 60:40 occupancy ratio, making it necessary to fix the C–C distances (d(C–C) = 1.420 Å) by creating rigid Cp rings and refining the minority carbon atoms isotropically. All computer programs are contained in the SHELXTL program library (version 5.1, Nicolet Corp., Madison, WI).

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen parameters for 1, 2, and 3 (13 pages); listings of structure factors (F_o vs F_c) for 1, 2, and 3 (53 pages). Ordering information is given on any current masthead page.