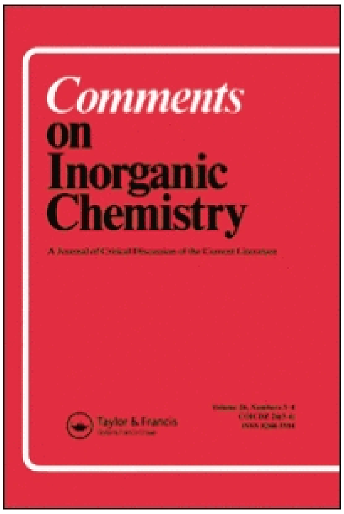


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Concerning the Spatial Nature of Metal-Thiolate π Bonding

Michael T. Ashby[a]
[a] Searle Chemical Laboratory, Department of Chemistry, 5735 South Ellis Avenue, The University of Chicago, Chicago, Illinois

To cite this Article Ashby, Michael T.(1990) 'Concerning the Spatial Nature of Metal-Thiolate π Bonding', Comments on Inorganic Chemistry, 10: 6, 297 — 313
To link to this Article: DOI: 10.1080/02603599008048654
URL: http://dx.doi.org/10.1080/02603599008048654

Concerning the Spatial Nature of Metal–Thiolate π Bonding

MICHAEL T. ASHBY[1]
Searle Chemical Laboratory,
Department of Chemistry,
5735 South Ellis Avenue,
The University of Chicago,
Chicago, Illinois 60637

Structural data obtained from published single-crystal X-ray studies of molecular transition metal complexes of terminal thiophenolate ligands are used to rationalize a model for M–S π bonding. The principal π-donor orbital of thiolates is the S 3p orbital which is oriented perpendicular to the M–S–C plane. Consequently, M–S–C bond angles are not indicative of the degree of M–S dπ-pπ bonding.

Key Words: *thiolate, π bonding, electronic structure, molecular structure*

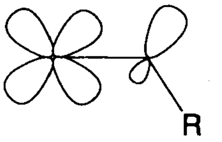
INTRODUCTION

Coordination chemists have long been attracted to thiolate ligands because of their proclivity for forming bridging bonds, an attribute useful in the synthesis of metal clusters.[2] Furthermore, terminal thiolate ligands may serve as π-donors, thereby stabilizing coordinatively unsaturated metal centers[3] and π-acceptor ligands bound to metals in high oxidation states.[4] However, the greatest attention has been paid by chemists interested in the role thiolates play as

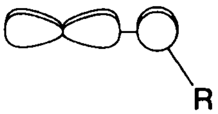
Comments Inorg. Chem.
1990, Vol. 10, No. 6, pp. 297–313
Reprints available directly from the publisher
Photocopying permitted by license only

ancillary ligands in metalloproteins.[5] An understanding of the relationship between the molecular and electronic structures of terminal metal–thiolate complexes is fundamental to appreciating their chemistry and spectroscopy.

Many models have emerged for the bonding of thiolate ligands to transition metals. The simplest model, which involves sp^3 hybridization of the sulfur orbitals to give tetrahedrally disposed sulfur lone pairs, is frequently invoked. However, when it comes to describing subtle structural and spectroscopic features, this model is as inadequate for thiolate ligands as it is for simple organic thioethers.[6] Theorists describe thiolate ligands as possessing two potential π-donor orbitals[3c–e,7]:



1



2

The in-plane orbital (**1**) will be referred to here as $\pi_{\parallel}$ and the out-of-plane orbital (**2**) will be referred to here as $\pi_{\perp}$. Both $\pi_{\parallel}$ and $\pi_{\perp}$ are largely S 3p in character. However, whereas $\pi_{\parallel}$ has σ-bonding as well as a π-bonding component with respect to the metal and the R-group, $\pi_{\perp}$ is strictly π-bonding with respect to the metal and the R-group. Furthermore, the $\pi_{\perp}$ orbital typically lies somewhat higher in energy than the $\pi_{\parallel}$ orbital. Among those who embrace this latter model, there appears to be confusion as to whether the $\pi_{\parallel}$[8,9] or the $\pi_{\perp}$[3c–e,7f] orbital is the better π-donor orbital.

Thiolate ligand complexes offer five structural parameters pertinent to a discussion of bonding: 1. the M–S bond distance, 2. the S–C bond distance, 3. the M–S–C bond angle, 4. the rotational orientation about the S–C bond, and 5. the rotational orientation about the M–S bond. Previous discussions of the relationship between the structure and bonding of thiolate ligands have considered all of these structural parameters; however, only two of the parameters directly address the question of the spatial nature of the M–S dπ-pπ bond: the M–S–C bond angle and the rotational orientation about the M–S bond. Nearly linear M–O–C bond angles are often cited as evidence for M–O dπ-pπ bonding interactions between transition metals and alkoxide ligands.[10,11] However, structural and theoretical studies of coordinatively unsaturated transition metal complexes suggest the out-of-plane lone pair is the preferred thiolate ligand π-donor orbital.[3c–e] If this is correct, M–S–C bond angles should be insensitive to the extent of M–S dπ-pπ bonding. Surprisingly, despite the fact that hundreds of crystal structures of metal complexes containing thiolate ligands have been reported, even the most recent reviews of the chemistry of thiolate ligands neglect to discuss M–S–C angles.[2,12] We report here that, indeed, M–S–C bond angles are independent of the electronic nature of the metal fragment.

MOLECULAR STRUCTURES OF METAL–THIOLATE COMPLEXES

M–S Bond Distances. Chisholm *et al.* have analyzed M–S bond lengths in metal–thiolate complexes by comparison with analogous metal–alkyl complexes.[13] By assuming M–C bond lengths represent σ-only bonds, the covalent radius of a metal can be determined by subtracting the covalent radius of carbon (radius of C(sp^3) = 0.77 Å) from the M–C bond length. The covalent radius of the sulfur atom is determined by subtracting the covalent radius of carbon from the S–C bond length. The M–S bond distances in Chisholm's compounds were found to be about 0.07 Å shorter than the sum of the covalent radii of the metal and the sulfur atoms. It is difficult, however, to argue the significance of this difference given that the M–S and M–C distances were obtained from different compounds. Since Chisholm's analysis, a better benchmark compound has been reported by Legzdins *et al.*[14] CpW(NO)(SCH$_2$SiMe$_3$)(CH$_2$SiMe$_3$) is a coordinatively unsaturated 16-electron complex. The rotational orientation of the thiolate ligand observed in the solid-state structure of CpW(NO)(SCH$_2$SiMe$_3$)(CH$_2$SiMe$_3$) maximizes M–S dπ-pπ bonding (*vide infra*). Both the alkyl and the thiolate ligand are bound to the same metal center and are in the same coordination environment. Furthermore, the alkyl group bound to the metal is the same as that bound to the sulfur atom. Using the same method of analysis as Chisholm, we calculate that the covalent radii of W and S are 1.36 and 1.08 Å, respectively. The sum (2.44 Å) is 0.14 Å longer than the observed W–S distance (2.30 Å), which indicates the importance of M–S π bonding in $CpW(NO)(SCH_2SiMe_3)(CH_2SiMe_3)$.

M–S–C Bond Angles. Consider now the influence of the nature of the metal fragment on M–S–C bond angles. Only terminal, monodentate thiolate ligands are suitable for such a comparison. Therefore, we will confine our discussion to a single R-group, phenyl, and observe the effect of various metal fragments on the M–S–C bond angles. Thiophenolates were chosen for the following discussion because more crystal structures containing thiophenolates have been reported than for any other R-group.[15] Any potential ambiguity introduced as a result of different steric and electronic effects imposed by different R-groups may be avoided by comparing only thiophenolate ligand complexes. We note here that aryl thiolates apparently prefer to orient the aryl group coplanar with respect to the M–S–C plane so as to facilitate a π-type interaction between the aryl π-system and the S 3p lone pair. The significance of this orientation has been discussed previously.[16] It is important to point out that, although π conjugation is possible for thiophenolates, they are not unique in the context of the subsequent discussion. Thiolate complexes possessing other R-groups could be discussed to the same end.[17]

Figure 1 summarizes the available crystallographic data for molecular thiophenolate complexes. The data used to construct the histogram of Fig. 1 are summarized in the Appendix. Only molecular monomeric and symmetric dimeric compounds containing terminal thiophenolate ligands are included in these data. Some of the thiolate ligands in the structures from which these data were derived are related by crystallographic symmetry and for one entry two crystallographically independent molecules were found. For those compounds that contain more than one terminal thiophenolate ligand, only the data for those structures in which individual M–S–C bond angles were reported are included in Fig. 1. The data for a total of 24 compounds containing 14 different transition metals and 68 thiophenolate ligands are represented in Fig. 1.

It is clear from Fig. 1 that the M–S–C bond angles are distrib-

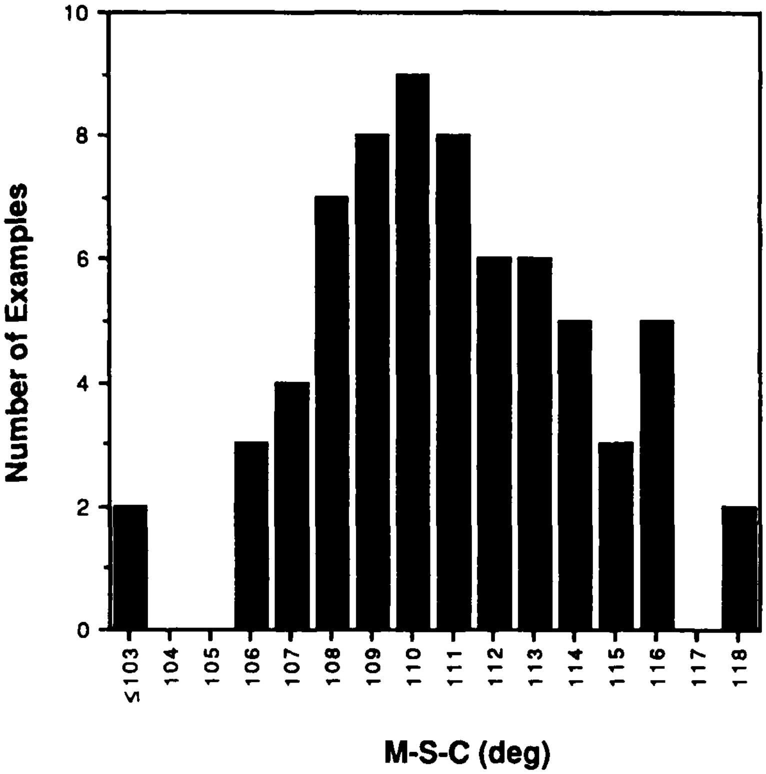


FIGURE 1 Distribution of M–S–C bond angles in thiophenolate–metal complexes.

uted over a very narrow arc with respect to a mean value of 110.8(3.4)°. This is in sharp contrast to the M–O–C bond angles of alkoxide ligands, which vary from 130° to nearly 180°.[10,11] The significance of Fig. 1 becomes apparent with the discussion of particular complexes (*vide infra*).

M–SR Rotational Orientations. The most compelling evidence for metal–thiolate dπ-pπ bonding is found in the observed rotational orientations of thiolate ligands bound to coordinatively unsaturated transition metal fragments, which, according to theory, have available dπ acceptor orbitals. Table I summarizes examples of such complexes. The electronic structures of some of the com-

TABLE I

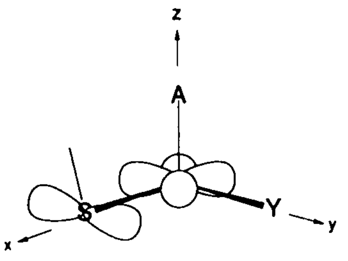
Compounds which exhibit conformations that maximize Mdπ–Spπ bonding

Compound	Expected[a] (deg)	Observed (deg)	M–S–C (deg)	Ref.
5 $CpMo(NO)(SPh)_2$	0,180	12,186	108,111	3e
6 $CpW(NO)(CH_2SiMe_3)(SCH_2SiMe_3)$	180	174	110	14
7 $CpMo(CO)(C_2(CF_3)_2)(SC_6F_5)$	180	176	106	18
8 $CpMo(O)(C_2(CF_3)_2)(SC_6F_5)$	90	76	108	18
9 $CpMo(CO)(C_2Me_2)(SC_6H_4$-*o*-SPh)	180	179	109	19
10 $CpMo(P(OMe)_3)(C_2Me_2)(SC_6H_4$-*o*-$NO_2)$	180	179	110	19
11 $Mo\{HB(Me_2Pz)_3\}(NO)(I)(Scy)$	0	11	112	20
12 $Ti(Cl)_2(diars)(S^tBu)_2$	±90	65,-65	120,120	21
13 $Mo(CN^tBu)_4(S^tBu)_2$	±90	102,-101	119,120	3b,c
14 $Mo(CN^tBu)_2(C_2H_2)(S^tBu)_2$	90	81,83	118,120	3d
15 $Mo(CN^tBu)_2(C_2Ph_2)(S^tBu)_2$	90	76,81	120,120	3d
16 $Cp_2Ti(SMe)_2$	±90	57,-57	110,110	31
17 $Cp_2Ti(SPh)_2$	±90	61,-65	113,115	15a
18 $[Cp_2Nb(SPh)_2][PF_6]$	±90	67,-68	112,112	15d

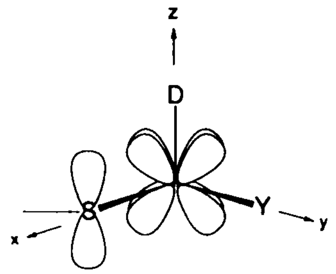
[a] For **5–11**, the compounds LM(X)(Y)(SR), where L is a tridentate ligand (Cp or $\{HB(Me_2Pz)_3\}$), X is a double-sided π-bonding ligand (NO, CO, O, PR_3), and Y can be anything (e.g., π-nonbonding (CH_2SiMe_3), single-sided π-bonding (SR,C_2R_2), or double-sided π-bonding (I) ligand), the C–S–M–X torsion angle. For **12–18**, the C–S–M–S torsion angle.

pounds listed in Table I, as they relate to metal–thiolate $d\pi$-$p\pi$ bonding, have been discussed elsewhere.[3c–e,17] Only one class of compounds, the three-legged piano stool complexes, will be mentioned here. The expected rotational orientations of the other compounds of Table I may be rationalized similarly.[23]

Three-legged piano stool complexes CpM(X)(Y)(SR), where X is a double-sided (cylindrical) π-acceptor (A) or π-donor (D) ligand and Y may be either a π-nonbonding or a single-sided π-donor ligand, have been investigated theoretically using the Extended Hückel[27] and Fenske–Hall[3c] methods. These compounds are best described as pseudo-octahedral. For the examples in Table I where X is a double-sided π-acceptor ligand, and the metal has a d^4 electron configuration (e.g., $CpMo(CO)(C_2(CF_3)_2)(SC_6F_5)$), the two M $d\pi$ orbitals that interact with the π-acceptor ligand orbitals will be occupied and the $d\pi$ orbital that is perpendicular to the M–X axis will be unoccupied. In all cases, the thiolate ligands orient themselves such that their S 3p lone pair(s) donate to the empty $d\pi$ orbital (**3**, the empty M$d\pi$ orbital is illustrated). In contrast, for $CpMo(O)(C_2(CF_3)_2)(SC_6F_5)$, X is a π-donor oxo ligand and the metal has a d^2 electron count. The occupation of the M $d\pi$ orbitals is opposite from that of the other piano stool compounds of Table I (for **3**, the d_{xz} and d_{yz} orbitals are filled and the d_{xy} orbital is empty, whereas, for **4**, the d_{xz} and d_{yz} are empty and the d_{xy} orbital is filled). Accordingly, the thiolate ligand rotates by 90° (**4**, the two empty M$d\pi$ orbitals are illustrated, only one of which may be π-donated to by the SR ligand, the other M$d\pi$ orbital is π-donated to by the alkyne).

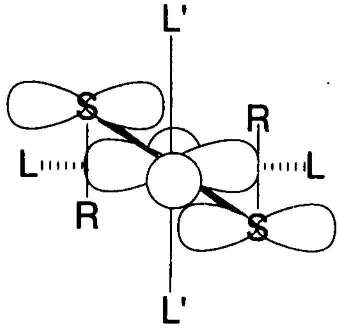


3



4

While the orientations of the thiolate ligands in the compounds of Table I are approximately what we might expect based upon the simple-minded electronic arguments presented here, the orientations in several of the complexes deviate somewhat from ideal. We note here another trend in the structures of the compounds of Table I that possess two *cis* thiolate ligands that are oriented such that their out-of-plane lone pairs are approximately coplanar (i.e., **5**, **12–18**). One might attribute the deviation to steric or solid-state effects, but the principal cause is more subtle; all of these structures exhibit the molecular distortion shown diagrammatically below:



The S/M/S planes of these compounds are twisted with respect to the L/M/L planes. The effect of this distortion is to make the C–S–M–S′ torsion angles more acute than if the S/M/S and L/M/L planes were coplanar. For **12** and **13** the dihedral angles between the S/M/S and L/M/L planes are 11.1° and 11(1)°, respectively. The related dihedral angles for **14** and **15** (where the L/M/L plane is defined to be 90° less than the least-squares plane containing the metal, the alkyne carbon atoms, and the carbon atoms of the two *trans* isocyanide ligands) are 9.8° and 9.5°. The related distortions in compounds **5** and **16–18** are evident in the interatomic angles of the molecules (e.g., the S–Mo–NO angles of **5** are 90.6(1)° and 96.1(1)°). The dihedral distortions observed in compounds **5** and **12–18** may have an electronic origin. Intramolecular S 3p lone pair–S 3p lone pair repulsion is evidenced by the obtuse S–M–S angles in compounds **5** and **12–18** (100–115°). The bond and dihedral angular distortions may be an effort to minimize intramolecular S–S repulsions while maximizing M–S bonding. The salient point is that the C–S–M–S′ torsion angles of these compounds are not entirely representative of the orientation of the S 3p lone pairs with respect to the inferred metal-based LUMO's.

We conclude this discussion by pointing out the lack of correlation between the electronic requirements of the metal fragment and M–S–C bond angles. Consider **5**, the only three-legged piano stool compound of Table I that possesses thiophenolate ligands. The Mo–S–C bond angles for **5** are 107.2(2)° and 110.6(2)°, very close to the mean M–S–C bond angle of all thiophenolate ligand complexes (110.8°). Clearly for this class of three-legged piano stool complexes the M–S bond distances, the rotational orientation of the thiolate ligands about the M–S bond, and *the M–S–C bond angles* suggest that $\mathrm{Md\pi{-}Sp\pi_{\perp}}$ bonding (as opposed to $\mathrm{Md\pi{-}Sp\pi_{\parallel}}$ bonding) is significant. The only other compounds of Table I that possess thiophenolate ligands are **17** and **18**. For **17**, the Ti–S–C bond angles are 112.9° and 115.4°, which are relatively large. However, the Nb–S–C bond angles of 112.0(4)° observed for **18**, which is valence isoelectronic with **17**, indicate that intramolecular steric factors may play a role in these eight-coordinate complexes. The two thiophenolate complexes with the largest M–S–C angles (118°) are $\mathrm{Mo\{HB(Me_2pz)_3\}(O)(SPh)_2}$[15h] and $\mathrm{[NMe_4][Mo(\mu\text{-}O)(O)(SPh)_2]_2}$.[15i] The former compound contains a 3,5-dimethylpyrazolylborate ligand, which is renowned for its steric demands, and the latter happens to crystallize with two independent molecules per unit cell, only one of which has a Mo–S–C angle of 118°; the other angles in both molecules are within 3° of the mean value for all thiophenolate ligands.

CONCLUSIONS

The significance of M–S dπ-pπ bonding is evidenced by relatively short M–S bond lengths and apparent in the chemistry of thiolate ligand complexes. Structural studies have demonstrated the spatial and electronic nature of the M–S dπ-pπ bond. The principal π-donor orbital of thiolate ligands is the out-of-plane S 3p lone pair. Accordingly, M–S–C bond angles do not reflect the degree of π donation. In contrast, there exists strong evidence for a correlation between M–O–C bond angles and the extent of M–O dπ-pπ bonding in metal–alkoxide compounds. M–O–C bond angles range from 130° to nearly 180°. Why then are M–O–C bond angles sensitive and M–S–C bond angles insensitive to the electronic nature of the metal fragment? One is tempted to ascribe the difference to alkoxides being better π-donor ligands than thiolates. However, we are reminded of the trend apparent when first row heteroatom-containing compounds are compared to their heavier congeners: e.g., the more obtuse H–X–H angle in H_2O (104.5°) as compared to H_2S (92.1°) and in NH_3 (106.7°) as compared to PH_3 (93.3°). The barriers to inversion of the latter two compounds (5.8 vs. 30–36 kcal mol^{-1}, respectively) also reflect the reluctance of the heavier congeners to bend their bonds. These trends must reflect a greater tendency for the 2s and 2p orbitals of first row atoms to mix as compared to the 3s and 3p orbitals of second row atoms.

APPENDIX

Table II lists all known transition metal complexes containing terminal thiophenolate ligands that have been structurally characterized by single-crystal X-ray crystallography, including the compounds and structural data used to prepare the histogram of Fig. 1. Table II is organized according to the formal oxidation states of the transition metals.

TABLE II

Structurally characterized examples of metal complexes that contain terminal thiophenolate ligands

Compound	M–S (Å)	M–S–C (deg)	Ref.
Ti(IV)			
$Cp_2Ti(SPh)_2$	2.395(8)	115.4	15a
	2.424(8)	112.9	

TABLE II (*continued*)

Structurally characterized examples of metal complexes that contain terminal thiophenolate ligands

Compound	M–S (Å)	M–S–C (deg)	Ref.
Zr(IV)			
[Cp$_2$Zr(μ-O)$_{1/2}$(SPh)]$_2$	2.542(2)	105.9(2)	15b
	2.554(2)	110.9(2)	
V(IV)			
Cp$_2$V(SPh)$_2$	2.448(3)	115.5	15a
	2.470(2)	113.6	
[PhCH$_2$NMe$_3$]$_2$[V(S)(SPh)$_4$]	2.377(2)	110.96(18)-	15c
	2.388(2)	112.36(21)	
	2.405(2)		
	2.392(2)		
Nb(V)			
[Cp$_2$Nb(SPh)$_2$][PF$_6$]	2.417(1)	112.0(1)	15d
Mo(II)			
CpMo(NO)(SPh)$_2$	2.345(1)	110.6(2)	3e
	2.339(1)	107.2(2)	
[NHEt$_3$][Mo(NO)(SPh)$_4$]	2.317(2)	108.9(2)	15e
	2.326(3)	110.3(3)	
	2.337(2)	110.0(3)	
	2.524(2)	116.2(3)	
Mo(IV)			
[Cp$_2$Mo(NH$_3$)(SPh)][PF$_6$]	2.465(5)	115.5(5)	7f
Mo(V)			
[CpMo(μ-O)$_{1/2}$(O)(SPh)]$_2$	2.369(3)	a	15f
[AsPh$_4$][Mo(O)(SPh)$_4$]	2.401(4)	107.3(5)	15g
	2.401(4)	111.4(5)	
	2.397(3)	111.7(5)	
	2.411(4)	108.8(4)	
Mo{HB(Me$_2$Pz)$_3$}(O)(SPh)$_2$	2.384(2)	117.7(2)	15h
	2.380(2)	112.5(3)	
[NMe$_4$][Mo(μ-O)(O)(SPh)$_2$]$_2$	2.452(4)	118.1(4)	15i
	2.437(4)	111.9(4)	
	2.463(4)	114.2(4)	
	2.452(3)	110.6(4)	
	2.422(3)	109.6(4)	
	2.458(3)	108.0(4)	
	2.414(4)	110.3(4)	
	2.476(3)	110.6(4)	

TABLE II (*continued*)

Structurally characterized examples of metal complexes that contain terminal thiophenolate ligands

Compound	M–S (Å)	M–S–C (deg)	Ref.
Mo(VI)			
$[PPh_4][Mo(O)(NNMe_2)(SPh)_3$	2.432(4)	109.5(3)	15j
	2.465(3)	111.2(3)	
	2.415(4)	109.4(3)	
W(II)			
$[PPh_4][W(Cl)(NO)(SPh)_3]$	2.328(4)	110.0(4)	15e
	2.315(4)	110.6(6)	
	2.320(4)	113.4(5)	
Mn(II)			
$[PPh_4]_2[Mn(SPh)_4]$	2.454(3)	109.7(2.2)[b]	15k
	2.445(3)		
	2.421(3)		
	2.449(3)		
Re(III)			
$Re(NCMe)(PPh_3)(SPh)_3$	2.248(7)	a	15l
	2.555(6)		
	2.264(7)		
Re(V)			
$[AsPh_4][Re(O)(SPh)_4]$	2.337(3)	112.8(3)	15m
	2.339(3)	112.1(3)	
	2.342(3)	115.9(3)	
	2.345(3)	116.4(3)	
$Re(NPPh_3)(SPh)_4$	2.337(2)	a	15l
	2.323(3)		
	2.318(2)		
	2.330(3)		
Fe(O)			
$[PPN][PhSFe(CO)_4]$	2.332(5)	111.3(6)	15n
Fe(II)			
$CpFe(CO)(PMe_3)SPh$	a	a	15o
$[PPh_4][Fe(SPh)_4]$	2.359(2)	114.1(2)	15p
	2.360(2)	109.9(2)	
	2.338(2)	110.3(4)	
	2.355(2)	109.2(3)	
$[NMe_4][Fe(\mu\text{-}o\text{-}(SCH_2)_2C_6H_4)(SPh)]_2$	2.303(1)	a	15q

TABLE II (*continued*)

Structurally characterized examples of metal complexes that contain terminal thiophenolate ligands

Compound	M–S (Å)	M–S–C (deg)	Ref.
Fe(III)			
[NEt$_4$][Fe(SPh)$_4$]	2.297(3)	112.8(4)	15v
	2.295(3)	112.5(4)	
	2.289(3)	112.4(5)	
	2.303(3)	107.8(5)	
Fe(ttp)(HSPh)(SPh)	2.27(2)	a	15s
[K][Fe(ttp)(SPh)$_2$]	2.336(2)	108.7	15t
Fe(oep)(SPh)	2.299(3)	102.5(3)	15u
Co(II)			
[PPh$_4$]$_2$[Co(SPh)$_4$]	2.326(4)	109.9(2.2)^{b}	15k
	2.342(4)		
	2.316(4)		
	2.328(4)		
Ni(II)			
[PPh$_4$][Ni(SPh)$_4$]	2.303(4)	108.5(2.4)^{b}	15k
	2.289(5)		
	2.272(4)		
	2.287(4)		
Ni(bipy)(SPh)$_2$	2.444(2)	107.6(2)	15v
	2.445(2)	108.3(2)	
Cu(I)			
[NEt$_4$][Cu(SPh)$_3$]	2.253(2)	113.7(2)	15w
	2.258(2)	114.8(2)	
	2.239(2)	115.1(2)	
[PPh$_4$][Cu(SPh)$_3$]	2.274(4)	110.2(5)	15x
	2.335(4)	107.8(4)	
	2.276(4)	114.4(4)	
Cu(II)			
Cu(Pre-H)(SPh)	2.424(1)	99.4(1)	15y
Zn(II)			
[PPh$_4$]$_2$[Zn(SPh)$_4$]	2.362(3)	109.6(2.2)^{b}	15k
	2.363(3)		
	2.329(3)		
	2.357(3)		
[PPh$_4$]$_2$[Zn$_2$(SPh)$_6$]	2.293(1)	108.1(1)	15z
	2.302(1)	108.9(1)	

TABLE II (*continued*)

Structurally characterized examples of metal complexes that contain terminal thiophenolate ligands

Compound	M–S (Å)	M–S–C (deg)	Ref.
Cd(II)			
$[PPh_4]_2[Cd(SPh)_4]$	2.540(4) 2.546(4) 2.517(3) 2.535(3)	108.8(2.1)[b]	15k
$[PPh_4]_2[Cd_2(SPh)_6]$	2.477(1) 2.478(1)	106.7(1) 105.9(1)	15z

[a] Information not available in the original reference.
[b] An average of four angles.

Acknowledgments

Portions of this work were done at the University of Arizona and directed by Prof. J. H. Enemark. Dr. M. A. Bruck and Mr. M. Carducci are thanked for their assistance with the Cambridge Data Files. The National Science Foundation (CHE-8808446) is gratefully recognized for their financial support while this manuscript was prepared.

References

1. Current address: Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Rm. 208, Norman, Oklahoma 73019.
2. I. G. Dance, Polyhedron **5**, 1037 (1986).
3. (a) S. Otsuka, M. Kamata, K. Hirotsu and T. Higuchi, J. Am. Chem. Soc. **103**, 3011 (1981). (b) M. Kamata, T. Yoshida, S. Otsuka, K. Hirotsu and T. Higuchi, J. Am. Chem. Soc. **103**, 3572 (1981). (c) M. Kamata, K. Hirotsu, T. Higuchi, K. Tasumi, R. Hoffmann, T. Yoshida and S. Otsuka, J. Am. Chem. Soc. **103**, 5772 (1981). (d) M. Kamata, T. Yoshida, S. Otsuka, K. Hirotsu, T. Higuchi, M. Kito, K. Tatsumi and R. Hoffmann, Organometallics **1**, 227 (1982). (e) M. T. Ashby and J. H. Enemark, J. Am. Chem. Soc. **108**, 730 (1986).
4. M. M. Millar, T. O'Sullivan, N. de Vries and S. A. Koch, J. Am. Chem. Soc. **107**, 3714 (1985).
5. For example, cytochrome P450, blue copper plastocyanin, rubredoxin and other iron–sulfur proteins, and the oxo-transfer type molybdoenzymes sulfite oxidase and xanthine dehydrogenase.
6. Localized MO theory (hybridization) does not account for the fact that the two lone pairs of thiolate ligands (or H_2S for that matter) are energetically inequivalent. See also: I. N. Lavin, *Quantum Chemistry*, 3rd ed. (Allyn and Bacon, Boston, 1983), pp. 434–42.

7. (a) K. W. Penfield, A. A. Gewirth and E. I. Solomon, J. Am. Chem. Soc. **107**, 4519 (1985). (b) J. G. Norman, Jr. and S. C. Jackels, J. Am. Chem. Soc. **97**, 3833 (1975). (c) L. Noodleman, J. G. Norman, J. H. Osborne, A. Aizman and D. A. Case, J. Am. Chem. Soc. **107**, 3418 (1985). (d) M. Takahashi, I. Watanabe, S. Ikeda, M. Kamata and S. Otsuka, Bull. Chem. Soc. Jpn. **55**, 3757 (1982). (e) N. Ueyama, T. Sugawara, K. Tatsumi and A. Nakamura, Inorg. Chem. **26**, 1978 (1987). (f) M. J. Calhorda, M. Carrondo, M. H. Garcia and M. B. Hurthouse, J. Organomet. Chem. **342**, 209 (1988).
8. Both $\mathrm{Md}\pi\text{-}\mathrm{Sp}\pi_{\parallel}$ and $\mathrm{Md}\pi\text{-}\mathrm{Sp}\pi_{\perp}$ orbital interactions are believed important in stabilizing a Ru(IV)–CO complex: M. M. Millar, T. O'Sullivan and S. A. Koch, J. Am. Chem. Soc. **107**, 3714 (1985).
9. It has been suggested that $\mathrm{Fe(d}\pi)\text{-}\mathrm{S(p}\pi_{\parallel})$ orbital interactions are important in Cytochrome P450: (a) P. M. Champion, B. R. Stallard, G. C. Wagner and I. C. Gunsalus, J. Am. Chem. Soc. **104**, 5469 (1982). (b) P. M. Champion, J. Am. Chem. Soc. **111**, 3433 (1989).
10. M–O–C bond angles vary from 130° to nearly 180°.[11] The larger bond angles are not attributed to steric factors.[11j]
11. (a) M. L. Listemann, R. R. Schrock, J. C. Dewan and R. M. Kolodziej, Inorg. Chem. **27**, 264 (1988). (b) L. B. Handy and C. K. Fair, Inorg. Nucl. Chem. Letters **11**, 496 (1975). (c) L. B. Handy, Acta Crystallogr. **B31**, 300 (1975). (d) M. H. Chisholm, F. A. Cotton, M. W. Extine and R. L. Kelly, J. Am. Chem. Soc. **100**, 3354 (1978). (e) M. H. Chisholm, F. A. Cotton, M. W. Extine and R. L. Kelly, Inorg. Chem. **18**, 116 (1979). (f) M. H. Chisholm, J. F. Corning and J. C. Huffman, Inorg. Chem. **23**, 754 (1984). (g) R. R. Schrock, M. Wesolek, A. H. Liu, K. C. Wallace and J. C. Dewan, Inorg. Chem. **27**, 2050 (1988). (h) E. C. Walborsky, D. E. Wigley, E. Roland, J. C. Dewan and R. R. Schrock, Inorg. Chem. **26**, 1615 (1987). (i) G. Erker, U. Dorf, R. Lecht, M. T. Ashby, M. Aulbach, R. Schlund, C. Krüger and R. Mynott, Organometallics **8**, 2037 (1989). (j) R. Karia, G. R. Willey and M. G. B. Drew, J. Chem. Soc. Dalton Trans. 2493 (1986). (k) G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi and M. Freni, Inorg. Chim. Acta **72**, 29 (1983). (l) V. W. Day and T. J. Marks, J. Am. Chem. Soc. **106**, 2907 (1984). (m) D. A. Wright and D. A. Williams, Acta Crystallogr. **B24**, 1107 (1968). (n) A. A. Pinkerton, D. Schwarzenbach, L. G. Hubert-Pfalzgraf and J. G. Riess, Inorg. Chem. **15**, 1196 (1976). (o) U. Schubert, D. Neugebauer and W. Scharf, J. Organomet. Chem. **206**, 159 (1981). (p) A. J. Nielson and J. M. Waters, Polyhedron **1**, 561 (1982). (q) T. V. Lubben, P. T. Wolczanski and G. D. VanDuyne, Organometallics **3**, 977 (1984). (r) C. J. Boreham, G. Buisson, E. Duee, J. Jordanov, J.-M. Latour and J.-C. Marchon, Inorg. Chim. Acta **70**, 77 (1983). (s) J. L. Hoard, M. J. Hamor, T. A. Hamor and W. S. Caughey, J. Am. Chem. Soc. **87**, 2312 (1965). (t) C. Riche, M. Chiaroni, M. Perree-Favuet and A. Gaudemer, Acta Crystallogr. **B34**, 1868 (1978). (u) R. H. Heyn and T. D. Tilley, Inorg. Chem. **28**, 1768 (1989). (v) I. M. Gardiner, M. A. Bruck and D. E. Wigley, Inorg. Chem. **28**, 1769 (1989). (w) C. P. Casey, R. F. Jordan and A. L. Rheingold, J. Am. Chem. Soc. **105**, 665 (1983). (x) D. J. Brauer and C. Krüger, Organometallics **1**, 204 (1982).
12. P. J. Blower and J. R. Dilworth, Coord. Chem. Rev. **76**, 121 (1987).
13. M. H. Chisholm, J. F. Corning and J. C. Huffman, Inorg. Chem. **22**, 38 (1983).
14. S. V. Evans, P. Legzdins, S. J. Rettig, L. Sanshez and J. Trotter, Organometallics **6**, 7 (1987).
15. (a) E. G. Muller, S. F. Watkins and L. F. Dahl, J. Organomet. Chem. **111**, 73 (1976). (b) J. L. Peterson, J. Organomet. Chem. **166**, 179 (1979). (c) J. R.

Nicholson, J. C. Huffman, D. M. Ho and G. Christou, Inorg. Chem. **26**, 3030 (1987). (d) M. Y. Darensbourg, R. Silva, J. Reibenspies and C. K. Prout, Organometallics **8**, 1315 (1989). (e) P. T. Bishop, J. R. Dilworth, J. Hutchinson and J. Zubieta, J. Chem. Soc. Dalton Trans. 967 (1986). (f) I. B. Benson, S. D. Killops, S. H. R. Knox and A. J. Welch, J. Chem. Soc. Chem. Commun. 1137 (1980). (g) J. R. Bradbury, M. F. MacKay and A. G. Wedd, Aust. J. Chem. **31**, 2423 (1978). (h) W. E. Cleland, Jr., K. M. Barnhart, K. Yamanouchi, D. Collison, F. E. Mabbs, R. B. Ortega and J. H. Enemark, Inorg. Chem. **26**, 1017 (1987). (i) I. G. Dance, A. G. Wedd and I. W. Boyd, Aust. J. Chem. **31**, 519 (1978). (j) R. J. Burt, J. R. Dilworth, G. J. Leigh and J. A. Zubieta, J. Chem. Soc. Dalton Trans. 2295 (1982). (k) D. Swenson, N. C. Baenziger and D. Coucouvanis, J. Am. Chem. Soc. **100**, 1932 (1978). (l) J. R. Dilworth, B. D. Neaves, J. P. Hutchinson and J. A. Zubieta, Inorg. Chim. Acta **65**, L223 (1982). (m) A. C. McDonell, T. W. Hamble, M. R. Snow and A. G. Wedd, Aust. J. Chem. **36**, 253 (1983). (n) W.-F. Liaw, C. Kim. M. Y. Darensbourg and A. L. Rheingold, J. Am. Chem. Soc. **111**, 3591 (1989). (o) K. J. Haller, P. M. Triechel and A. C. A. Summer, **11**, 46 (1983). (p) D. Coucouvanis, D. Swenson, N. C. Baenziger, C. Murphy, D. G. Holah, N. Sfarnas, A. Simopoulos and A. Kostikas, J. Am. Chem. Soc. **103**, 3350 (1981). (q) G. Henkel, W. Tremel and B. Krebs, Angew. Chem. Int. Ed. Engl. **22**, 319 (1983). (r) S. A. Koch, L. E. Maelia and M. Millar, J. Am. Chem. Soc. **105**, 5944 (1983). (s) J. P. Collman, T. N. Sorrell, K. O. Hodgson, A. K. Kulshrestha and C. E. Strouse, J. Am. Chem. Soc. **99**, 5180 (1977). (t) M. P. Byrn, B. A. Katz, N. L. Keder, K. R. Levan, C. J. Magurary, L. M. Millar, J. W. Prit and C. E. Strouse, J. Am. Chem. Soc. **105**, 4916 (1983). (u) K. M. Millar and C. E. Strouse, Acta Crystallogr. **C40**, 1324 (1984). (v) K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka and Y. Sasada, Acta Crystallogr. **C40**, 85 (1984). (w) C. D. Garner, J. R. Nicholson and W. Clegg, Inorg. Chem. **23**, 2148 (1984). (x) D. Coucouvanis, C. N. Murphy and S. K. Kanodia, Inorg. Chem. **19**, 2993 (1980). (y) O. P. Anderson, C. M. Perkins and K. K. Brito, Inorg. Chem. **22**, 1267 (1983). (z) I. L. Abrahams, C. D. Garner and W. Clegg, J. Chem. Soc. Dalton Trans. 1577 (1987).

16. D. Coucouvanis, D. Swenson, N. C. Baenziger, C. Murphy, D. G. Holah, N. Sfarnas, A. Simopoulos and A. Kostikas, J. Am. Chem. Soc. **103**, 3350 (1981).
17. The ability of aryl thiolate π-systems to conjugate with the S 3p lone pair apparently has no effect on the M–S–R bond angles. The observed differences in M–S–R bond angles for different R-groups may be largely attributed to steric effects. Accordingly, the mean M–S–R bond angle observed for R = Ph(110°) is about the same as for R = secondary alkyl (112°), but M–S–R bond angles become more acute when R = primary alkyl (107°) and more obtuse when R = tertiary alkyl (119°): M. T. Ashby, Dissertation, University of Arizona (1986).
18. J. A. K. Howard, R. F. D. Standsfield and P. Woodward, J. Chem. Soc. Dalton Trans. 246 (1976).
19. S. R. Allen, T. H. Glauert, M. Green, K. A. Mead, N. C. Norman, A. G. Orpen, C. J. Schaverien and P. Woodward, J. Chem. Soc. Dalton Trans. 2747 (1984).
20. J. A. McCleverty, A. S. Drane, N. A. Bailey and J. M. A. Smith, J. Chem. Soc. Dalton Trans. 91 (1983).
21. R. A. Jones, S. T. Schuab and B. R. Whittlesey, Polyhedron **3**, 505 (1984).
22. M. A. A. F. De, C. T. Carrondo and G. A. Jeffrey, Acta Crystallogr. **C39**, 42 (1983).

23. For example, the electronic structures of bent metallocene complexes of the type Cp_2MX_2 have been modeled using the Extended Hückel[24] and Fenske–Hall[25,26a] methods and have been experimentally investigated by single-crystal electron paramagnetic resonance spectroscopy[26b,c] and gas-phase photoelectron spectroscopy.[25] The results of these studies indicate that the LUMO of the d^0 and the HOMO of the d^1 and d^2 analogues is spatially localized in the plane containing the MX_2 fragment and is normal to the plane that bisects the X–M–X angle. All of the bent metallocene compounds in Table I have a d^0 electron configuration and are coordinatively unsaturated. Accordingly, the orientations observed for the thiolate ligands in these complexes indicate that the $Sp\pi_\perp$ orbitals donate to the LUMO. In contrast, the thiolate ligands in bent metallocene compounds that have a d^2 electron configuration and are coordinatively saturated are rotated 90° so as to minimize interaction between the metal-localized HOMO and the thiolate ligand $Sp\pi_\perp$ orbitals.[17]

24. J. W. Lauher and R. Hoffmann, J. Am. Chem. Soc. **103**, 7713 (1981).

25. J. L. Peterson, D. L. Lichtenberger, R. F. Fenske and L. F. Dahl, J. Am. Chem. Soc. **97**, 6433 (1975).

26. (a) J. L. Peterson and L. F. Dahl, J. Am. Chem. Soc. **96**, 2248 (1974). (b) *ibid.* **97**, 6416 (1975). (c) *ibid.* **97**, 6422 (1975).

27. Hoffmann *et al.*[28] have reported that the Extended Hückel method does not predict the conformation of $CpMo(O)(C_2(CF_3)_2)(SC_6F_5)$ observed in the solid-state as the electronically preferred conformation. However, we repeated these calculation and found that when the S–Mo–(C$\equiv$C centroid) angle is opened up to ca. 120°, an energy minimum is found very close to the geometry predicted by the simple-minded electronic model presented here.

28. B. E. R. Schilling, R. Hoffmann and J. W. Faller, J. Am. Chem. Soc. **101**, 592 (1979).