Synthesis, Structure, and Reactivity of the Complexes Fe(η^3-S₂CPR₃)(CO)₃. Electronic Factors Affecting the Dichotomy between η^2 and η^3 Coordination Modes in Transition Metal Complexes of Dithiocarboxy Ligands

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The reaction of Fe(BDA)(CO)₃ (BDA = benzylidene acetone) (**1**) with the dithiocarboxy adduct S₂CPR₃ affords complexes of formula Fe(η^3-S₂CPR₃)(CO)₃ (**2**). The pseudoallylic coordination of the SCS grouping is ascertained by an X-ray determination on the cyclohexyl derivative, **2a**. The primary geometry of the complexes **2** is also maintained upon the electrophilic attack of a methyl cation to one of the sulfur atoms. This piece of information was obtained by solving the structure of the complex [Fe{η^3-CH₃SC(S)PCy₃}(CO)₃]CF₃SO₃ (**3a**). Unfortunately, the complete set of X-ray data for the latter cannot be completed due to the high disorder affecting the CF₃SO₃ anion. Altogether, these and the other experimental data available for a variety of ML$_n$(S₂CX) complexes have prompted a general theoretical study (based on EHMO calculations) of the factors affecting the $\eta^3-\eta^2$ coordination dichotomy of the dithiocarboxy ligands, S₂CX. The Fe(CO)₃ fragment, also in view of one extra vacant coordination site, appears better suited than other 14-electron metal fragments, such as Mo(CO)₂(PR₃)₂ and Fe(PR₃)Cp, to favor the pseudo-allylic coordination of the SCS grouping. In any case, an energetic barrier is observed for the η^2/η^3 interconversion. This is due to an initial four-electron repulsion between the overall π-bonding S₂CX level and a d$\pi_\perp$ metal orbital. A HOMO−LUMO *avoided crossing* transforms the repulsion into a bonding attraction between the metal and the central carbon atom.

Introduction

The understanding of the factors governing the formation of metal to carbon bonds constitutes the fundamental core of organometallic chemistry[1] and carries a great relevance to more practical aspects such as the synthesis of new molecules[2] or their use to improve catalytic reactions.[3]

On the other hand, it is well-known that metal complexes containing sulfur ligands are involved in catalytic processes of great importance such as oil hydrotreating[4] or coal liquefaction.[5] In this field, con-

siderable efforts have been made, in the last two decades, to apply the knowledge derived from fundamental or synthetic organometallic chemistry to the modeling of the more complicated heterogeneous systems.[6]

Studies on the coordination chemistry of the dithiocarboxy molecules S₂CPR₃ have revealed that the bonding of the central carbon atom to the metal is no longer a curiosity. In particular, this feature has been frequently observed in binuclear complexes,[7] in which the S₂CPR₃ ligand acts invariably as an asymmetric bridge between the metals with the following possible

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coordination modes: $\eta^3(S,C,S')$;$\eta^1(S)$,[7a,g] $\eta^2(S,C,)$;$\eta^1(S')$,[7m] and $\eta^3(S,C,S')$;$\eta^2(S,S')$.[7b–k] Concerning the latter $\eta^3-\eta^2$ species, the experimental trends[7c,j–k] seem to indicate that the carbon atom is preferentially coordinated to the metal in the lower oxidation state. Simple theoretical considerations[8] have suggested that the larger diffuseness of the orbitals over the S_2C face *vs* the η^2 side favors the C-coordination to the metal with more diffuse orbitals and, in turn, with the lower oxidation state. The point is only qualitative, and an *ad-hoc* study on all of the influencing factors would be needed.

In this paper, we will concentrate only on mononuclear complexes containing ligands of the type S_2CX^{n-} ($n = 1$, X = H, alkyl, aryl; $n = 0$, X = phosphine). The $\eta^3(S,C,S')$ coordination of the latter has been definitely observed only for a couple of species, namely MoCl(NO)-$(PMe_3)_2(\eta^3-S_2CPMe_3)$[9] and M$(\eta^3-S_2CPMe_3)(CO)_2(PMe_3)_2$ (M = Mo, W).[10] In the latter, the ancillary fragment is of the type ML_4-d^6 with a pseudo-C_{2v} symmetry. Formally, the 18-electron configuration can be attained through the donation of the 4 π electrons of the S_2CPR_3 ligand. The electron saturation of the carbon atom can be achieved through a back-donation from one of the pseudo "t_{2g}" metal lone pairs, although this implies an stereochemically difficult linking of the metal to seven different atoms. Now, we have been able to synthesize and characterize (also by X-ray) the compounds Fe$(\eta^3-S_2CPR_3)(CO)_3$ (R = cyclohexyl (Cy), isopropyl (Pr^i)) in which the ancillary fragment is of the pyramidal type, ML_3-d^8. The latter are conceptually simpler models for a theoretical investigation, not only because all of the coligands have an unique nature (carbon monoxide) but also because the coordination of the dithiocarboxy ligand through the S and C atoms would naturally complete the pseudo-octahedral geometry of the 14-electron fragment. By contrast, the known complexes of ML_3-d^8 fragment with dithiocarboxy ligands have η^2-coordination geometry (the structurally characterized case is that of the cation[11] [Ir$(\eta^2$-$S_2CPPh_3)(CO)(PPh_3)_2]^+$).

In this paper, beside the synthesis and characterization of a novel Fe(CO)$_3$ complex with unprecedented η^3-SCS coordination, we present a detailed EHMO study of the electronic factors affecting the potential $\eta^3-\eta^2$ dichotomy.

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Experimental Section

All reactions were carried out in dry solvents under a nitrogen atmosphere. Details of instrumentation and experimental procedures have been given elsewhere.[7g] Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated.

Fe(η^3-S_2CPCy_3)(CO)$_3$ (2a). A mixture of Fe(BDA)(CO)$_3$ (**1**, BDA = benzylidene acetone) (0.50 g, 1.75 mmol)[12] and S_2CPCy_3 (0.71 g, 2.00 mmol), in CH$_2$Cl$_2$ (20 cm^3), was stirred overnight at room temperature. The solvent was then evaporated *in vacuo*, and the solid residue was chromatographed in alumina (activity III, 2.5 × 15 cm column). Elution with a 1:5 Et$_2$O/hexane mixture gave a red band which was collected. Slow evaporation at reduced pressure gave **2a** as deep red microcrystals. Yield: 0.35 g, 40%. Anal. Calcd for C$_{22}$H$_{33}$FeO$_3$PS$_2$: C, 53.23; H, 6.70. Found: C, 53.05; H, 6.43.

Fe(η^3-$S_2CPPr^i_3$)(CO)$_3$ (2b). To a solution of PPr$^i_3$ (380 μL, 2.00 mmol), in a mixture of CH$_2$Cl$_2$ (20 mL) and CS$_2$ (3 mL), was added compound **1** (0.5 g, 1.75 mmol).[12] The mixture was stirred overnight at room temperature and **2b** was isolated following a procedure similar to that described for **2a**. Yield: 0.243 g, 37%. Anal. Calcd for C$_{13}$H$_{21}$FeO$_3$PS$_2$: C, 41.50; H, 5.63. Found: C, 41.43; H, 5.68.

[Fe{η^3-CH$_3$SC(S)PCy$_3$}(CO)$_3$]CF$_3$SO$_3$ (3a). To a solution of **2a** (0.20 g, 0.40 mmol), in CH$_2$Cl$_2$ (20 mL), was added methyl triflate, CF$_3$SO$_3$Me (46 μL, 0.40 mmol), and the mixture was stirred for 5 min and then filtered through kieselguhr. The solvent was removed in vacuo, the residue was washed with Et$_2$O (2 × 5 mL) dissolved in CH$_2$Cl$_2$ (5 mL), and the solution was layered with hexane (20 mL) and kept in a refrigerator at −20 °C for several days. When the diffusion was complete, compound **3a** was obtained as a microcrystalline orange-red solid. Yield: 0.22 g, 83%. Anal. Calcd for C$_{24}$H$_{36}$F$_3$FeO$_6$PS$_3$: C, 43.64; H, 5.49. Found: C, 43.87; H, 5.62.

[Fe{η^3-CH$_3$SC(S)PPr$^i_3$}(CO)$_3$]CF$_3$SO$_3$ (3b). Compound **3b** was prepared as described above for **3a**, from **2b** (0.2 g, 0.532 mmol) and methyl triflate (0.087 g, 0.532 mmol). Yield: 0.215 g, 75%. Anal. Calcd for C$_{15}$H$_{24}$F$_3$FeO$_6$PS$_3$: C, 33.34; H, 4.48. Found: C, 33.55; H, 4.79.

X-ray Diffraction Studies of 2a and 3a. Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into concentrated solutions of the compounds (**2a** and **3a**) in CH$_2$Cl$_2$ at −20 °C. Relevant crystallographic details for **2a** are given in Table 3. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Corrections were made for Lorentz and polarization effects. An empirical absorption correction was applied with DIFABS.[13] Structures were solved by direct methods with SHELX86[14] and subsequent Fourier maps. Refinement and other calculations were made with CRYSTALS.[15] Non-hydrogen atoms with the exception of carbon atoms of cyclohexyl rings were refined anisotropically. Refinements were carried out in four blocks by minimizing the function $\sum w(F_o - F_c)^2$, with unit weights. Hydrogen atoms were placed in calculated positions. A perspective drawing for **2a** (Figure 1) was made with ORTEP.[16]

The crystal structure of **3a** could not be successfully completed mostly on account of the high disorder affecting the anion CF$_3$SO$_3$. The lattice parameters were determined as

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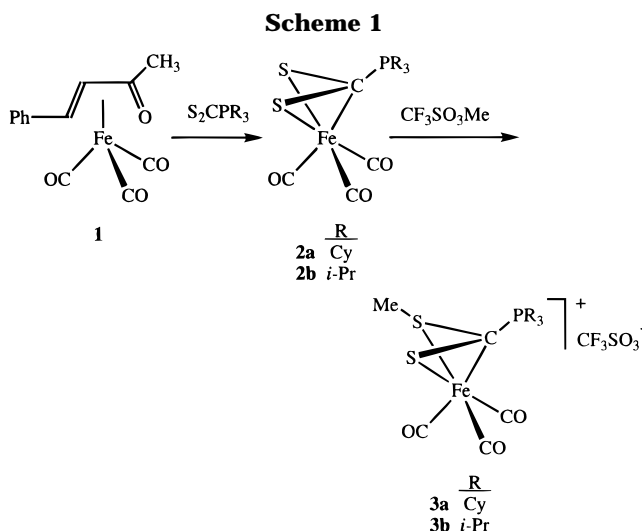
follows: monoclinic, space group $C2/c$, $a = 25.926(9)$ Å, $b = 18.086(4)$ Å, $c = 15.858(8)$ Å, $\beta = 115.75(1)°$, $Z = 8$, $R = 0.182$, $R_w = 0.211$. Additional data are reported as Supporting Information. By using the available observed reflections (1461), it was possible to establish the basic structure of the cationic complex, but the CF_3SO_3 anion caused serious problems for the refinement. The final R factor cannot become lower than 18%, and the coordinates remain affected by high standard deviations. Accordingly we provide the available structural parameters only as Supporting Information. Only a CAMERON[17] drawing of the cation is reported in the text (Figure 2), which shows the gross structural features. Any detailed discussion of the geometry is avoided.

Computational Details. All the MO calculations were of the extended Hückel type[18] (EHMO) using a weighted-modified Wolfsberg–Helmholz formula[19] and standard atomic parameters.[20] The 3D drawings and correlation diagrams were performed with the program CACAO.[21] The selected geometrical parameters used for the dithio acid ligands are C–S = 1.75 Å, C–P = 1.78 Å, C–H = 1.05 Å, Fe–S = 2.3 Å, Mo–S = 2.5 Å, and S–C–S = 117°. Other bond distances and angles have been taken from experimental structures.

Results and Discussion

Synthesis of Fe(η³-S₂CPR₃)(CO)₃ Compounds (R = Cy (2a), Prⁱ (2b)). Crystal Structure of 2a. As it has been pointed out above, only a few mononuclear complexes containing η^3-S_2CPR_3 ligands have been reported[9,10] which contain at least two types of ancillary ligands apart from S_2CPR_3. Our interest in the coordination of the central carbon of the S_2CPR_3 ligand to a metal center prompted us to prepare even simpler mononuclear complexes with a minimum number of coligands, possibly all of the same nature. By freeing one coordination site with respect to the other known ancillary fragments, the S_2CPR_3 should better adapt to the metal. Moreover, the potential η^3–η^2 dichotomy would be definitely less hindered.

In previous synthetic work relative to some binuclear species,[7c,j–k] we found that the η^3 coordination of the SCS carbon atom occurs preferentially at the site of the metal in the lower oxidation state, usually zerovalent. This prompted us to try the synthesis of mononuclear species containing M^0L_3 fragments with 14 valence electrons, such as $Fe(CO)_3$ or $Ru(CO)_3$. As mentioned, they should favor the η^3 coordination of the S_2CPR_3 ligands. After several unsuccessful attempts, starting from $Fe(CO)_5$, $Fe_2(CO)_9$, and $M_3(CO)_{12}$ (M = Fe, Ru), it was found that the tricarbonyl iron(0) complex Fe(BDA)-$(CO)_3$ (BDA = benzylidene acetone) (1)[12] reacts slowly in CH_2Cl_2 at room temperature with trialkylphosphonio dithiocarboxy adducts, S_2CPR_3, to afford, after overnight stirring, a dark red solution from which the desired complexes $Fe(\eta^3$-$S_2CPR_3)(CO)_3$ (2a,b; see Scheme 1) were isolated in moderate yields (37–40%). In fact, the reaction of 1 with carbon disulfide and trialkylphosphines had been explored some years ago by Dixneuf *et al.*[22] In their work, they used smaller phosphines, such

as PMe_3, PBu_3, or PMe_2Ph, and the reaction produced low yields of the carbon disulfide compounds Fe(η^2-$CS_2)(PR_3)_2(CO)_3$, instead of complexes with S_2CPR_3. The result is not surprising since, as we have pointed out before, the use of bulky *and* basic phosphines (*i.e.* PCy_3 or PPr^i_3) is often necessary to obtain stable complexes with S_2CPR_3 ligands.[7b] The analytical and spectroscopic data of complexes 2a,b (Tables 1 and 2) were fully consistent with their formulation as containing η^3-phosphonio dithiocarboxy ligands. Highly significant was the presence, in the $^{13}C\{^1H\}$ NMR spectra, of the signal attributable to the central carbon of the ligand [δ 74.6, ^1J(PC) = 66 Hz for 2a, and δ 74.3, ^1J(PC) = 67 Hz for 2b], in the region expected for η^3 coordination.[7b,10] In order to attain a detailed knowledge of the structural features, useful also for the subsequent MO studies, a single crystal of compound 2a was subjected to an X-ray determination. The results are summarized in Table 4 (bond lengths and angles). Figure 1 shows a schematic view of one of the two crystallographically independent (although chemically equivalent) molecules contained in the asymmetric unit.

The molecule of 2a consists of a pyramidal $Fe(CO)_3$ fragment, to which the tricyclohexylphosphonio dithiocarboxy ligand is bound in a pseudoallylic η^3 fashion through the two sulfur and the central carbon atom. The distance Fe–C(1) of 1.96(1) Å is close to Fe–C(carbon disulfide) of 1.983(8) Å found for the complex Fe(η^2-$CS_2)(PPh_3)_2(CO)_2$.[22] Also, it is significantly shorter than the distance to the central allyl carbon atom [2.083(13) Å], found in the complex Fe(η^3-$CH_3CHCHCHPh)(SnPh_3)_2$-$(CO)_3$.[23] The overall geometry of the molecule can be

Scheme 1

	R
2a	Cy
2b	*i*-Pr

	R
3a	Cy
3b	*i*-Pr

Table 1. IR and ³¹P{¹H} NMR Data for the New Complexes

compd	IR (CH_2Cl_2): ν(CO), cm⁻¹	³¹P{¹H} NMR:[a] δ(S₂C*P*)
Fe(η^3-S₂CPCy₃)(CO)₃ (2a)	2043 vs, 1974 s, 1952 m	38.2
Fe(η^3-S₂CPPrⁱ₃)(CO)₃ (2b)	2045 vs, 1975 s, 1954 m	47.4
[Fe(η^3-MeSC(S)PCy₃)(CO)₃]- [CF₃SO₃] (3a)	2086 vs, 2029 s, 2012 s	41.0
[Fe(η^3-MeSC(S)PPrⁱ₃)(CO)₃]- [CF₃SO₃] (3b)	2087 vs, 2029 s, 2014 s	51.1

[a] In solutions of CD_2Cl_2, δ (ppm) from internal 85% H_3PO_4.

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Table 2. ^{1}H and ^{13}C\{^{1}H\} NMR Data for the New Complexes[a]

compd	^{1}H NMR: δ, ppm	^{13}C\{^{1}H\} NMR: δ, ppm
2a	2.64 [m, 3H, C*H* of Cy], 2.32−1.31 [m, br, 30 H, C*H$_2$* of Cy]	213.6 [s, 1 × Fe*C*O], 210.7 [s, 2 × Fe*C*O], 74.6 [d (66), S$_2$*C*P], 33.9 [d (42), *C^1* of Cy], 27.8 [d (3), *C^2* and *C^6* of Cy], 27.3 [d (11), *C^3* and *C^5* of Cy], 26.0 [s, *C^4* of Cy]
2b	2.95 [m, 3H, C*H* of Pr^i], 1.54 [dd (15 and 7), 18 H, C*H$_3$* of Pr^i]	213.4 [s, 1 × Fe*C*O], 210.7 [s, 2 × Fe*C*O], 74.3 [d (67), S$_2$*C*P], 24.6 [d (44), *C*H of Pr^i], 17.9 [s, *C*H$_3$ of Pr^i]
3a	2.80 [m, 3H, C*H* of Cy], 2.27 [s, 3H, C*H$_3$*S], 2.40−1.28 [m, br, 30 H, C*H$_2$* of Cy]	206.5 [d (3), Fe*C*O], 204.8 and 203.2 [s, Fe*C*O], 67.8 [d (56), S$_2$*C*P], 33.7 [d (39), *C^1* of Cy], 27.4 [s, *C^2* and *C^6* of Cy], 26.4 [d (11), *C^3* and *C^5* of Cy], 25.2 [s, *C^4* of Cy], 12.7 [d (2), *C*H$_3$S]
3b	3.03 [m, 3H, C*H* of Pr^i], 2.14 [s, 3H, C*H$_3$*S], 1.50 [dd (16 and 7), 18 H, C*H$_3$* of Pr^i]	206.3 [d (2), Fe*C*O], 204.6 and 202.8 [s, Fe*C*O], 67.7 [d (58), S$_2$*C*P], 24.3 [d (41), *C*H of Pr^i], 17.3 [s, *C*H$_3$ of Pr^i], 12.1 [d (2), *C*H$_3$S]

[a] From CD$_2$Cl$_2$ solutions. Coupling constants, in Hz, in parentheses.

Table 3. Crystal Data and Refinement Details for Fe(η^3-S$_2$CPCy$_3$)(CO)$_3$ (2a)

formula	C$_{22}$H$_{33}$FeO$_3$PS$_2$
fw	496.44
cryst system, space group	monoclinic, $P2_1/n$
a, Å	22.409(9)
b, Å	10.749(7)
c, Å	22.132(7)
β, deg	112.36(4)
V, Å^3	4930(5)
molecules/cell	8
T, K	293
ρ_{calc}, g cm^{-3}	1.34
$F(000)$	2096
diffractometer	Philips PW1100
λ(Mo Kα), Å	0.71069
cryst size, mm	0.65 × 0.50 × 0.45
cryst color	red
μ, cm^{-1}	18.1
method of collcn	$\omega/2\theta$ scan
scan range, deg	$0 \leq \theta \leq 25$
collcn limits	h, −25,23; k, 0.12; l, 0.25
no. of reflcns measd	8492
no. of reflcns obsd, $I \geq 3\sigma(I)$	2962
no. of params	339
residuals R, R_w	0.055, 0.059

[a] $R = (|\Delta F|)/\Sigma|F_o|$; $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1$.

approximated to a C_s symmetry, with a staggered disposition of the pseudoallyl SCS group with respect to the three carbonyl ligands. The two Fe−C(carbonyl) distances *trans* to the sulfur atoms [1.76(1) and 1.78(1) Å] are shorter than the Fe−C(carbonyl) *trans* to the central carbon of S$_2$CPCy$_3$ [1.84(1) Å]. This may reflect a larger *trans* influence of the coordinated carbon with respect to the sulfur atoms. According to the spectroscopic data available for **2a**, the inequivalency of the carbonyl groups persists in solution at room temperature. Two signals, of relative intensity 2:1, are observed for the carbonyl groups in the ^{13}C NMR spectra. This is consistent with the existence of a rotation barrier of the pseudoallyl system around the C_3 axis of the Fe(CO)$_3$ fragment. Unfortunately heating of complexes **2a,b** in solution leads to extensive decomposition within few minutes, and this precluded an experimental measure of the rotational barrier.

Reactivity of Fe(η^3-S$_2$CPR$_3$)(CO)$_3$ (2a,b) with Electrophiles. Crystal Structure of [Fe\{η^3-CH$_3$SC-(S)PCy$_3$\}(CO)$_3$]CF$_3$SO$_3$ (3a). Electron-rich compounds containing η^3-S$_2$CPR$_3$ ligands, such as M(η^3-S$_2$CPMe$_3$)-(CO)$_2$(PMe$_3$)$_2$ (M = Mo, W), can be alkylated with MeI on one of the sulfur atoms to give a phosphonio dithioester or protonated to afford, ultimately, the phosphoniodithioformate ligand.[10] All the attempts to obtain stable compounds from the protonation of complexes **2a,b** have been fruitless so far. Upon addition of strong acids, such as HBF$_4$·OEt$_2$ or HCl, an instantaneous reaction takes place, and the IR monitoring

### Table 4. Selected Bond Lengths (Å) and Angles (deg) for Fe(η^3-S$_2$CPCy$_3$)(CO)$_3$ (2a)

molecule 1		molecule 2	
Fe(1)−S(1)	2.322(3)	Fe(51)−S(51)	2.328(3)
Fe(1)−S(2)	2.300(3)	Fe(51)−S(52)	2.311(3)
Fe(1)−C(1)	1.96(1)	Fe(51)−C(51)	1.99(1)
Fe(1)−C(2)	1.78	Fe(51)−C(52)	1.80(1)
Fe(1)−C(3)	1.76(1)	Fe(51)−C(53)	1.77(1)
Fe(1)−C(4)	1.84(1)	Fe(51)−C(54)	1.83(1)
S(1)−C(1)	1.73(1)	S(51)−C(51)	1.76(1)
S(2)−C(1)	1.76(1)	S(52)−C(51)	1.774(9)
P(1)−C(1)	1.80(1)	P(51)−C(51)	1.76(1)
P(1)−C(10)	1.84(1)	P(51)−C(60)	1.83(1)
P(1)−C(20)	1.812(9)	P(51)−C(70)	1.81(1)
P(1)−C(30)	1.83(1)	P(51)−C(80)	1.83(1)
O(2)−C(2)	1.13(1)	O(52)−C(52)	1.13(1)
O(3)−C(3)	1.15(1)	O(53)−C(53)	1.15(1)
O(4)−C(4)	1.13(1)	O(54)−C(54)	1.12(1)
S(2)−Fe(1)−S(1)	78.6(1)	S(52)−Fe(51)−S(51)	78.4(1)
C(1)−Fe(1)−S(1)	46.8(3)	C(51)−Fe(51)−S(51)	47.3(3)
C(1)−Fe(1)−S(2)	47.9(3)	C(51)−Fe(51)−S(52)	47.8(3)
C(2)−Fe(1)−S(1)	158.0(4)	C(52)−Fe(51)−S(51)	156.9(4)
C(2)−Fe(1)−S(2)	88.6(4)	C(52)−Fe(51)−S(52)	88.4(4)
C(2)−Fe(1)−C(1)]	111.7(5)	C(52)−Fe(51)−C(51)	110.2(5)
C(3)−Fe(1)−S(1)	93.2(4)	C(53)−Fe(51)−S(51)	91.9(3)
C(3)−Fe(1)−S(2)	156.8(4)	C(53)−Fe(51)−S(52)	157.3(3)
C(3)−Fe(1)−C(1)	111.3(5)	C(53)−Fe(51)−C(51)	111.0(4)
C(3)−Fe(1)−C(2)	91.8(6)	C(53)−Fe(51)−C(52)	93.4(5)
C(4)−Fe(1)−S(1)	101.2(4)	C(54)−Fe(51)−S(51)	102.5(4)
C(4)−Fe(1)−S(2)	103.7(4)	C(54)−Fe(51)−S(52)	102.7(4)
C(4)−Fe(1)−C(1)	135.1(5)	C(54)−Fe(51)−C(51)	135.8(5)
C(4)−Fe(1)−C(2)	99.1(6)	C(54)−Fe(51)−C(52)	98.8(5)
C(4)−Fe(1)−C(3)	99.1(5)	C(54)−Fe(51)−C(53)	99.4(5)
C(1)−S(1)−Fe(1)	55.5(3)	C(51)−S(51)−Fe(51)	56.2(3)
C(1)−S(2)−Fe(1)	55.8(3)	C(51)−S(52)−Fe(51)	56.5(3)
S(1)−C(1)−Fe(1)	77.7(4)	S(51)−C(51)−Fe(51)	76.6(4)
S(2)−C(1)−Fe(1)	76.3(4)	S(52)−C(51)−Fe(51)	75.7(4)
S(2)−C(1)−S(1)	113.9(6)	S(52)−C(51)−S(51)	112.5(5)
P(1)−C(1)−Fe(1)	136.8(6)	P(51)−C(51)−Fe(51)	135.7(6)
P(1)−C(1)−S(1)	121.0(6)	P(51)−C(51)−S(51)	122.9(5)
P(1)−C(1)−S(2)	119.5(6)	P(51)−C(51)−S(52)	120.0(6)
O(2)−C(2)−Fe(1)	178.7(12)	O(52)−C(52)−Fe(51)	178.2(11)
O(3)−C(3)−Fe(1)	176.0(10)	O(53)−C(53)−Fe(51)	178.7(9)
O(4)−C(4)−Fe(1)	176.5(12)	O(54)−C(54)−Fe(51)	177.5(11)

reveals the appearance of ν(CO) bands at frequencies very close to those of the methyl derivatives **3a,b**. However, extensive decomposition occurs within minutes, giving rise to a complex mixture of signals in the IR and ^{31}P NMR spectra.

It seems that the Fe(CO)$_3$ fragment is not electron-rich enough to stabilize the cationic complex with the resulting (trialkylphosphonio)dithioformate ligand. The same effect could be responsible of the diminished nucleophilicity of the S$_2$C system in **2a,b** when compared with the above mentioned complexes of Mo and W, containing the electron-richer fragment M(CO)$_2$-(PMe$_3$)$_2$. Thus, compounds **2a,b** do not react with methyl iodide upon prolonged stirring. Nonetheless, by using a more electrophilic reagent, such as methyl
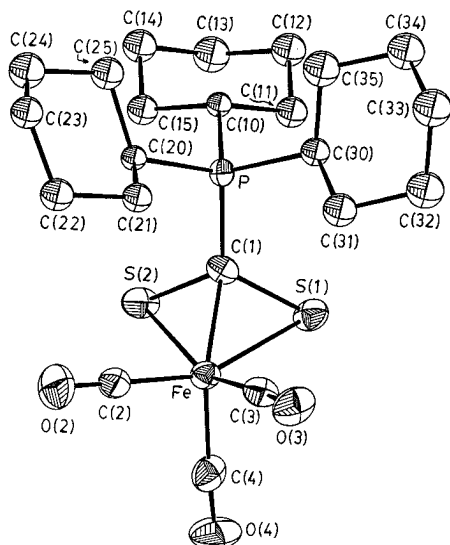
Figure 1. Perspective view (ORTEP)[16] of one of the two independent molecules in the asymmetric unit of Fe(η^3-S$_2$-CPCy$_3$)(CO)$_3$ (**2a**), showing the atom numbering.
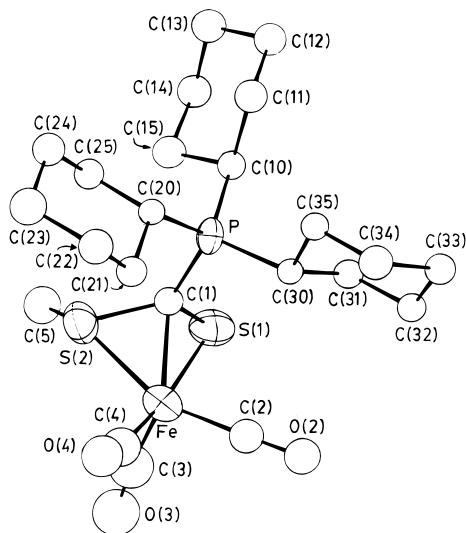
Figure 2. Perspective view (CAMERON)[17] of the cation [Fe{η^3-CH$_3$SC(S)PCy$_3$}(CO)$_3$] in **3a**, showing the atom numbering.

triflate, the alkylation can be accomplished in a few minutes affording, after appropriate workup, the expected trialkylphosphonio dithioesters **3a,b** (see Scheme 1) in good yield (83 and 71%, respectively). Analytical and spectroscopic data of **3a,b** (see Tables 1 and 2) are in good agreement with the structure proposed for them in Scheme 1. Again, the ^{13}C NMR spectra display the signals attributable to the central carbon of the ligand as weak doublets in the region expected for η^3(S,C,S′) coordination [δ 67.8, ^1J(PC) = 56 Hz for **3a**, and δ 67.7, ^1J(PC) = 58 Hz for **3b**]. To confirm this point, an X-ray determination of **3a** was attempted. Unfortunately, it has been impossible to refine the structure to a reasonable level of accuracy, mainly due to the high disorder affecting the triflate anion. Accordingly, we present in Figure 2 only the gross structural features.

Essentially, the tricyclohexylphosphonio dithioester, resulting from the addition of methyl group to one sulfur atom of S$_2$CPCy$_3$, is bonded to the iron atom in a pseudoallylic fashion, as was previously found[10] for [M{η^3-CH$_3$SC(S)PMe$_3$}(CO)$_2$(PMe$_3$)$_2$]$^+$ (M = Mo, W). The

overall disposition of the SCS grouping with respect to the Fe(CO)$_3$ fragment remains staggered as in complex **2a**. Notice that the presence of the methyl group destroys the C_s symmetry of the parent complex **2a** and renders inequivalent the three CO ligands. Accordingly, the ^{13}C{^{1}H} NMR spectrum of **3a** in solution exhibits three different signals for the carbonyl groups. The one at the highest frequency appears as a doublet with a small coupling, ^3J(PC) = 3 Hz, and can be tentatively assigned to the carbonyl group *trans* to the central carbon of the dithioester ligand. The spectrum of the triisopropylphosphine derivative, **3b**, shows similar features.

Qualitative MO Description of the η^2 and η^3 Dichotomy. Dithiocarboxy ligands of the type S$_2$CX^{n-} (n = 1, X = H, alkyl, aryl; n = 0, X = phosphine) with four π electrons do remarkably associate good donor properties (*via* the sulfur atoms) to residual acceptor capabilities at the central carbon atom. In particular, upon an efficient donation to the metal atom, the species are susceptible of becoming significantly carbocationic.[24] In turn, the electron-richer metal activates one of its nonbonding orbitals (*lone pair*) and back donates or even transfers electrons into the carbon atom itself. A different class of dithiocarboxy ligands contains formally six π electrons (X = NR$_2$, OR, SR, O, etc.). Also in this case the η^3 coordination is occasionally attainable,[25] although it is evident that the electron-rich metal has to compete not only with the sulfur atoms but also with the additional π-donor substituent to quench the cationic character of the central carbon atom. Thus, in order to limit the complexity of the problem the following discussion will be focused only on the structural $\eta^2-\eta^3$ dichotomy of dithiocarboxy complexes with only four π electrons.

Most of the arguments are based on the results of MO calculations of the extended Hückel type.[18] The basic parameter of the $\eta^2-\eta^3$ interconversion is the *ca.* 90° rotation of the whole dithiocarboxy ligand about the S$\cdots$S vector, as shown in I. Also other subtle structural
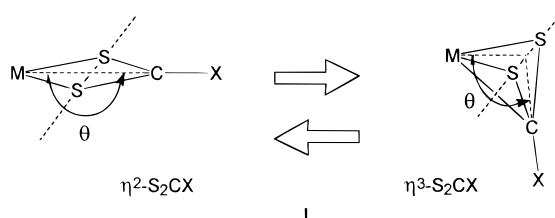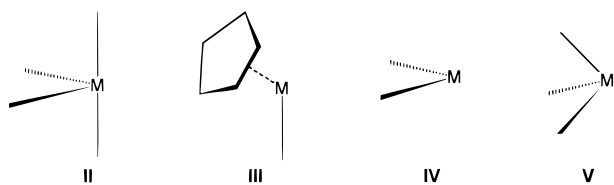
(24) For some examples that evidence the carbon electrophilic character, see: (a) Miguel, D.; Miguel, J. A.; Riera, V.; Solans, X. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1014. (b) Faridoon; Spalding, T. R.; Fergurson, G.; Kennedy, J. D.; Fontaine, X. L. R. *J. Chem. Soc., Chem. Commun.* **1989**, 906. (c) Bianchini, C.; Meli, A.; Dapporto, P.; Tofanari, A.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 3677. (d) Bianchini, C.; Mealli, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 141. (e) Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4161 and 4166. (f) Bianchini, C.; Meli, A.; Nuzzi, F.; Dapporto, P. *J. Organomet. Che.* **1982**, *236*, 245. (g) Ashworth, T. V.; Singleton, E.; Laing, M. *J. Chem. Soc., Chem. Commun.* **1976**, 875. (h) Einstein, F. W.; Enwall, E.; Flitcroft, N.; Leach, J. M. *J. Inorg. Nucl. Chem.* **1972**, *34*, 885.
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parameters (essentially those relative to the ancillary metal fragment) can affect the $\eta^2-\eta^3$ dichotomy, but, due to the limitations of the computational method, they can be hardly optimized. Nor can the energetics involved be a tool of quantitative discernment but only a useful guideline for the most reasonable interconversion pathway. Most important is the identification of the major orbital interactions as well as their evolution. This goal is facilitated by the graphic interface package CACAO,[21] which helps to disclose MO arguments of chemical significance and macroscopic evidence.

Let us first summarize a few well-known aspects of the stereochemistry of the monomeric transition metal complexes with dithiocarboxylate ligands. The supporting metal fragments seem to fall in one of the following categories: (i) butterfly shaped ML_4-d^6 fragments (see II); (ii) a variation of the type above where a cyclopen-

tadienyl ligand replaces three single ligands in a *fac* arrangement, MCp(L) (see III); (iii) planar ML_2-d^8 fragments, isolobal with the ML_4-d^6 ones (see IV); (iv) pyramidal ML_3-d^8 fragments (see V).

With the possible exception of the fragments of type IV (most suited for the η^2 mode), all of the other fragments have been found to support either the η^2 or the η^3 coordination mode of the dithiocarboxylate ligands. Some of the most significant examples, which have been characterized by X-ray methods, are summarized in Table 5 (η^2 complexes) and Table 6 (η^3 complexes).

In fact, there is only one fully documented case of real $\eta^2-\eta^3$ dichotomy. This is provided by the compound[30] $FeCp(S_2CCH_3)(\eta^1\text{-dppm})$ (dppm = $Ph_2PCH_2PPh_2$) for which both coordination modes are evident in solution. In this case, different crystallization procedures have also allowed the separation and the X-ray characterization of the two isomers. The differences affecting the geometry of the fragment FeCp(L) in the two structures are very small, thus confirming that the governing factors of the dichotomy are very subtle. In the other cases, the η^2 and the η^3 conformation seems to depend on parameters such as the nature and charge of the metal itself, the nature and disposition of the ancillary

Table 5. Selected X-ray-Characterized Examples of M(η^2-S₂CX) Compounds

complexes η^2-S₂CX	dists (Å)		angle (deg)	ref
	M–S	C–S	S–C–S	
ML₄-d⁶ Fragment				
MnBr(CO)₃(η^2-S₂CCMe₂PPh₃)	2.351(1)	1.691(5)	112.5(3)	26
	2.380(1)	1.675(5)		
ReBr(CO)₃(η^2-S₂CCMe₂PPh₃)	2.488(1)	1.717(4)	113.6(2)	26
	2.503(1)	1.664(4)		
[Fe(depe)₂(η^2-S₂CH)](BPh₄)	2.326(5)	1.66(2)	110.0(9)	27
	2.312(5)	1.69(2)		
[Fe(depe)₂(η^2-S₂CPEt₃)](BPh₄)₂	2.261(3)	1.68(1)	109.9(5)	27
	2.305(3)	1.68(1)		
RuCl(CO)(PPh₃)₂(η^2-S₂CH)	2.447(2)	1.67(1)	115(1)	28
	2.427(2)	1.67(1)		
[W(CO)₄(η^2-S₂CCH₃)](PPN)	2.557(5)	1.67(2)	113(1)	29
	2.565(5)	1.71(2)		
Fe(Cp)(η^1-dppm)(η^2-S₂CCH₃)	2.265(2)	1.683(6)	109.0(4)	30
	2.260(2)	1.676(7)		
[Mn(CO)₃(η^1-S₂CPCy₃)-(η^2-S₂CPCy₃)]ClO₄	2.383(2)	1.66(1)	116.4(5)	31
	2.361(3)	1.673(7)		
[Mn(CO)₂(PEt₃)₂(η^2-S₂CPEt₃)]ClO₄	2.375(1)	1.680(3)	113.5(2)	32
	2.354(1)	1.677(3)		
Mn(CO)₂(PEt₃)₂(η^2-S₂CH)	2.422(2)	1.651(7)	115.9(8)	31
	2.422(2)	1.651(7)		
Mn(CO)₃(SnCl₃)(η^2-S₂CPCy₃)	2.362(2)	1.676(8)	113.9	33
	2.348(3)	1.663(7)		
ML₃-d⁸ Fragment				
[Ir(CO)(PPh₃)₂(η^2-S₂CPPh₃)]BF₄	2.307(5)	1.66(2)	110.7(4)	11
	2.377(5)	1.70(2)		
ML₂-d⁸ Fragment				
Pd(C₆F₅)₂(η^2-S₂CPCy₃)	2.368(2)	1.672(4)	19.0(3)	34
	2.415(2)	1.662(6)		

ligands, and, finally, also the flexibility of the metal fragment itself to reorganize geometrically.

ML₃(S₂CX) Complexes. Ultimately, the MO picture of the $\eta^2-\eta^3$ dichotomy in dithiocarboxylate complexes is comparable for all of the different types of metal fragments depicted in **II–V**, but perhaps the neatest analysis is carried out with the fragments of the type ML_3-d^8. In this case, the d_π frontier metal orbital, which is able to switch from a metal lone pair (η^2 coordination) into a donor σ-hybrid, is easily identified. In the other cases, at least two metal orbitals have suited symmetry and topology and their reciprocal mixing somewhat complicates the picture. Two examples of alternative coordination modes supported by the fragments ML_3 can be quoted: (i) the cation[11] $[Ir(\eta^2\text{-}S_2CPPh_3)(CO)(PPh_3)_2]^+$ (**VI**); (ii) the complex $Fe(\eta^3\text{-}S_2CPCy_3)(CO)_3$ (**2a, VII**).
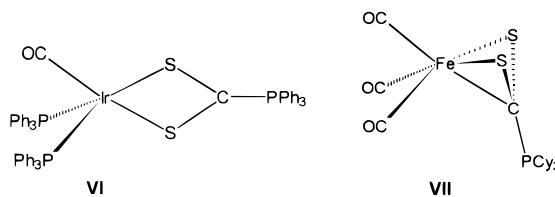
The 3 + 2 rotamer in the iridium complex **VI** adapts to a pseudo-trigonal bipyramid, TBP (one axial and one equatorial sulfur atom), while the conversion to the η^3-coordination mode (of type **VII**) implies an initial reorientation of the S₂CX ligand to a pseudo-square pyramidal η^2-conformer (SP). Specific calculations, by using the fragment $[Ir(CO)(PH_3)_2]^+$, show that the pseudo-η^2-TBP geometry **VI** is more stable than the SP one by *ca.* 15−20 kcal/mol, which has sulfur and phosphorus atoms quasi coplanar. This is attributable to the unique nature of one terminal ligand (CO), and

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Table 6. Selected X-ray-Characterized Examples of M(η^3-S$_2$CX) Compounds

| complexes η^3-S$_2$CX	dists (Å)			angle (deg)	torsion angle (deg)	
	M–S	C–S	M–C	S–C–S	M–S–C–S	ref
Ru(Cp)(η^3-S$_2$CCHMeC$_6$H$_4$PPh$_2$)	2.426(1)	1.728(4)	2.175(4)	121.3(2)	97	35
	2.418(1)	1.722(4)				
MoCl(NO)(PMe$_3$)$_2$(η^3-S$_2$CPMe$_3$)	2.492(8)	1.75(2)	2.14(3)	123(2)	91	9
	2.50(1)	1.76(3)				
Fe(Cp)(η^1-dppm)(η^3-S$_2$CCH$_3$)	2.291(1)	1.735(3)	2.039(3)	118.4(2)	95	30
	2.300(1)	1.711(3)				
W(CO)$_2$(PMe$_3$)$_2$(η^3-S$_2$CPMe$_3$)	2.505(8)	1.73(2)	2.12(2)	117(1)		10
	2.541(7)	1.77(2)				
Fe(CO)$_3$(η^3-S$_2$CPCy$_3$)	2.322(3)	1.73(1)	1.96(1)	113.9(6)		this work
(molecule 1 of **2a**)	2.300(3)	1.76(1)				

likely, a freezing of the observed TBP geometry for η^2 prevents the subsequent attainment of the η^3 conformer. Conversely the TBP–SP rearrangement of the η^2 conformer has no sizable barrier for a cylindrically symmetric pyramidal fragments such as Fe(CO)$_3$. The frontier MOs of the latter are well-known[36] and are in the following order: a high-lying σ-hybrid, two degenerate and orthogonal d$_\pi$ hybrids (shown in **VIII**), and three lower "t$_{2g}$-reminiscent" levels.
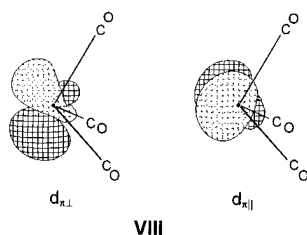

VIII

The dithiocarboxy ligand S$_2$CPH$_3$ is characterized by two major in-plane combinations of sulfur *lone pairs* (one in phase and one out-of-phase) and by the S$_2$C π-delocalized system. The three combinations, π-S$_2$C, n_π-S$_2$C, and π^*-S$_2$C are shown in **IX**–**XI**, respectively.

IX   **X**   **XI**

At the η^2-SP coordination (see the diagram **XII** for the most simplified case of a FeH$_3^{3-}$ fragment), the two in-plane sulfur *lone pairs* (S$\sigma_{i.p.}$ and S$\sigma_{o.o.p.}$) interact well with the metal σ-hybrid and the d$_{\pi\parallel}$ hybrid (the rightmost in **VIII**). The other filled orthogonal d$\pi_\perp$ FMO does instead interfere with the S$_2$C π system which carries already four electrons. Thus, the resulting MS$_2$C planar ring has two more electrons than the simplest four-membered ring, C$_4$H$_4$ (*i.e.*, it compares with an hypothetical cyclobutadiene dianion).[37] The π electron density may be inconsistent with the planarity of the ring, and as a qualitative explanation, the system may choose to rearrange to the η^3 coordination. Most important is the interplay of the S$_2$C combinations **IX** and **XI**. The empty π^*-S$_2$C FMO (**XI**) is close in energy to the metal d$\pi_\perp$ orbital; thus their bonding interaction is favored. However, the presence of the lower and filled π-S$_2$C FMO (**IX**) destabilizes the HOMO (see **XII**). The
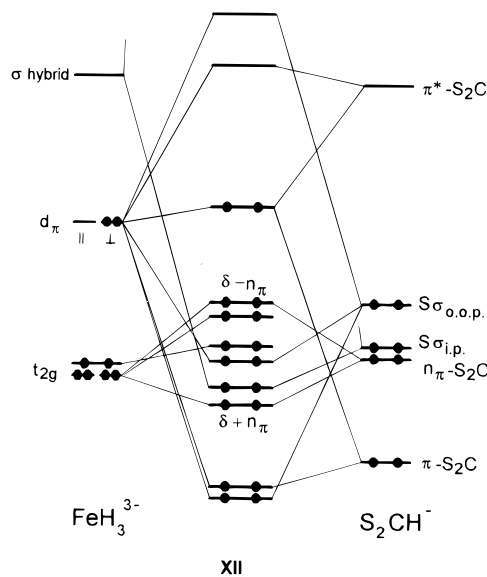
XII

mixing, typical of a three-center interaction, deletes the sulfur p$_\pi$ contribution to the latter HOMO which is shown in **XIII**. Notice that the π electron density accumulates at the *trans*-diagonal metal and carbon atoms.
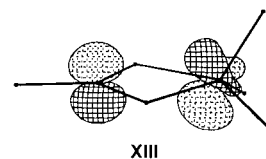
XIII

The evolution of the η^2 MO picture **XII** on bending the ligand S$_2$CH toward the η^3 mode is monitored in Figure 3. There is an evident energy barrier (of *ca.* 0.8 eV) which is comparable for the FeH$_3^{3-}$ and the Fe(CO)$_3$ fragments.

Also, the absolute energy minimum is generally calculated at the side of the η^2 conformers. For instance, the η^2 minimum is *ca.* 0.4 eV deeper for the Fe(CO)$_3$ adduct. Indeed, the EHMO method is hardly reliable for predicting correct energetics while it provides significant pieces of chemical information such as those associated to the HOMO–LUMO mixing along the pathway and their *avoided crossing*.

It is implicit from the nature of the HOMO (η^2 side) that the bending of the dithiocarboxy ligand induces initially its destabilization due to the antibonding relationship between the metal and carbon atoms. As observed for (η^3-allyl)metal complexes,[38] the antibonding

(36) See for example: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital interactions in Chemistry*; Wiley: New York, 1985.

(37) The total of π electrons in the four-membered ring can be as many as 8 since the metal carries also a filled δ-type orbital in the t$_{2g}$ set which is repulsive toward the out-of-phase combination of sulfur *lone pairs* (n_π-S$_2$C, **X**).

(38) Carfagna, C.; Galarini, r.; Linn, K.; Lopez, J. A.; Mealli, C.; Musco, A. *Organometallics* **1993**, *12*, 3019.
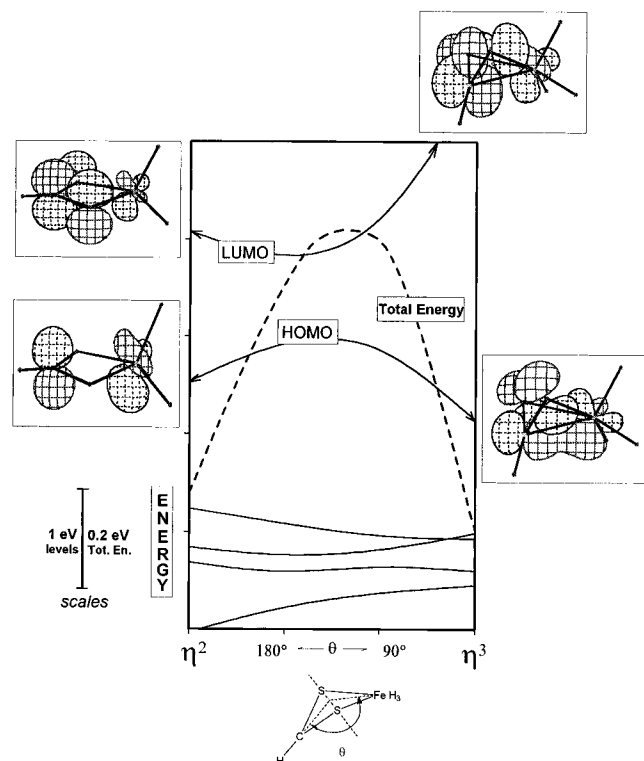
Figure 3. Diagram showing the evolution of the MOs and the total energy for the interconversion of the $\eta^2-\eta^3$ coordination modes in the model complex $FeH_3(S_2CH)^{4-}$.

interaction between $d\pi_\perp$ and the overall π bonding FMO **IX** is predominant at some stage of the interconversion (see HOMO). Soon however, the mixing with the descending LUMO (the $d\pi_\perp-\pi^*-S_2C$ antibonding combination, which, however, carries in-phase metal and carbon components) overcomes the HOMO's destabilization. Over a certain stage, the direct metal−carbon σ bond prevails in the HOMO which stabilizes toward η^3. The drawing of the latter (right side of Figure 3) shows clearly the acquired metal−carbon σ-bonding character as well as residual π^*-S_2C features. Analogously, the LUMO appears metal−carbon antibonding in character with residual π^*-S_2C character as well. In both cases, the S_2C p_π components have lost part of their initial parallelism.

The chemical and structural consequences of the metal−carbon bond formation are evident. There is a net electron density accumulation in the dithiocarboxy ligand with consequent electron loss by the metal. Indicatively, the Mulliken analysis suggests a transfer of *ca.* 0.5 electrons subsequent to the η^3 rearrangement. At the same time, the accumulation of the electrons in the π^*-S_2C level is responsible for a decrease of the C−S overlap populations, which matches well with the experimental results (longer C−S distances for the compounds of Table 6 compared with those in Table 5).

Most importantly, the visual MO approach shows that, although a new metal−carbon bond is formed, the original features of the S_2C π system (see the MOs **IX**−**XI**) are somewhat preserved. This could be well consistent with the simplest metal back-donation picture, namely an electrostatic interaction which does not alter significantly the character of the components. The evident HOMO−LUMO *avoided crossing* suggests another possibility. At η^2, the two electrons in the HOMO do clearly belong to the metal. On bending of the

dithiocarboxy ligand, an improved back-donation into the emptry π^*-S_2C level would be simply indicated by the diverging HOMO−LUMO levels (a normally increasing two-center/two-electron interaction). Conversely, the HOMO destabilizes rather than stabilizes on account of the prevailing four-electron repulsion between the metal d_π orbital and the low filled $\pi-S_2C$ FMO. This means that also the latter level with its electrons participates actively into the HOMO−LUMO interplay and their *avoided crossing*. Through the mixing, the two levels can exchange their character and eventually the ownership of the electrons is reversed. In this respect, the system seems to undergo an oxidative addition process of some sort which accumulates metal electrons into the dithiocarboxy ligand and in particular at the carbon atom. The latter is only one of the two limiting descriptions, with the metal being converted from a d^8 to a d^6 species and the S_2CX ligand becoming capable of donating as many as three electron pairs to the metal (a very peculiar case of octahedral d^6 complex). The alternative description is, as mentioned, the simplest back-donation which perturbs only a little of the character and electron distribution of the S_2C moiety, hence allowing the maintenance of its original features with four π electrons. As it is often the case in chemistry, the actual description is in between the two limiting models.

A final remark can be made about the regioselectivity of the electrophilic attack by a methyl cation to the complexes **2** to give the complexes **3**. These maintain the η^3 coordination of the SCS grouping. As evidentiated in Figure 3, the composition of the high-lying HOMO is quite different between η^2 and η^3 conformers. In particular, the absence of any sulfur atomic orbital contribution seems to dismiss the possibility that such a regioselective attack can occur at η^2 or that the alkylated product can convert to this coordination mode. Although the HOMO of the η^3 conformer is largely metal−carbon bonding in character (see above), the sulfur orbitals are well developed and appear to point in the same direction as the S−C_{alkyl} bond observed in the crystal structure (compare Figures 2 and 3).

$ML_4(S_2CX)$ Complexes. The underpinnings of the $\eta^2-\eta^3$ dichotomy, illustrated above for the complexes of the type $ML_3(S_2CX)$, can be generalized also for the species containing the fragments ML_4-d^6. In these cases (the most numerous in Tables 5 and 6), the switching from η^2 to η^3 coordination mode is accompanied by a structural rearrangement of the metal fragment itself. Thus, beside the nature of the metal (the oxidation state and the charge are of importance) and that of the coligands, the effects of geometry need to be evaluated.

A ML_4 fragment of type **II** has well-characterized FMOs.[36] In particular, there is a relatively high σ-hybrid, a well-hybridized frontier d_π orbital (in-plane), and a lower set of "t_{2g}-reminiscent" orbitals. As for the η^2 coordination mode of the ML_3 fragment, one σ and one in-plane d_π hybrid accept the donation of electrons from two symmetry adapted combinations of sulfur *lone pairs*. Practically, this is like reconstructing a pseudo-octahedral d^6 complex from a ML_4 fragment and a chelate ligand. At variance with the ML_3 fragments, there is no high-lying $d\pi_\perp$ hybrid apt to back-donate into the carbon atom of the dithiocarboxy ligand. Two symmetry-suited candidates are found only in the low-

lying t$_{2g}$ set. These are the orbitals *xz* (**XIV**) and *x^2 −
y^2* (**XV**), respectively. In any case, the energy separation
from π*-S$_2$C (**XII**) is large but *xz* makes a better overlap
with the latter.

Also consider that in ML$_4$ fragments, containing
ligands with good π-acceptor capabilities (*e.g.* carbon
monoxide), any of t$_{2g}$ orbitals **XIV** and **XV** as well as *yz*
(with δ character) can be depressed (*vide infra*). In
particular, if *xz* is significantly stabilized by the interac-
tion with π*$_{CO}$, the η^3 coordination becomes more
difficult to achieve. This can be compensated by a
deformation of the fragment **II** into that shown in **XVI**.
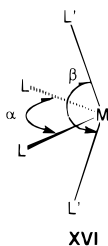
The two angles α and β do in general vary from 90 to
110° and from 180 to 150°, respectively. Particularly,
the latter appears to be the *governing* parameter as it
affects significantly the energy and the hybridization
of the orbital *xz*, **XIV**. As soon as the two axial σ donors
(L′) move away from the node, *xz* is rapidly destabilized
(for the increasing M−L′ σ* character), the gap with the
π*-S$_2$C diminishes, and the back-donation is facilitated.

Moreover, the loss of C$_{2v}$ symmetry (when the dithio-
carboxy ligand moves away from η^2) allows the orbital
x^2 − y^2 (**XV**), also symmetric with respect to the L′ML′
plane, to mix with *xz*, so their lobes are redirected. One
of the two orbitals, acting as a donor, is directed toward
the S$_2$C carbon atom (as to maximize the overlap) while
the other maintains the former character of *lone pair*
(at η^2) and points over the MS$_2$ plane [see in **XVII** the
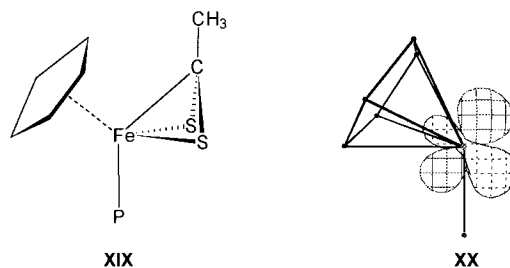relative FMOs calculated for the simplest model
[MoH$_4$(η^3-S$_2$CPH$_3$)]$^{4-}$.
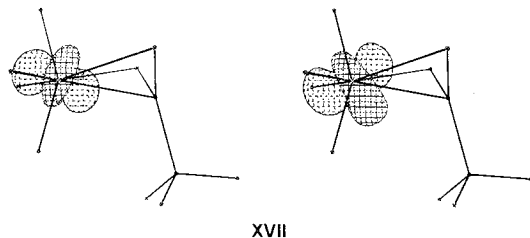
An *ad-hoc* MO analysis of the $\eta^2-\eta^3$ dichotomy in the
model of the Mo(S$_2$CPMe$_3$)(CO)$_2$(PMe$_3$)$_2$ compound (**XVI-
II**) does not confirm that the η^3 structure, determined
experimentally,[10] is energetically favored. The calcu-
lated barrier is *ca.* 0.7 eV. Also the most stabilized
conformer appears to be η^2. Although the same results
were obtained for the ML$_3$ iron complexes, the energet-
ics involved were lower in that case. In spite of this
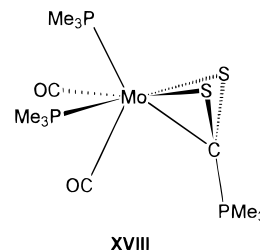
poor response, the preferential disposition of the pairs
of CO and phosphine ligands at η^3 can be understood.
A reasonable explanation why the COs are neither both
axial or both equatorial (see **XVIII**) has been already
presented together with a rationale for the observed
fluxional propeller behavior of the S$_2$CPMe$_3$ with respect
to the ML$_4$ fragment.[39] The importance of the α and β
parameters (defined in **XVI**) in governing this process
has been also underlined.

MCp(L)(S$_2$CX) Complexes. This category includes
the very special case of one metal fragment (type **III**)
which is able to accommodate both η^2 and η^3 coordina-
tion modes of a dithiocarboxy ligand. This is the already
mentioned complex FeCp(S$_2$CCH$_3$)(η^1-dppm).[30] The
drawing **XIX** schematizes the structure of the η^3 con-

former. The frontier FMOs of FeCp(PH$_3$) are closely
related to those of the fragments ML$_4$, namely they
consist of two higher hybrids (σ and d$\pi_{||}$) and three "t$_{2g}$-
reminiscent" orbitals. Given a metal of the first transi-
tion row (iron), the "t$_{2g}$" levels are at least 1 eV lower
in energy than those of Mo(CO)$_2$(PH$_3$)$_2$, even in the
absence of any stabilizing π-acceptor CO ligands. More-
over, due to the presence of the Cp ring, the d$\pi_\perp$ orbital
(**XX**) has lobes best suited for back-donation and lies
ca. 0.3 eV higher than the other "t$_{2g}$" levels.

The orbital **XX** destabilizes on closing from 120° the
angle Cp(centroid)−Fe−P.[40] This is expected to facili-
tate its interaction with the π*-S$_2$C level, hence the
metal back-donation (the model S$_2$CH is used in the
calculations). However, in both the η^2 and η^3 structures
of the compound FeCp(S$_2$CCH$_3$)(η^1-dppm) the experi-
mental values of the angle remain very close to 120°.
On the other hand, one of the "t$_{2g}$" levels with δ
symmetry triggers a significant 4e-repulsion with the
FMO n$_\pi$-S$_2$C (**X**) thus being a factor of destabilization
for the η^2 coordination mode. Experimentally, the ratio
between the η^2 and η^3 forms depends on the nature of
the terminal substituents in the dithiocarboxy ligand
(the percentage of the η^2 form increases in the order H
> CH$_3$ > Ph). At the EHMO level, the higher energy
(*ca.* 0.6 eV) is once again calculated for the η^2 form and
it may be due to an overestimation of the repulsion

(39) Galindo, A.; Mealli, C. *Inorg. Chem.* **1996**, *35*, 2406.
(40) Hofmann, P.; Padmanabhan, M. *Organometallics* **1983**, *2*, 1273.

(**XXI**) between the in-phase sulfur σ *lone pair* combina-

XXI
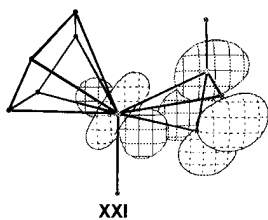
tion ($S\sigma_{i.p.}$) and the other symmetric "t_{2g}" FMO. Notice that $S\sigma_{i.p.}$ is engaged in one major σ-bonding combination at the η^2 structure, whereas at the η^3 coordination it is simply a *lone pair*, which can trigger four-electron repulsions.

The Mulliken analysis accounts for the different bond distances found in the η^2 and η^3 isomers containing the dithioacetate ligand. Namely, the C–S and Fe–S separations appear longer in the η^3 coordination (compare Tables 5 and 6). The back-donation to the central carbon atom weakens the C–S overlap populations by *ca.* 10%. Also the slight decrease of the Fe–S overlap population mirrors the antibonding relation between the metal and the sulfur orbitals shown in **XXI**.

Conclusions

The synthesis and structural characterization of the complex Fe(η^3-S$_2$CPCy$_3$)(CO)$_3$ (**2a**), compared to other known systems, such as Mo(η^3-S$_2$CPMe$_3$)(CO)$_2$(PMe$_3$)$_2$[10] and FeCp(S$_2$CCH$_3$)(η^1-dppm),[30] prompted us to investigate theoretically the problem of the structural η^2–η^3 dichotomy in complexes of dithiocarboxylate ligands containing four π electrons. Intuitively, the rearrangement depends on several parameters such as the nature and the charge of the metal, the nature and the disposition of the coligands, and the geometric features of the ancillary metal fragment. Due to the well-known limitations of the EHMO method, no structural optimization was attempted. Also, not much weight was attributed to the fact that the total energetics seems in general to favor the η^2 coordination mode. The discussion was mainly focused on the arguments of chemical significance which stem from the comparison of the orbital interactions in the two isomers as well as from their monitoring along the η^2–η^3 interconversion pathway. On the basis of the latter, the existence of an energetic barrier can be justified.

Most critical for the η^3 coordination is the nature of the filled metal d$\pi_\perp$ orbital suited to interact with the empty π^*-S$_2$C level centered on the carbon. The more hybridized and destabilized is the metal FMO, the better is the back-donation. In general, the HOMO of ML$_n$(η^3-S$_2$CX) complexes appears as the bonding combination between the two levels in question. However, the interconversion from η^2 (modeled through a simple 90° rotation of the dithiocarboxy ligand at the S···S vector) shows that, before the M–C bonding relationship is established, there is an initial repulsion between the metal d$\pi_\perp$ and the low-lying π-S$_2$C filled FMOs. The repulsion is eventually overcome by an *avoided crossing* with the descending LUMO (d$\pi_\perp$-π^*-S$_2$C bonding in character). The strength of the *avoided crossing* determines, case by case, whether the system is stabilized at the η^2 or η^3 conformation.

The general η^3 MO description stands between two limiting situations. The first picture is consistent with the typical model of two synergistic donations (from the sulfur atoms) and back-donation (to the carbon atom). This metal–ligand interaction resembles, for example, that attributed to other π-four electron donor ligands[41] (*e.g.* 1,3-butadiene). The second interpretation suggests that the oxidative addition of the metal may have occurred in going from η^2 to η^3 on account of the HOMO–LUMO *avoided crossing*. As a consequence, the electron density which accumulates at the dithiocarboxy ligand reduces the C–S overlap populations according in full agreement with the longer C–S bond distances experimentally found for the η^3 derivatives.

Supporting Information Available: Tables of complete coordinates and isotropic and anisotropic thermal parameters and complete bonds distances and angles for the structures of **2a** and **3a** and a table of crystal data for **3a** (9 pages). Ordering information is given on any current masthead page.

OM950977Q

(41) Similar ML$_4$-d^6 deformations have been reported for other π-four electron donor ligands: (a) Wink, D. J.; Creagan, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 8585. (b) Wang, N.-F.; Wink, D. J.; Dewan, J. C. *Organometallics* **1990**, *9*, 335.