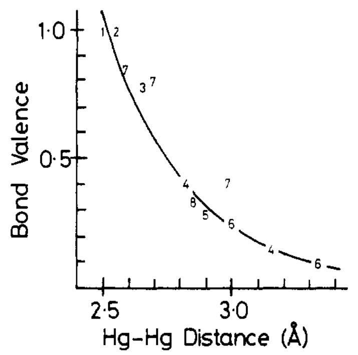

Figure 2. Relation between the bond valence (*y* axis) and bond length (*x* axis) in angstroms for Hg–Hg bonds. The line corresponds to the following equation: bond valence = exp((2.51 – distance)/0.35). The points correspond to (1) Hg_2^{2+},[15] (2) Hg_3^{2+},[1,2] (3) $Hg_{3-\delta}AsF_6$,[8] (4) β-Hg,[14] (5) Hg_3NbF_6, (6) α-Hg,[15] (7) $Hg_4^{2+}(AsF_6)_2$,[3] and (8) $KHgC_4$.[12]

bonded Hg atoms. In these sheets each Hg has six other Hg atoms as neighbors, at a distance of 2.90 (1) Å. Its coordination is completed by six F atoms from the two adjacent fluorine sheets, at distances of around 3.2 Å.

On being heated to 120 °C, the silver Hg_3NbF_6 crystals were transformed in about 30 min to the golden $Hg_{3-\delta}NbF_6$ crystals, as was confirmed by an X-ray powder photograph. Despite the apparent difference in the composition of these compounds, no mercury was observed to be formed in the transformation. When the golden crystals were cooled to room temperature and below, the silver crystals were not re-formed. Thus, it appears that this transformation is not reversible in the absence of the liquid SO_2 that was present during the formation of the silver crystals from the initially formed golden crystals.

Hg–Hg bonds occur in many compounds, but Hg_3NbF_6 and Hg_3TaF_6 are unusual in that this bonding occurs in sheets. In most cases the Hg atom has a strong tendency to form two collinear bonds as in Hg_3^{2+} and Hg_4^{2+}. Infinite linear chains are found in β-Hg and $Hg_{3-\delta}MF_6$ (M = As, Sb, Nb, Ta).

Mercury atoms can be found in sheets in the graphite intercalate $KHgC_4$.[10] Although the Hg–Hg distances are similar in both the intercalate and Hg_3NbF_6 (2.85 and 2.90 Å, respectively), the sheets differ in that in the Nb compound each Hg has six nearest Hg neighbors and a formal charge of $^1/_3$ +, while in the intercalate each Hg has only three Hg neighbors and a formal charge of 0.

Following the approaches of Pauling[11] and Brown and Shannon,[12] it is possible to correlate the lengths of Hg–Hg bonds with their bond strength (or bond valence) as shown in Figure 2. The bond valences have been assigned as follows: For Hg_2^{2+} and Hg_3^{2+} a bond valence of 1.00 is assumed. For Hg_4^{2+} the terminal Hg atoms are assumed to form bonds to F of 0.58 valence unit (vu) and to the inner Hg of 0.36 vu, giving bond valences of about 0.85 for the central bond, 0.80 for the terminal bond, and 0.40 for the weak bridging bond between Hg_4^{2+} ions. For $Hg_{3-\delta}AsF_6$ the atomic valence of the Hg atom (2.00) is diminished by its formal charge (0.36 vu, being the valence of the bonds formed to F) and by a further 0.10 to allow for the bonding to the adjacent perpendicular chains (because of the incommensurate nature of this structure, bond lengths vary from one atom to another). In β-Hg there are two short bonds and eight longer bonds, and the valences of these have been chosen so that they sum to 2.0 at each Hg atom. A similar method of assigning valences has been used for α-Hg, where there are six short and six longer bonds. The bond valence expected for Hg_3NbF_6 is the atomic valence of Hg (2.00) less the valence of the bonds to F (0.33 = formal charge on each Hg) divided by the number of Hg–Hg bonds (6). The solid curve in Figure 2 corresponds to the expression

$$\text{bond valence} = \exp((2.51 - \text{distance})/0.35)$$

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for the operating grants that made this work possible.

Registry No. $Hg(NbF_6)_2$, 93255-71-1; $Hg(TaF_6)_2$, 93255-75-5; Hg_3NbF_6, 93255-73-3; Hg_3TaF_6, 93255-74-4; Hg, 7439-97-6.

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Reactivity of the Monodentate Dithiocarbamate Ligand in $CpFe(CO)_2(\eta^1\text{-}SC(S)NR_2)$

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Received November 16, 1983

The most convenient route to $CpFe(CO)_2(\eta^1\text{-}SC(S)NR_2)$ (**1**) is the reaction between $CpFe(CO)_3{}^+PF_6{}^-$ (**2**) and Na^+dtc^- in acetone. Chelation of **1**, which proceeds in very low yield thermally, is induced by $PPh_3 + CS_2$, $Mo(CO)_6$, or Cp_2TiCl_2. Reaction of **1** with $NO^+PF_6{}^-$ leads to replacement of both carbonyls in **1** by NO^+ together with chelation of the dtc ligand, giving $[CpFe(NO)(\eta^2\text{-dtc})]^+PF_6{}^-$ (**3**). Transmetalation of the dtc ligand in **1** is obtained upon heating with $Fe_2(CO)_9$ or $[CpMo(CO)_3]_2$, giving the known complexes $Fe(CO)_2(\eta^2\text{-dtc})_2$ (**4**) and $CpMo(CO)_2(\eta^2\text{-dtc})$ (**5**), respectively. Reaction of **1** with KCN in methanol gives the new anionic metallacycle $K^+[Cp\overline{Fe(CO)(SC(NR_2)(SC}N))]^-$ (**6**), which can be acylated by PhCOCl to give $Cp\overline{Fe(CO)(SC(NR_2)SC}NCOPh)$ (**7**). The reaction of **1** with electrophiles gives different products depending on whether the counteranion of the electrophilic reagent is a potential ligand: the action of CH_3I leads to $CpFe(CO)_2I$ and $MeSC(S)NMe_2$ whereas that of $Me_3O^+BF_4{}^-$ gives $[CpFe(CO)_2(\eta^1\text{-}SC(SMe)(NMe_2))]^+BF_4{}^-$ (**8**). This reaction also demonstrates the nucleophilic properties of the uncoordinated sulfur atom in a monodentate dtc complex.

Dithiocarbamate complexes (dtc = dimethyl- or diethyldithiocarbamate) are one of the most extensively used and studied families in inorganic chemistry, and their various aspects have been thoroughly reviewed.[2] However, it is

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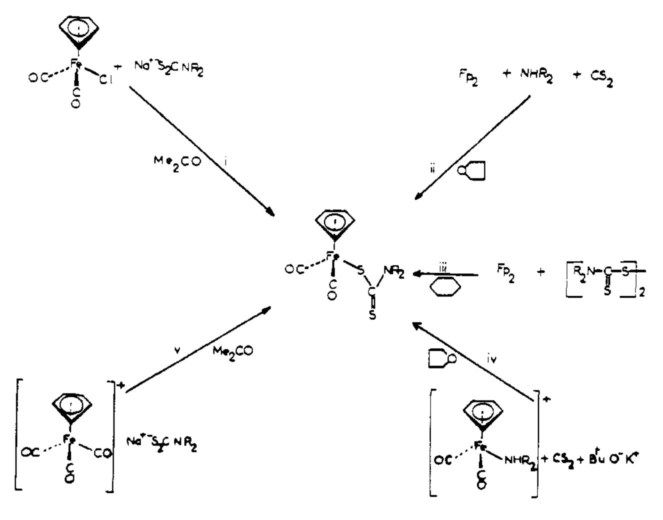
Scheme I

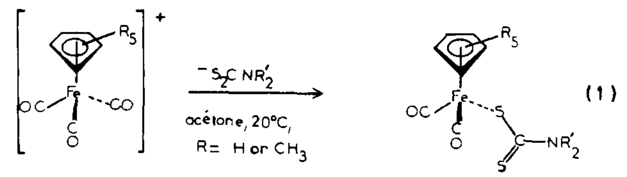


	R	T(°C)	t (h)	Yield(%)	Ref.
i	Me	20	24	70	4
ii	Et	65	4	50	5
iii	Et	101	4	70	7 this work
iv	Me, Et, Me_3Si	20	0.5	90	this work
v	Me	20	0.1	91	this work

noteworthy that the reactivity of monodentate dtc complexes has not, to our knowledge, been examined. This is certainly due to the fact that only a few monodentate dtc complexes have been made because of the tremendeous driving force toward chelation brought about by the entropy effect. Since monodentate dtc complexes are known for the very common and easily available $CpFe(CO)_2$ (Fp) series, we were interested in the specific reactivity of the monodentate form of this ligand, in particular because the free sulfur atom might interact with additional transition metal centers, electrophiles, etc. On the other hand, it was of interest to see how chelation could be effected, if not spontaneously or thermally, and to compare the spectroscopic properties of monodentate and bidentate complexes in the same series. In a preceding article, we described the synthesis of amine complexes of Fp^+ and the access to mono- and bidentate dtc complexes by insertion of CS_2.[5] Some of the results presented here have been reported in a communication[6] also including the full details of the crystal structure study of the heterometallacyclic complex **7**. In this article, we present a new, improved synthesis of the monodentate complex $CpFe(CO)_2(\eta^1\text{-}SC(S)NMe_2)$ (**1**) and various aspects of its reactivity: chelation induced by $PPh_3 + CS_2$, $Mo(CO)_6$, or Cp_2TiCl_2, transmetalation of the dtc ligand by reaction with $Fe_2(CO)_9$ or $Cp_2Mo_2(CO)_6$, formation of the metallacycle $K^+[\overline{CpFe(CO)(SC(NR_2)SCN})]^-$ (**6**) and its benzoylation at the N atom of the incoming CN group, reactions with electrophiles leading to dtc displacement from **1** by I^- using MeI, and methylation of the free sulfur of the η^1-dtc ligand of **1** using $Me_3O^+BF_4^-$

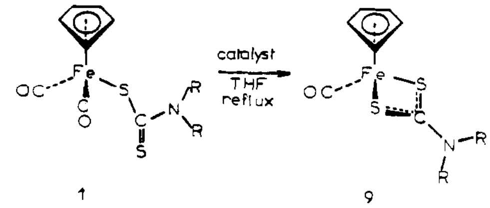
Results

Synthesis of 1 from $Fp(CO)^+PF_6^-$ (2). There are several known methods for the synthesis of $Fp(\eta^1\text{-dtc})$ (**1**) (Scheme I). First, Wilkinson et al. reported the reaction between FpCl and Na(dtc)[4] (sodium salt of dimethyldithiocarbamate). Cotton and McCleverty[7] reported that the chelate $CpFe(CO)(\eta^2\text{-dtc})$ (**9**) is obtained upon refluxing Fp_2 with dithiuram ($(dtc)_2$) in cyclohexane for 18 h, but we found that **1** can be obtained in this way if the reaction is stopped after 3–4 h. We also found that **1** could be synthesized directly from Fp_2, NHR_2, and CS_2 in 50% yield but some chromatographic purification is needed; we synthesized **1** with various *N*-alkyl substituents more cleanly in two steps, namely isolation of the amine complexes $(FpNHR_2)^+PF_6^-$ and then insertion of CS_2 using *t*-BuOK.[5] We now find that a more convenient route is to react $CpFe(CO)_3^+PF_6^-$ (**2**) (easily accessible from ferrocene, $AlCl_3$, and CO)[8] with Na^+dtc^- in acetone at room temperature (eq 1). This method is fast and extremely easy and requires no separation. The reaction is immediate, and the crude yield is quantitative. Applied to $C_5Me_5Fe(CO)_3^+PF_6^-$ (**10**), this route is the only one leading to the monodentate complex $C_5Me_5Fe(CO)_2(\eta^1\text{-dtc})$ (**11**), since in this case, all the other methods give the chelate $C_5Me_5Fe(CO)(\eta^2\text{-dtc})$ (**12**)[5] directly.



(1)

Chelation of the Monodentate dtc Ligand: Displacement of a CO Ligand by the Free Sulfur Atom (Eq 2). Thermal chelation of the dtc ligand in **1** is a very difficult process.[5] The thermal reaction in cyclohexane proceeds at 81 °C with ex-



(2)

1 9

Catalyst	Time(h)	Yield (%)
Ph_3P/CS_2	8	75
$Mo(CO)_6$	10	40
Cp_2TiCl_2	10	47

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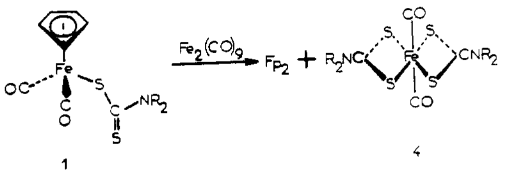
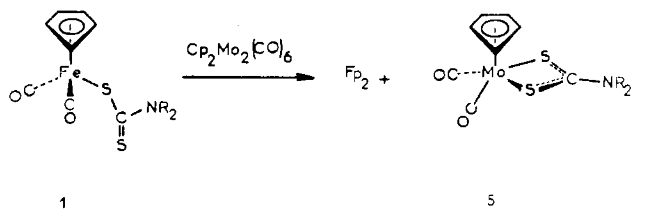
tensive decomposition. Thus we have looked for reagents that would facilitate this process: $PPh_3 + CS_2$ (1/1), $Mo(CO)_6$, and Cp_2TiCl_2 all are successful to some extent since, when added in less than equimolecular amount (10%), they greatly increase the rate and yield of the chelation in refluxing THF.

Whereas the thermal reaction yields no chelate at all in refluxing THF (more drastic conditions are needed), yields of $CpFe(CO)(\eta^2\text{-dtc})$ (**9**) obtained under these conditions are 75% (8 h) with $PPh_3 + CS_2$ (namely $Ph_3P^+CS_2^-$; PPh_3 or CS_2 alone is inefficient), 40% (10 h) with $Mo(CO)_6$, and 47% (10 h) with Cp_2TiCl_2. In each case, **9** is obtained pure by chromatographic separation on thick (1 mm) silica gel plates and these unoptimized yields are given after subsequent recrystallization. No search was made for byproducts, which were only found in minor or trace amounts by chromatography, aside from decomposition products.

Transmetalations. Coordination of the free sulfur in **1** to other transition metals has been attempted via reaction with some transition-metal carbonyl or halide complexes. The reaction of $Mo(CO)_6$ described above simply leads to chelation at a single metal center. The reaction of $Fe_2(CO)_9$ gives transfer of the monodentate ligand from one iron center to another, leading to $Fe(CO)_2(\eta^2\text{-dtc})_2$ (**4**), a long known complex[3] (eq 3). A similar reaction is found with $Cp_2Mo_2(CO)_6$, leading to $CpMo(CO)_2(\eta^2\text{-dtc})$ (**5**), another known dtc complex[4] that can be made quantitatively from $Cp_2Mo_2(CO)_6$, $NHEt_2$, and CS_2 (eq 4).[5]



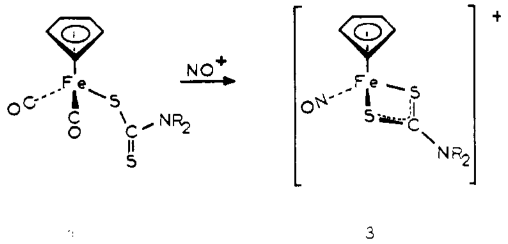
(3)



(4)

In the first case, the transmetalation is complex since two dtc ligands are found on the same metal. However, we know that both dtc ligands have been transmetalated since the fate of the Fp moiety is to form Fp_2. In the case of molybdenum, only clean, intermolecular transfer of the dtc ligand is found.

Chelation Subsequent to Ligand Exchange of CO by NO⁺. Reaction of **1** with $NO^+PF_6^-$ at room temperature in CH_2Cl_2 is complete in 1 h and results in the removal of both CO ligands and their replacement by NO^+ and η^2-dtc. Exchange of CO by NO^+ in **1** would leave a cationic intermediate in which chelation of dtc is presumably favored since the uncoordinated sulfur atom is nucleophilic. Thus this reaction leads to the red complex $CpFe^+(NO)(\eta^2\text{-dtc})$ (**3**) in 62% yields after recrystallization (eq 5).



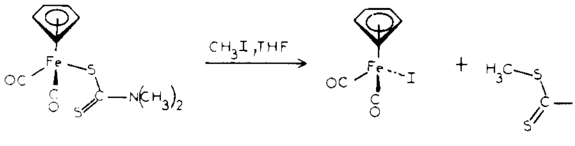
(5)

It may be noted that, in the NMR spectra of the cationic complexes, $\delta_{Cp}(^1H)$ is 1.5 ppm larger than in neutral analogues and $\delta_{Cp}(^{13}C)$ is shifted by 20 ppm.[11] This indicates that electronic effects are transmitted well through iron; such effects have been noted previously.[12]

The Mössbauer parameters for **3** are close to those recorded for neutral CpFe(dtc) complexes, indicating that the positive charge does not interfere much with the iron orbital and electron density (IS, 0.06 mm s^{-1} vs. Fe; QS, 1.754 mm s^{-1}, 293 K).

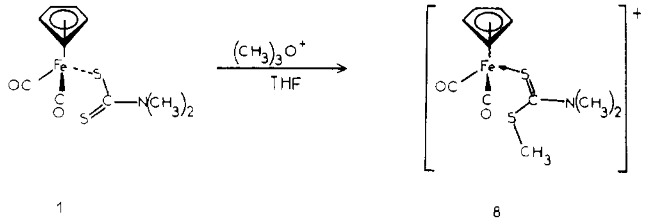
The combined NMR and Mössbauer data indicate that the effects of the positive charge are seen on the ligands, not on the metal.

Electrophilic Character of the Free Sulfur in 1: Reaction with MeI and Alkylation with $Me_3O^+BF_4^-$. We attempted to alkylate the free sulfur in **1** using various electrophiles. The reaction of **1** with MeI requires heating in THF (reflux, 2 h) and leads to the formation of FpI and $MeSC(S)NMe_2$ (eq 6).



(6)

The reaction of $Me_3O^+BF_4^-$ with **1** proceeds in THF at room temperature, giving a 70% (crude) yield of the red complex $[Fp(\eta^1\text{-SC(SMe)(NMe}_2))]^+BF_4^-$ (**8**) (eq 7), which after recrystallization gives large bordeaux crystals (50% overall yield).



(7)

The ^1H and ^{13}C NMR spectra of CD_2Cl_2 solutions of **8** show the presence of both *S*-methyl and *N*-methyl groups. The CS carbon is now shifted to 204.5 ppm. The infrared spectrum (Nujol) shows two strong CO stretches (ν_{CO} 2060 and 2000 cm^{-1}), confirming the presence of two carbonyls. The Mössbauer parameters are consistent with a complex of the $(FpL)^+$ series, and the elemental analysis for C, H, N, S, and Fe confirms the molecular structure.

So far, dtc has always been considered to be an odd-electron ligand, giving one or three electrons.[2] Medtc, a stable molecule, can also bind to transition metals in the form of a η^1 two-electron ligand via the lone pair on sulfur, in the same way as a dialkyl sulfide.

In the light of this reaction, it can be understood how MeI reacts to give FpI and $MeSC(S)NMe_2$. The first step is, as with $Me_3O^+BF_4^-$, alkylation of the free sulfur giving **8**, in which the counteranion is I^-, and this counteranion reacts further with the cationic metal center to displace the ligand $MeSC(S)NMe_2$ (eq 8).

Formation of Heterometallacycles FeS_2C_2 by Reaction with CN⁻. The reaction of KCN in methanol with transition-metal carbonyl complexes leads to the replacement of one or several carbonyl ligands by CN^- ligands. Subsequent alkylation with

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(11) A study of the ^{15}N chemical shifts and of the rotation barriers about the C⁻N bond is under way: Martin, M.; Mabon, M.; Román, E.; Catheline, D.; Astruc, D., work in progress.

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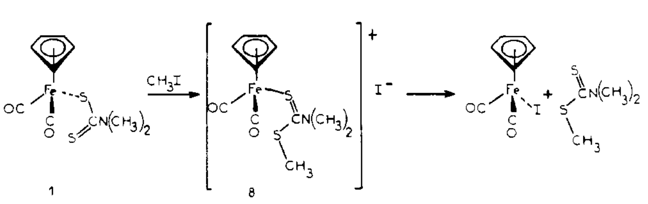


(8)

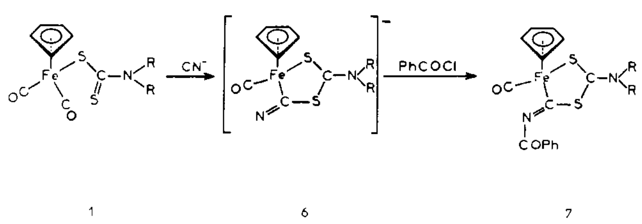
CH_3I or benzoylation with PhCOCl gives the N-alkylated or benzoylated isocyanide complexes (eq 9).[13]

$$L_nMCO \xrightarrow[MeOH]{KCN} [L_nM(CN)]^- K^+ \xrightarrow{RX} L_nMCNR + KX \qquad (9)$$

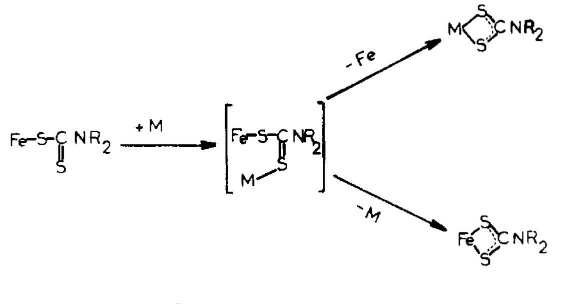
We investigated this type of reaction in which the starting metal carbonyl bears the monodentate ligand in **1**. The reaction between **1** and KCN in dry methanol (3 h) gives, after workup in CH_2Cl_2 and precipitation by ether, the salt $K^+[CpFe(CO)(SC(SCN)(NMe_2))]^-$ (**6**) as a very air-sensitive red-purple powder (Scheme II). **6** was characterized by ^1H and ^{13}C NMR (in CD_2Cl_2), infrared, and Mössbauer spectra, by elemental analysis, and by benzoylation with PhCOCl. After reflux for 3 h with excess PhCOCl in CH_2Cl_2, workup and chromatographic purification give the neutral, red heterometallacyclic complex $CpFe(CO)(SC(SCNCOPh)(NEt_2))$, which was characterized by X-ray diffraction.[6] The essential features of this crystal structure, the full details of which were published in a preliminary communication, are the formation of a metallacycle and its consequences for the geometries of the dtc and benzoyl isocyanide ligands. A covalent bond (1.83 Å) is found between these two ligands ($C_{CN}\text{-}S_{dtc}$). Since the dtc moeity is once again part of a chelate ring, this ligand is almost symmetrical, its two CS bonds being of nearly identical length (1.69 and 1.72 Å). The benzoyl isocyanide ligand, which was found to be quasi-linear in CrCNC,[13] where no strong interaction with neighboring ligands occurs, is bent in **6** (∠FeCN = 134°). The geometry of **7** is represented in Figure 1, with indications of bond lengths and angles. The isocyanide infrared stretch (1760 cm^{-1}, Nujol) is much lower than in $(\eta^6\text{-arene})Cr(CO)_2CNCOPh$ complexes (2020 cm^{-1}), in which the isocyanide ligand is quasi-linear as in normal alkyl isocyanides. The lowering of the CN bond order in **7** is due to the presence of a covalent bond between the CN carbon atom and the S atom of the dtc ligand. dtc complexes usually show two characteristic absorptions in the infrared spectra: the CS_2 stretch at 1000–1100 cm^{-1} and the thioureide stretch (C=N) at 1400–1500 cm^{-1}. According to Bonati,[14] chelating dtc shows only one CS_2 band whereas, for monodentate dtc complexes, two bands are found, owing to the dissymmetry of the ligand. The thioureide band is located at higher frequencies for chelating than for monodentate dtc complexes because of the greater delocalization of the lone pair on the N atom. These criteria apply to the metallacycles **6** and **7**.

Like **1**, the metallacycle **7** does not exhibit the molecular peak (M^+) in the mass spectrum, but $(M - CO)^+$ (relative intensity 40%), the base peak, as generally encountered for $CpFe(CO)_x(\eta^n\text{-dtc})$ ($x = 2, n = 1$; $x = 1, n = 2$) complexes, is $(CpFedtc)^+$. For the first time, to our knowledge, in functional isocyanide complexes, the ion $(CNCOPh)^+$ is observed (relative intensity 12%).

Scheme II



Scheme III



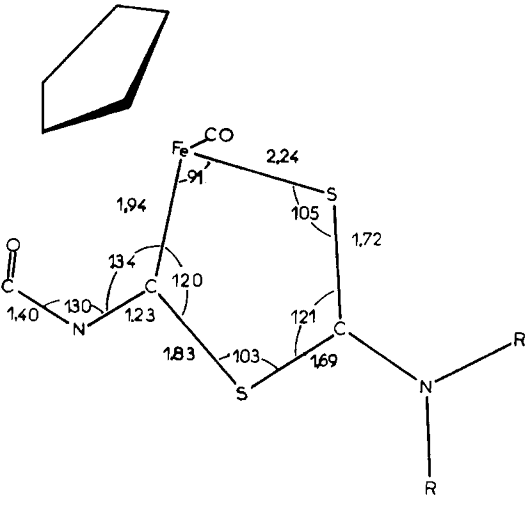


Figure 1. Geometry of **7**, with selected bond lengths (Å) and angles (degrees).

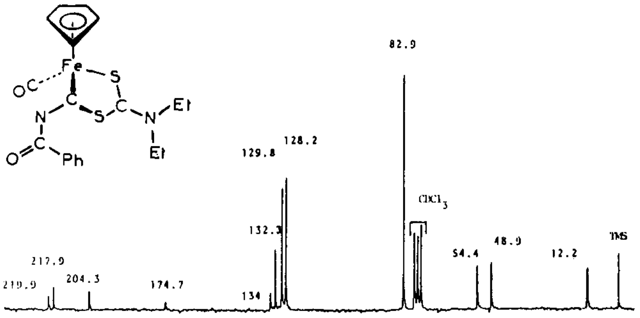


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of the benzoylated metallacycle **7** in $CDCl_3$.

The Mössbauer parameters of **6** and **7** are essentially identical within experimental error (IS, −0.01 mm s^{-1} vs. Fe; QS, 1.9 mm s^{-1}). They are also extremely close to those of the chelate complex $CpFe(CO)(\eta^2\text{-dtc})$ (IS, +0.02 mm s^{-1} vs. Fe; QS, 1.8 mm s^{-1}), but distinct from those of the monodentate complex **1** (IS, −0.15 mm s^{-1} vs. Fe; QS, 1.68 mm s^{-1}).

It is noteworthy that, in the $^{13}C\{^1H\}$ NMR spectrum of **7**, δ_{CN} is lower (217 or 219 ppm) than in $(arene)Cr(CO)_2CNCOPh$ (232 ppm)[13] (Figure 2).

Discussion

The multifaceted chemistry of the monodentate dtc complex **1** results from the reactivity of the free sulfur atom of the dtc

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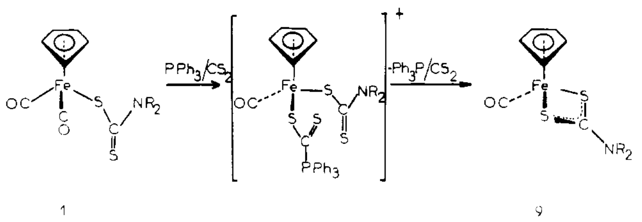
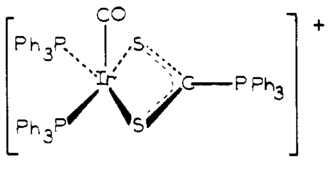
Scheme IV



ligand in this mode of coordination. Coordination of this free sulfur to a transition-metal center leads to either chelation or transmetalation. Its electrophilic character and its ability to form heterometallacycles have also been demonstrated. The intermolecular coordination of the free sulfur to a transition metal follows two different reaction pathways, depending on the nature of the metal species involved in this process (Scheme III).

Bimetallic complexes such as the intermediate depicted in Scheme III have been isolated, but when they are unstable, subsequent reaction is expected, giving chelation to either transition-metal center. The entropy effect is a strong driving force toward chelation in this chemistry. When M = Fe, the dtc chooses the metal having electron-releasing ligands, but when M $\neq$ Fe, several factors may intervene: not only the respective affinity of Fe and M for S but also the ability of unsaturated M to react with the ligands of the iron complex, such as CO. Note, for instance, that $Mo(CO)_6$ induces chelation about iron whereas $Cp_2Mo_2(CO)_6$ traps the dtc ligand. In the first case, thermal decoordination of CO leaves a 16-electron $Mo(CO)_5$ species, whereas in the second case, thermal cleavage of the Mo–Mo bond leaves the 17-electron species $CpMo(CO)_3$, which needs an odd-electron ligand such as dtc. That $Ph_3P^+{-}C^-S_2$ also induces the chelation may be interpreted in terms of removal of CO by this zwitterion, which was indeed found to behave as a ligand toward several transition metals, as for instance in $[Ir(CS_2PPh_3)(CO)(PPh_3)_2]^+$ (**9**). We know



9

that anionic ligands such as CN^- can displace a CO ligand in **1**. $Ph_3P^+{-}C^-S_2$ probably cannot achieve a stable, chelate-type coordination, as in the Ir complex **9** and is thus easily displaced at this point by chelation of the dtc ligand (Scheme IV).

In the case of Cp_2TiCl_2, a coordination site is also available for the attack of dtc, but in absence of more detailed studies, the mechanism remains obscure.

Chelation of the monodentate dtc ligand upon reaction with NO^+ is presumably due to the appearance of a cationic charge on the metal following ligand exchange between NO^+ and CO in the neutral complex **1**. However, the reverse, e.g. interaction of NO^+ with the free sulfur, occurs; thus assisting chelation before coordination of NO^+ is not rigorously excluded. Indeed, the electrophilic properties of this sulfur atom are shown by the reaction with MeI and $Me_3O^+BF_4^-$, irreversibly forming S–C bonds; subsequent coordination of this alkylated sulfur atom is not observed. Before this demonstration of the electrophilic properties of the free sulfur atom in **1**, it was not clear whether CN^- would attack **1** at the metal carbonyl group (path B, Scheme V) or if it would attack the free sulfur directly before coordination (path A, Scheme V). That the free sulfur is electrophilic rather than nucleophilic excludes this latter suggestion and establishes that path B is correct. The interaction between the coordinated CN^- and the free sulfur atom of the monodentate dtc is clearly shown by the X-ray crystal structure and by the dramatic change in the properties of the benzoyl isocyanide part of the heterometallacyclic ligand as, for instance, the lowering of the isocyanide IR stretch by 260 cm^{-1} as compared to the normal linear situation found in chromium complexes.[13] The striking analogies between the spectroscopic properties of anion **6** and of the benzoylated complex **7** afford conclusive evidence that ring closure of the metallacycle had occurred prior to benzoylation and, thus, that the anionic heterometallacycle **6** could be N-alkylated or functionalized by other reagents. The formation and reactivity of the FeS_2C_2 metallacycle[16] obtained from the common metal carbonyl complex $[CpFe(CO)_3]^+$ (**2**) by successive coordination of the simple reagents dtc^- and CN^- are noteworthy. No attempt has been made yet to remove the organic part from the metal, but this could be a goal for future studies.

Experimental Section

Reagent grade tetrahydrofuran (THF) and diethyl ether were predried on Na foil and distilled before use. Toluene was distilled and stored under nitrogen. Reagent grade pentane was degassed with nitrogen before use. All other chemicals were used as received. All manipulations were done with use of Schlenk techniques in a nitrogen-filled Vacuum Atmospheres Dri-Lab or in glovebags. The infrared spectra of **3** and **5** were recorded with a Beckman IR 12 spectrometer; solid samples were suspended in Nujol between CsI disks. The other infrared spectra were recorded with a Pye-Unicam SP 1100 spectrometer; samples were suspended in Nujol between KBr disks. ^{1}H and ^{13}C NMR spectra were recorded by M. Mabon in the laboratory of Professor Maryvonne Martin (University of Nantes) using a Varian XL 100 spectrometer and by S. Sinbandhit at the Center of Physical Measurements of Rennes (see Table I). The mass spectrum of **7** was recorded by Dr. P. Guênot (University of Rennes) using a Varian MAT 311 spectrometer (double focalization). Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne.

1. Synthesis of 1 Using $[CpFe(CO)_3]^+PF_6^-$ (2). To 10 mmol of **2** (prepared as previously reported[8] from ferrocene and aluminum chloride under CO pressure) and 10 mmol of $Na^+dtc^-\cdot 2H_2O$ is added under N_2 100 mL of acetone at room temperature. The yellow solution rapidly turns orange. After the mixture is stirred for 5 min, thin-layer chromatography on silica gel plates (elution by hexane/ether (85/15), R_f 0.3) indicates that **1** is the only product in the reaction mixture. After removal of acetone in vacuo, workup with ether, and recrystallization from hexane/ether, 2.7 g of orange-red crystals of **1** is obtained (91%). **1** was identified by comparison with ^{1}H NMR, infrared spectra, and R_f of authentic samples.

2. Chelation of 1 Induced by Inorganic Reagents. Attempts to chelate **1** thermally were reported previously.[5]

a. Chelation Induced by PPh_3 + CS_2. A THF solution containing 3 mmol of **1** (974 mg), 0.3 mmol of PPh_3 (80 mg), and a few drops of CS_2 is refluxed for 10 h. After removal of the solvent in vacuo, chromatographic separation on thick-layer (1 mm) silica gel plates (eluent hexane/ether (4/1)), and crystallization from hexane/ether, 668 mg of $CpFe(CO)(\eta^2\text{-dtc})$ (**9**) is obtained (75%). In the absence of PPh_3 or CS_2, **1** remains unchanged after refluxing 72 h in THF.

b. Chelation Induced by $Mo(CO)_6$ and Cp_2TiCl_2. The same reaction carried out under the conditions noted above using either $Mo(CO)_6$ or Cp_2TiCl_2 instead of PPh_3 + CS_2 results in a 40% yield of $CpFe(CO)(\eta^2\text{-dtc})$ (**9**) when $Mo(CO)_6$ is used and 47% yield in the case of Cp_2TiCl_2. In all cases, it was verified by TLC that **1** had completely disappeared after the reaction. This was not so for shorter reaction times. The chelate is stable under the reaction conditions, and yields are not decreased when reaction is continued for 24 h.

3. Synthesis of $[CpFe(NO)(\eta^2\text{-dtc})]^+PF_6^-$ (3) from 1 and $NO^+PF_6^-$. To a CH_2Cl_2 solution (40 mL) of **1** (3 mmol, 974 mg) under N_2 is added, with magnetic stirring, $NO^+PF_6^-$ as a solid (3 mmol, 525 mg) at room temperature. The light red solution immediately turns brown.

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[16] The FeS_2C_2 metallacycle in the present arrangement has been postulated as an intermediate in the mechanism of disproportionation of isothiocyanates: Themissen, D. H. M. W.; Van Gaal, H. L. M. *J. Organomet. Chem.* **1979**, *172*, 69.

Scheme V

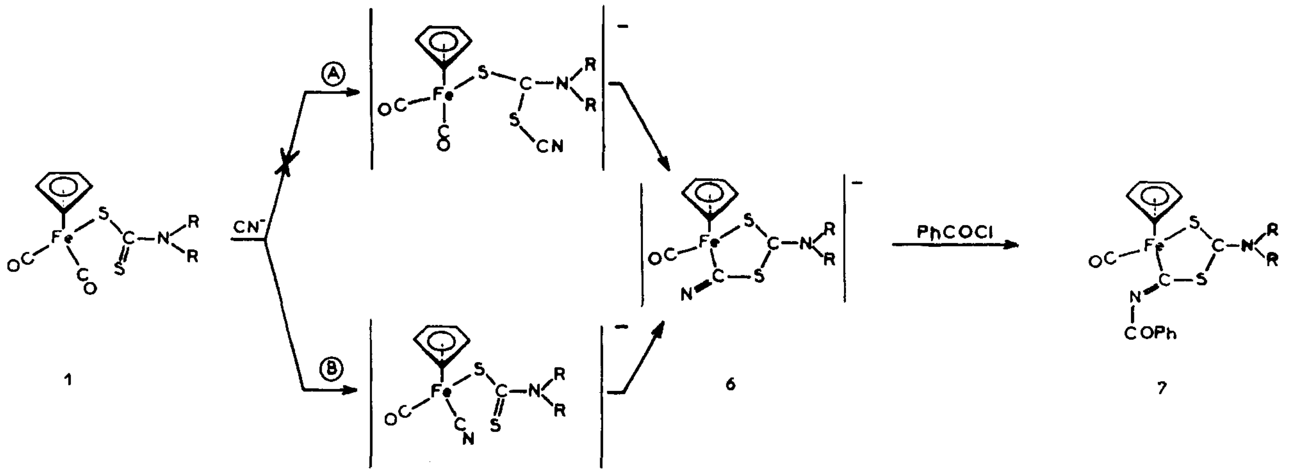
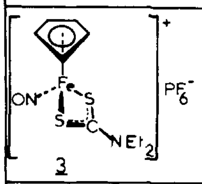
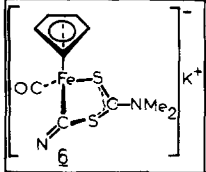
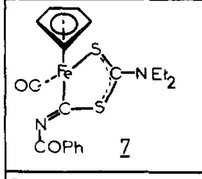
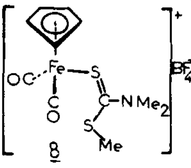


Table I

	NMR[δ vs Me_4Si][a]										Mössbauer[b]		Infrared[c]		
	^1H NMR				^{13}C NMR										
	Solvent	Cp	CH_2	CH_3	Solvent	Cp	CO	CN	CH_2	CH_3	I.S.	Q.S.	ν_{CO}	ν_{CS}	ν_{CN}
 3	CD_3COCD_3	6.32 s,5H	3.90 q,4H	1.35 t,6H	CD_2Cl_2	100.0		201.1	44.5	12.5	+0.060	1.754		1005 w	1545 s
 6	CD_2Cl_2	4.63 s,5H		3.53 s,6H	CD_2Cl_2	83.4	210.9	195.3		46.0	-0.010	1.940	2080 s 2030 s	995 w 940 w	1500m
 7	$CDCl_3$	4.79 s,5H	3.78 m,4H	1.30 m,6H	$CDCl_3$	82.8	219.8 174.8	204.3 217.8	54.4 48.9	12.2 11.9	-0.016	1.855	1975 s 1660 s	1075w	1575 m 1715 m
		Ph: 7.52,m,3H 8.22,m,2H				Ph: 134.1, 132.3, 129.8, 128.2									
 8	CD_2Cl_2	5.36 s,5H		3.66 s,6H	CD_2Cl_2	87.0	211.2	204.3		47.6	+0.110	1.880	2060 s 2000 s		1560 m
		SCH_3: 2.79 s,3H				SCH_3 : 21.5									

[a] ^{15}N chemical shift and rotation barriers about the C–N bond were subjected to a special study and will be published in a future paper. For the Et group, δ is given below the temperature of coalescence. [b] IS values are reported in mm s^{-1} vs. Fe; QS values are reported in mm s^{-1}. The accuracy of both IS and QS is 0.005 mm s^{-1}. Spectra were computer fitted. [c] Spectra were recorded as Nujol mulls. Wavenumbers are given in cm^{-1} (accuracy ±2 cm^{-1}). Legend: s, strong; m, medium; w, weak.

After 1 h, TLC indicates that no starting material **1** remains (**3** does not migrate with hexane/ether as the eluent). The solvent is removed in vacuo, and the solid residue is dissolved in acetone. After filtration of this solution and precipitation by ether, the salt **3** is recrystallized from acetone, giving 826 mg of red plates (62%). Anal. Calcd for $C_{10}H_{15}FeN_2OS_2PF_6$: C, 27.03; H, 3.57; Fe, 12.58; N, 6.30. Found: C, 26.79; H, 3.48; Fe, 12.0; N, 6.31.

4. Transmetalation of the dtc Ligand in 1. a. Reaction of 1 with $Fe_2(CO)_9$. **1** (650 mg, 2 mmol) and $Fe_2(CO)_9$ (364 mg, 1 mmol) are reacted in benzene under N_2 at reflux until TLC indicates **1** has totally disappeared (4 h). After removal of the solvent in vacuo, thick-layer chromatography affords the separation of 90% of Fp_2 and 40% of the known complex $Fe(CO)_2(\eta^2\text{-dtc})_2$ (**4**)[3] identified by its infrared and ^1H NMR spectra and elemental analysis.

b. Reaction of 1 with $[CpMo(CO)_3]_2$. A THF solution (50 mL) containing $[CpMo(CO)_3]_2$ (392 mg, 0.8 mmol) and **1** (520 mg, 1.6 mmol) is refluxed under N_2 for 10 h, the reaction being followed by TLC. After this reaction time, **1** has disappeared and workup allows the isolation of the known complexes $CpMo(CO)_2(\eta^2\text{-dtc})$ (**5**)[4,5] (430 mg, 74%) and Fp_2 (30%).

5. Reaction of 1 with KCN and Synthesis of the Heterometallacycles 6 and 7. a. Synthesis of $K^+[CpFe(CO)(SC(NR_2)(SCN))]^-$ (6) from 1 and KCN. **1** (3.25 g, 10 mmol) is dissolved in 50 mL of methanol (freshly distilled from Mg), and KCN (65 mg, 10 mmol) is added as a solid. After the mixture is stirred for 3 h at room temperature, TLC indicates that **1** has been consumed. The solvent is removed in vacuo and 20 mL of CH_2Cl_2 added (freshly distilled from P_2O_5); this solution is filtered and 100 mL of anhydrous ether is added, which precipitates **6** (**2**, 985 mg, 85%) as an extremely air- and water-sensitive purple powder. Anal. Calcd for $C_{10}H_{11}N_2S_2OFeK$: C, 35.93; H, 3.31; N, 8.38; S, 19.18; Fe, 16.70. Found: C, 35.07; H, 3.58; N, 8.36; S, 19.34; Fe, 17.15.

b. Synthesis of $CpFe(CO)(SC(SCNCOPh)CNEt_2)$ from 6 and

PhCOCl. To **6** (1 g, 2.7 mmol) obtained as noted above, 20 mL of CH_2Cl_2 and 20 mL of PhCOCl are added under N_2 and the solution is refluxed for 3 h. After removal of the solvent in vacuo and chromatographic separation on thick silica gel plates (eluent ether) the brown-red solid **7** is obtained (R_f 0.3) and recrystallized from ether (80%). Some of these crystals were selected for the X-ray crystal structure determination. Anal. Calcd for $C_{19}H_{20}FeN_2O_2S_2$: C, 53.31; H, 4.67; Fe, 13.04; N, 6.54; S, 14.95. Found: C, 53,41; H, 4.62; Fe, 13.00; N, 6.48; S, 14.87.

6. Alkylation of 1 with CH_3I. A THF solution (30 mL) of **1** (0.3 g, 1 mmol) is refluxed with CH_3I (0.06 mL, 1.1 mmol) for 2 h. After this reaction time, TLC indicates that all **1** has reacted. The solvent is removed in vacuo, and the solid residue is dissolved in ether and passed through a short column of alumina; FpI and MeSC(S)NMe_2 are isolated as the only reaction products (respectively 70 and 60%); their identity was verified by ^1H NMR ($CDCl_3$, δ, Me_4Si): FpI, Cp at 5.12; MeSC(S)NMe_2, NMe at 3.60 and SCH_3 at 2.79.

7. Synthesis of $[CpFe(CO)_2(\eta^1\text{-}SC(SMe)(NMe_2))]^+BF_4^-$ from 1 and $Me_3O^+BF_4^-$. To a THF solution (30 mL) of **1** (2.55 g, 8.6 mmol) under N_2 is added $Me_3O^+BF_4^-$ (2.15 g, 10 mmol). After the mixture is stirred 2 h at room temperature, the THF is removed in vacuo; the solid residue is dissolved in 10 mL of CH_2Cl_2, this solution is filtered, and 100 mL of ether is added to precipitate **8**. Recrystallization from acetone yields 1.7 g of large bordeaux red crystals (50%), stable in air (dec pt 141 °C). Anal. Calcd for $C_{11}H_{14}NS_2O_2FeBF_4$: C, 33.11; H, 3.54; N, 3.51; S, 16.07; Fe, 14.14. Found: C, 33.26; H, 3.55; N, 3.49; S, 15.96; Fe, 14.14.

Acknowledgment. We are grateful to Professor Maryvonne Martin (University of Nantes) and to Professor François Varret (University of Maine) for NMR and Mössbauer facilities and for invaluable discussions. We thank BASF (Ludwigshafen, West Germany) for a generous gift of iron carbonyl.

Registry No. **1**, 75900-10-6; **2**, 38834-26-3; **3**, 93085-05-3; **4**, 36309-89-4; **5**, 52201-61-3; **6**, 82404-92-0; **7**, 82404-95-3; **8**, 93085-06-4; **9**, 12128-65-3; FpI, 12078-28-3; Na^+dtc^-, 128-04-1; $Mo(CO)_6$, 13939-06-5; Cp_2TiCl_2, 1271-19-8; $[CpMo(CO)_3]_2$, 12091-64-4; $Fe_2(CO)_9$, 15321-51-4; CS_2, 75-15-0; $NO^+PF_6^-$, 16921-91-8; KCN, 151-50-8; PhCOCl, 98-88-4; CH_3I, 74-88-4; MeSC(S)NMe_2, 3735-92-0; $Me_3O^+BF_4^-$, 43625-65-6.

Contribution from the Department of Chemistry,
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Quantitative Studies on the Coordination Chemistry of Tetrakis(*n*-butyrato)diruthenium Chloride

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Earlier work on the coordination chemistry of metal carboxylate dimers is extended to the ruthenium system tetrakis(*n*-butyrato)diruthenium chloride, $Ru_2(but)_4Cl$. Calorimetric measurements are made of the enthalpies of adduct formation to $Ru_2(but)_4Cl$ by the Lewis bases acetone, *N*-methylimidazole, tetrahydrothiophene, dimethyl sulfoxide, 4-picoline *N*-oxide, acetonitrile, and pyridine. UV–visible spectroscopy, conductivity measurements, and reactivity studies are performed to validate the calorimetric measurements. A dipyridine adduct of $Ru_2(but)_4Cl$ is reported as the first complex of this type. Comparison of the calorimetric data obtained for $Ru_2(but)_4Cl$ with previous data on analogous systems shows a higher Lewis acidity for $Ru_2(but)_4Cl$. This is attributed to the higher overall charge of the metal dimer unit. A synergistic mechanism is offered to explain how this charge is transmitted to the acceptor Ru atom through the metal–metal bond. This synergism leads to a strong electrostatic base interaction (as indicated by the high E_A value of 7.73). The covalent contribution to the Lewis acidity of this system (indicated by the C_A value of 1.27) is intermediate between the Rh and Mo systems. The covalent contribution to the acidity of these metal–metal-bonded systems depends inversely on the metal–metal bond strength. Higher than predicted enthalpies of adduct formation with pyridine and acetonitrile are observed. These are attributed to a π-back-bonding interaction between the partly filled π^* orbitals of the Ru dimer and empty π^* orbitals on these bases, in agreement with previous results on rhodium(II) dimers.

Introduction

Metal–metal-bonded systems have been widely studied.[1] The nature of the metal–metal bond itself and the coordination chemistry of metal–metal-bonded complexes compared to analogous mononuclear complexes are of great interest. Previous work from this laboratory has concentrated on understanding metal–metal bonding and ligand coordination chemistry of the Rh(II) and Mo(II) carboxylate dimers.[2] Thermodynamic and spectroscopic studies of complexes such as $Rh_2(but)_4$ (but = *n*-butyrate), $Rh_2(pfb)_4$ (pfb = perfluoro-*n*-butyrate), and $Mo_2(pfb)_4$ have led to some interesting conclusions concerning the relationship between structure and reactivity by providing evidence for a synergistic metal–metal interaction. In particular, the rhodium dimers appeared to undergo more than a simple σ-type interaction with certain Lewis bases while the molybdenum dimer showed only σ interactions. This difference in reactivity was attributed to the difference in the populations of their respective molecular orbitals. The rhodium system contains π^* electron density while the molybdenum system does not. Therefore, in those cases involving a Lewis base capable of accepting π^* electron density from the rhodium dimer, π stabilization was observed. This was manifested by the observed Rh–base adduct bond enthalpies being higher than that predicted by the *E* and *C* equation, which considers only σ-type interactions. It is therefore reasonable to expect that if this interpretation is valid, the diruthenium(II,III) carboxylate system would also show instances of π stabilization with the proper bases. A simplified MO scheme for this dimer is shown in Figure 1. This quantitative scheme has been confirmed in calculations by Norman et al.[3] There are a total of 11 d electrons, which

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[‡] University of Illinois.

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982; and references therein.

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