using laser flash photolysis.[18] It is worth noting that the reaction ratio of k_{Me}/k_{Et} (=65) for the reactions of alkylcobalamins with $Sn^{II}Cl_x^{2-x}$ is quite similar to the reported rate ratio of k_{Me}/k_{Et} (=80) for the reactions of alkylcobalamins with Cr^{2+}.[16] The smaller rate constant for C_2H_5-B_{12} than for CH_3-B_{12} is probably due to the steric hindrance of methyl group of C_2H_5-B_{12}.

Endicott et al. have recently unified the mechanisms of halide- and methyl-bridged electron-transfer reactions of cobalt complexes with macrocyclic ligands.[19] The relatively slow rates for methyl-bridged reactions are interpreted in terms of a three-center–three-electron (Co–CH_3–Co) bonding description of the transition state. This three-center–three-electron bonding description can also be applied to the methyl transfer from CH_3-B_{12} to $Sn^{II}Cl_x^{2-x}$. It should be noted that the one-electron reduction potential of base-off CH_3-B_{12} has been estimated to be −1.46 V (vs. aqueous SCE) at 19 °C.[20] Consequently, compared with the reduction potential of H_2O-B_{12}^+ which has been measured to be 0.15 V under the same experimental conditions,[21] CH_3-B_{12} is an extremely weak oxidant. Indeed, we have shown that there is no reaction between CH_3-B_{12} and $Ru(NH_3)_6^{2+}$, an apparent outer-sphere one-electron reductant, for several days under argon. Apparently, the rate constant of 1.04 M^{-1} s^{-1} (at 23 °C, 1.0 M HCl) for the methyl transfer from CH_3-B_{12} to Sn^{II} is due to the "bridging" of the methyl group.

The pH-dependent kinetics for the reaction between methylcobalamin and $Sn^{II}Cl_x^{2-x}$ are somewhat puzzling, because it has been shown that there is no pH dependence for the reactions between platinum(IV) and $Sn^{II}Cl_x^{2-x}$ (at pH 0–1),[6] and between CH_3-B_{12} and Cr^{2+}.[16] One explanation for the increasing rate with increasing [H^+] in the present study is that the base-off CH_3-B_{12} includes forms in which water occupies the sixth coordination position and in which it does not. An increase in [H^+] may increase the five-coordinated CH_3-B_{12} which is more reactive to $Sn^{II}Cl_x^{2-x}$ than the six-coordinated form.

In conclusion, our observation that CH_3-B_{12} possesses the capability of methylating inorganic tin is noteworthy because the organometallic forms of heavy metals are invariably more toxic than their inorganic precursors. This study may be pertinent to the toxicity of tin in the environment.

Acknowledgment. We wish to thank the Freshwater Biological Research Foundation and in particular its founder, Mr. Richard G. Gray Sr., for providing an excellent atmosphere for doing this research. We are also grateful to Drs. Joe Pignatello, Tom Frick, and Mr. Paul Tomasek for their valuable discussions and comments on this paper. This research is supported by NIH Grant AM18101.

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(19) (a) Durham, B.; Endicott, J. F.; Wong, C. L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 847. (b) Endicott, J. F.; Wong, C. L.; Ciskowski, J. M.; Balakrishman, K. P. *Ibid.* **1980**, *102*, 2100. (c) Endicott, J. F.; Balakrishman, K. P.; Wong, C. L. *Ibid.* **1980**, *102*, 5519.

(20) Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3220. The reduction potential for base-off CH_3-B_{12} is taken from the reduction potential of methylcobinamide.

(21) Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 2786.

Novel Boron-to-Sulfur Alkyl Group Transfer in Reactions of Lithium Triethylborohydride-Derived Bis(μ-thiolato)-bis(tricarbonyliron) Dianion with Mercuric Chloride and Alkylmercuric Chlorides

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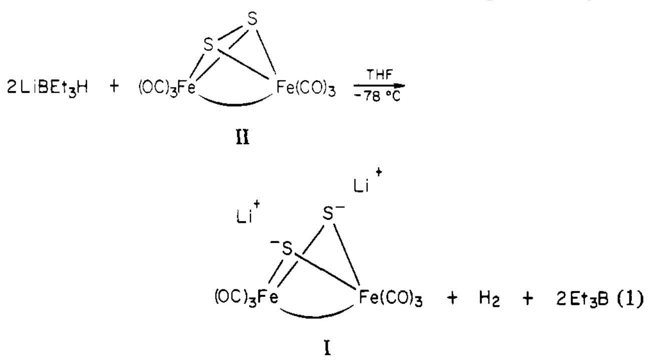
Abstract: In addition to the expected products, (μ-RHgS)$_2$Fe$_2$(CO)$_6$, the reaction of LiBEt$_3$H-derived (μ-LiS)$_2$Fe$_2$(CO)$_6$ with methyl- and ethylmercuric chloride gave products of the type (μ-C_2H_5S)(μ-RHgS)Fe$_2$(CO)$_6$, i.e., into which ethyl groups from the complex hydride had been incorporated. An experiment in which KB(s-C_4H_9)$_3$H was used to generate the dianion from (μ-S_2)Fe$_2$(CO)$_6$ gave evidence of the generality of this process. Possible intermediates in this novel chemistry are considered.

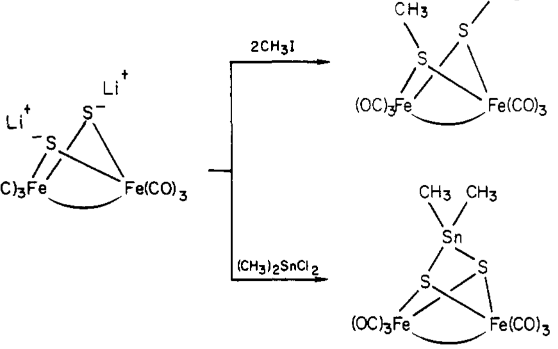
We have reported previously concerning the generation of the bis(μ-thiolato)-bis(tricarbonyliron) dianion (I) by reaction of (μ-dithio)-bis(tricarbonyliron) (II) with lithium triethylborohydride (eq 1).[1] The reactions of dianion I with various organic, inorganic, and organometallic halides were quite straightforward, giving the products expected from nucleophilic displacement of halogen from the carbon or the metal(loid) atom, e.g., eq 2 and 3.[1,2]



II

I

(1)



(2)

(3)

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(1) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.

(2) Seyferth, D.; Henderson, R. S.; Gallagher, M. J. *J. Organomet. Chem.* **1980**, *193*, C75.

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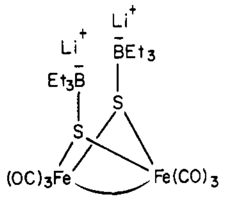
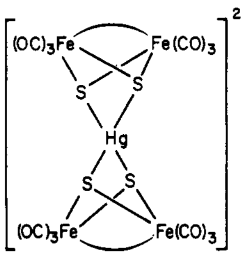
In this procedure for the generation of dianion I triethylborane also is produced. In principle, triethylborane, a Lewis acid, might be expected to be associated with the dianion, a charged Lewis base, as in III. If such is the case, it does not affect the reactivity at the nucleophilic sulfur centers, and only the expected products were isolated in the reactions which were carried out. During the extension of our investigations of the reactivity of dianion I to its reactions with mercury(II) halides, we have found that ethyl groups from the $LiBEt_3H$ reagent can become incorporated into the iron-carbonyl product. We report here the details of these studies.



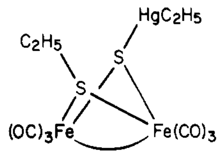
III

Results and Discussion

Our initial objective in this investigation was the synthesis of salts of anion IV by the reaction of 2 molar equiv of dianion I with 1 molar equiv of mercuric chloride, followed by treatment with an appropriate complex cation, e.g., Et_4N^+. Such a procedure had been successful in the preparation of the Ni(II) analogue of IV.[3] However, the 2/1 $I/HgCl_2$ reaction in ethanol/THF medium took an unexpected course. The principal product, formed in 38% yield on the basis of II initially charged, which was isolated as air-stable red crystals, was identified on the basis of its NMR (^1H, ^{13}C, ^{199}Hg) and infrared spectra, its mass spectrum, and its C/H analysis as (μ-ethythio)-(μ-ethylmercurithio)-bis(tricarbonyliron) (V). [An X-ray crystallographic study by Professor C. C. Chieh (University of Waterloo) (to be published) has confirmed the structure of V.] Further experiments in which the ethanol was replaced by methanol and propanol and in which THF was the only solvent used quickly showed that the ethyl substituents on mercury and on sulfur originated with the $(C_2H_5)_3B$ component of the $LiB(C_2H_5)_3H$ reagent since in all cases V again was the product which was isolated.



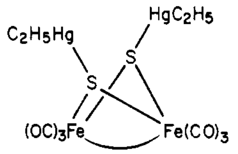
IV



V

The transfer of alkyl groups from trialkylboranes to mercury(II) derivatives is a well-known process,[4] so the appearance of a C_2H_5Hg substituent in V is not difficult to understand. On the other hand, the alkylation of a mercaptide-type sulfur atom by a trialkylborane is, to our knowledge, without precedent, and thus the formation of V was quite surprising.

If indeed ethylmercuric chloride had been formed by the ethylation of mercuric chloride by triethylborane or by the borate complex III, one might have expected bis(μ-ethylmercurithio)-bis(tricarbonyliron) (VI) to have been a major product. Since VI conceivably could be a precursor to V, we turned our efforts to its synthesis. Again, the results were unexpected. Addition of 2 molar equiv of ethylmercuric chloride to a $(\mu\text{-}LiS)_2Fe_2(CO)_6$ solution, prepared by reaction of 2 equiv of $LiBEt_3H$ with 1 equiv of II at −78 °C, gave not only the desired VI in 21% yield but also a 17% yield of V. The former, a deep red, crystalline solid, was quite stable. That the ethyl substituent on sulfur was derived from $LiBe_3H$ was demonstrated by a reaction of $(\mu\text{-}LiS)_5Fe_2(CO)_6$ (from $LiBEt_3H$) with 2 molar equiv of methylmercuric chloride. Two products again were obtained: the expected $(\mu\text{-}CH_3HgS)_2Fe_2(CO)_6$ (33% yield) as well as $(\mu\text{-}C_2H_5S)(\mu\text{-}CH_3HgS)Fe_2(CO)_6$ (26% yield). Further evidence on this point was provided when the dianion I (with K^+ counterion) was generated by using $KB(s\text{-}Bu)_3H$. A reaction with 2 equiv of methylmercuric chloride resulted in formation of $(\mu\text{-}CH_3HgS)_2Fe_2(CO)_6$ (23%) and $(\mu\text{-}C_2H_5(CH_3)CHS)(\mu\text{-}CH_3HgS)Fe_2(CO)_6$ (28%). The appearance of the *sec*-butylthio substituent in the latter product confirms the generality of the process under consideration.



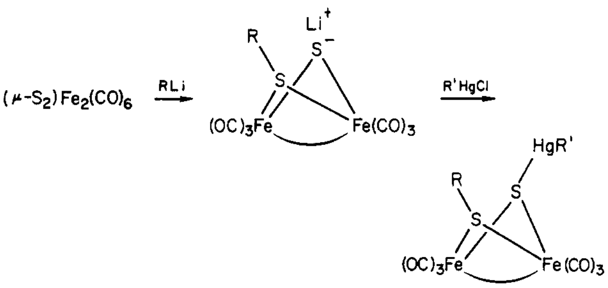
VI

The bis(μ-thiolato)-bis(tricarbonyliron) dianion also may be generated, albeit in rather lower yield, by the action of 2 molar equiv of potassium hydride on II.[5] When 2 equiv of methylmercuric chloride was added to such a solution of the dianion, $(\mu\text{-}CH_3HgS)_2Fe_2(CO)_6$ was the only product formed, although its yield was low (16%). Another complex hydride which we have found may be used to generate reagent I is $LiAl(O\text{-}t\text{-}Bu)_3H$ (eq 4). The reaction of a dianion solution prepared in this way with

$$\underset{\text{II}}{(\mu\text{-}S_2)Fe_2(CO)_6} + 2LiAl(O\text{-}t\text{-}Bu)_3H \xrightarrow{THF,\ -78\ ^\circ C} Al(O\text{-}t\text{-}Bu)_3 + H_2 + (\mu\text{-}LiS)_2Fe_2(CO)_6 \xrightarrow{CH_3I} \underset{82\%}{(\mu\text{-}CH_3S)_2Fe_2(CO)_6} \quad (4)$$

methylmercuric chloride gave only $(\mu\text{-}CH_3HgS)_2Fe_2(CO)_6$ (23%). A similar reaction with ethylmercuric chloride produced $(\mu\text{-}C_2H_5HgS)_2Fe_2(CO)_6$ in 29% yield. As might have been expected, addition of separately prepared triethylborane to a solution of $(\mu\text{-}KS)_2Fe_2(CO)_6$ (filtered to remove unconverted KH), followed by addition of methylmercuric chloride, gave $(\mu\text{-}C_2H_5S)(\mu\text{-}CH_3HgS)Fe_2(CO)_6$ as well as $(\mu\text{-}CH_3HgS)_2Fe_2(CO)_6$.

Our previously reported cleavage of the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ by organolithium reagents[5] provided a route for the specific synthesis of compounds of type $(\mu\text{-}RS)(\mu\text{-}R'HgS)Fe_2(CO)_6$ (eq 5). Complex VIIa was in all respects identical with $(\mu\text{-}C_2H_5S)(\mu\text{-}CH_3HgS)Fe_2(CO)_6$ obtained in the reaction of the $LiBEt_3H$-derived dianion with CH_3HgCl, thus providing further proof of structure of the "anomalous" products.



(5)

VIIa, R = Et, R' = Me
VIIb, R = Me, R' = Me
VIIc, R = Me, R' = Et

We now may inquire into the mode of formation of the products of type $(\mu\text{-}RS)(\mu\text{-}R'HgS)Fe_2(CO)_6$ in reactions of the bis(μ-

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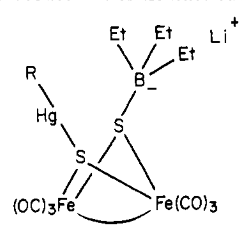
[3] Song, L.-C., unpublished work.

[4] (a) Brown, H. C. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; Chapters 5 and 6. (b) Onak, T. "Organoborane Chemistry"; Academic Press: New York, 1975; Chapter 3. (c) Straub, H.; Zeller, K. P.; Leditschke, H. "Houben-Weyl Methoden der Organischen Chemie"; Georg Thieme-Verlag: Stuttgart, 1974; Vol. XIII/2b, pp 76–83.

[5] Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508.

thiolato)-bis(tricarbonyliron) dianion, generated by the action of MBR_3H reagents on $(\mu\text{-}S_2)Fe_2(CO)_6$, with alkylmercuric halides. We note first of all that these reactions are not "clean". The product yields in general are low, and some metallic mercury usually is formed. In the dianion/$HgCl_2$ reaction small globules of mercury were observed. In the RHgCl/dianion reactions the gray, insoluble solid which always was present gave a positive qualitative test for mercury. We may assume that the first step, the formation of the dianion, is straightforward. The trialkylborane may be associated with the dianion, as in III, but alkyl transfer from boron to sulfur does not take place since "normal" products are obtained when the dianion solution is treated with alkyl iodides and various metal dihalides. In the second step, the alkylmercuric chloride is added to the dianion solution at −78 °C. At this low temperature, the solubility of CH_3HgCl and C_2H_5HgCl is quite low, and we may expect their sequential reactions with the dianion to give first $(\mu\text{-RHgS})(\mu\text{-LiS})Fe_2(CO)_6$, and then $(\mu\text{-RHgS})_2Fe_2(CO)_6$, to be quite slow.

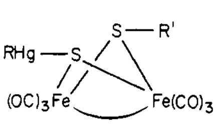
The formation of elemental mercury suggests that the RHgCl species is acting as an oxidizing agent, undergoing reduction to Hg(0),[11] while a mercurated intermediate such as VIII is oxidized.



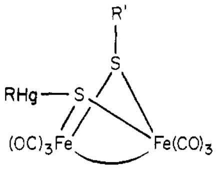
VIII

Oxidation of VIII, i.e., abstraction of an electron from this species, could result in ethyl group transfer from boron to sulfur to give, ultimately, the observed product, V, in the case of ethylmercuric chloride. The fate of the Et_2B moiety remains unknown. It might be expected that if RHgCl is in part consumed in such a redox process, then the use of an excess of RHgCl in such a reaction might give better yields of both the "expected" and the "anomalous" products. However, there was no such yield improvement in a reaction in which the dianion produced by reaction of 4.7 mmol of $LiBEt_3H$ with 2.33 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$ was treated with 9.32 mmol of methylmercuric chloride in THF at −78 °C. In the absence of more definitive experimental evidence, this discussion of possible mechanisms of this novel mercury-induced boron-to-sulfur alkyl-transfer process is only speculation and the mechanism remains undefined.

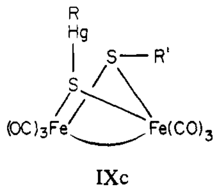
The proton and ^{13}C NMR spectra of all of the products of types $(\mu\text{-R'S})(\mu\text{-RHgS})Fe_2(CO)_6$ and $(\mu\text{-RHgS})_2Fe_2(CO)_6$ showed that in each reaction in which they were formed only one isomer was present. For complexes of type $(\mu\text{-R'S})(\mu\text{-RHgS})Fe_2(CO)_6$ four different isomers, IXa–d, are possible.[6] The position of the SCH_3 resonance in $(\mu\text{-}CH_3S)(\mu\text{-}CH_3HgS)Fe_2(CO)_6$ and $(\mu\text{-}CH_3S)(\mu\text{-}C_2H_5HgS)Fe_2(CO)_6$, δ 2.17 and 2.15, respectively, are indicative of isomer IXa or c [based on assignments made for the two $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$ which were isolated by King[7]], which have exo SCH_3 substituents. The RHg resonances for $(\mu\text{-R'S})(\mu\text{-RHgS})Fe_2(CO)_6$ and $(\mu\text{-RHgS})_2Fe_2(CO)_6$ complexes are identical. For the latter exo alkylmercury substituents are suggested (see below). Thus, we consider IXa to be the more probable isomer. In the case of the $(\mu\text{-RHgS})_2Fe_2(CO)_6$ complexes, three isomers, Xa–c, are possible, and we consider Xa to be the most likely on steric grounds.



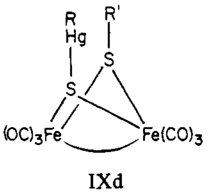
IXa



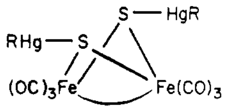
IXb



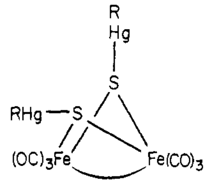
IXc



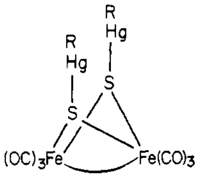
IXd



Xa



Xb



Xc

The proton NMR parameters for the methylmercury derivatives prepared during the course of this study ($\delta(CH_3HgS)$ 0.83–0.86 ($^2J_{HgH}$ = 160–162 Hz)) fall within the range reported by Bach and Weibel[8] for a number of CH_3HgSR compounds ($\delta(CH_3HgS)$ 0.76–0.92 ($^2J_{HgH}$ = 150–167 Hz)). Like all other $(\mu\text{-RS})(\mu\text{-R'S})Fe_2(CO)_6$ (R = R′ or R ≠ R′), the $(\mu\text{-RS})(\mu\text{-R'HgS})Fe_2(CO)_6$ and $(\mu\text{-R'HgS})_2Fe_2(CO)_6$ complexes which we report here are fluxional at room temperature, their ^{13}C NMR spectra showing only one sharp signal for the CO ligand carbon atoms. [For a variable-temperature ^{13}C NMR study of the fluxional nature of $(\mu\text{-RS})(\mu\text{-R'S})Fe_2(CO)_6$ complexes, see ref 9.]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen in flame-dried glassware. Solvents were rigorously dried before use. The progress of the reactions was monitored by thin-layer chromatography (J.T. Baker Silica Gel 1B). Full-scale column chromatography generally was not required in the isolation of products. Instead, filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100 mesh silicic acid (ca. 200 mL) in a 350-mL glass-frit filter funnel, was used in most cases. The eluting solvent then was passed through with suction filtration.

Infrared spectra were obtained by using a Perkin-Elmer Model 457A double-beam grafting infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 NMR spectrometer. The proton NMR spectra were obtained at room temperature at 250 MHz and the ^{13}C NMR spectra, also at room temperature, at 62.83 MHz operating in the broad-band decoupled mode. The ^{199}Hg NMR spectrum was recorded by using a JEOL FX-90Q spectrometer at 15.96 MHz. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70 eV. Melting points are uncorrected.

$(\mu$-Dithio)-bis(tricarbonyliron) was prepared by the method of Hieber and Gruber.[10] The hydride reagents ($LiBEt_3H$, $KB(s\text{-}Bu)_3H$, $LiAl(O\text{-}t\text{-}Bu)_3H$) were purchased from Aldrich Chemical Co., methyl- and ethylmercuric chloride, potassium hydride, and CH_3Li–LiBr from Alfa/Ventron. Ethyllithium was prepared by reaction of lithium chips and bromoethane in diethyl ether at −30 °C.

Reaction of Lithium Triethylborohydride-Derived $(\mu\text{-LiS})_2Fe_2(CO)_6$ with Mercuric Chloride. A 200-mL three-necked, round-bottomed flask equipped with two serum caps, a magnetic stir-bar, and a nitrogen inlet tube was flushed with nitrogen, charged with 1.00 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ and 75 mL of dry THF, and cooled to −78 °C. During the course of 1 h 6.00 mL of 1 M $LiBEt_3H$ (6 mmol) in THF was added. The color of the solution changed from dark red to emerald green at the midpoint of the addition (corresponding to formation of $(\mu\text{-LiS})(\mu\text{-HS})Fe_2(CO)_6$) and remained that color for the rest of the addition. The mixture was stirred for 10 min, and then a solution of 0.82 g (3 mmol) of $HgCl_2$ in 50 mL of absolute ethanol was added by syringe during 10

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[6] Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 328.

[7] King, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2460.

[8] Bach, R. D.; Weibel, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 6241.

[9] Aime, S.; Milone, L.; Rosetti, R.; Stanghellini, P. L. *Transition Met. Chem.* **1979**, *4*, 322.

[10] Hieber, W.; and Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91.

[11] There is precedence for such an oxidization by Hg(II) of an anionic species when nucleophilic substitution at mercury might have been expected. A recent example of such behavior is the reaction of $HgCl_2$ with $K^+(3)\text{-}1,2\text{-}C_2B_9H_{12}^-$ in THF or pyridine: Zakharkin, L. I.; Kalinin, V. N.; Zhigareva, G. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2376.

min. A light red reaction mixture resulted. This mixture was stirred under nitrogen for 2 h at −78 °C and overnight at room temperature. The brown-red mixture which had formed was evaporated at reduced pressure. The residue was dissolved in pentane and subjected to filtration chromatography on silicic acid. Pentane eluted 0.17 g (0.49 mmol, 17%) of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$, mp 45–47 °C, identified by means of its IR and mass spectra. Subsequently, 10% dichloromethane/pentane eluted 0.67 g (1.11 mmol, 38%) of the product which was identified as $(\mu\text{-EtHgS})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$. Recrystallization from pentane gave air-stable, red plates (mp 113–114 °C): the mass spectrum showed the molecular ion at m/e 602 (based on ^{200}Hg) and fragment ions due to the successive loss of the six carbon monoxide ligands; IR (CO region, in $\mathrm{CHCl_3}$, cm^{-1}) 2070 (s), 2034 (vs), 1997 (sh), 1987.5 (vs); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.33 (t, $J = 7.5$ Hz, 3 H, $\mathrm{CH_3}$ of SEt), 1.35 (t, $J_{\mathrm{HH}} = 7.5$ Hz, $^3J_{\mathrm{HgH}} = 242$ Hz, 3 H, $\mathrm{CH_3}$ of HgEt), 1.66 (q, $J_{\mathrm{HH}} = 7.5$ Hz, $^2J_{\mathrm{HgH}} = 160$ Hz, 2 H, $\mathrm{CH_2}$ of HgEt), 2.47 (q, $J = 7.5$ Hz, 2 H, $\mathrm{CH_2}$ of SEt); ^{13}C NMR ($\mathrm{CDCl_3}$) δ_{C} 13.041 ($\mathrm{CH_3}$ of HgEt), 17.751 ($\mathrm{CH_3}$ of SEt), 33.117 ($\mathrm{CH_2}$ of HgEt), 35.737 ($\mathrm{CH_2}$ of SEt), 209.888 (CO ligands) (The assignments are based on the SEt and HgEt carbon atom resonances observed in the ^{13}C NMR spectra of $(\mu\text{-EtHgS})_2\mathrm{Fe_2(CO)_6}$, $(\mu\text{-EtHgS})(\mu\text{-CH_3S})\mathrm{Fe_2(CO)_6}$, and $(\mu\text{-CH}_3\text{HgS})(\mu\text{-C}_2\text{H}_5\text{S})\mathrm{Fe_2(CO)_6}$ (see below)); ^{199}Hg NMR ($\mathrm{CDCl_3}$) 121 ppm downfield from external $\mathrm{Ph_2Hg}$ in $\mathrm{CDCl_3}$ [or −627 ppm (upfield) from internal neat dimethylmercury]. Anal. Calcd for $\mathrm{C_{10}H_{10}O_6S_2Fe_2Hg}$: C, 19.93; H, 1.67. Found: C, 19.91; H, 1.73.

A similar experiment carried out in 50 mL of *n*-propyl alcohol by using the same quantities of reagents (0.5 h at −78 °C, 2 h at room temperature) gave 0.57 g (0.95 mmol, 33%) of $(\mu\text{-EtHgS})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ and 0.31 g (0.64 mmol, 33%) of $\mathrm{S_2Fe_3(CO)_9}$ (mp 116 °C (dec)), whose IR spectrum was identical with that of authentic material prepared by the method of Hieber and Grubber.[10] A reaction carried out in anhydrous methanol (2 h at −78 °C, overnight at room temperature) resulted in the formation of $(\mu\text{-EtHgS})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$ (17%) and $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ (15%). In another experiment 0.82 g of solid $\mathrm{HgCl_2}$ was added to a solution of dianion I (from 0.91 mmol of II) in 75 mL of THF at −78 °C. A reaction time of 1 h at −78 °C and 1 h at room temperature followed. Workup as above gave a small amount of a mixture of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ and $\mathrm{S_2Fe_3(CO)_9}$ and 0.27 g (15%) of $(\mu\text{-EtHgS})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}$.

Reaction of the Lithium Triethylborohydride-Derived Bis(μ-thiolato)-bis(tricarbonyliron) Dianion with Alkylmercuric Chlorides. (a) Ethylmercuric Chloride. A solution of $(\mu\text{-LiS})_2\mathrm{Fe_2(CO)_6}$ was prepared as described above from 2.91 mmol of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ and 6 mmol of $\mathrm{LiEt_3BH}$ in THF at −78 °C. To the green solution was added, against a brisk countercurrent of nitrogen, 1.59 g (6 mmol) of solid EtHgCl and the resulting mixture was stirred at −78 °C for 30 min. A light red solution was formed which was allowed to warm to room temperature and stirred for another 2 h. The brown-red mixture was examined by TLC; hexane eluted four bands, yellow, purple, yellow, and orange in color. The mixture was evaporated at reduced pressure, and the residue was dissolved in hexane and resolved by filtration chromatography. Pentane eluted two bands (yellow and purple) whih contained only trace amounts of material. An orange and a red band were eluted with 10% $\mathrm{CH_2Cl_2}$/hexane. The solids which could be isolated from these were recrystallized from pentane. The product which had been eluted first (0.3 g, 17% yield), red crystals (mp 112–113 °C) was identified (mp, IR, NMR) as $(\mu\text{-C}_2\text{H}_5\text{S})(\mu\text{-C}_2\text{H}_5\text{HgS})\mathrm{Fe_2(CO)_6}$. The second product (0.5 g, 0.62 mmol, 21% yield), dark red crystals (mp 93–94 °C), was identified as $(\mu\text{-C}_2\text{H}_5\text{HgS})_2\mathrm{Fe_2(CO)_6}$: the mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of the six CO ligands; IR (CO region, in $\mathrm{CHCl_3}$, cm^{-1}): 2066 (s), 2030 (vs), 1992 (sh), 1976 (vs); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.265 (t, $J_{\mathrm{HH}} = 7.5$ Hz, $^3J_{\mathrm{HgH}} = 239$ Hz, 6 H, $\mathrm{CH_3}$), 1.65 (q, $J_{\mathrm{HH}} = 7.5$ Hz, $^2J_{\mathrm{HgH}} = 160$ Hz, 4 H, $\mathrm{CH_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ_{C} 13.091 ($\mathrm{CH_3}$ of Et), 32.049 ($\mathrm{CH_2}$ of Et), 210.498 (CO). Anal. Calcd for $\mathrm{C_{10}H_{10}O_6S_2Fe_2Hg_2}$: C, 14.95; H, 1.26. Found: C, 14.62; H, 1.35.

(b) Methylmercuric Chloride. A solution of the dianion I was prepared as described above from 2.91 mmol of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ and 6 mmol of $\mathrm{LiBEt_3H}$ in THF at −78 °C, and then 1.51 g (6 mmol) of $\mathrm{CH_3HgCl}$ was added as the solid. The mixture changed from green to light red; it was stirred at −78 °C for 1 h and then for 1.5 h at room temperature. The resulting brown-red mixture was evaporated at reduced pressure. The residue was dissolved in pentane and subjected to filtration chromatography. Pentane eluted trace quantities of material (yellow and purple bands) which was discarded and then an orange band from which $(\mu\text{-C}_2\text{H}_5\text{S})(\mu\text{-CH}_3\text{HgS})\mathrm{Fe_2(CO)_6}$ was isolated. Elution with 10% $\mathrm{CH_2Cl_2}$/pentane gave a red band from which $(\mu\text{-CH}_3\text{HgS})_2\mathrm{Fe_2(CO)_6}$ was obtained.

$(\mu\text{-C}_2\text{H}_5\text{S})(\mu\text{-CH}_3\text{HgS})\mathrm{Fe_2(CO)_9}$: obtained in 26% yield (0.45 g, 0.76 mmol), red plates; mp ~124 °C (dec) (from pentante); the mass spectrum showed the molecular ion and fragment ions with m/e corresponding to $[\mathrm{M} - n\mathrm{CO}]^+$ ($n = 1$–6); IR (CO region, in $\mathrm{CHCl_3}$, cm^{-1}) 2071 (s), 2036 (vs), 1998 (sh), 1984 (vs); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.86 (s, $^2J_{\mathrm{HgH}} = 161$ Hz, $\mathrm{CH_3Hg}$), 1.35 (t, $J = 7.5$ Hz, 3 H, $\mathrm{CH_3}$ of Et), 2.47 (q, $J = 7.5$ Hz, 2 H, $\mathrm{CH_2}$ of Et); ^{13}C NMR ($\mathrm{CDCl_3}$) δ_{C} 17.448 ($\mathrm{CH_3Hg}$), 17.595 ($\mathrm{CH_3}$ of Et), 35.699 ($\mathrm{CH_2}$ of Et), 209.763 ppm CO). Anal. Calcd for $\mathrm{C_9H_8O_6S_2Fe_2Hg}$: C, 18.37; H, 1.37. Found: C, 18.48; H, 1.51.

$(\mu\text{-CH}_3\text{HgS})_2\mathrm{Fe_2(CO)_6}$: obtained in 33% yield (0.74 g, 0.95 mmol), deep red microcrystals; mp ~113 °C (dec) (from 10% $\mathrm{CH_2Cl_2}$/pentane); the mass spectrum showed the molecular ion and fragment ions with m/e corresponding to the successive loss of the six CO ligands; IR (CO region, $\mathrm{CHCl_3}$, cm^{-1}) 2066 (s), 2032 (vs), 1993 (sh), 1978 (vs); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.834 (s, $\mathrm{CH_3Hg}$, $^2J_{\mathrm{HgH}} = 159$ Hz). Anal. Calcd for $\mathrm{C_8H_6O_6S_2Fe_2Hg_2}$: C, 12.39; H, 0.78. Found: C, 12.04; H, 1.09.

In another experiment, the solution of $(\mu\text{-LiS})_2\mathrm{Fe_2(CO)_6}$ (via $\mathrm{LiBEt_3H}$) was treated with 1 (rather than 2, as above) molar equiv of $\mathrm{CH_3HgCl}$. The resulting reaction mixture was brown-green (rather than red) in color. Workup as above gave only $(\mu\text{-C}_2\text{H}_5\text{S})(\mu\text{-CH}_3\text{HgS})\mathrm{Fe_2(CO)_6}$ (0.26 g, 0.422 mmol, 15%).

Reaction of Potassium Tri-*sec*-butylborohydride-Derived $(\mu\text{-KS})_2\mathrm{Fe_2(CO)_6}$ with Methylmercuric Chloride. To 1.00 g (2.91 mmol) of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ in 75 mL of THF at −78 °C was added, with stirring and under nitrogen, 12 mL of 0.5 M potassium tri-*sec*-butylborohydride in THF (6 mmol), during the course of 1 h. The usual red-to-green color change was observed after 6 mL of the hydride solution had been added. After the dianion solution had been stirred for 25 min at −78 °C, 1.51 g (6 mmol) of solid $\mathrm{CH_3HgCl}$ was added rapidly. Within 5 min the color of the solution had changed to light red. The mixture was stirred at −78 °C for 1.5 h and at room temperature for 1 h. Workup followed using the general procedure described above. Filtration chromatography (elution with 10% $\mathrm{CH_2Cl_2}$/pentane) gave two products.

$(\mu\text{-C}_2\text{H}_5(\text{CH}_3)\text{CHS})(\mu\text{-CH}_3\text{HgS})\mathrm{Fe_2(CO)_6}$: initially isolated as a red oil which slowly solidified to give a red solid; 0.50 g (0.81 mmol, 28% yield); mp 92–94 °C (from pentane); the mass spectrum showed M$^+$ and $[\mathrm{M} - n\mathrm{CO}]^+$ ($n = 1$–6); IR (CO region, $\mathrm{CHCl_3}$, cm^{-1}) 2073 (s), 2039 (vs), 1996 (sh), 1985 (vs); ^{1}H NMR (60 MHz, $\mathrm{CDCl_3}$) δ 0.84 ($\mathrm{CH_3Hg}$), 0.91–2.23 (m, *s*-Bu). Anal. Calcd for $\mathrm{C_{11}H_{12}O_6S_2Fe_2Hg}$: C, 21.43; H, 1.96. Found: C, 21.25; H, 2.01.

$(\mu\text{-CH}_3\text{HgS})_2\mathrm{Fe_2(CO)_6}$: red solid; mp ~112 °C (dec), 0.51 g (0.66 mmol, 23% yield), identified by its melting point and IR and NMR spectra.

Reaction of Potassium Hydride-Derived $(\mu\text{-KS})_2\mathrm{Fe_2(CO)_6}$ with Methylmercuric Chloride. The standard apparatus was charged with 0.29 g (7.23 mmol) of potassium hydride and 25 mL of dry THF. The suspension was stirred at room temperature and then a solution of 1.00 g (2.91 mmol) of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ in 25 mL of THF was added (by cannula) to the KH suspension. The brown-green mixture was stirred for 20 h at room temperature. Subsequently it was filtered into a 250 mL, three-necked reaction flask (nitrogen pressure) and 1.51 g (6 mmol) of $\mathrm{CH_3HgCl}$ was added. The reaction mixture was stirred under nitrogen for 20 h. Workup followed the procedure above. Filtration chromatography (10% $\mathrm{CH_2Cl_2}$/pentane) gave 0.37 g (0.48 mmol, 16% yield) of $(\mu\text{-CH}_3\text{HgS})_2\mathrm{Fe_2(CO)_6}$, which was identified by comparison (mp, IR, NMR) with authentic material.

Reaction of Lithium Tri-*tert*-butoxyaluminohydride-Derived $(\mu\text{-LiS})_2\mathrm{Fe_2(CO)_6}$ with Alkylmercuric Chlorides. The usual apparatus was charged with 1.00 g (2.91 mmol) of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ and 75 mL of THF. The solution was cooled to −78 °C, and then 1.644 g (5.82 mmol) of $\mathrm{LiAl(O\text{-}}t\mathrm{\text{-}Bu)_3H}$ (powder, 90% minimum) was added as the solid in one portion under a stream of nitrogen. The color of the solution turned from red to brown-green. Stirring at −78 °C for 2 h gave a green solution. To this solution was added 1.51 g (6 mmol) of solid $\mathrm{CH_3HgCl}$. The resulting light red solution was stirred at −78 °C for 1 h and at room temperature for 2 h. The usual workup, followed by filtration chromatography (pentane, first to remove small amounts of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ and $\mathrm{S_2Fe_3(CO)_9}$ and then to elute product) gave 0.52 g (0.67 mmol, 23%) of $(\mu\text{-CH}_3\text{HgS})_2\mathrm{Fe_2(CO)_6}$ (mp ~113 °C (dec)) identified by melting point and IR and ^{1}H NMR spectra.

A similar reaction, carried out on the same scale with ethylmercuric chloride, gave $(\mu\text{-C}_2\text{H}_5\text{HgS})_2\mathrm{Fe_2(CO)_6}$ (mp 93–95 °C) in 29% yield. The product was identified by melting point and IR and ^{1}H NMR spectra.

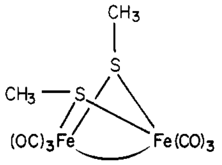
Preparation of $(\mu\text{-RS})(\mu\text{-R'HgS})\mathrm{Fe_2(CO)_6}$ Complexes by the Organolithium Route. The preparation of $(\mu\text{-CH}_3\text{S})(\mu\text{-C}_2\text{H}_5\text{HgS})\mathrm{Fe_2(CO)_6}$ is described to illustrate the procedure used.

The usual apparatus was charged with 1.00 g (2.91 mmol) of $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ and 75 mL of THF. The solution was cooled to −78 °C and then 2.1 mL of $\mathrm{CH_3Li\text{–}LiBr}$, 1.45 M in diethyl ether (~3 mmol), was added by syringe over the course of 10 min. The resulting emerald green solution was stirred at −78 °C for 10 min, and subsequently 0.8 g (2.9 mmol) of solid ethylmercuric chloride was added in one portion in a brisk stream of nitrogen. The mixture rapidly turned brown-red. It was stirred at −78 °C for 1 h and at room temperature for several hours. The usual workup, including filtration chromatography (10% CH_2Cl_2/pentane) and recrystallization from pentane, gave 0.8 g (1.36 mmol, 47%) of red (μ-CH_3S)(μ-C_2H_5HgS)$Fe_2(CO)_6$ (mp ~118 °C (dec)): IR (CO region, $CHCl_3$, cm^{-1}) 2070 (s), 2033 (vs), 1995 (sh), 1987 (vs); ^1H NMR ($CDCl_3$) δ 1.31 (t, J_{HH} = 7.5 Hz, $^3J_{HgH}$ = 242.5 Hz, 3 H, CH_3 of Et), 1.645 (q, J_{HH} = 7.5 Hz, $^2J_{HgH}$ = 162.6 Hz, 2 H, CH_2 of Et), 2.15 (s, 3 H, SCH_3); ^{13}C NMR ($CDCl_3$) δ_C 13.033 (CH_3 of Et), 24.189 (SCH_3), 33.43 (CH_2 of Et), and 209.792 (CO). Anal. Calcd for $C_9H_8O_6S_2Fe_2Hg$: C, 18.37; H, 1.37. Found: C, 18.38; H, 1.43.

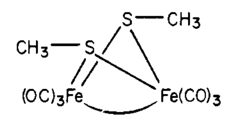
The addition of 2.9 mmol of CH_3HgCl to such a solution of (μ-LiS)(μ-CH_3S)$Fe_2(CO)_6$ (from 2.91 mmol of (μ-S_2)$Fe_2(CO)_6$ gave, after the usual workup, 0.52 g (0.91 mmol, 31%) of red crystals of (μ-CH_3S)(μ-CH_3HgS)$Fe_2(CO)_6$ (mp ~137 °C (dec) (recrystallized from 1:1 CH_2Cl_2/pentane)): the mass spctrum showed the molecular ion at *m/e* 574 (based on ^{200}Hg) and fragment ions corresponding to the successive loss of the six CO ligands; IR (CO region, $CHCl_3$, cm^{-1}) 2073 (s), 2036 (vs), 1998 (sh), 1988 (vs); ^1H NMR ($CDCl_3$) δ 0.85 (s, $^2J_{HgH}$ = 162.5 Hz, CH_3Hg), 2.17 (s, SCH_3); ^{13}C NMR ($CDCl_3$) δ_C 17.507 (CH_3Hg), 24.130 (SCH_3), 209.733 (CO). Anal. Calcd for $C_8H_6O_6S_2Fe_2Hg$: C, 16.72; H, 1.05. Found: C, 16.76; H, 1.11.

The 1:1 reaction of ethyllithium in Et_2O with (μ-S_2)$Fe_2(CO)_6$ in THF at −78 °C (2.9-mmol scale), followed by addition of CH_3HgCl to the solution of (μ-LiS)(C_2H_5S)$Fe_2(CO)_6$ thus produced, gave 0.75 g (1.274 mmol, 44%) of (μ-C_2H_5S)(μ-CH_3HgS)$Fe_2(CO)_6$ (mp ~124 °C (dec)), which was identified by melting point and IR and ^1H NMR spectral comparison with the same compound obtained in the reaction of CH_3HgCl with the $LiBEt_3H$-derived (μ-LiS)$_2Fe_2(CO)_6$ reagent.

Preparation of (μ-CH_3S)$_2Fe_2(CO)_6$ by the LiAl(O-*t*-Bu)$_3$H Route. A solution of (μ-LiS)$_2Fe_2(CO)_6$ in THF at −78 °C was prepared as described above by the reaction of 6 mmol of LiAl(O-*t*-Bu)$_3$H with 2.91 mmol of (μ-S_2)$Fe_2(CO)_6$. To the resulting green solution was added 1 mL (16 mmol) of iodomethane by syringe, which resulted in a rapid color change from green to light red. The reaction mixture was stirred briefly at −78 °C and for 90 :min at room temperature. It then was evaporated at reduced pressure. The residue was dissolved in pentane and submitted to filtration chromatography. Elution with pentane gave a red solid which was recrystallized from pentane: 0.53 g (1.55 mmol, 53%); mp 67–68 °C; ^1H NMR (60 MHz, $CHCl_3$) δ 1.62 (s), 2.12 (s). This is indicative of isomer XIIa of (μ-CH_3S)$_2Fe_2(CO)_6$ (lit.[7] mp 65–67.5 °C).



XIIa



XIIb

Elution with 10% CH_2Cl_2/pentane gave a red solid which was recrystallized from pentane: 0.32 g (0.86 mmol, 29%); mp 105–106 °C. The 60-MHz proton NMR spectrum (in $CHCl_3$) of this product showed a singlet at δ 2.05, indicative of isomer XIIb of (μ-CH_3S)$_2Fe_2(CO)_6$ (lit.[7] mp 101.5–103.5 °C). The total product yield thus was 82%.

Reaction of Potassium Hydride-Derived (μ-KS)$_2Fe_2(CO)_6$ with Triethylborane and Methylmercuric Chloride. The reaction of KH (7.93 mmol) with 2.91 mmol of (μ-S_2)$Fe_2(CO)_6$ in 50 mL of THF, using the procedure described above, served to give (μ-KS)$_2Fe_2(CO)_6$. The mixture was filtered to give a brown-green solution. To this solution was added a solution of Et_3B in THF (prepared by the reaction of ethylene with 10.7 mL of 0.56 M BH_3 (6 mmol) in THF). No color change was noted. Then 0.73 g (2.91 mmol) of CH_3HgCl was added as the solid, all at once. The reaction mixture soon turned brown-red. After it had been stirred at room temperature for 2 h, the usual workup followed. Filtration chromatography gave trace amounts of (μ-S_2)$Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$ (elution with pentane). Elution with 10% CH_2Cl_2/pentane gave an orange and a red band. The products in these bands were isolated and recrystallized from pentane and 10% CH_2Cl_2, respectively. They were identified (mp, mmp, IR, NMR) as (μ-C_2H_5S)(μ-CH_3HgS)$Fe_2(CO)_6$ (0.15 g, 0.25 mmol, 9% yield, based on (μ-S_2)$Fe_2(CO)_6$) and (μ-CH_3HgS)$_2Fe_2(CO)_6$ (0.52 g, 0.67 mmol, 23% yield).

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Synthesis and Characterization of a Novel Family of Dimeric Nickel(II) Complexes—Bimetallic Species Separated by a Persistent Void

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Abstract: A novel family of ligands has been synthesized and characterized as their nickel(II) complexes. The ligands are comprised of pairs of 16-membered macrocyclic ligating sites held in an approximate face-to-face orientation by various bridging moieties, including $(CH_2)_n$, where n = 2–8, *m*- and *p*-xylyl, and duryl. They are prepared by condensation reactions from monomeric macrocyclic precursor complexes. The same reactions also yield monomeric *lacunar* complexes in many cases. The dimeric bimetallic complexes were purified by fractional crystallization and/or chromatography and characterized by the usual physical means. A specific route has been devised for dimer synthesis. On an NMR time scale the structures typically possess two symmetry elements, e.g., a mirror plane and an inversion center. An X-ray structure determination of the *m*-xylene-bridged complex reveals the details of the structure: the Ni–N distance and the related bond angles are normal for square-planar diamagnetic nickel(II) (Ni–N = 1.87 (average) Å, N–Ni–N angle (average) = 89.9°). Of greatest importance, the structure shows the size and nature of the persistent void caused by the rigid components of the molecule. The metal ions are 13.6 Å apart, separated by an empty cavity that is from 3.87 to 6.18 Å wide.

The cooperative functioning of pairs or quartets of metal atoms in a substantial array of natural products (e.g., hemoglobin, cytochrome oxidase, hemerythrin, hemocyanine, and laccase) has attracted attention to dimeric complexes in which the metal ion proximity is enforced by the ligands. Side-by-side dimers based on the systems first prepared by Pilkington and Robson[1] have