Charge Distribution and Nucleophilic Reactivity in Sulfur Ligand Chelates. Dialkyl Derivatives of Nickel(II), Palladium(II), and Platinum(II) Bis(*cis*)ethylenedithiolates

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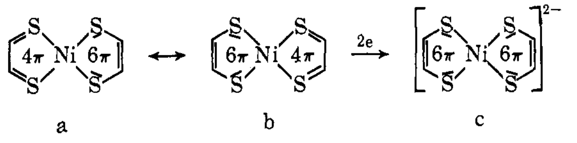
Abstract: Model calculations of the charge distribution in the species $NiS_4C_4R_4^{0,-,2-}$ indicate a considerable localization of charge on the four sulfur atoms in the dianion. In accord with this result, it is demonstrated that the sulfur atoms in Ni(II), Pd(II), and Pt(II) bis(*cis*)ethylenedithiolato dianions possess nucleophilic character. On reaction with alkylating agents, new, neutral, diamagnetic complexes of composition $M(R'_2S_4C_4R_4)$ were obtained which are shown to be the 1,4-S-bisdialkyl derivatives. The complexes are remarkably resistant to acids and bases and show no tendency to undergo reversible oxidation–reduction. The electronic spectra resemble those of the $MS_4C_4R_4^{2-}$ systems in agreement with the proposed planar structure. The complex with M = Ni, $R' = CH_2C_6H_5$, and $R = C_6H_5$ is debenzylated on irradiation with visible light. Some of the previously described adducts of the neutral group VIII metal dithienes, $MS_4C_4R_4$, with olefins are proposed to be Diels–Alder adducts and are probably related to the new complexes. Preliminary experiments indicate that the dianions $MS_6C_6Ph_6^{2-}$ (M = V, Mo, or W) undergo 1,4-S-dialkylation followed by decomposition.

The neutral bis- and "trisdithiene" or "dithiolene" complexes[1a,b] $MS_4C_4R_4$ or $MS_6C_6R_6$ are now well known to be electronically delocalized systems.[2] On the basis of MO calculations and group theoretical considerations, a theory has been advanced[3,4] according to which the metal-bound ligands are regarded to be in a state between dithiodiketones, RC(=S)C(=S)R, and dithiolato dianions, $RC(S^-)=C(S^-)R$. This theory provides the basis for the proper formulation of the state of the ligands and the assignment of oxidation numbers of the metals in these complexes. It also allows unconstrained explanations for most of their unusual chemical properties and simple limiting ground-state formulations in terms of valence bond theory, without invoking unusual valence states of the metals. On reduction to the dianions $MS_4C_4H_4^{2-}$ (eq 1), the dithiene ligands are converted into chelated dithiolato dianions. Accordingly, a significant part of the negative charge in structure c is expected to be localized on the sulfur atoms. This also follows from a MO model calculation of the charge distribution. Using the extended ω technique of Nakajima[5] and den-Boer, *et al.*,[6] essentially in the form recently applied by Boyd and Singer,[7] self-consistent HMO charges and bond orders were obtained (Figure 1). Details of the method of calculation are given in the Appendix.



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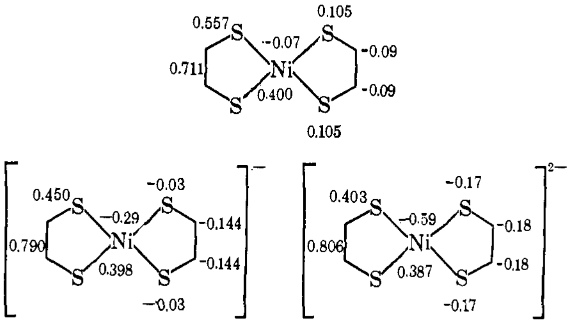

Figure 1. Calculated charges and π bond orders of the system $NiS_4C_4H_4^{0,-,2-}$.

Occupation of the $3b_{2g}$ MO of the neutral complex $MS_4C_4R_4$ with one or two electrons causes the expected[3] increase of the C–C and a decrease in the C–S and Ni–S π bond orders. The charge on the sulfur atoms in the monoanion is small, but rather significant in the dianions. The sulfur atoms in the dianions were therefore expected to exhibit considerable nucleophilicity. The subsequent study of the reactions of various dianions, $MS_4C_4R_4^{2-}$, with alkylating agents led to the discovery of a new class of neutral sulfur ligand complexes to be reported in the present paper.

Complexes of Composition $M[R'_2S_4C_4R_4]$ by the Alkylation of Ions $MS_4C_4R_4^{2-}$. Methylation of $NiS_4C_4Ph_4^{2-}$. Bis(diphenyldithiene)nickel, $NiS_4C_4Ph_4$ (**1**), was reduced to the dianion with $NaBH_4$ in methanol solution. The subsequent addition of excess methyl iodide, dimethyl sulfate, or methyl tosylate afforded olive-green, air-stable, and diamagnetic crystals of $Ni(CH_3)_2S_4C_4Ph_4$ (**2**), in 85% yield. In the nmr spectrum of **2** the phenyl and methyl group proton signals are observed as single peaks at 7.19 and 2.36 ppm, indicating that the methyl groups are bonded to equivalent sites. On heating **2** decomposes above 247° into nickel stilbenedithiolate (**3**) plus a mixture of *cis*- and *trans*-α,α′-bismethyl-

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(1) (a) Suggested nomenclature for complexes containing ligands intermediate between 1,2-dithiodiketones and 1,2-ethylenedithiolato dianions (*cf.* from G. N. Schrauzer in "Transition Metal Chemistry," Vol. IV, R. C. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, pp 299–335); (b) J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *J. Am. Chem. Soc.*, **89**, 6082 (1967).

(2) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **88**, 5174 (1966).

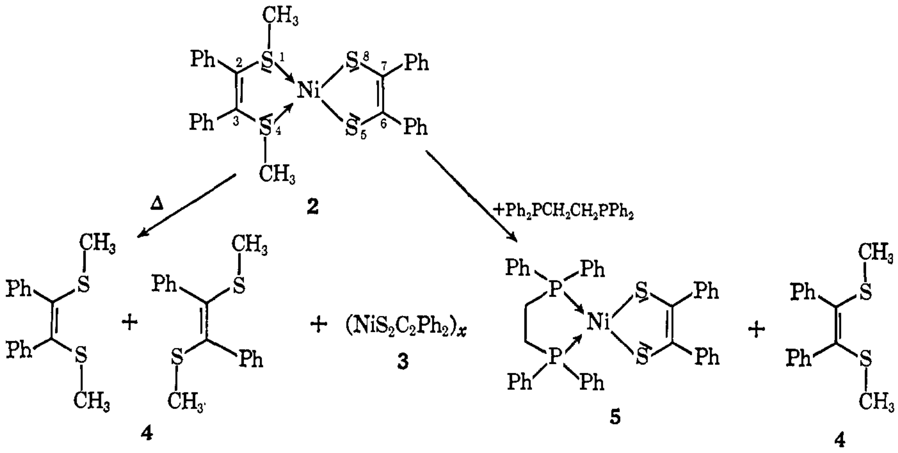
(3) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 3585 (1965).

(4) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **88**, 3235 (1966).

(5) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963).

(6) P. C. Boer-Veenendaal, J. A. Vliegenhart, and D. H. W. den-Boer, *Tetrahedron*, **18**, 1325 (1962).

(7) G. V. Boyd and N. Singer, *ibid.*, **22**, 3383 (1966).



(1)

thiostilbene. To eliminate the possibility that this product formed by an alkyl group migration reaction, during the thermolysis, different methods of decomposition were employed. With ethylenebisdiphenylphosphine **2** reacts under milder conditions (boiling xylene), yielding a mixture of mainly *cis*-α,α'-bismethylthiostilbene, small amounts of the *trans* isomer, plus the known complex **5**[8] as the only products. A similarly smooth displacement of **4** also occurs on gentle heating of **2** with α,α'-bipyridyl.

These experiments show that **2** is 1,4-dimethylbis(diphenylethylenedithiolato)nickel. No evidence for the formation of any other isomer than **2** was found. The complex is remarkably resistant to acids and bases. It can be dissolved in concentrated sulfuric acid without decomposition and is not attacked by hydrochloric acid. However, protolysis occurs slowly in contact with 70% $HClO_4$ *via* a dark green protonated intermediate.

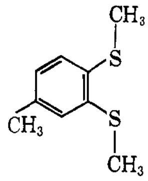
A slow ligand displacement reaction was also observed with concentrated warm KCN solution. Pyridine or other nitrogen bases were found not to form adducts or to cause significant changes in the absorption spectra. In view of the similarity of the spectra of **2** with those of the dianions $MS_4C_4R_4^{2-}$, the complex is assumed to be planar.

Related Compounds. The alkylation of $NiS_4C_4Ph_4^{2-}$ could be effected with equal success with many alkyl halides. Some of the complexes prepared to date are listed in Table I. The bis(2-hydroxyethyl) derivative mentioned in Table I was obtained by the reaction of the dianion with chlorohydrin as well as with ethylene oxide. The complexes were shown to be the 1,4-bisalkyl derivatives, *e.g.*, by the reaction with $Ph_2PCH_2CH_2PPh_2$, α,α'-bipyridyl, and/or the thermal decomposition, and only this one isomer formed in all cases studied to date.

It is remarkable that the nickel bismaleonitrile dianion could not be converted into a dimethyl derivative. Several bisbenzyl derivatives of group VIII metal dithienes have also been synthesized. These behave just as the alkyl derivatives, but $Ni(PhCH_2)_2S_4C_4Ph_4$ was found to be light sensitive in solution. On irradiation in the presence of air, $NiS_4C_4Ph_4$ plus mainly benzaldehyde are formed. Under anaerobic conditions photodebenzylation occurs as well, though at a slower rate, producing bibenzyl as one of the products.

A notable property of some of these complexes is their thermochromism which occurs on heating to temperatures above 60° (Table I). The effect is probably caused by a change in the crystal modification, since heating in solution initiates only slight color changes.

The complexes represent the first well-documented examples for the ability of aliphatic unsaturated 1,2-dithioethers to coordinate with transition metals. Ligands of this type, *e.g.*, dithioveratrole (**6**), are normally poor chelating agents;[9] the same is also true for α,α'-bismethylthiostilbene. Stable complexes of these ligands are evidently capable of existence if synthesized from a suitable metal chelate precursor. The only other complexes known which may be regarded as derivatives of isomers of our compounds are the presumably planar Ni^{2+}, Pd^{2+}, and Pt^{2+} complexes of *o*-methylthiobenzenethiol (**7**) briefly reported by Livingstone.[10,11]



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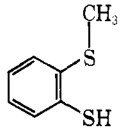

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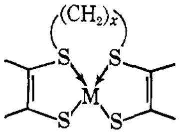
Attempted Synthesis of Similar Complexes. Attempts to direct the addition of the second alkyl group onto another but the 4 sulfur atom so far remained without success. In particular, a macrocyclization to **8** or **9**, which in some ways would have been analogous to reactions described by Busch,[12] could not be achieved. Both **8** and **9** should be capable of existence. However, **8** is evidently not accessible by this route, while **9** would require larger values of x than so far have been employed. To explain the obvious preference of the second alkyl group for sulfur atom 4, we assume that the charge density on this atom increases over that of the remaining sulfur atoms as the first alkyl group is attached. It is conceivable that this is due to a change



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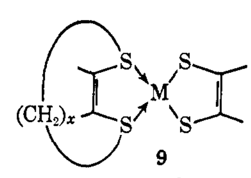

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[8] G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **88**, 5174 (1966).

[9] (a) L. Tshugaev, *Ber.*, **41**, 2222 (1908); (b) R. Backhouse, M. E. Foss, and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

[10] S. E. Livingstone, *ibid.*, 437 (1956).

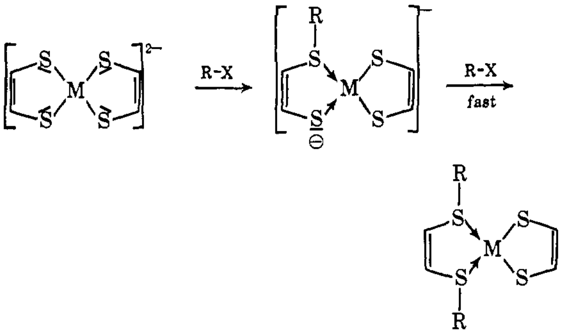
[11] S. E. Livingstone, *ibid.*, 1042 (1956).

[12] D. H. Busch, *et al.*, *J. Am. Chem. Soc.*, **86**, 3642, 3651 (1964).

Table I. Some Properties of Complexes M[R$'_2$($S_4C_4R_4$)]

No.	M	R	R′	Mp, °C dec	Color (solid)	Thermochromic transition temp, °C	Thermochromic color
1	Ni	Ph	CH_3	247	Dark green	. . .	. . .
2	Ni	Ph	Et	267	Brown	70	Red-brown
3	Ni	Ph	*n*-Pr	248	Brown	. . .	. . .
4	Ni	Ph	*n*-Bu	235	Orange	. . .	. . .
5	Ni	Ph	*t*-Bu	245–250	Deep purple	75	Dark green
6	Ni	Ph	*sec*-Octyl	182	Orange	. . .	. . .
7	Ni	Ph	CH_2CH_2OH	256	Green	130–150	Brown
8	Ni	Ph	CH_2Ph	193	Dark red	. . .	. . .
9	Ni	CH_3	CH_2Ph	135	Brown-yellow	. . .	. . .
10	Pd	Ph	CH_2Ph	196	Red-brown	. . .	. . .
11	Pt	Ph	CH_2Ph	202	Yellow	186	Yellow-green

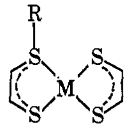
in the hybridization of both the 1 and the 4 sulfur atoms, and that it is ultimately responsible for an increase in the nucleophilicity of the 4 sulfur atom (eq 2).



(2)

The nucleophilicity of the sulfur atoms may be expected to depend on the inductive effect of the ethylenedithiol carbon substituents. We explain our difficulties to methylate Ni(MNT)$_2^{2-}$ on this basis.

Attempted Alkylation of Ions $MS_4C_4R_4^-$. The Ni(II), Pd(II), and Pt(II) monoradical anions $MS_4C_4R_4^-$ could not be alkylated under similar and different conditions to produce isolable free radicals of the type M[R′($S_4C_4R_4$)]. The reaction of $NiS_4C_4Ph_4^-$ with benzyl bromide afforded a pink solution which exhibited a weak esr signal, but the radical could not be isolated. Although the existence of compounds such as **10** cannot be discounted, it appears that they are not accessible in this way, or rather unstable in solution.



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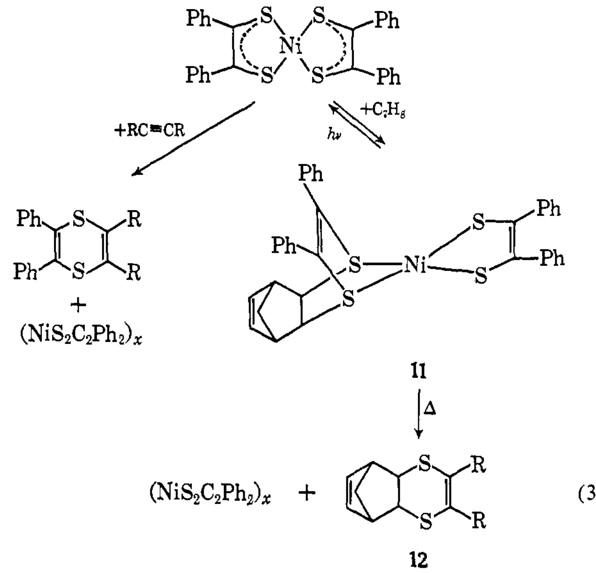
The "Diels–Alder Adducts" of Olefins with Group VIII Metal Dithienes. Certain olefin adducts of group VIII metal bisdithienes reported earlier[13] may be related to the complexes described here. In analogy to the reactions of the nickel bisdithienes with alkynes, some of the compounds (*e.g.*, **11**) were formulated[13] as "Diels–Alder adducts" of the olefin with one of the ligands (eq 3). As a further confirmation of this view we now find that the reaction of $NiS_4C_4Ph_4$ with norbornadiene under slightly more vigorous conditions produces the 1,4-Diels–Alder adduct (**12**) of the hypothetical 1,3-diene, dithiobenzil. The residual 1,3-diene reactivity may be regarded as another compelling piece of evidence in favor of our description of bonding in the neutral group VIII metal bisdithienes and related compounds.



(3)

The spectra of the olefin adducts have been reported to resemble those of the $MS_4C_4R_4^{2-}$ dianions. The adduct of $NiS_4C_4Ph_4$ with norbornadiene furthermore was found to be light sensitive, decomposing into $NiS_4C_4Ph_4$ and norbornadiene. In view of these analogies we conclude that these adducts are thus related to the dialkylbisdithiolato complexes obtained through the alkylation reactions.

Alkylation of Trisdithiene Complex Dianions. On reduction of the trisdithienes to the mono- and dianions, the C–C stretching frequency of the dithiene ligand (ω_1 in ref 4) increases very nearly to the same extent as in the series of the nickel complexes $NiS_4C_4R_4^{0,-,2-}$. The dithiene ligands thus also become more nearly dithiolato dianions in the anions of the tris complexes, a fact which is readily explained on the basis of the proposed[4] electronic structures. Accordingly, the sulfur atoms in the dianions of the complexes exhibit some nucleophilicity. The neutral, prismatic trisdithienes $MS_6C_6Ph_6$ of V, Mo, and W were reduced to the dianions with $NaBH_4$ in methanol and allowed to react with methyl tosylate. The desired complexes $M(CH_3)_2S_6C_6Ph_6$ could not be isolated, but bismethylthiostilbene was obtained, indicating that the 1,4-dialkylation had occurred. Apparently, the dialkyls $MR'_2S_6C_6R_6$ are unstable under the conditions employed. Work is in

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[13] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 87, 1483 (1965).

Table II. Optical Spectra (in Methanol)

Complex			Frequency, cm^{-1} (ϵ)		
M	R	R′			
Ni	Ph	CH_3	14,110 (565)	21,500 sh (2500)	26,300 sh (15,000) 28,700 (27,000)
Ni	Ph	C_2H_5	14,204 (470)	21,500 sh (2500)	25,900 sh (15,600) 28,900 (24,700)
Ni	Ph	n-C_3H_7	14,164 (500)	*a*	
Ni	Ph	n-C_4H_9	14,225 (478)	*a*	
Ni	Ph	t-C_4H_9	14,180 (510)	*a*	
Ni	Ph	CH_2Ph	14,050 (558)	21,500 sh (2500)	25,900 sh (15,500) 28,600 (25,000)
Pd	Ph	CH_2Ph	18,700 (1100)	23,000 sh (2000)	28,500 sh (15,000) 30,600 (22,000)
Pt	Ph	CH_2Ph	25,900 (sh) (7500)	*b*	

[a] Spectra are essentially identical with those above. [b] Spectrum is not resolved.

progress with the rhenium compound as well as with the complexes of iron and cobalt.

Electronic Spectra. In Figures 2 and 3 spectra of several dialkyl derivatives of the ions $MS_4C_4R_4^{2-}$ are shown together with those of the free anions. From the observed similarities, we conclude that the dialkyl derivatives are also planar, at least within the MS_4 moiety, and that their electronic structures must be similar. Accordingly, we may assume that the sequence of the d orbitals is the same as calculated[2,14] for $NiS_4C_4H_4^{2-}$ and for $Ni(MNT)_2^{2-}$, $d_{yz} < d_{z^2} < d_{xz} < d_{x^2-y^2} \ll d_{xy}$. The band observed around 14,000 cm^{-1} is therefore assigned to the $d_{x^2-y^2} \rightarrow d_{xy}$ transition ($^1A_1 \rightarrow {}^1A_2$, assuming C_{2v} symmetry). In the spectra of the dianions the corresponding band is observed in the range between 11,500 and 12,900 cm^{-1}.[3,14] The ligand field splitting in the dianions is thus slightly smaller. It is conceivable that electrostatic repulsion between the ligands is diminished in the neutral dialkyl derivatives, leading to stronger metal–ligand interactions and hence to an effectively stronger d orbital splitting. The corresponding d–d transition in the analogous Pd and Pt complexes is observed at higher energies, as expected (Table II). The intensity of the $^1A_1 \rightarrow {}^1A_2$ transition is consistently higher than that of the corresponding transition of the dianions. This is plausibly explained by the lower symmetry of the neutral compounds and a possibly small asymmetric charge distribution between the $R'_2S_2C_2R_2$ and the $R_2C_2S_2^{2-}$ ligands.

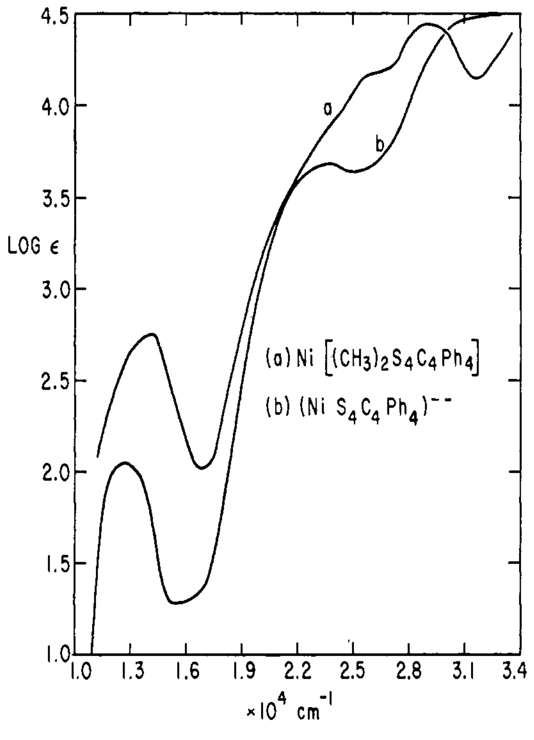

Figure 2. Absorption spectra of $Ni[(CH_3)_2S_4C_4Ph_4]$ (a, in methanol) and of $NiS_4C_4Ph_4^{2-}$ (b, in hydrazine solution).

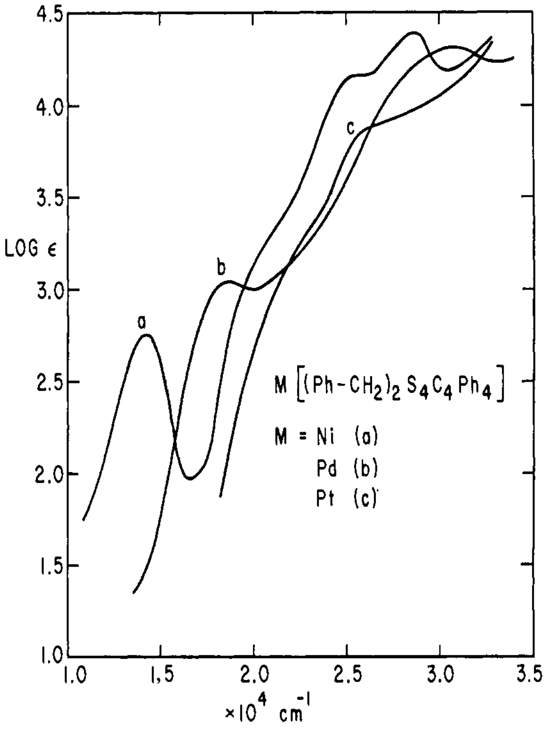

Figure 3. Absorption spectra of complexes $M(PhCH_2)_2S_4C_4Ph_4$ (M = Ni, Pd, Pt) in methanol.

A slight alternating effect was noted in the series of the bis-n-alkyl derivatives as a function of the alkyl chain length (Table II). This is suggestive of small periodic variations of the effective ligand field strength

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(14) S. I. Shupack, E. Billig, R. T. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

due to a combination of small steric displacements and subtle electronic substituent effects.

In the spectra of most dialkyldithiolato complexes two shoulders are observed around 22,000 and 28,000 cm^{-1}, while in the spectra of the dianions usually only one shoulder is present (Figures 2 and 3). In the case of the latter this absorption was assigned to a $\mathrm{N}_{=\mathrm{S}} \rightarrow \mathrm{d}_{xy}$ transition.[3] Maintaining this assignment we conclude that the two transitions in the dialkylbisdithiolato complexes may result from the nonequivalence of the $R'_2S_2C_2R_2$ and $R_2C_2S_2^{2-}$ ligands present in the molecule.

Experimental Section

General Alkylation Procedure, Exemplified for the Methylation of $NiS_4C_4Ph_4^{2-}$. Complex **1** (20 g), prepared by the benzoin–P_4S_{10} method,[13,15,16] was suspended in 300 ml of methanol. After the addition of 10 ml of 50% (wt) of NaOH solution the complex was reduced to the dianion by adding 1.5 g of $NaBH_4$ and heating to 50° for 60 min. To this solution methyl iodide (12 g, slight excess over stoichiometric amount) was added. Green crystals of the methyl derivative precipitated after standing overnight. The reaction mixture was filtered, affording 18.2 g (86% of the theoretical amount) of product. For purification the crude was recrystallized from methylene chloride, affording olive-green crystals, mp 247° dec.

Anal. Calcd for $C_{30}H_{26}S_4Ni$: C, 62.85; H, 4.57; Ni, 10.24; mol wt, 573.2. Found: C, 62.45, H, 4.60; Ni, 10.44; mol wt, 570.

The infrared spectrum showed main bands (cm^{-1}, in KBr) at 1587, 1567, 1545, 1477, 1430, 1406, 1253, 1166, 1072, 1028, 981, 962, 909, 862, 801, 764, 740, and 694.

Remarks. The reduction of the starting dithiene complexes of the group VIII metals can also be achieved with $LiBH_4$, sodium amalgam, or hydrazine. The sodium borohydride method was found to be the most convenient, however.

The procedure can be used without major modification for the preparation of most of the other alkyl and aralkyl derivatives. Occasionally the reaction times have to be varied, *e.g.*, if the alkyl halides are less reactive because of steric hindrance. To obtain a yield of 10% of the bis-*t*-butyl derivative of $NiS_4C_4Ph_4$ using *t*-butyl bromide as the alkylating agent, the reaction solution was allowed to stand at room temperature for 10 days until work-up. Acyl halides, diphenylchloromethane, diphenylchlorophosphine, ethyl chloroformate, and trimethylchlorosilane reacted with $NiS_4C_4Ph_4^{2-}$ without producing stable analogous complexes. Instead, $NiS_4C_4Ph_4$ was reisolated. Properties, analyses, and nmr data of various complexes prepared are summarized in Tables III and IV.

Table III. Analyses of Complexes **2–11** of Table I

No.	Compound	C, % Calcd	C, % Found	H, % Calcd	H, % Found
2	$NiC_{32}H_{30}S_4$	63.91	63.95	4.99	4.95
3	$NiC_{34}H_{34}S_4$	64.88	64.75	5.40	5.38
4	$NiC_{36}H_{38}S_4$	65.77	65.31	5.78	5.55
5	$NiC_{36}H_{38}S_4$	65.77	65.60	5.78	5.86
6	$NiC_{44}H_{54}S_4$	68.68	68.42	7.02	6.90
7	$NiC_{32}H_{30}S_4O_2$	60.68	60.33	4.74	4.75
8	$NiC_{42}H_{34}S_4$	69.53	69.45	4.69	4.75
9	$NiC_{22}H_{28}S_4$	55.13	55.05	5.84	5.81
10	$PdC_{42}H_{34}S_4$	65.24	65.20	4.40	4.60
11	$PtC_{42}H_{34}S_4$	58.53	57.99	3.93	3.85

Table IV. ^1H Nmr Spectra in CS_2

Compound	Nmr signals: Chemical shift in ppm from TMS (relative intensity)
$Ni[Me_2S_4C_4Ph_4]$	Peak: 2.36 (3), 7.19 (10)
$Ni[Pr_2S_4C_4Ph_4]$	Triplet: 0.81, 0.92, 1.00; multiplet: 1.74–2.28 (2) Triplet: 2.46 (2), 2.58, 2.70; peak: 7.08 (10)
$Ni[Bu_2S_4C_4Ph_4]$	Triplet: 0.62 (3), 0.82, 0.98; multiplets: 1.30 (2), 1.86 (2), 2.48 (2) Peak: 7.16 (10)
Ni[*t*-$Bu_2S_4C_4Ph_4$]	Peak: 1.55 (1), 7.13 (1)
$Ni(CH_2Ph)_2S_4C_4Ph_4$	Peak: 3.91 (1), 7.03 (4) 7.22 (2)
$Ni(CH_2Ph)_2S_4C_4Me_4$	Peak: 1.74 (3), 1.90 (3), 4.04 (2), 7.22 (5)
$Pt(CH_2Ph)_2S_4C_4Ph_4$	Peak: 4.20 (2), 7.02 (15)

Thermal Decomposition. Complex **2** (2.0 g) was placed into a vacuum sublimation apparatus and was heated to 250° at a pressure of approximately 10^{-2} mm. A faintly yellow sublimate formed. Recrystallized from hot methanol, its nmr spectrum displayed two pairs of signals in the aromatic and the aliphatic regions (7.23, 6.96 and 1.87, 1.66 ppm relative to TMS, respectively), with the integrated intensities of 5:3. The melting point indicated the presence of two types of crystals, one melting at 94–95°, the other at 141–143°.

Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.60; H, 5.87; S, 23.53. Found: C, 70.68; H, 5.83; S, 22.50.

After recrystallization from methanol the first fraction of crystals obtained had mp 145–147° (lit.[17] mp (for *trans*-α,α′-bismethylthiostilbene) 146.5–148°).

Anal. Found: C, 70.60; H, 5.88.

The nmr spectrum showed the phenyl and methyl signals at 7.23 and 1.66 ppm relative to TMS (in $CDCl_3$), intensity ratio 5:3. The nonvolatile sublimation residue (1.08 g) was purified by adding *n*-hexane to the solution in CH_2Cl_2, mp 360° dec. The infrared spectrum was identical in every respect with the nickel dithiobenzoin complex $(NiS_2C_2Ph_2)_x$ reported earlier.[13]

Anal. Calcd for $C_{14}H_{10}S_2Ni$: C, 55.85; H, 3.34. Found: C, 55.72; H, 3.30.

Reaction with Ethylenebisdiphenylphosphine. Complex **2** (1.0 g) was mixed with 1 g of $Ph_2PCH_2CH_2PPh_2$ and carefully heated in a small glass vessel to 150–180° for 15 min. After cooling the melt was dissolved in 10 ml of CH_2Cl_2. To the filtered solution methanol was slowly added while the methylene chloride was being evaporated. Cooling of the saturated methanol–CH_2Cl_2 mixture afforded 0.87 g of product, which was recrystallized from CH_2Cl_2–methanol, mp 150° (lit.[8] mp 153–155°). The infrared spectrum was identical with that of authentic $NiS_2C_2Ph_2 \cdot Ph_2PCH_2CH_2PPh_2$. Further evaporation of the filtrates afforded colorless crystals, mp 94–96° (0.4 g), of *cis*-α,α-bismethylthiostilbene, contaminated with 22% of the *trans* isomer (estimated by nmr spectroscopy). This reaction was carried out with all the dialkyl derivatives of $NiS_4C_4Ph_4$ reported in this paper. In all cases $NiS_2C_2Ph_2 \cdot Ph_2PCH_2CH_2PPh_2$ was isolated out of the reaction mixture. The reaction with the chelating phosphine also takes place in refluxing xylene.

Reaction with α,α′-Bipyridyl. Complex **2** was allowed to react with α,α′-bipyridyl under the same conditions as described in the previous experiment. After cooling, the melt was extracted with benzene. The benzene solution was evaporated to dryness and the residue recrystallized from CH_2Cl_2–methanol, yielding a mixture of *cis*- and *trans*-α,α′-bismethylthiostilbene. The benzene-insoluble residue was extracted with methylene chloride and the product, $NiS_2C_2Ph_2 \cdot$bipyridine, isolated by adding benzene, mp 229° dec, identified by its nmr spectrum.

Photolysis of $Ni(PhCH_2)_2(S_4C_4Ph_4)$. A dilute solution of the complex in benzene was irradiated under nitrogen using a 75-W photoflood lamp (GE). After 24 hr the originally yellow solution was deeply green. The electronic spectrum was identical with that of $NiS_4C_4Ph_4$. Glpc analysis indicated the presence of bibenzyl and two as yet unidentified volatile products in the solution. When the irradiation was performed in air, photolysis was appreciably faster, yielding benzaldehyde as the main organic by-product (identified by glpc).

Diels–Alder Addition of Norbornadiene to $NiS_4C_4Ph_4$. A suspension of 3 g of $NiS_4C_4Ph_4$ in 50 ml of freshly distilled norbornadiene was heated to 85° for 4 hr. During this time the black crystals of the starting complex changed completely into a brown material. After cooling and filtration, the solid product was identified as $(NiS_2C_2Ph_2)_x$. The filtrate was evaporated to dryness and the residue recrystallized three times from xylene–methanol, affording

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Table V. Calculated Metal Configurations and Total Charges

z		Ni charge
0	$3d^{7.79}4s^{0.81}4p^{1.47}$	−0.075
−1	$3d^{8.03}4s^{0.81}4p^{1.45}$	−0.292
−2	$3d^{8.44}4s^{0.78}4p^{1.36}$	−0.593

Table VI. Observed and Calculated Bond Lengths (Å) in the Complexes $NiS_4C_4R_4^{0,-,2-}$ [a]

Ni–S		C–S		C–C			
Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Compound	Ref
2.101	0.002	1.71 (0.01)	1.70	1.37 (0.014)	1.39	$NiS_4C_4Ph_4$	25
2.146	0.001	1.71 (0.004)	1.72	1.35 (0.007)	1.37	$Ni(MNT)_2^-$	*b*
2.165	0.005	1.75 (0.01)	1.73	1.33 (0.02)	1.37	$Ni(MNT)_2^{2-}$	24

[a] Standard deviations in parentheses. [b] C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966).

colorless needles, mp 147°. *Anal.* Calcd for $C_{21}H_{18}S_2$: C, 75.42; H, 5.42. *Found:* C, 75.35; H, 5.48.

The ^1H nmr spectrum in $CDCl_3$ showed the following (intensities in parentheses): 7.00 (10) (phenyl protons); 6.19 (2); 3.56 (2), 3.04 (2), 1.80 (quartet, 2) ppm relative to TMS. The chemical shifts of the norbornadiene protons correspond closely to those of tricyclo[4.2.1.0^{2,5}]nona-2,7-diene derivatives which were assigned to have the *exo* configuration.[18]

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Appendix

Model Calculation of the Charge Distribution in the Species $NiS_4C_4H_4^{0,-,2-}$. In the ω–β technique,[5–7] an improvement of simple HMO results is achieved by a combination of the conventional ω technique with a variation of the resonance integrals β. For the variation of the charges a linear dependence of the diagonal terms on the net charge was assumed as usual with $\omega = 1.4\beta_0$ ($\beta_0 = -3.00$ eV) for all atoms. The C–C bond distances were related to the calculated bond orders by the known[19] equation $r_{ij}(\text{C–C}) = 1.511 - 0.173p_{ij}$. For the dependence of β_{ij} on the distance, the exponential function $\beta_{ij} = \beta_{ij}^0 \exp b(r_0 - r_{ij})$ with $b = 5.007$[19] was used.

The β bond distance and the bond order–bond distance relations were combined and expressed in a power series

$$k_{ij} = k_0 + k_1p_{ij} + k_2p_{ij}^2 + k_3p_{ij}^3 + \cdots$$

The k_i values for C–C bonds are 0.5679 (k_0), 0.5081 (k_1), 0.1364 (k_2), and 0.1302 (k_3). For the C–S distances the r_{ij}–p_{ij} relation was approximated by the equation $r_{ij}(\text{C–S}) = 1.82 - 0.22p_{ij}$, and the same exponential dependence of β on the bond order as for the C–C bonds was assumed. The Ni–S bonds were not varied. The calculation was performed using a ω–β program written by Dr. J. A. Schachtschneider, Shell Development Co., Emeryville, Calif. The input energies and off-diagonal elements for $NiS_4C_4H_4$ were the same as in ref 3, except that slightly different metal Coulomb terms were used (Ni 3d, −10.03; 4s, −8.96; 4p, −5.15 eV, corresponding to VSIE's of the configurations $3d^{n-1}4s$, $3d^{n-2}4s^2$, and $3d^{n-2}4p^2$, respectively).[20]

The calculation was started with a set of assumed net charges q_i^0 and bond orders p_{ij}^0. After the solution of the secular equation new sets of charges and bond orders were obtained which were used for the calculation of the corrected diagonal and off-diagonal matrix elements. The values calculated in each cycle were compared with the previous numbers until all Δq_i and Δp_{ij} were less than 0.005. This was the case after 10–12 cycles.[21]

Charges and calculated configurations of the metal and calculated and observed bond lengths are given in Tables V and VI.

The lowest unoccupied π MO ($3b_{2g}$) in $NiS_4C_4H_4$ according to the HMO treatment[3] was calculated to have 82% ligand π and 18% metal $3d_{xz}$ character. The "self-consistent" MO's of the ω–β technique indicate ligand π and metal d_{xz} characters of 49 and 51%, respectively, *in the monoanion.* This is in excellent agreement with the recent estimation on the basis of measurement of the ^{33}S and ^{61}Ni esr hyperfine interactions in $Ni(MNT)_2^-$.[22] Polarographic data[23] suggest a greater ligand character (∼80%). Since the calculations and experimental estimates are endowed with elements of uncertainty, the physically realistic conclusion at present is that the $3b_{2g}$ oribital has a ligand π character between 50 and 85%.

Correlation with Optical Data. The energy of the very intense near-infrared band in the spectra of $NiS_4C_4R_4$ and $NiS_4C_4R_4^-$ [3,14] ($2b_{1u} \rightarrow 3b_{2g}$) is calculated in very good agreement with experiment. The shift of the $2b_{1u} \rightarrow 3b_{2g}$ transition to lower energy in $NiS_4C_4H_4^-$ is correctly predicted.

Transition $2b_{1u}$–$3b_{2g}$(π–π*)	$NiS_4C_4H_4$	$NiS_4C_4H_4^-$
Calcd, cm^{-1}	14,740	11,273
Obsd, cm^{-1}	13,870	11,495

Bond Lengths. The calculated bond lengths agree with most of the available experimental data except for the C–C distance in the dianion. However, the experimental value was obtained from $Ni(MNT)_2^{2-}$,[24] whereas the calculation was done for $NiS_4C_4H_4^{2-}$. A further shortening of the C–C bond is expected to result if the change in the hybridization of the sulfur atoms from sp^2 to sp^3 is fully taken into account. In addition, consideration of the inductive effect of the CN substituents could improve the agreement with the experiment. The increase of the Ni–S bond lengths with increasing *z* is probably significant[25] and is paralleled by a decrease in the calculated (Figure 1) Ni–S π bond orders.

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