tion of polarized water molecules around the anion is postulated to form an electron trap when the anion is neutralized by proton transfer induced by irradiation.[13] This local orientation is apparently similar in both glassy and polycrystalline phases when formed by rapid freezing, the main difference in these phases being in the long-range order. This is also shown by the fact that the line width is not significantly different in the two phases. The latter observation implies that the charge density of the trapped electron is not extremely delocalized.

However, since a significant cation contribution to the line width is observed, we know that the charge

density distribution of the trapped electron cannot be too highly localized. At 2–5 M concentrations the average distance to a cation is about 5–4 Å. By using the theory of Kip, et al.,[10] the proton contribution to the line width can be shown to correspond to interaction of the trapped electron with about eight protons.[3,13] Thus the total interaction of the charge density of trapped electrons in alkaline ices encompasses several water molecules and one or more cations. This is consistent with the physical picture of an anion vacancy as the trapping site.

(13) L. Kevan in "Progress in Chemistry of the Solid State," Vol. 2, H. Reiss, Ed., Pergamon Press, New York, N. Y., 1965, pp. 304–329.

Preparation, Reactions, and Structure of Bisdithio-α-diketone Complexes of Nickel, Palladium, and Platinum[1,2]

G. N. Schrauzer and V. P. Mayweg

Contribution from the Department of Inorganic Chemistry, The University, Munich, Germany, and Shell Development Company, Emeryville, California. Received December 3, 1964

Preparation and properties of complexes M(RCSCSR)₂ (R = aryl or alkyl, M = Ni, Pd, Pt) are reported. From theoretical considerations and X-ray and spectroscopic evidence, it is inferred that the compounds are planar bis-chelates of semi-α-dithiodiketones with the metals in the +2 state. Reactions of the complexes with hydrazines, phosphines, alkynes, and olefins are reported. With alkynes, thiophene derivatives are obtained via dithiadienes as intermediates. With a number of diolefins, labile 1:1 adducts are formed, the structure of which is discussed.

Since their discovery,[3] complexes of the type $M(RCSCSR)_n$ (M = a transition metal, n = 2 or 3, R = aryl or alkyl) were available only with difficulties and low yields, e.g., from the reaction of alkynes with certain metal sulfides. A new method of synthesis has now been developed,[4] details of which will be published shortly. It makes these interesting compounds accessible from simple starting materials, according to reaction sequence 1. By this method we have prepared a large number of complexes of this type of most

transition metals. In the present paper some results of our work on complexes of nickel, palladium, and platinum are reported.

$$(n = 2 \text{ or } 3)$$
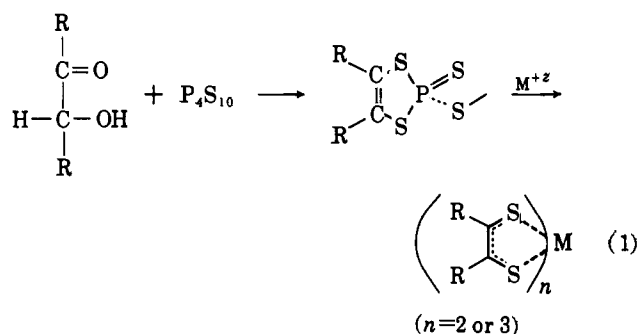
Preparation and Properties. The bisdithio-α-diketone complexes of composition M(RCSCSR)₂ with R = phenyl, substituted phenyl, or alkyl and M = Ni and Pt were prepared according to eq. 1. Bis(dithiobenzil)palladium was obtained similarly, but the analogous methyl-substituted complex of this metal so far has resisted isolation. All compounds were well crystallized, air stable, and intensely colored solids. The X-ray analysis of bis(dithiobenzil)nickel has now been completed[5] and confirms the initially proposed structure I. The analogous complexes of Pd and Pt are isostructural with the nickel compound, space group P2₁/a. The methyl-substituted complexes are vacuum sublimable. The dithiobenzil complexes of

(1) Paper VI of the series "Chemistry of the Coordination Compounds"; Paper V: G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 1080 (1964).

(2) Partly abstracted from the Ph.D. Thesis of V. P. M., The University, Munich, Germany, 1964.

(3) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(4) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 381 (1964); G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Angew. Chem.*, **76**, 715 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 639 (1964).

(5) M. R. Truter, Leeds, personal communication.

nickel and platinum decompose at 292 or 310°, respectively, producing 2-phenylthionaphthene as the exclusive organic product. The palladium derivative is somewhat less stable and decomposes at 254° into a mixture of 2-phenylthionaphthene and tetraphenylthio-

I
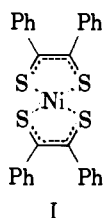
phene. All complexes show limited solubilities in common organic solvents. They are insoluble in water and are not affected by moderately concentrated mineral acids. However, they react with a number of nitrogen bases (e.g., piperidine, pyridine, or hydrazine) forming salts of the ions $M(RCSCSR)_2^{-z}$, $z = 1$ or 2. This is a general feature of complexes of this type and was independent of our own work found by Davison, Edelstein, Holm, and Maki.[6,7] The reduction reactions are reversible; polarographic half-wave potentials are listed in Table I. The potentials depend on the sub-

Table I. Polarographic Half-Wave Potentials (in Volts) of Complexes $M(RCSCSR)_2^a$

M	R	I[b]	II[c]
Ni	CH_3	−0.051	−0.982
Pt	CH_3	−0.089	−0.963
Ni	C_6H_5	+0.188	−0.818
Pd	C_6H_5	+0.232	−0.586
Pt	C_6H_5	+0.145	−0.800

^{a} At 25° in dimethylformamide with 0.1 M $LiClO_4$ and a Ag–AgCl reference electrode, $C_{HCl} = 1.05 M$. ^{b} I = couple $M(Lig)_2^0 \rightleftharpoons M(Lig)_2^-$. ^{c} II = couple $M(Lig)_2^- \rightleftharpoons M(Lig)_2^{-2}$.

stituents R. For CF_3-substituted complexes they have already been reported[8] and are considerably more positive, indicating the strong inductive effect of this substituent.

Among the dithiobenzil complexes, that of palladium is most easily reduced, an observation which is in keeping with the chemical and spectroscopic properties (vide infra). Various salts of the ions $M(RCSCSR)_2^{-z}$, $z = 1$ or 2, have already been prepared.[8,9] The dianion salts of the phenyl-substituted nickel complex are very air sensitive and difficult to isolate. With hydrazine, well-defined hydrazonium salts which are less sensitive are formed. The orange-yellow salt of bis(dithiobenzil)nickel dianion has the composition $(N_2H_5^+)_2Ni(PhCSCSPh)_2^{2-} \cdot (N_2H_4)_2$. The unexpectedly high hydrazine content suggests the presence of hydrogen-bridged $(N_2H_5 \cdot N_2H_4)^+$ ions, whose formation is apparently favored by the large size of the anions. Accord-

(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, Inorg. Chem., 2, 1227 (1963).
(7) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, J. Am. Chem. Soc., 85, 2029 (1963).
(8) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, Inorg. Chem., 3, 814 (1964).
(9) G. N. Schrauzer and V. P. Mayweg, Z. Naturforsch., 19b, 192 (1964).

ingly, with 1,2-dimethylhydrazine only the "normal" hydrazonium salt, $(CH_3NH_2NHCH_3^+)_2Ni(PhCSCSPh)_2^{2-}$, was obtained. The dithiobenzil complexes of palladium and platinum behave similarly. Although bis(dithiobenzil)nickel dissolves in triphenylphosphine at elevated temperature, no defined adduct could be isolated. The palladium and platinum complexes combine readily, forming compounds of composition $M(Ph-CSCSPh)_2 \cdot 2P(C_6H_5)_3$. The compounds are not salt-like, and the phosphines cannot be removed without destruction of the whole complex. The bistriphenylphosphine adduct of $Pt(CH_3CSCSCH_3)_2$ has also been prepared; its n.m.r. spectrum (in CH_2Cl_2 solution) shows in addition to the phenyl protons at 7.21 p.p.m. only one peak of the methyl protons at 1.88 p p.m. relative to TMS.

Reaction with Alkynes. The reaction of bis(dithiobenzil)nickel with alkynes yields thiophene derivatives.[3,9] In view of the improved method of preparation of the complexes this reaction may find use in the synthesis of otherwise difficultly accessible substituted thiophene derivatives. In Table II a number of

Table II. Thiophene Derivatives from the Reaction of Bisdithiodiketone Complexes with Alkynes

Alkyne	Complex (M/R)	Reaction temp., °C.	Thiophene yield, %
$C_6H_5-C_2-C_6H_5$	Ni/C_6H_5	140	78
$RO_2C-C_2-CO_2R$	Ni/C_6H_5	80–100	85
$CH_3-C_2-CH_3$	Ni/C_6H_5	140	71
$CF_3-C_2-CF_3$	Ni/C_6H_5	160	69
$C_6H_5-C_2-C_2-C_6H_5$	Ni/C_6H_5	140	68[a] 70[b]
$C_6H_5-C_2-H$	Ni/C_6H_5	60	42[c]
$CH_3-C_2-CH_3$	Pd/C_6H_5	160	20
$CH_3-C_2-CH_3$	Pt/C_6H_5	160	15
$CF_3-C_2-CF_3$	Ni/CH_3	160	46

^{a} Employing a ratio of complex to alkyne of 1:1, hexaphenyl-bithiophenyl is formed ^{b} At ratio complex to alkyne of 1:4, the product is phenylethynyltriphenylthiophene. ^{c} After distillation; 2,3,4-triphenylthiophene is the only isomer formed.

examples are listed. The reactivity of the alkynes depends on the substituents; among the most reactive were phenylacetylene and acetylene dicarboxylic esters. With the former the reaction already takes place at 60°, but if the reaction mixture is worked up avoiding high temperatures the product is actually triphenyldithiadiene. Similarly, the reaction of bis(dithiodiacetyl)-nickel with 2-butyne produces tetramethyldithiadiene. If the reaction of bis(dithiobenzil)nickel with alkynes is conducted under the mildest conditions possible, the yields would frequently be somewhat less than 50%, suggesting that only one dithiobenzil molecule per complex underwent reaction. Accordingly, the metal-containing residues of such reactions were not nickelous sulfide but a complex $(C_6H_5CSCSC_6H_5)_4Ni_4$ as indicated by analysis. This material is air-stable, forming yellow-brown crystals and may be considered as the tetrameric Ni^{+2} salt of dithiobenzoin. It is also formed by allowing bis(dithiobenzil)nickel to react with metallic nickel or with $Ni(CO)_4$. With alkynes it is relatively inert. Hence, the reaction of the dithiodiketone com-

plexes with acetylene derivatives in the first step consists in the formation of a dithiadiene derivative and the complex fragment Ni(RCSCSR). The latter may either associate to the unreactive tetramer or at elevated temperature react with another alkyne to produce a thiophene and NiS (eq. 2). The corresponding complexes of palladium and platinum are much less reactive (Table II).


$$(2)$$
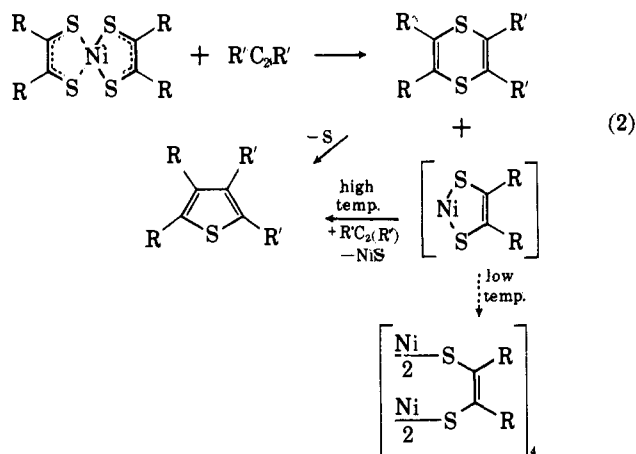
Reaction with Olefins. We have observed that bisdithiobenzil complexes of Ni, Pd, and Pt absorb certain dienes and other unsaturates to form 1:1 adducts. Thus, if butadiene is bubbled through a suspension of bis(dithiobenzil)palladium in CH_2Cl_2 at 20°, yellow-red crystals of composition Pd(Ph-CSCSPh)$_2$·C_4H_6 are isolated. The adduct is sparingly soluble in most solvents, air stable, and decomposes at 165° into butadiene and bis(dithiobenzil)palladium. Similar adducts have been obtained and characterized with 2,3-dimethylbutadiene, isoprene, 1,3-cyclohexadiene, and norbornadiene. Qualitatively, the existence of analogous adducts of 2-chloroprene, 1,3-cycloocta-diene, 1,3,5-cyclooctatriene, cyclooctatetraene, and piperylene was detected. No complex formation occurred with 2,5-dimethyl-2,4-hexadiene, methyl sorbate, muconic ester, acrylonitrile, and several simple olefins. However, the double bond in norbornene is reactive enough to afford an adduct and this shows that conjugation or homoconjugation of the olefin is not essential. Bis(dithiobenzil)nickel also forms complexes of this kind, but these are generally more labile. Bis(dithiobenzil)nickel–norbornadiene, *e.g.*, decomposes at room temperature if exposed to daylight. The nickel complex was found no longer capable of fixing isoprene and butadiene. Bis(dithiobenzil)platinum even forms less stable adducts than the nickel compound. The 2,3-dimethylbutadiene adduct already decomposes at 100°. The possible nature of these adducts will be discussed in a later section.

Electronic Structure and Spectra. In our first report[3] on bis(dithiobenzil)nickel we proposed that it is a square-planar d^8 nickel complex in which the two positive charges of the metal ion are compensated by two electrons occupying a low-lying molecular orbital extending over the whole molecule. This suggestion has later been supported by molecular orbital and group theoretical considerations.[9] The essential feature of the electronic structure lies in the behavior of the pair of

lowest unoccupied ligand π-MO's upon interaction with the central metal. In an arrangement with D_{2h} symmetry the two originally degenerate MO's transform as $2b_{2g}$ and $2b_{1u}$. The former can only interact with the metal d-orbitals of the nd_{zz} or nd_{yz} type, the latter only with the $(n + 1)p_z$ metal orbital. Since the first unoccupied π-MO in the hypothetical α-dithiodiketones is only weakly antibonding,[10] the energetic sequence for the isolated orbitals must be $nd > 2b_{2g}/2b_{1u} > (n + 1)p$. Consequently, the $2b_{1u}$ MO will be stabilized whereas $2b_{2g}$ becomes labilized upon interaction with the metal orbitals. In complexes of the type $M(RCSCSR)_2$ (R = alkyl or aryl, M = Ni, Pd, or Pt) the $2b_{2g}$ MO is most likely the lowest unoccupied level, followed by the occupied $(d_{x^2-y^2})$-type metal orbital.

Early attempts to correlate the electronic spectra with this electronic structure brought encouraging results.[9] In Table III the observed transitions for a series of planar bis complexes of dithiodiketones with Ni, Pd, and Pt are shown. The most characteristic absorptions are ν_1, ν_2, ν_6, and ν_7 which were observed in all cases. ν_3, ν_4, and ν_5 are either less intense or not generally observable. The first transition ν_1 occurs in the ·near-infrared region. On account of its high intensity it was assigned to the first allowed inter-π-transition, $2b_{1u} \rightarrow 2b_{2g}$. It is affected by substituents and hence it must indeed involve molecular orbitals extending over the whole molecule. The second band (ν_2) is of moderate intensity and was initially considered to be the n $\rightarrow$ π transition between the nonbonding electron pairs at the sulfur atoms and the $2b_{2g}$ MO. Owing to their high intensity, ν_6 and ν_7 are inter-π-transitions. No assignments for ν_3, ν_4, and ν_5 are being made in view of the complexity of the spectra. In this region mainly $n_{=s} \rightarrow \pi^*$, and metal–ligand charge-transfer bands are to be expected. A quantitative MO treatment of a representative complex is in progress which will allow more definite assignments of these transitions. If the proposed electronic structure is accepted, the reversible reduction of the complexes to the mono- and dianions must be the occupation of the $2b_{2g}$ MO by one or two electrons, respectively. In the monoanions the $2b_{1u} \rightarrow 2b_{2g}$ transition is still present, albeit shifted somewhat to longer wave lengths and with diminished intensity. The spectrum of the dianion bears no resemblance any longer to that of the uncharged compound. The intense near-infrared transition ν_1 is absent. In the dianions the ligands have lost their chromophoric character; a change of the original structure to complexes containing two dithiolate dianions (II) may be envisaged and it must be conceded that the reduction of the complexes does not change the formal +2 oxidation state of the nickel, palladium, or platinum atoms.

II
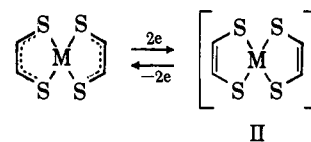
The nature of the complexes may also be made more nearly understood in terms of conventional valence

(10) H. E. Simmons, A. D. West, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962).

Table III. Electronic Transitions in Complexes M(RCSCSR)₂[a]

M	R	Solvent	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
Ni	C₆H₅	CCl₃H	866	602	417	377		316	270
			(4.49)	(3.34)	(3.71)	(4.08)		(4.71)	(4.57)
Ni	p-CH₃C₆H₄	CHCl₃	885	607	450		(340)	320	277
			(4.50)	(3.33)	(3.54)		(4.28)	(4.65)	(4.59)
Ni	p-CH₃OC₆H₄	CHCl₃	925	640	460		330	302	285
			(4.40)	(3.22)	(3.46)		(4.39)	(4.53)	(4.49)
Ni	p-ClC₆H₄	CHCl₃	865	601	450	(380)		320	277
			(4.43)	(3.29)	(3.58)			(4.62)	(4.56)
Ni	CH₃	CHCl₃	774	569	400	370		304	278
			(4.45)	(3.37)	(3.39)	(3.42)		(4.57)	(4.51)
Ni	C₂H₅	CHCl₃	777	569	410	360		307	280
			(4.29)	(3.18)	(3.18)	(3.28)		(4.40)	(4.28)
Ni	n-C₃H₇	CHCl₃	780	572	410	360		309	281
			(4.29)	(3.17)	(3.17)	(3.31)		(4.39)	(4.31)
Ni	CF₃	n-C₅H₁₂	715	553	410			295	230
			(4.09)	(3.28)	(3.30)			(4.39)	(4.31)
Pd	C₆H₅	CHCl₃	885	545	430	364		292	268
			(4.61)	(3.32)	(3.45)	(3.94)		(4.73)	(4.72)
Pt	C₆H₅	CHCl₃	802	529	435	360		303	252
			(4.63)	(3.28)	(3.02)	(3.82)		(4.22)	(4.85)
Pt	CH₃	C₂H₅OH	735	520	410	377	333	289	250
			(4.50)	(3.39)	(2.78)	(2.74)	(3.06)	(3.79)	(4.0)

[a] Wave lengths in mμ; log ε in parentheses.

bond structures. The fact that two metal electrons occupy molecular orbitals extending over the whole complex leads to the proposal of a mesomeric ground state. Resonance between the two mainly contributing limiting structures III may be assumed.


III
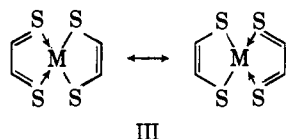
Both the MO and VB description, however, render the previously used nomenclature inadequate. A "bis-(dithiobenzil)nickel" would actually be a Ni(0) complex and should not be planar. Hence, the term "bis-(dithiosemibenzil)nickel" would appear to be more appropriate. It must be pointed out that these views differ from Davison, et al.,[9] who considered at least the planar CF₃-substituted complexes as derivatives of the dianions
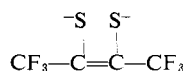
with the metals in the +4 state. The electronic spectrum of Ni(CF₃CSCSCF₃)₂ is very similar to that of alkyl-substituted nickel complexes (Table III), indicating analogous electronic structures. It would also be difficult to see why dithiolate dianions should be capable of stabilizing the +4 valence state of the nickel atom and why the complexes should be so strongly colored. The existence of bisphosphine adducts of the palladium and platinum complexes (IV), on the other hand, suggests that the coordination of the phosphine ligands leads to the promotion of electrons into the 2b₂g orbital. In the electronic spectra of these adducts the intense near-infrared (2b₁ᵤ → 2b₂g) transition is absent as in the spectra of dianionic species. Hence, four metal electrons occupy pre-

dominantly ligand-based MO's in these cases, and the adducts may be regarded as derivatives of Pd(IV) and Pt(IV). The +4 valence state of the latter two metals is much more common than in the case of nickel which may account for the nonexistence of similar stable phosphine adducts of nickel complexes.
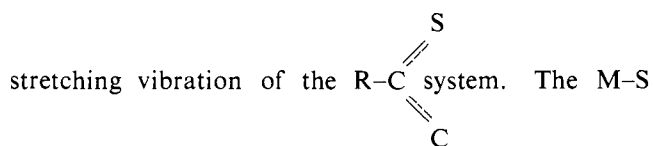

IV
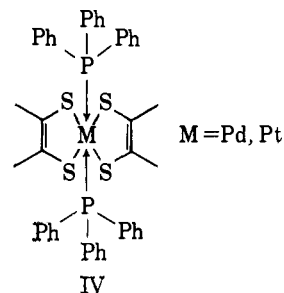
Infrared Spectra. The infrared spectra of complexes M(RCSCSR)₂ are similar to each other. Apart from bands which are obviously due to the presence of phenyl groups, three characteristic absorptions ω_1, ω_2, and ω_3 are observed in the 3000–600-cm.⁻¹ range (Table IV). These are undoubtedly combination bands

Table IV. Characteristic Absorption Bands in the Infrared Region of Complexes M(RCSCSR)₂ in KBr

M	R	ω_1	ω_2	ω_3	ω_4	ω_5
Ni	CH₃	1333	914	558	435	333
Pt	CH₃	1324	908	563	405	<310
Ni	C₆H₅	1359	1136	882	408	354
Pd	C₆H₅	1342	1136	884	401	352
Pt	C₆H₅	1351	1139	877	403	373

and probably coupled to each other. Their rigorous assignment would require a normal coordinate treatment. Qualitatively ω_1 may be assigned to a vibration predominantly consisting of the perturbed C=C

stretch, whereas ω_2 may correspond to that of the perturbed C=S bond. ω_3 appears at 558 cm.$^{-1}$ in bis-(dithiodiacetyl)nickel and at 882 cm.$^{-1}$ in bis(dithiobenzil)nickel. It thus depends rather strongly on the substituents and therefore is tentatively assigned to a

$$\begin{array}{c} S \\ \diagup\!\!\!\!/ \\ R-C \\ \diagdown\!\!\!\!\diagdown \\ C \end{array}$$

stretching vibration of the R–C system. The M–S

stretching bands (ω_4 and ω_5) appear in the region expected (Table IV). No systematic changes were observed in the sequence Ni–Pd–Pt. For the planar bisdithiooxalato dianion, Nakamoto and Fujita[11] report Pt–S stretching frequencies of 440–420 and 320 cm.$^{-1}$, respectively.

In the spectra of dianion salts, ω_2 and ω_3 are missing, but a band probably corresponding to the perturbed C=C stretch occurs at 1481 cm.$^{-1}$. The infrared spectrum of the tetrameric nickel salt of dithiobenzoin, $Ni_4(PhCSCSPh)_4$, is practically identical with that of a dianion salt with $Ni(PhCSCSPh)_2{}^{2-}$ present. The perturbed C—C stretch is assigned to a band at 1474 cm.$^{-1}$. In the CsBr region, however, only one Ni–S stretching vibration is observed at 345 cm.$^{-1}$. In the spectrum of salts containing the $Ni(PhCSCSPh)_2{}^-$ ion, ω_1, ω_2, and ω_3 appear at 1428, 1168, and 869 cm.$^{-1}$, respectively. These shifts with respect to the band positions in the neutral complex suggest a higher C=C double bond character in the monoanions. Thus, there cannot be any doubt that the reduction of the complexes primarily affects the ligands.

Constitution of the Olefin Adducts. The remarkable ability of the complexes to "fix" dienes is evidently a function of both the ligands and the metal. For the adducts the observed (thermal) stability sequence is Pd > Ni > Pt which coincides with the increase of the first excitation energy ($2b_{1u} \rightarrow 2b_{2g}$ transition). The corresponding dithiodiacetyl complexes were not found capable of adding unsaturated hydrocarbons; there the $2b_{1u} \rightarrow 2b_{2g}$ separation is even greater than in the bis(dithiobenzil)platinum complex which already shows little tendency to form adducts itself. The infrared spectra of the adducts show the absence of the characteristic absorptions ω_1, ω_2, and ω_3 and resemble those of dianionic species. In the electronic spectra the intense $2b_{1u} \rightarrow 2b_{2g}$ transition is completely absent. This indicates that the adducts are not simple transition metal–π–complexes of the olefins but that the ligands are involved as well. The extreme lability of some of the adducts makes it unlikely, however, that new C—C bonds have been formed and this suggests that the olefins are bonded *via* labile C—S bonds. In the C=C region, no bands characteristic of isolated C=C bonds are detected but in all cases a new band of medium intensity is observed around 1540 cm.$^{-1}$ which may be tentatively assigned to the C=C stretch of the bonded olefin. The low frequency of this band suggests interaction of the double bond with the metal and leads to the proposal of structure V for the adducts.

(11) K. Nakamoto and J. Fujita, cited in K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 214.

In the norbornadiene adducts the infrared spectra do not show the characteristic nortricyclene absorption at 800 cm.$^{-1}$, but a band at 1538 cm.$^{-1}$ in the nickel and at 1515 cm.$^{-1}$ in the palladium complex adduct may be assigned to the remaining C=C bond, supporting structure VI. In the corresponding palladium complex with norbornene the band at 1515 cm.$^{-1}$ is absent (structure VII). Limited solubility of the complexes prevented n.m.r. measurements. Final elucidation of the structure of these interesting olefin adducts therefore will require X-ray analysis.

V   VI

VII
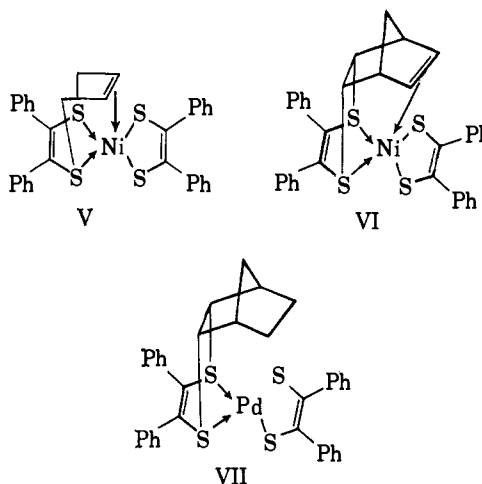
Experimental

Preparation of Complexes. Bis(dithiobenzil)nickel. Benzoin (100 g.) is refluxed with 150 g. of P_4S_{10} in 700 cc. of dioxane for 2 hr. During this time the thiophosphoric esters of dithiobenzoin are formed and hydrogen sulfide is evolved. To the cooled and filtered reaction solution 50 g. of $NiCl_2 \cdot 6H_2O$ in 200 cc. of water are added and the reaction mixture is heated on a steam bath for 2 hr. Black crystals of the complex are formed and are collected by filtering the cooled solution. Purification is effected by extraction with boiling toluene or dichloromethane, yield 45 g. (35% based on benzoin), m.p. 292° dec.

Anal. Calcd. for $C_{28}H_{20}S_4Ni$: C, 61.7; H, 3.7; S, 23.6; Ni, 10.8. Found: C, 61.7; H, 3.7; S, 23.5; Ni, 10.7.

Bis(dithiobenzil)palladium and -platinum. The complexes of these metals are obtained as described above. However, it is advantageous to employ a large excess of dithiobenzoin ester solution in order to avoid loss of the metals. For 100 g. of benzoin, 6 g. of K_2PdCl_4 and 8 g. of K_2PtCl_4 were used, yielding the complexes in practically quantitative amounts, based on the metals.

Anal. Calcd. for $C_{28}H_{20}S_4Pd$ (m.p. 254° dec.): C, 56.8; H, 3.4; S, 21.6; Pd, 18.2. Found: C, 56.8; H, 3.7; S, 21.5; Pd, 18.2. Calcd. for $C_{28}H_{20}S_4Pt$ (m.p. 310°): C, 49.4; H, 2.94. Found: C, 50.1; H, 3.1.

Complexes of Substituted Dithiobenzils and of Alkyl-α-dithiones. The complexes mentioned in this paper were obtained by procedures similar to that described for bis(dithiobenzil)nickel, using substituted benzoins and acyloins as starting materials.[4] Results are given in Table V.

Reaction of Bisdithiobenzil Complexes with Hydrazines. To a suspension of 2 g. of the bisdithiobenzil complexes of nickel, palladium, or platinum, respectively, in 50 cc. of absolute ethanol, 5 cc. of anhydrous hydrazine was added. The reaction mixture was gently warmed on a steam bath for about 10 min. Upon cooling, orange crystals precipitated which were filtered off and washed with 3 cc. of ethanol in an inert atmosphere and dried at 60° *in vacuo.*

Reaction with Triphenylphosphine. Bis(dithiobenzil)-palladium (1 g.) was suspended in a solution of 5 g. of triphenylphosphine in 20 cc. of toluene at room temperature. After 2 min. the color changed to blue and after 30 min. filtration afforded blue crystals of the adduct, m.p. 213–214° dec.

Anal. Calcd. for $C_{64}H_{50}S_4P_2Pd$: C, 68.8; H, 4.5; S, 11.5; P, 5.5. Found: C, 67.8; H, 4.8; S, 10.5; P, 6.1.

Table V. Prepared Metal Complexes of Substituted Dithiobenzils and of Alkyl-α-dithiones

M	R	M.p., °C.	Yield,[a] %	Calcd. C	Calcd. H	Found C	Found H
Ni	p-CH₃C₆H₄	337 dec.	37	64.2	4.7	64.2	4.9
Ni	p-CH₃OC₆H₄	329 dec.	34	58.0	4.25	56.9	4.2
Ni	p-ClC₆H₄	335 dec.	38	49.3	2.3	50.0	2.8
Ni	CH₃	256 dec.	27	32.6	4.1	32.9	3.7
Ni	C₂H₅	112	22	41.1	5.7	41.5	5.7
Pt	CH₃	>360 dec.	97[b]	22.2	2.8	21.9	2.8

[a] Based on employed acyloin. [b] Based on platinum.

Anal. Calcd. for $C_{28}H_{38}N_8S_4Ni$ (m.p. 140° dec.): C, 49.8; H, 5.7; N, 16.6. Found: C, 49.6; H, 5.7; N, 16.4. Calcd. for $C_{28}H_{38}N_8S_4Pd$ (m.p. 132° dec.): C, 46.6; H, 5.3; N, 15.5; S, 17.7. Found: C, 46.7; H, 6.2; N, 15.5; S, 17.0. Calcd. for $C_{28}H_{38}N_8$-

Bis(dithiobenzil)platinum (1 g.) suspended in 20 cc. of a solution of 5 g. of triphenylphosphine in *p*-xylene was refluxed for 5 hr. After cooling, small amounts of unreacted starting complex could be recovered by filtration. The yellow filtrate was evaporated under

Table VI. Thiophene Derivatives from Reaction with Alkynes

R	M	Alkyne	Reaction temp., °C.	Time, hr.	Yield, %	M.p., °C.	Identification
C₆H₅	Ni	C₆H₅C₂C₆H₅	140	24	78	184	M.p., m.m.p., infrared spectrum
C₆H₅	Ni	CH₃O₂CC₂CO₂CH₃	80–100	24	84	92	*Anal.* Calcd.: C, 68.2; H, 4.57 Found: C, 67.7; H, 4.6
C₆H₅	Ni	C₂H₅O₂CC₂CO₂C₂H₅	80–100	24	82	85	*Anal.* Calcd.: C, 69.4; H, 5.3 Found: C, 69.5; H, 5.3
C₆H₅	Ni	CH₃C₂CH₃	140	24	71	103	*Anal.* Calcd.: C, 81.8; H, 6.1 Found: C, 81.5; H, 6.2
C₆H₅	Ni	C₆H₅C₂–C₂C₆H₅ (1:1)	140	24	76	284	*Anal.* Calcd.[a]: C, 85.0; H. 4.9 Found: C, 84.8; H, 4.7
C₆H₅	Ni	C₆H₅C₂–C₂C₆H₅ (1:4)	140	24	79	230	*Anal.* Calcd.[b]: C, 87.4; H, 4.9 Found: C, 87.1; H, 4.8
C₆H₅	Ni	C₆H₅C₂H	60	15 min.	42	216[c]	*Anal.* Calcd.: C, 84.6; H, 5.2 Found: C, 84.3; H, 5.0
C₆H₅	Ni	CF₃C₂CF₃	140	24	69	78	*Anal.* Calcd.: C, 58.0; H, 2.7; S, 8.6 Found: C, 57.9; H. 2.7; S, 9.3
C₆H₅	Pd	CH₃C₂CH₃	140	24	20	103	M.p., m.m.p., infrared spectrum
C₆H₅	Pt	CH₃C₂CH₃	140	24	15	103	M.p., m.m.p., infrared spectrum
CH₃	Ni	C₆H₅C₂C₆H₅	140	24	45	103	M.p., m.m.p., infrared spectrum
CH₃	Ni	CF₃C₂CF₃	160	24	46	Liq. b.p. 168° (758 mm.)	*Anal.* Calcd.: C, 38.7; H. 2.4 Found: C, 38.6; H, 2.5

[a] Calculated for hexaphenylbithienyl. Only one isomer is formed, probably the 2,2',3,3',4,4'-hexaphenylbithienyl-5,5'. [b] Probably 2-phenylethinyl-3,4,5-triphenylthiophene. [c] The melting point of 2,3,5-triphenylthiophene was checked by independent synthesis.

S_4Pt (m.p. 146° dec.): C, 41.2; H, 4.7; N, 13.8; S, 15.8. Found: C, 41.1; H, 4.7; N, 14.0; S, 15.2.

The analogous reaction of bis(dithiobenzil)nickel with 1,2-dimethylhydrazine yielded orange crystals, m.p. 170°.

Anal. Calcd. for $C_{32}H_{38}N_4S_4Ni$: C, 57.5; H, 6.0; N, 8.4. Found: C, 55.8; H, 6.1; N, 8.7.

reduced pressure. The residue upon addition of acetone converted into yellow crystals. Recrystallization from a dichloromethane–*n*-hexane mixture yields the complex, m.p. 310° dec.

Anal. Calcd. for $C_{64}H_{50}S_4P_2Pt$: C, 63.8; H, 4.2; S, 10.6; P, 5.1. Found: C, 63.5; H, 4.4; S, 9.0; P, 5.4.

The adduct of $Pt(CH_3CSCSCH_3)_2$ with triphenyl-

Table VII. Olefin Adducts of Bisdithiobenzil Complexes of Ni, Pd, and Pt

M	Olefin	Decompn. point, °C.	Analyses, Calcd. (Found)			
			C	H	S	M
Ni	2,3-Dimethyl-1,3-butadiene	100	65.3	4.8	20.5	9.8
			(65.0)	(5.2)	(20.0)	(9.7)
Ni	Norbornadiene	165	66.1	4.4	20.2	9.6
			(65.0)	(4.4)	(19.8)	(9.2)
Pd	Butadiene	165	59.4	4.0	19.8	
			(59.1)	(4.1)	(20.1)	
Pd	Isoprene	159	60.0	4.2	19.4	
			(59.6)	(4.4)	(18.2)	
Pd	2,3-Dimethyl-1,3-butadiene	200	60.7	4.4	19.0	16.4
			(60.9)	(4.7)	(18.0)	(15.8)
Pd	1,3-Cyclohexadiene	110	60.8	4.2	19.1	
			(60.9)	(4.4)	(17.2)	
Pd	Norbornadiene	252	61.4	4.1	18.7	
			(60.4)	(4.2)	(16.1)	
Pt	2,3-Dimethyl-1,3-butadiene	100	53.3	3.9	16.8	
			(53.3)	(4.0)	(16.7)	
Pd	Norbornene	236	61.3	4.4		
			(61.5)	(4.2)		

phosphine was obtained similarly and was recrystallized from hot benzene, yielding yellow crystals, m.p. (darkening at 280°) 306° dec.

Anal. Calcd. for $C_{44}H_{45}S_4P_2Pt$: C, 55.3; H, 4.4; P, 6.5; Pt, 20.2. Found: C, 56.0; H, 4.3; P, 6.9; Pt, 20.0.

The n.m.r. spectrum of this compound was recorded in CH_2Cl_2. The phenyl protons appear at 7.21 p.p.m., the single peak of the methyl protons at 1.88 p.p.m. relative to TMS.

Reaction with Alkynes. Weighed amounts of the complexes were allowed to react with an excess of the alkyne except in the case of diphenyldiacetylene where stoichiometric amounts also were employed. The solvent was benzene and the reactions were performed in sealed tubes at conditions indicated in Table VI. The work-up procedure consisted in evaporation of the filtered reaction solutions and subsequent vacuum distillation of the residue.

Isolation of Dithiudienes. When bis(dithiobenzil)-nickel was allowed to react with phenylacetylene at 60° and the reaction products were worked up by chromatography on silica gel, using petroleum ether as solvent, triphenyldithiadine was obtained, m.p. 115°.

Anal. Calcd. for $C_{22}H_{16}S_2$: C, 76.6; H, 4.69. Found: C, 76.5; H, 4.6.

Thermal decomposition produced sulfur and triphenylthiophene, m.p. 216°. Reaction of bis(dithiodiacetyl)nickel with 2-butyne in benzene at 140° for 24 hr. afforded 48% of product, m.p. 85–86°, analyzing for tetramethyldithiadiene.

Anal. Calcd. for $C_8H_{12}S_2$: C, 55.8; H, 7.0; mol. wt., 172. Found: C, 55.8; H, 7.0; mol. wt., 192.

Preparation of the Nickel Salt of Dithiobenzoin. Further elution of the chromatography column of the above experiment with benzene yielded brown crystals, m.p. >360°.

Anal. Calcd. for $(C_{28}H_{20}S_4Ni_2)_2$: C, 55.85; H, 3.34; Ni, 19.5; mol. wt., 1204. Found: C, 55.5; H, 3.3; Ni, 19.2; mol. wt., 1260.

The complex is not affected by air and is insoluble in water. With warm hydrazine it forms metallic nickel and the dianion of bis(dithiobenzil)nickel. The same complex is also obtained by allowing bis(dithiobenzil)-nickel to react with $Ni(CO)_4$ or nickel powder.

Reaction with Olefins. In most cases suspensions of the dithiobenzil complexes in the pure olefins were stirred at room temperature until the color of the original complexes changed into yellow-brown. The olefin adducts were filtered off and dried *in vacuo* at room temperature. In the case of butadiene the olefin was simply bubbled through a suspension of the palladium complex in acetone at room temperature. Under similar and varied conditions (heating under pressure) no complex formation of butadiene with the complexes of nickel and platinum was observed.

The thermal decomposition of the complexes was performed with the palladium complexes of norbornadiene, dimethylbutadiene, and the nickel complex of norbornadiene and dimethylbutadiene. The infrared spectra of the volatile olefins were identical with those of authentic samples. The nonvolatile residues consisted of the unchanged complexes except in the case of the palladium–norbornadiene adduct where the thermal decomposition of the complex took place as well.