Sulfur-Containing Metal Complexes. 12.[1] Reactions of α-Thio Carbanions with Carbene Complexes of the Type $[M(CO)_5\{O(alkyl)Ar\}]$ and with the Carbyne $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2(CPh)][BCl_4]$

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A series of pentacarbonyl thiocarbene complexes of chromium and tungsten such as $[M(CO)_5\{C(Ph)SCH{=}C(OR^1)Ph\}]$ [M = Cr, R^1 = Me (**8**); M = W, R^1 = Et (**9**)] can be prepared by reaction of Fischer-type carbene complexes with lithiothioacetals or derivatives thereof. The products that form indicate that the synthesis involves double nucleophilic attack of each lithio compound on two carbene centers. The same class of carbenes produces a group of structurally different thione complexes when it reacts with $LiC({=}S)NMe_2$ or $LiC({=}S)NPh_2$. Lithium diisopropylamide plays a decisive role in some of these transformations. Two of the resulting complexes, $[Cr(CO)_5\{S{=}C(C_6H_4Ph\text{-}o)CH{=}C(Me)NHCHMe_2\}]$ (**18**) and $[W(CO)_5\{S{=}C(NPh_2)CH_2NPh_2\}]$ (**20**), have been identified by X-ray crystallography. Reaction of the carbyne complex $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2CPh][BF_4]$ with $LiC({=}S)NMe_2$ affords the compound $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2\{S{=}C(Ph)SCH_2C({=}S)NMe_2\}]$ (**23**) which has been completely characterized by X-ray crystallography. Treatment of the Fischer carbene $[Cr(CO)_5\{C(OEt)Ph\}]$ with $Li\overline{C{=}N(C_6H_4)S}\text{-}o$ furnishes upon subsequent alkylation a Lappert-type carbene complex, $[Cr(CO)_5\overline{CN(Et)(C_6H_4)S}\text{-}o]$ (**26**). It can be prepared in higher yield by trapping of the free carbene in solution. The structures of the new complexes and the mechanisms of their formation are discussed. Crystal data for **18**: $CrC_{24}H_{21}NO_5S$, M_r = 487.49, monoclinic, space group $C2/c$, a = 13.76 (1) Å, b = 20.14 (1) Å, c = 17.92 (1) Å, β = 98.3 (1)°, U = 4916 Å^3, Z = 8, D_{calcd} = 1.32 g cm^{-3}. Crystal data for **20**: $WC_{31}H_{22}N_2O_5S$, M_r = 718.41, triclinic, space group $P\bar{1}$, a = 14.20 (2) Å, b = 10.48 (2) Å, c = 9.92 (2) Å, α = 97.6 (1)°, β = 97.2 (1), γ = 93.8 (1)°, U = 1446 Å^3, Z = 2, D_{calcd} = 1.65 g cm^{-3}. Crystal data for **23**: $MnC_{19}H_{20}NO_2S_3$, M_r = 445.59, triclinic, space group $P\bar{1}$, a = 14.62 (1) Å, b = 11.56 (1) Å, c = 6.51 (1) Å, α = 91.6 (1)°, β = 96.7 (1)°, γ = 108.8 (1)°, U = 1032 Å^3, Z = 2, D_{calcd} = 1.43 g cm^{-3}.

Introduction

Metalated thioacetals, such as $Li\overline{CHS(CH_2)_3S}$, react with group 6 metal carbonyl complexes to afford, by formal carbonyl insertion, heterometallocyclic carbene thioether chelates.[2] Reactions with amines,[3] phosphines,[4] and simple organolithium compound[5] have established the electrophilicity of the carbene carbon atom in Fischer-type carbene complexes $[M(CO)_5\{C(OR^1)R^2\}]$ (M = Cr, W; R^1 = Me, Et; R^2 = Me, Ph). The latter class of compounds should, therefore, also be susceptible to attack by lithiothioacetals, and such reactions were investigated. The conversions with two other α-thio types of carbanions $LiC({=}S)NR_2$ (R = Me, Ph) and $Li\overline{C{=}N(C_6H_4)S}\text{-}o$, which have both recently been used in synthetic organic reactions,[6,7] were also examined. Since an electrophilic site in carbyne complexes is likewise situated on the metal-bonded carbyne carbon atom, carbon–carbon bond formation is also to be expected between such compounds and carbanions.[8] The cation $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2CPh]^+$ was thus also included in this study.

We have reported before that unstable carbenes containing no heteroatoms form more stable compounds by formal S insertion into the metal–carbene bond.[9] In the presence of $LiC({=}S)NR_2$ (R = Me, Ph), similar reactions occurred.

We report in this paper the major products obtained from the title reaction types. They include thiocarbene complexes, thione derivatives, and Lappert-type carbene complexes. Plausible mechanisms for some of the con-

Scheme I

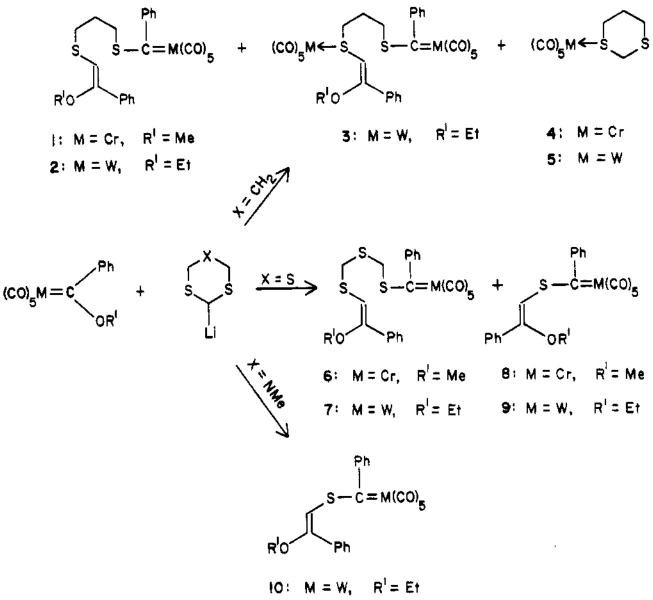

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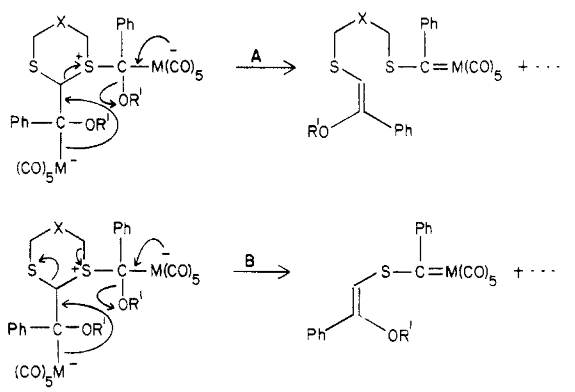
Table I. ^{13}C NMR Spectroscopic Results (-30 °C) of 1, 2, 3, and 8

complex	δ ($CDCl_3$, relative to Me_4Si)
1	362.0 (C-carbene), 228.8 (CO trans to C-carbene), 215.6 (CO cis to C-carbene)
2	327.0 (C-carbene), 208.7 (CO trans to C-carbene), 196.9 (CO cis to C-carbene)
3	328.6 (C-carbene), 209.3 (CO trans to C-carbene), 197.4, 197.2 (CO cis to C-carbene)
4	345.7 (C-carbene), 228.6 (CO trans to C-carbene), 215.9 (CO cis to C-carbene)

Scheme II

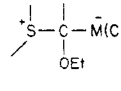


versions are proposed and discussed. The results of three crystal structure determinations are presented. A portion of this work appeared in a preliminary report.[10]

Results and Discussion

Reactions of Metalated Thioacetals and Derivatives Thereof with Carbene Complexes. Reaction of Fischer-type carbene complexes with the compounds $LiCHSCH_2XCH_2S$ (X = CH_2, S, NMe) produced ionic compounds (thin-layer chromatography) which upon treatment with solid SiO_2 yielded a series of compounds 1–10 (Scheme I) of which the thiocarbene complexes are new. During the synthesis involving 2-lithio-1,3,5-trithiane and 2-lithio-4,5-dihydro-5-methyl-1,3,5-dithiazine, additional neutral products were also formed but their yields were too low for isolation. The composition of the compounds was determined by elemental analysis. Only 8, 9, and 10 gave molecular ions in their mass spectra. ^{13}C NMR measurements of 1, 2, 3, and 8 (Table I) established the presence of a carbene carbon atom in these complexes. Crystal structures of 6 and 8 have been determined,[10] and the proposed structures for the other unknown compounds were based on correspondence of their spectroscopic data with that of the known compounds. The two thioether complexes 4 and 5 have been described before.[2]

From the composition of the major products, it follows that the reactant carbanions have displayed two centers of reactivity toward the carbene complexes, i.e., one located at the negatively charged carbon atom and the other on a sulfur atom. The nucleophilicity of the latter atom is enhanced by the neighboring negative charge, since apart from substitution,[11] no other reaction between neutral sulfides and carbene complexes has been found. The interaction at the sulfur atom has to involve a hitherto unknown type of sulfur ylide complex



of which phosphorus analogues have previously been fully characterized.[12] Direct supportive evidence for such a postulate has been obtained from the product formed from $LiCH(SPh)_2$ and $[Cr(CO)_5\{C(OMe)Ph\}]$. At −60 °C in ether a yellow, extremely thermolabile compound, precipitated. It decomposed back into the red carbene complex above −20 °C, but the C, H, and Cr elemental analyses agreed within 0.4% with the calculated values for the adduct $[Cr(CO)_5\{C(OMe)Ph\}\cdot PhSCHLiSPh\cdot 2Et_2O]$. The neutral phosphine ylides referred to above decompose similarly at room temperature.

The rare ring-opening reactions, which occur under extremely mild reaction conditions, can be explained in terms of (i) initial adduct formation which involves both active sites of the carbanion and (ii) rearrangement on subsequent acidification. Two modes of bond breaking (A and B) can be envisioned (Scheme II), both of which are probably initiated by the loss of an OR^1 group on acidification with SiO_2. In the dominant route for 2-lithio-1,3-dithiane (A) the charge on the sulfonium ion is neutralized by β-elimination of the $M(CO)_5$ group. The deprotonated *sym*-trithiane also reacts in this way, but the major product is formed, as with $LiCHSCH_2NMeCH_2S$, by a double C–S bond cleavage which follows the β-elimination affording a much simpler thiovinyl derivative (route B). The $W(CO)_5$ moiety can be trapped during the reaction with litiated 1,3-dithiane affording compound 3 (Scheme I). It is not clear why different isomers of the same compound (9 and 10) have been effected by reaction with the two different thioacetal derivatives, and this result is being investigated. Apart from the situation in 10 in which it occurs cis to the nearest sulfur atom, the phenyl group is always situated trans to this sulfur.

Caserio and co-workers[13] have established that thioacetals and thioketals can be activated by methylthiolation. We have now shown that a two-center interaction with carbene complexes may be followed upon subsequent acidification by a cleavage of a carbon–sulfur bond of the cyclic thioacetal function. In *derivatives* of thioacetals two additional C–S bonds are broken under similar reaction conditions.

Reactions of $LiC(=S)NR_2$ (R = Me, Ph) with Carbenes of the Type $[M(CO)_5\{C(OEt)Ar\}]$ (Ar = Ph, PhC_6H_4). The different carbenes used, and analytically pure products isolated from these reactions after acidification and column chromatography, are summarized in Scheme III. When the experiment was first carried out, impure [(ethoxyphenyl)carbene]chromium complex 11 was reacted with excess $LiC(=S)NMe_2$, prepared from dimethylformamide and lithium diisopropylamide (LDA, −100 °C, tetrahydrofuran).[6] Upon acidification with acetic acid, the products 14, 16, 17, and 18 were formed. Compound 14 is a substitution product. It has been used before to synthesize trithiocarbonate and triselenocarbonate complexes of chromium.[9] Elucidation of the structures of 17 and 18 indicated that the LiPh solution used in the preparation of the carbene complexes contained some

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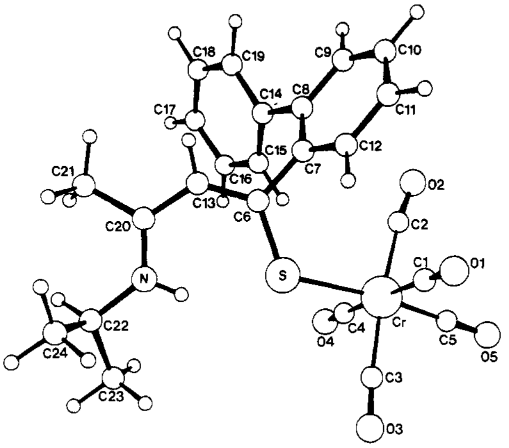

Figure 1. Structure of $[Cr(CO)_5\{S{=}C(C_6H_4Ph\text{-}o)CHC(Me)NHCHMe_2\}]$ showing the atom labeling scheme.

LiC_6H_4Ph. This was confirmed by the isolation of crystalline biphenyl after treatment of the reactant solution with H_2O. In subsequent experiments, as described in Experimental Section, and below, the carbene complexes employed were meticulously purified by column chromatography before use. The new, very stable carbene complex $[Cr(CO)_5\{C(OEt)C_6H_4Ph\text{-}o\}]$ (**12**) was also prepared (70%) in the usual way from LiC_6H_4Ph and $[Cr(CO)_6]$ and was fully characterized. Compound **18** was prepared in 8% yield from this complex. Except for **15** and **20** which decomposed in the mass spectrometer, all the other compounds gave molecular ions.

Alkoxycarbene complexes react with LiPh to produce, after subsequent acidification, a diphenylcarbene complex.[14] With group 6 metals and alkyllithium reactants, the products are very unstable at room temperature. In the formation of compound **16**, the intermediately formed unstable carbene complex $[Cr(CO)_5\{C(Ph)C({=}S)NMe_2\}]$ has presumably been converted into a more stable thione complex by sulfur insertion into the metal–carbene bond. The latter type of reaction under mild reaction conditions has been noted by us before,[9] and Fischer has studied the mechanism of a sulfur insertion reaction by using isothiocyanides as source of sulfur.[15] Similar conversions as those applicable to the formation of **16** did not occur when the tungsten alkoxycarbene complex $[W(CO)_5\{C(OEt)Ph\}]$ (**13**) or the compound $[Cr(CO)_5\{C(OEt)C_6H_4Ph\text{-}o\}]$ (**12**) were used. Two clearly separated singlets at τ 6.40 and 6.81 assigned to the methyl groups in the ^1H NMR spectrum of **16** indicated appreciable double-bond character in the N–C bond neighboring the uncoordinated sulfur atom. Infrared measurements in the ν(CO) region and the consecutive loss of five carbonyl groups from the molecular ion in the mass spectrum established the compound as a monosubstituted carbonyl complex. The infrared spectrum exhibits a shoulder on the lowest frequency band that has previously been found for pentacarbonyl thioether complexes of chromium[2] and which is also a feature of all the pentacarbonyl thione complexes we have prepared up to now.

It was not possible to draw conclusive evidence regarding the structures of compounds **17** and **18** from their respective elemental analyses and rather similar IR and ^1H NMR spectra. Finally, an X-ray structure determination of 1 provided the structure and evidence that (i) during the formation of **17** and **18** LDA had reacted with the carbene in a hitherto unknown manner in which CH acidity was shown at the saturated carbon atom β to the nitrogen atom and (ii) once again (see above), the formed non-heteroatom-containing carbene complex had been converted into a more stable thione complex by formal sulfur insertion. The structure of **18** is shown in Figure 1 and Table II contains the final fractional atomic coordinates while selected bond distances and angles are summarized in Tables III and IV.

Table II. Final Fractional Atomic Coordinates ($\times 10^4$) and Their Esds for $[Cr(CO)_5\{SC(C_6H_4Ph\text{-}o)CHCMeNHCHMe_2\}]$ (18)[a]

atom	x	y	z
Cr	2624 (0)	1677 (0)	2211 (0)
S	3766 (1)	1350 (1)	1336 (1)
O(1)	3433 (3)	653 (2)	3383 (2)
O(2)	813 (2)	849 (2)	1668 (2)
O(3)	4177 (2)	2618 (2)	2963 (2)
O(4)	1795 (3)	2729 (2)	1105 (3)
O(5)	1365 (3)	2222 (2)	3281 (2)
C(1)	3131 (3)	1024 (2)	2931 (2)
C(2)	1525 (3)	1129 (2)	1840 (2)
C(3)	3627 (3)	2258 (2)	2656 (2)
C(4)	2128 (3)	2331 (2)	1515 (3)
C(5)	1865 (4)	2012 (2)	2866 (3)
C(6)	3465 (2)	694 (2)	740 (2)
C(7)	2767 (3)	182 (2)	943 (2)
C(8)	1913 (3)	0 (2)	458 (2)
C(9)	1344 (3)	−517 (2)	675 (2)
C(10)	1606 (4)	−856 (2)	1339 (3)
C(11)	2450 (3)	−676 (2)	1818 (2)
C(12)	3017 (3)	−162 (2)	1618 (2)
C(13)	3847 (3)	592 (2)	86 (2)
C(14)	1588 (2)	356 (2)	−263 (2)
C(15)	1521 (3)	1038 (2)	−299 (2)
C(16)	1222 (3)	1361 (2)	−974 (2)
C(17)	990 (3)	995 (3)	−1624 (3)
C(18)	1043 (3)	312 (3)	−1598 (3)
C(19)	1333 (3)	−8 (2)	−920 (2)
C(20)	4480 (3)	986 (2)	−281 (2)
N	4920 (2)	1517 (2)	30 (2)
C(21)	4644 (3)	788 (2)	−1061 (2)
C(22)	5601 (3)	1957 (2)	−298 (2)
C(23)	5508 (3)	2651 (2)	−6 (2)
C(24)	6649 (3)	1687 (2)	−103 (3)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure.

Table III. Interatomic Distances (Å) with Esds for $[Cr(CO)_5\{SC(C_6H_4Ph)CHCMeNHCHMe_2\}]$ (18)

Cr–S	2.466 (1)	C(11)–C(12)	1.375 (6)
Cr–C(1)	1.902 (4)	C(7)–C(12)	1.395 (5)
Cr–C(2)	1.913 (4)	C(8)–C(14)	1.489 (5)
Cr–C(3)	1.894 (4)	C(14)–C(15)	1.378 (6)
Cr–C(4)	1.874 (5)	C(15)–C(16)	1.384 (6)
Cr–C(5)	1.810 (5)	C(16)–C(17)	1.377 (6)
C(1)–O(1)	1.137 (5)	C(17)–C(18)	1.376 (8)
C(2)–O(2)	1.135 (6)	C(18)–C(19)	1.383 (6)
C(3)–O(3)	1.133 (5)	C(14)–C(19)	1.389 (6)
C(4)–O(4)	1.138 (6)	C(6)–C(13)	1.369 (5)
C(5)–O(5)	1.164 (7)	C(13)–C(20)	1.412 (5)
S–C(6)	1.712 (3)	C(20)–C(21)	1.502 (5)
C(6)–C(7)	1.490 (5)	N–C(20)	1.313 (5)
C(7)–C(8)	1.406 (5)	N–C(22)	1.475 (5)
C(8)–C(9)	1.394 (5)	C(22)–C(23)	1.504 (5)
C(9)–C(10)	1.374 (6)	C(22)–C(24)	1.533 (5)
C(10)–C(11)	1.390 (6)		

The interatomic distances and angles around the octahedrally coordinated chromium atom compare well with those previously determined for the complex $[Cr(CO)_5(SCMe_2)]$.[16] The weak trans influence of the thione in the

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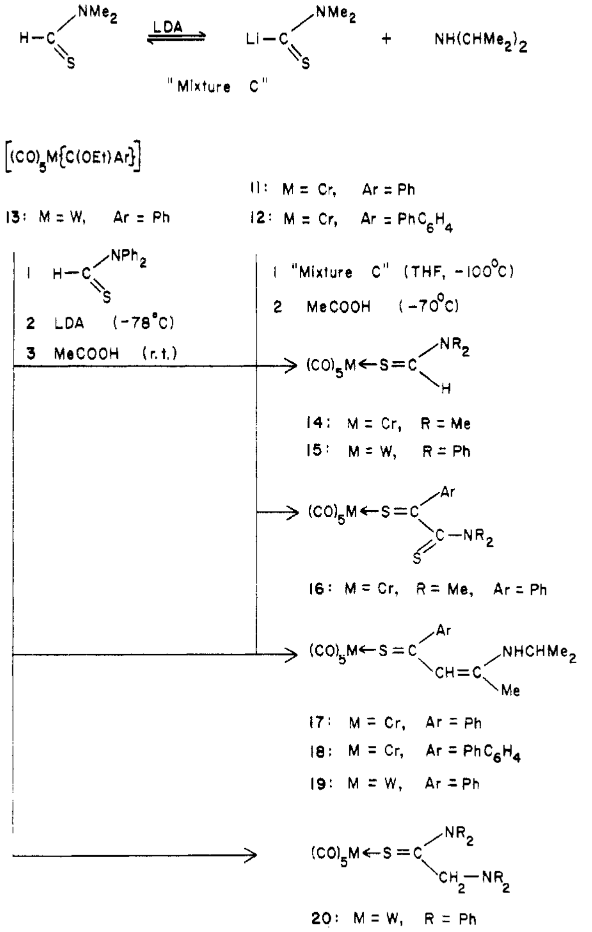
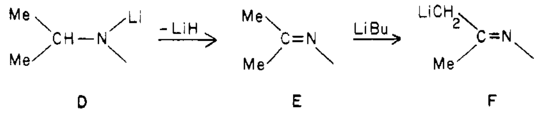
Table IV. Bond Angles (deg) with Esds for [Cr(CO)$_5${SC(C$_6$H$_4$Ph)CHCMeNHCHMe$_2$}] (18)

C(1)-Cr-S	92.3 (2)	O(2)-C(2)-Cr	172.0 (4)	C(11)-C(12)-C(7)	121.5 (3)
C(2)-Cr-S	99.7 (1)	O(3)-C(3)-Cr	174.4 (4)	C(20)-C(13)-C(6)	131.0 (3)
C(2)-Cr-C(1)	91.8 (2)	O(4)-C(4)-Cr	177.4 (5)	C(15)-C(14)-C(8)	121.9 (3)
C(3)-Cr-S	86.6 (1)	O(5)-C(5)-Cr	179.0 (4)	C(19)-C(14)-C(8)	119.3 (3)
C(3)-Cr-C(1)	88.1 (2)	C(7)-C(6)-S	119.2 (3)	C(19)-C(14)-C(15)	118.7 (4)
C(3)-Cr-C(2)	173.7 (2)	C(13)-C(6)-S	124.3 (3)	C(16)-C(15)-C(14)	121.3 (4)
C(4)-Cr-S	88.2 (2)	C(13)-C(6)-C(7)	116.5 (3)	C(17)-C(16)-C(15)	119.4 (4)
C(4)-Cr-C(1)	179.1 (2)	C(8)-C(7)-C(6)	122.7 (3)	C(18)-C(17)-C(16)	120.2 (4)
C(4)-Cr-C(2)	88.8 (2)	C(12)-C(7)-C(6)	118.0 (3)	C(18)-C(19)-C(14)	120.2 (4)
C(4)-Cr-C(3)	91.2 (2)	C(12)-C(7)-C(8)	119.2 (3)	N-C(20)-C(13)	122.4 (4)
C(5)-Cr-S	173.1 (2)	C(9)-C(8)-C(7)	118.3 (3)	C(21)-C(20)-C(13)	118.1 (3)
C(5)-Cr-C(1)	90.4 (2)	C(14)-C(8)-C(7)	122.1 (3)	C(21)-C(20)-N	119.5 (3)
C(5)-Cr-C(2)	86.5 (2)	C(14)-C(8)-C(9)	119.5 (3)	C(22)-N-C(20)	126.8 (3)
C(5)-Cr-C(3)	87.2 (2)	C(10)-C(9)-C(8)	121.8 (4)	C(23)-C(22)-N	109.2 (3)
C(5)-Cr-C(4)	89.0 (2)	C(11)-C(10)-C(9)	119.8 (4)	C(24)-C(22)-C(23)	112.0 (3)
C(6)-S-Cr	119.0 (1)	C(12)-C(11)-C(10)	119.4 (4)		
O(1)-C(1)-Cr	177.1 (4)				

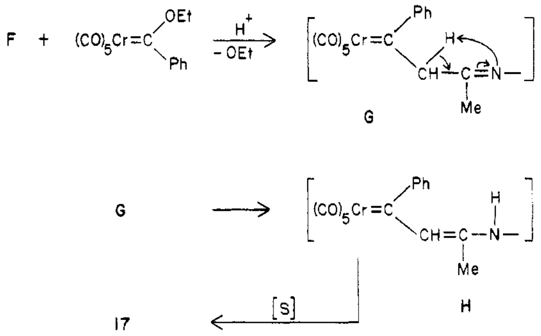
Scheme III



Scheme IV



Scheme V



present compound is apparent in the short Cr–C(trans) bond length of 1.810 (5) Å compared to an average of 1.896 (4) Å for the remaining Cr–C distances. The Cr–S distance [2.466 (1) Å] is 0.089 Å longer than the value for [Cr(CO)$_5$(SCMe$_2$)] while the C=S separation of 1.712 (3) Å compares with 1.618 (8) Å. The dihedral angle between the aromatic rings is 50.5°. The following dihedral angles have been reported for 4-acetyl-2′-X-biphenyl, X = Cl, 49.3°,[17] X = NO$_2$, 50.0°,[18] and X = F, 50.4°.[19] The existence of an N–H···S hydrogen bond in the complex is apparent when comparing the N–S and H···S distances of respectively 3.03 and 2.27 Å with the two larger corresponding van der Waals distances (3.35 and 3.00 Å).[20] The two carbon bonds C(13)–C(6) [1.369 (5) Å] and C(13)–C(20) [1.412 (5) Å] are nearly equal and significantly shorter than the C(6)–C(7) single bond distance of 1.490 (5) Å. This result, the relatively short C(20)–N distance [1.313 (5) Å compared to 1.475 (5) Å for C(22)–N], and the relatively long C=S bond length are consistent with delocalized π bonding between the atoms in the S–C(6)–C(13)–C(2-)–N chain.

Too much speculation on the mechanisms of low-yield products is inappropriate, but the following remarks seem relevant to the formation of **17** and **18**. The formation of these compounds probably necessitates the conversion of LDA into a carbanion that is lithiated β to the nitrogen atom. The initial LiH abstraction in Scheme IV to afford E could facilitate such a metalation in F. Previously, Richey et al.[21,22] have rationalized the formation of imines from amines and alkyllithium reagents by reaction sequences in which eliminations of LiH from lithiated amines alternate with addition of organolithium compounds to the formed products. [The neutral product (G, Scheme V) formed from carbanion F and the carbene complex after the loss of the OEt group could then rearrange by migra-

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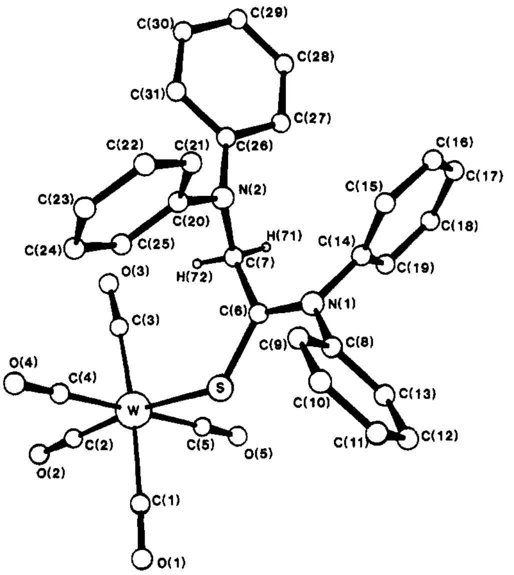
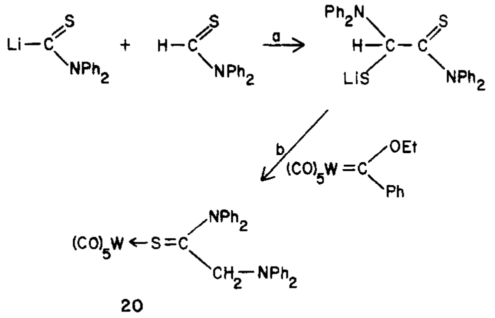


Figure 2. ORTEP drawing of atoms in $[W(CO)_5\{S{=}C(NPh_2)CH_2NPh_2\}]$ showing the labeling scheme. Phenyl hydrogens omitted for clarity.

Scheme VI



tion of the acidic hydrogen atom α to the carbene carbon[23] to the basic nitrogen atom with concomitant alkene formation to furnish an unstable intermediate, H. Final stabilization occurs by sulfur insertion.]

All the above remarks are also applicable to the formation of **19** from a mixture of $[W(CO)_5\{C(OEt)Ph\}]$ (**13**) and $HC(=S)NPh_2$ upon treatment with LDA (Scheme III) and subsequent acidification.

Seebach and co-workers have established that the lithiocarbamoyl derived from phenyl-substituted thioformamide is very unstable and dimerizes, but in situ reactions proved feasible for trapping the carbanion. We found, however, that even at −100 °C addition of carbene complex and $HC(=S)NPh_2$ to an LDA solution furnishes in addition to **19** a product (**20**) during the formation of which dimerization of the thioformamide has occurred. The explanation in Scheme VI is consistent with Seebach's proposals (step a) and with the structure of **20** as determined by single-crystal X-ray analysis. In step b the sulfide is reductively desulfurized (generally, $LiAlH_4$ or Raney Nickel are used in synthetic reactions[6]) and then the remaining bicovalent sulfur donor ligand substitutes the carbene ligand.

The origin of the hydride for the reduction is not known. It is notable, however, that LiH is abstracted from LDA according to our previous proposal for the formation of **19** (Scheme IV) and, furthermore, when lithium tetramethylpiperidide was used as base,[24] complex **20** did not form at all. The molecular structure of **20** is illustrated in Figure 2, the positional parameters are displayed in Table V, and the bond lengths and angles are given in Tables VI and VII.

The W–S bond distance [2.572 (1) Å] in the essentially octahedral complex is in good agreement with the same bond lengths in two other tungsten thione complexes, [W-

Table V. Final Fractional Coordinates (×10^4) and their Esds for $[W(CO)_5\{SC(NPh_2)CH_2NPh_2\}]$ (20)

atom	*x*	*y*	*z*
W	1360 (0)	224 (0)	2931 (0)
S	1332 (1)	−1599 (1)	915 (2)
O(1)	−915 (4)	−168 (5)	2235 (6)
O(2)	1067 (4)	2401 (5)	5270 (6)
O(3)	3543 (4)	1025 (6)	4024 (6)
O(4)	1308 (5)	−1755 (6)	5071 (6)
O(5)	1379 (4)	2230 (5)	788 (6)
N(1)	2293 (3)	−2846 (4)	−845 (5)
N(2)	3909 (3)	−2549 (5)	1287 (5)
C(1)	−90 (5)	−73 (6)	2453 (7)
C(2)	1181 (5)	1599 (6)	4393 (7)
C(3)	2760 (5)	688 (7)	3589 (7)
C(4)	1324 (5)	−1063 (7)	4284 (7)
C(5)	1381 (5)	1511 (6)	1546 (7)
C(6)	2347 (4)	−1993 (5)	294 (5)
C(7)	3329 (4)	−1478 (6)	1016 (7)
C(8)	1464 (4)	−3723 (5)	−1371 (6)
C(9)	1319 (5)	−4807 (6)	−760 (7)
C(10)	553 (5)	−5691 (7)	−1289 (9)
C(11)	−51 (5)	−5500 (7)	−2423 (8)
C(12)	97 (5)	−4412 (7)	−3020 (7)
C(13)	862 (5)	−3512 (6)	−2500 (6)
C(14)	3029 (4)	−2798 (6)	−1729 (6)
C(15)	3478 (5)	−3905 (6)	−2107 (6)
C(16)	4157 (5)	−3844 (8)	−2989 (8)
C(17)	4379 (6)	−2711 (10)	−3484 (7)
C(18)	3934 (6)	−1613 (9)	−3108 (7)
C(19)	3228 (5)	−1664 (6)	−2241 (6)
C(20)	3533 (4)	−3500 (6)	2037 (6)
C(21)	3698 (5)	−4776 (6)	1693 (7)
C(22)	3349 (5)	−5709 (7)	2400 (9)
C(23)	2826 (5)	−5394 (7)	3438 (8)
C(24)	2646 (5)	−4127 (7)	3791 (7)
C(25)	2988 (4)	−3181 (6)	3091 (6)
C(26)	4913 (4)	−2339 (6)	1400 (6)
C(27)	5336 (5)	−1866 (6)	332 (7)
C(28)	6325 (5)	−1712 (7)	441 (8)
C(29)	6894 (5)	−2026 (7)	1544 (10)
C(30)	6481 (5)	−2469 (7)	2597 (9)
C(31)	5505 (5)	−2612 (6)	2539 (7)

Table VI. Interatomic Distancs (Å) with Esds for $[W(CO)_5\{SC(NPh_2)CH_2NPh_2\}]$ (20)

W–S	2.572 (1)	C(12)–C(13)	1.389 (9)
W–C(1)	2.048 (7)	C(8)–C(13)	1.374 (8)
W–C(2)	1.957 (7)	C(14)–C(15)	1.392 (9)
W–C(3)	2.020 (7)	C(15)–C(16)	1.384 (10)
W–C(4)	2.028 (7)	C(16)–C(17)	1.376 (14)
W–C(5)	2.051 (7)	C(17)–C(18)	1.380 (13)
S–C(6)	1.692 (6)	C(18)–C(19)	1.403 (11)
C(1)–C(1)	1.161 (9)	C(14)–C(19)	1.379 (9)
C(2)–O(2)	1.162 (8)	C(20)–C(21)	1.379 (9)
C(3)–O(3)	1.155 (9)	C(21)–C(22)	1.378 (11)
C(4)–O(4)	1.135 (10)	C(22)–C(23)	1.362 (12)
C(5)–O(5)	1.132 (9)	C(23)–C(24)	1.377 (11)
C(6)–N(1)	1.336 (7)	C(24)–C(25)	1.379 (10)
N(1)–C(8)	1.441 (7)	C(20)–C(25)	1.397 (9)
N(1)–C(14)	1.448 (8)	C(26)–C(27)	1.411 (10)
C(6)–C(7)	1.515 (8)	C(27)–C(28)	1.392 (10)
C(7)–N(2)	1.469 (8)	C(28)–C(29)	1.357 (12)
N(2)–C(20)	1.434 (8)	C(29)–C(30)	1.378 (13)
N(2)–C(26)	1.415 (7)	C(30)–C(31)	1.378 (10)
C(8)–C(9)	1.371 (9)	C(26)–C(31)	1.395 (9)
C(9)–C(10)	1.385 (9)	C(7)–H(71)	1.034 (55)
C(10)–C(11)	1.366 (11)	C(7)–H(72)	0.886 (59)
C(11)–C(12)	1.369 (11)		

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Table VII. Selected Bond Angles (deg) with Esds for $[W(CO)_5\{SC(NPh_2)CH_2NPh_2\}]$ (20)

C(1)-W-S	83.0 (2)	C(5)-W-C(2)	91.2 (3)	C(7)-N(2)-C(20)	117.7 (5)
C(2)-W-S	171.7 (2)	C(5)-W-C(3)	90.7 (3)	C(7)-N(2)-C(26)	118.8 (5)
C(2)-W-C(1)	88.8 (3)	C(5)-W-C(4)	179.2 (3)	C(20)-N(2)-C(26)	117.2 (5)
C(3)-W-S	104.1 (2)	W-C(1)-O(1)	175.6 (6)	S-C(6)-C(7)	122.9 (4)
C(3)-W-C(1)	179.2 (3)	W-C(2)-O(2)	178.9 (6)	S-C(6)-N(1)	119.2 (4)
C(3)-W-C(2)	84.2 (3)	W-C(3)-O(3)	175.2 (6)	C(7)-C(6)-N(1)	117.8 (5)
C(4)-W-S	91.5 (2)	W-C(4)-O(4)	178.0 (6)	C(6)-C(7)-N(2)	110.4 (5)
C(4)-W-C(1)	89.8 (3)	W-C(5)-O(5)	178.9 (6)	C(6)-C(7)-H(71)	109.3 (27)
C(4)-W-C(2)	89.2 (3)	W-S-C(6)	121.0 (2)	C(6)-C(7)-H(72)	116.5 (38)
C(4)-W-C(3)	90.0 (3)	C(6)-N(1)-C(8)	123.2 (5)	N(2)-C(7)-H(71)	109.8 (30)
C(5)-W-S	87.9 (2)	C(6)-N(1)-C(14)	120.2 (4)	N(2)-C(7)-H(72)	105.5 (41)
C(5)-W-C(1)	89.6 (3)	C(8)-N(1)-C(14)	116.9 (4)		

Scheme VII

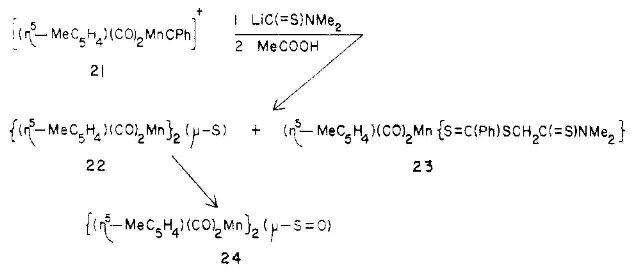

Table VIII. Final Fractional Atomic Coordinates ($\times 10^4$) and Their Esds for $[\eta^5\text{-}(MeCp)Mn(CO)_2\{SC(Ph)SCH_2C(S)NMe_2\}]$ (23)

atom	*x*	*y*	*z*
Mn	5 (0)	2419 (0)	1895 (1)
S(1)	1083 (1)	1508 (1)	2582 (1)
O(1)	1077 (2)	4866 (2)	3904 (4)
O(2)	542 (2)	3326 (3)	−2099 (4)
C(1)	685 (2)	3901 (3)	3124 (5)
C(2)	354 (3)	2961 (4)	−522 (6)
C(3)	−1180 (3)	2421 (4)	3526 (7)
C(4)	−1479 (2)	2390 (4)	1360 (7)
C(5)	−1415 (3)	1290 (4)	468 (7)
C(6)	−1086 (3)	672 (4)	2053 (8)
C(7)	−939 (3)	1358 (4)	3931 (7)
C(8)	−1851 (4)	3295 (6)	275 (10)
S(2)	2626 (1)	3602 (1)	1289 (1)
C(9)	2240 (2)	2156 (3)	2218 (5)
C(10)	2907 (2)	1431 (3)	2501 (5)
C(11)	2929 (3)	754 (3)	4235 (6)
C(12)	3486 (3)	−15 (4)	4365 (7)
C(13)	4013 (3)	−116 (4)	2799 (9)
C(14)	4012 (3)	574 (4)	1112 (7)
C(15)	3466 (3)	1346 (3)	968 (6)
S(3)	4638 (1)	6651 (1)	1858 (2)
C(16)	3907 (2)	4219 (3)	2476 (6)
C(17)	4080 (2)	5513 (3)	3276 (5)
C(18)	3285 (3)	4720 (4)	6325 (7)
C(19)	3887 (4)	6935 (4)	5865 (7)
N	3782 (2)	5704 (2)	5062 (4)

Table IX. Fractional Coordinates ($\times 10^4$) of the Hydrogen Atoms for $[\eta^5\text{-}(MeCp)Mn(CO)_2\{SC(Ph)SCH_2C(S)NMe_2\}]$ (23)

atom	*x/a*	*y/b*	*z/c*
H(31)	−1137 (26)	3064 (33)	4526 (57)
H(51)	−1550 (27)	999 (33)	−926 (58)
H(61)	−990 (25)	−182 (33)	1780 (53)
H(71)	−699 (26)	1127 (32)	5313 (58)
H(81)	−1598 (28)	4090 (34)	1143 (59)
H(82)	−2581 (28)	2944 (32)	−92 (54)
H(83)	−1657 (27)	3299 (34)	−1232 (57)
H(111)	2573 (28)	883 (35)	5297 (60)
H(121)	3445 (29)	−429 (36)	5564 (62)
H(131)	4346 (28)	−686 (35)	2801 (60)
H(141)	4361 (29)	477 (35)	27 (61)
H(151)	3444 (29)	1761 (35)	−169 (61)
H(161)	4301 (26)	4154 (31)	1390 (54)
H(162)	3979 (25)	3704 (32)	3585 (55)
H(181)	3540 (29)	4114 (34)	6301 (59)
H(182)	2696 (27)	4276 (34)	5609 (58)
H(183)	3125 (30)	5020 (37)	7260 (62)
H(191)	3832 (27)	6930 (33)	7260 (58)
H(192)	3419 (28)	7213 (35)	5161 (59)
H(193)	4455 (27)	7486 (34)	5598 (59)

$(CO)_5\{S{=}\overline{CNH(CH_2)_2S}\}]$[25] and $[W(CO)_5\{S{=}\overline{CNH(CH_2)_2SCH_2}\}]$[26] [2.56 (6) and 2.556 (8) Å, respectively]. The W–S–C(6) bond angle of 121.0 (2)° indicates sp^2 hybridization of the S donor atom and is 4° larger than the corresponding angles in the two above-mentioned compounds. The S donor atom in compound **20** exhibits a larger σ(donor)/π(acceptor) ratio than the carbonyl ligands with the result that the W–C(trans) bond lengths [1.957 (7) Å] is somewhat shorter than the average W–C(cis) distances [2.037 (7) Å], in accordance with the results for compound **18** above. In a *trisubstituted* chromium carbonyl complex containing thione groups, however, a significant lengthening of the Cr–C(trans) bond compared to the Cr–CO separations has been found.[27] A comparison of the bond lengths C(6)–N(1) [1.336 (7) Å] and C(7)–N(2) [1.469 (8) Å] indicates that the former bond is 0.13 Å shorter than the latter due to electron delocalization and concomitant bond shortening.

Reaction of $LiC(=S)NMe_2$ with $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2CPh][BCl_4]$. In principle, treatment of the manganese carbyne complex $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2CPh][BCl_4]$ (**21**) with $LiC(=S)NMe_2$ should produce after addition and sulfur insertion, a complex containing the same ligand as **16**. Only two other neutral compounds **22** and **23** (Scheme VII) were, however, formed in yields higher than 2% after completion of this reaction and subsequent acidification. The green dimer **22** (characterized only by a molecular ion in its mass spectrum) was extremely air sensitive and oxidized easily to a more stable pink complex, **24**. The formation of **22** reflects both the affinity of the manganese center for sulfur and the availability of sulfur from the thione. A comparable pair of compounds has been isolated from the reaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)]$ with S_8.[28]

Although elemental analysis for **23** indicated three sulfur atoms per molecule, the mass spectrum exhibited its highest peak at *m/z* 413 ($M^+ - S$). Furthermore, the chemical bonding in the new ligand could not be assigned with certainty from the available IR spectrum (dicarbonyl complex) and ^1H NMR data, and we embarked on a crystallographic study. Atomic coordinates are listed in Tables VIII and IX. The molecular structure is shown in Figure 3, and selected bond lengths and angles are given in Tables X and XI. Notable features of the structure are the following: (a) the fact that the two C=S bond

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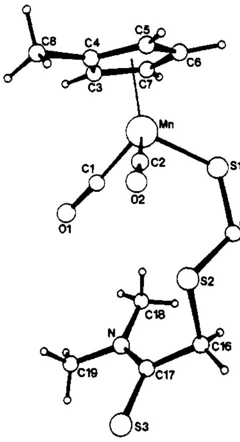


Figure 3. Structure of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_2\{\text{S=C(Ph)SCH}_2\text{C(=S)NMe}_2\}]$ showing the atom numbering scheme.

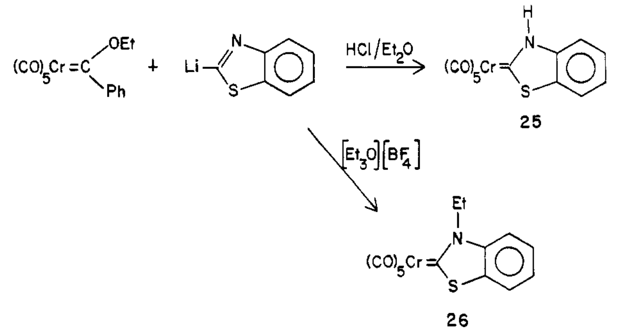
Table X. Interatomic Distances (Å) with Esds for $[\eta^5\text{-(MeCp)Mn(CO)}_2\{\text{SC(Ph)SCH}_2\text{C(S)NMe}_2\}]$ (23)

Mn-S(1)	2.173 (1)	S(1)-C(9)	1.664 (3)
Mn-C(1)	1.789 (3)	C(9)-C(10)	1.476 (5)
Mn-C(2)	1.780 (4)	C(10)-C(11)	1.395 (5)
Mn-C(3)	2.136 (4)	C(11)-C(12)	1.384 (6)
Mn-C(4)	2.145 (4)	C(12)-C(13)	1.372 (8)
Mn-C(5)	2.148 (3)	C(13)-C(14)	1.376 (7)
Mn-C(6)	2.148 (4)	C(14)-C(15)	1.374 (6)
Mn-C(7)	2.144 (4)	C(10)-C(15)	1.382 (5)
C(1)-O(1)	1.148 (4)	S(2)-C(9)	1.735 (3)
C(2)-O(2)	1.151 (5)	S(2)-C(16)	1.838 (3)
C(3)-C(4)	1.422 (6)	C(16)-C(17)	1.501 (5)
C(4)-C(5)	1.418 (6)	S(3)-C(17)	1.674 (3)
C(4)-C(8)	1.485 (8)	N-C(17)	1.326 (4)
C(5)-C(6)	1.397 (7)	N-C(18)	1.470 (5)
C(6)-C(7)	1.394 (6)	N-C(19)	1.457 (6)
C(3)-C(7)	1.407 (7)		

lengths corresponding to the coordinated and uncoordinated sulfur atoms [C(9)-S(1) and C(17)-S(3)] are the same [1.664 (3) and 1.674 (2) Å, respectively]; (b) the single C-S bond length [C(9)-S(2)] next to the thione linkage C(9)-S(1) is significantly influenced by the double bond and is shortened to 1.735 (3) Å compared to the 1.838 (3) Å distance of C(16)-S(2) [this effect is also observed for the C-N distance where the N atom is linked to the same carbon atom as the uncoordinated bicovalent sulfur atom: thus C(17)-N has a relatively short bond length of 1.326 (4) Å [the average value for C(18)-N and C(19)-N is 1.464 Å] and the thioamide moiety [C(16) to C(19) via N and S(3)] is planar]; (c) the Mn-S bond is 2.173 (1) Å which can be compared to a 2.193 (2) Å length in $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}\{\text{SC(Ph)C}_5\text{H}_4\}\text{Mn(CO)}_3]$ which also contains a bicovalent sulfur atom,[29] (d) the methyl group on the cyclopentadienyl ring is arranged away from the S donor ligand toward the center of the carbonyl groups, with the methyl carbon atom lying 0.08 Å out of the cyclopentadienyl plane; (e) the thione ligand in **23**, similar to SO_2 in $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_2(\text{SO}_2)]$,[30a] which occurs as a vertical conformer, is orientated with the ligand axis in the $(\text{MeC}_5\text{H}_4)\text{Mn(CO)}_2$ apparent but noncrystallographic mirror plane.[30b]

The low-yield (4%) formation of **23** not only involves the coupling of two thioformaldehyde units, the formation of a thiocarbene ligand by addition to the carbyne carbon atom, and a sulfur insertion into this metal-carbene bond, but also a very rare reductive deamination. The latter process is rather similar to the desulfurization used above to explain the formation of compound **20**. Sulfur insertion into the manganese-carbene bond has not been mentioned before. The present result is remarkable due to the mild reaction conditions employed and, furthermore, because S insertion into the metal-carbene bond of heteroatom-containing carbene complexes is unknown.

Scheme VIII



Reaction of 2-Lithiobenzothiazole with $[\text{Cr(CO)}_5\{\text{C(OEt)Ph}\}]$. The reaction of 2-lithiobenzothiazole (LiBtz) with $[\text{Cr(CO)}_5\{\text{C(OEt)Ph}\}]$ bears no resemblance to that of the other α-thio carbanions (see above). During this reaction, substitution of the alkoxyphenylcarbene ligand takes place and extremely stable Lappert-type carbene complexes result on acidification or alkylation.

The reactant anion was prepared by deprotonation of benzothiazole with LiBu at −78 °C in Et_2O.[31] The carbene complex was added and the reaction mixture stirred at room temperature before the solvent was removed and CH_2Cl_2 and an excess of either HCl in Et_2O or $[\text{Et}_3\text{O}][\text{BF}_4]$ were added. Two Lappert-type carbene complexes (**25** and **26** Scheme VIII) were obtained (yields respectively 1% and 5%) after purification of the filtered reaction mixture by column chromatography and crystallization.

The compounds crystallize as single crystals, are soluble in polar solvents such as CH_2Cl_2 (only **26** is appreciably soluble in hexane), and are stable both in the solid state and in solution at room temperature. Complex **25** was too insoluble to afford an infrared spectrum of a hexane solution, and a Nujol mull was resorted to. The infrared spectrum of **26** in the carbonyl region differs from that of the Lappert-type carbene complex $[\text{Cr(CO)}_5\{\text{CN(Et)(CH}_2)_2\text{NEt}\}]$[32] in that a weak B_1 band is present (1971 cm^{-1}) and distinction between the E (1937 cm^{-1}) and $\text{A}_1^{(2)}$ (1930 cm^{-1}) bands is possible.

The only existing examples of complexes in which *N*-alkylbenzothiazole coordinates as a carbene ligand are *cis*- and *trans*-$[\text{MX}_2\{\text{CN(Me)(C}_6\text{H}_4)\text{S-}o\}]$ (M = Pd, Pt; X = Cl, Br; R = Et, *n*-Bu).[33] The electron-rich olefin $\text{N(Me)(C}_6\text{H}_4)\text{S-}o\text{-C=CN(Me)(C}_6\text{H}_4)\text{S-}o$ has been employed as the source of carbene.

The anionic ligand can exist in an equilibrium mixture involving two forms

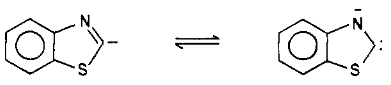


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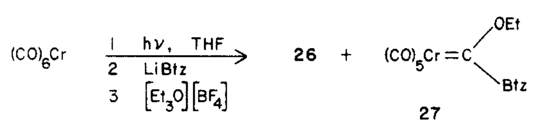
Table XI. Selected Bond Angles (deg) with Esds for [η^5-(MeCp)Mn(CO)$_2${SC(Ph)SCH$_2$C(S)NMe$_2$}] (23)

C(1)-Mn-S(1)	99.0 (1)	C(6)-Mn-C(5)	38.0 (2)	C(5)-C(4)-Mn	70.8 (2)
C(2)-Mn-S(1)	97.4 (1)	C(7)-Mn-S(1)	93.1 (1)	C(5)-C(4)-C(3)	106.7 (4)
C(2)-Mn-C(1)	89.3 (2)	C(7)-Mn-C(1)	110.2 (2)	C(8)-C(4)-Mn	127.1 (3)
C(3)-Mn-S(1)	129.0 (1)	C(7)-Mn-C(2)	156.2 (1)	C(8)-C(4)-C(3)	126.3 (4)
C(3)-Mn-C(1)	88.9 (2)	C(7)-Mn-C(3)	38.4 (2)	C(8)-C(4)-C(5)	126.8 (4)
C(3)-Mn-C(2)	133.3 (2)	C(7)-Mn-C(4)	64.6 (2)	C(4)-C(5)-Mn	70.6 (2)
C(4)-Mn-S(1)	151.3 (1)	C(7)-Mn-C(5)	63.9 (2)	C(6)-C(5)-Mn	71.0 (2)
C(4)-Mn-C(1)	105.5 (2)	C(7)-Mn-C(6)	37.9 (2)	C(6)-C(5)-C(4)	108.2 (4)
C(4)-Mn-C(2)	97.7 (2)	C(9)-S(1)-Mn	121.7 (1)	C(7)-C(6)-Mn	70.9 (2)
C(4)-Mn-C(3)	38.8 (2)	O(1)-C(1)-Mn	176.4 (4)	C(7)-C(6)-C(5)	108.9 (4)
C(5)-Mn-S(1)	116.5 (1)	C(17)-C(16)-S(2)	106.9 (2)	C(3)-C(7)-Mn	70.5 (2)
C(5)-Mn-C(1)	143.9 (2)	C(16)-C(17)-S(3)	118.3 (3)	C(6)-C(7)-Mn	71.2 (2)
C(5)-Mn-C(2)	92.3 (2)	N-C(17)-S(3)	122.9 (2)	C(6)-C(7)-C(3)	107.9 (4)
C(5)-Mn-C(3)	64.3 (2)	N-C(17)-C(16)	118.7 (3)	C(16)-S(2)-C(9)	102.7 (3)
C(5)-Mn-C(4)	38.6 (2)	O(2)-C(2)-Mn	176.9 (4)	S(2)-C(9)-S(1)	120.5 (2)
C(6)-Mn-S(1)	87.1 (1)	C(4)-C(3)-Mn	70.9 (2)	C(10)-C(9)-S(1)	118.7 (2)
C(6)-Mn-C(1)	148.0 (2)	C(7)-C(3)-Mn	71.1 (3)	C(10)-C(9)-S(2)	120.6 (2)
C(6)-Mn-C(2)	121.2 (2)	C(7)-C(3)-C(4)	108.3 (4)	C(18)-N-C(17)	123.9 (3)
C(6)-Mn-C(3)	63.8 (2)	C(3)-C(4)-Mn	70.3 (2)	C(19)-N-C(17)	121.2 (3)
C(6)-Mn-C(4)	64.2 (2)			C(19)-N-C(18)	114.8 (3)

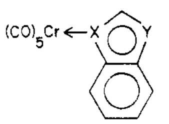
Scheme IX



Either of these would be able to effect substitution of the carbene ligand in [Cr(CO)$_5${C(OEt)Ph}]. It is also possible that substitution takes place only after alkylation of the free ligand, in which case the equilibrium suggested by Wanzlick and Kleiner[34] should pertain:

The second alternative was discarded when we established (TLC) that only a red ionic compound formed after the addition of the metalated benzothiazole.

The new carbene complex **26** was also obtained via rearrangement of the ligand after deprotonation (with LiBu) and subsequent alkylation of the mixed-donor complex **28**



28

in which X can be N or S and, correspondingly, Y then S or N. ^{1}H NMR spectroscopy showed the X donor:Y donor ratio to be 2:1 by integration of the two signals for the C(2) proton at respectively τ 0.72 and 0.90. A similar preparation (see Experimental Section) was previously reported to have yielded a solely N co-ordinated benzothiazole ligand.[35]

An attempt to trap the free carbene proposed in the first equilibrium yielded both the above-mentioned Lappert-type carbene complex **26** and a Fischer-type carbene complex, [Cr(CO)$_5${C(OEt)Btz}] (**27**), on addition of 2-lithiobenzothiazole to [Cr(CO)$_5$(THF)] and alkylation of the resulting ionic mixture (Scheme IX). The Fischer-type complex originates from unreacted [Cr(CO)$_6$] in the reaction mixture (reaction of 2-lithiobenzothiazole with [Cr(CO)$_6$] completely dissolved in THF yielded, after alkylation, only the Fischer-type carbene complex in the relatively high yield of 48%. When [Cr(CO)$_6$] was suspended in Et$_2$O, no reaction occurred).

In the above-mentioned reactions, stable Lappert-type carbene complexes have formed under extremely mild reaction conditions, compared to the established procedure according to which a solution of the particular carbonyl compound is boiled in the presence of an electron-rich olefin.[32]

Experimental Section

General Data. All reactions and manipulations were carried out under purified nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and distilled under nitrogen before use. Crystalline compounds were degassed under high vacuum and saturated with nitrogen before they were used in reactions. Proton NMR spectra were recorded on a Bruker WP 80 spectrometer, ^{13}C NMR spectra on a Bruker WP 20, and mass spectra on a Hitachi Perkin-Elmer RMU-6H (60 eV) apparatus, and for infrared measurements, a Perkin-Elmer 237 was used. Melting points (uncorrected) were determined on a Kofler hot-stage apparatus. Elemental analyses were carried out by the Mikroanalytisches Labor, Bonn, and at the Technical University, Münich. All the yields reported are for analytically pure compounds. The numbers of compounds refer to the drawings in the Results and Discussion.

Reactions of Carbene Complexes with Lithiated Thioacetals. The metalation of the thioacetals or derivatives thereof were carried out according to methods used in literature.[2] The following describes a typical experiment.

(a) Preparation of 1 and 4. A solution of $Li\overline{CHS(CH_2)_3S}$ (approximately 16 mmol) in tetrahydrofuran (THF) (10 mL) was added dropwise to a diethyl ether solution (50 mL) of [Cr(CO)$_5${C(OMe)Ph}][36] (5 g, 16 mmol) and stirred for 1 h at −60 °C. Enough SiO$_2$ (50 g) was added to absorb all the solvent, which was then removed under vacuum. Elution with ether and concentration of the eluate produced a residue which was chromatographed (−20 °C) on a SiO$_2$ column (2.8 × 35 cm) with ether–hexane (1:8) to remove unreacted carbene complex. The products were then eluted with ether, and the residue obtained after stripping of the solvent was transferred to a short column (4.5 × 12 cm) of silica gel and thoroughly washed with hexane (2 L). The sulfide complex [Cr(CO)$_5\overline{S(CH_2)_3SCH_2}$] (4) was obtained in less than 0.5% yield (based on carbene complex) from this step. After elution of the other products with CH$_2$Cl$_2$ and evaporation of the solvent under vacuum, chromatography with CH$_2$Cl$_2$–hexane (1:4, −20 °C) afforded at first a brown band which contained an unstable brown oily product [ν(CO) (hexane) 2071 (w), 1950 (sh), 1940 (s) cm^{-1}] which was not completely characterized. The second brown-red fraction eluted with CH$_2$Cl$_2$–hexane (1:1)

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yielded a reddish oil, which was precipitated from pentane (−80 °C) and dried under vacuum to give 1.8 g (44%) of **1** in analytically pure form.

(b) Preparation of 2, 3, and 5. To 5 g (10.9 mmol) of a cooled (−60 °C) solution of [W(CO)$_5${C(OEt)Ph}][36] in ether was added approximately 11 mmol of LiCHS(CH$_2$)$_3$S in THF. Subsequent workup was as for **1** and **4**. The known[2] sulfide complex [W(CO)$_5$S(CH$_2$)$_3$SCH$_2$] (**5**) was obtained from the hexane eluate in extremely low yield (<0.5%). Final chromatography yielded consecutively 1.2 g (11%) of **3** and 2.1 g (58%) of **2** as yellow-brown oils.

(c) Preparation of 6–10. LiCHSCH$_2$SCH$_2$S was prepared from 1.38 g (10 mmol) of *sym*-trithiane in THF and mixed with 3 g (9.6 mmol) of [Cr(CO)$_5${C(OMe)Ph}] in ether (−50 °C). Initial workup was as above. After the unreacted carbene had been removed (ether–hexane, 1:8), a purple band was eluted. Concentration under vacuum and recrystallization from pentane (−80 °C) gave 1.0 g (47%) of **8** as pink-purple crystals.

The polarity of the eluant was increased (CH$_2$Cl$_2$–hexane, 1:3). A broad orange zone (containing a mixture of low-yield compounds) followed by two brown bands was observed on the column. The latter two fractions were separately removed by pipette from the top of the column, and each was washed through a glass filter with cold (−15 °C) CH$_2$Cl$_2$. The composition of the more polar of the two compounds which had been obtained in extremely low yields [ν(CO) (hexane) 2024 (m), 1962 (m), 1938 (s), 1918 (m) cm^{-1}] was not established. The other was recrystallized twice from pentane (−80 °C) to afford 0.90 g (35%) of **6** as light brown needles.

Compounds **7** (brown oil) and **9** (red prisms) were prepared similarly from the tungsten carbene complex [W(CO)$_5${C(OEt)Ph}], however, both in only 4% yield.

From the reaction between [W(CO)$_5${C(OEt)Ph}] and LiCHSCH$_2$NMeCH$_2$S only one product, **10**, could be isolated in pure form (10%, brown-red crystals).

Reactions of LiC(=S)NR$_2$ with Carbene Complexes. (a) Preparation of the Carbene Complex [Cr(CO)$_5${C(OEt)C$_6$H$_4$Ph-*o*}] (12). A suspension of [Cr(CO)$_6$] (1.1 g, 5 mmol) in 20 mL of tetrahydrofuran (THF) was treated with 5 mmol of 2-lithiobiphenyl. After 10 min the solvent was removed under vacuum and the residue redissolved in 20 mL of CH$_2$Cl$_2$ and then alkylated with [Et$_3$O][BF$_4$] until thin-layer chromatography (in ether) showed no more of unreacted ionic yellow adduct. The solution was filtered and concentrated and the product precipitated by cooling (−30 °C). Recrystallization from ether–pentane (−30 °C) yielded 3.5 mmol (70%) of the dark red crystalline product.

(b) Preparation of the Thione Complexes 14, 16, 17, and 18. In a typical experiment 20 mmol (1.73 mL) of dimethylformamide in 20 mL of THF at −100 °C was added to 20 mmol (5.6 mL) of diisopropylamine in THF which had previously been treated with 12.5 mL of 1.6 M LiBu (in hexane). After being stirred for 2 min, the mixture was added to 10 mmol (2.2 g) of [Cr(CO)$_5${C(OEt)Ph}] in 30 mL of THF −100 °C. The temperature was allowed to rise to −70 °C over a period of 30 min, and 2 mL of glacial acetic acid was added. Final workup involved column chromatography (SiO$_2$, −20 °C, ether–hexane, 1:10 to 1:3). The substitution product **14** was obtained in <1% yield. Compound **16**, which appeared as a blue zone on the column, was recrystallized from CH$_2$Cl$_2$–pentane as black, needle-like crystals (0.068 g, 2%). Finally, 0.113 g (3%) of red needles of **17** was obtained after crystallization from ether–pentane (−30 °C).

From a similar experiment using 10 mmol (4.0, g) of the biphenyl carbene complex [Cr(CO)$_5${C(OEt)C$_6$H$_4$Ph-*o*}] as starting material, only compound **18** was eventually crystallized (0.40 g, 8%) as orange needles from pentane–ether (−30 °C).

(c) Preparation of the Thione Complexes 15, 19, and 20. A solution of *N,N*-diphenylthioformamide (1.88 g, 10 mmol) and [W(CO)$_5${C(OEt)Ph}] (4.58 g, 10 mmol) in THF (24 mL) was added dropwise over a period of 1 h to a solution of lithium diisopropylamide[6] at −78 °C. The temperature was allowed to rise to room temperature and glacial acetic acid (0.2 mL) added. The solvent was removed, degassed water and CH$_2$Cl$_2$ were added and the CH$_2$Cl$_2$ layer was filtered through a short column packed with SiO$_2$ and Na$_2$SO$_4$. This solution was concentrated and separated by chromatography on SiO$_2$ (−20 °C) with hexane–ether (1:1) into two fractions. After the solvent had been evaporated, further chromatography of the first fraction (−20 °C, CH$_2$Cl$_2$–hexane 1:4) yielded two products: **15**, which crystallized as yellow needles (0.38 g, 7%) from hexane–ether, and **20**, which could be obtained as orange prisms (0.36 g, 10%) after crystallization from hexane–ether. The second fraction was rechromatographed with hexane–CH$_2$Cl$_2$ (1:1) to yield, upon crystallization, 0.38 g (7%) of **19** (red prisms).

Reaction of LiC(=S)NMe$_2$ with [(η^5-MeC$_5$H$_4$)Mn(CO)$_2$CPh][BCl$_4$]. Preparation of 22, 23, and 24. To a cooled (−100 °C) solution of 4.32 g (10 mmol) of [(η^5-MeC$_5$H$_4$Mn(CO)$_2$CPh][BCl$_4$][37] in THF was added 17 mmol of LiC(=S)NMe$_2$ in THF over a period of 1 min. After 30 min the solution was allowed to warm to −70 °C and 2.3 mL (40 mmol) of glacial acetic acid added. The mixture was subsequently warmed to room temperature, the solvent removed, and the residue redissolved in ether–hexane and filtered through SiO$_2$. Two main products (green and purple zones) were separated from the series of minor ones by column chromatography (SiO$_2$, −20 °C) with a hexane–ether mixture of increasing polarity (hexane–ether, 30:1 to 1:1) as eluant. Evaporation of the solvent and crystallization from ether–hexane provided ca. 0.12 g (6%) of the unstable **22** and 0.095 g (4%) of **23** from the green and purple fractions, respectively.

Conversions of **22** to **24** took place on exposure of a solution of the former (0.12 g in ether) to atmospheric oxygen, and 0.11 g (91%, black needles) of **24** was obtained.

Reaction of 2-Lithiobenzothiazole with [Cr(CO)$_5${C(OEt)Ph}]. (a) Preparation of 25 and 26. The carbene complex [Cr(CO)$_5${C(OEt)Ph}] (1.30 g, 4 mmol) was added to a cooled (−78 °C) solution of 2-lithiobenzothiazole, prepared by adding LiBu (6 mmol) dropwise to benzothiazole (0.65 mL, 6 mmol) in Et$_2$O (15 mL) and stirring for 15 min at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1.5 h, after which the solvent was removed and the residue redissolved in CH$_2$Cl$_2$. To obtain complex **25**, the reaction mixture was acidified with excess HCl in ether. Alternatively, to obtain **26**, the solution was cooled to −10 °C and an excess of [Et$_3$O][BF$_4$] added. Each complex was purified by column chromatography (SiO$_2$, −20 °C, CH$_2$Cl$_2$–hexane, 1:1) and crystallization (−30° C) to yield yellow needles of either **25** (0.025 g, 1%) or **26** (0.085 g, 5%).

(b) Reaction of 2-Lithiobenzothiazole with [Cr(CO)$_5$THF]-[Cr(CO)$_6$] (Trapping of the Free Carbene). After [Cr(CO)$_6$] (0.66 g, 3 mmol) had been irradiated for 2.5 h in THF, the solution was cooled to −78 °C and a cooled (−78 °C) solution of 2-lithiobenzothiazole (see above) was added. The reaction mixture was warmed to room temperature, the solvent removed, and CH$_2$Cl$_2$ added. Addition of an excess of [Et$_3$O][BF$_4$] to the cooled (−10 °C) solution yielded, after separation and purification by column chromatography (SiO$_2$, −20 °C, CH$_2$Cl$_2$–hexane, 1:1) and crystallization (−30 °C), 0.076 g (7%) of **26** (yellow needles) and 0.030 g (3%) of **27** (red needles).

(c) Preparation of 27. Benzothiazole (0.33 mL, 3 mmol) in THF (15 mL) was cooled to −78 °C, and LiBu (3 mmol, 1.6 mL), diluted with an additional 15 mL of THF, was added slowly. After 10 min this solution was added to [Cr(CO)$_6$] (0.44 g, 2 mmol) in THF (75 mL) at −78 °C. The reaction mixture was stirred for 2 h until no more unreacted [Cr(CO)$_6$] could be seen in suspension and then allowed to warm to room temperature. The solvent was removed under vacuum; the brown residue was washed with hexane (15 mL), dissolved in CH$_2$Cl$_2$, and alkylated with [Et$_3$O][BF$_4$] (3 mmol) at −10 °C. The mixture was warmed to room temperature and filtered through SiO$_2$. After the solvent had been removed, the product was crystallized from ether–hexane at −80°C and 0.54 g (47%) of **27** was obtained.

(d) Preparation of 28. Irradiation of [Cr(CO)$_6$] (1.1 g, 5 mmol) in THF for 5 h and addition of benzothiazole (0.54 mL, 5 mmol) yielded a stable yellow product, which, after column chromatography (SiO$_2$, −20 °C, CH$_2$Cl$_2$–hexane, 1:1) and crystallization (−30 °C), was characterized as (benzothiazole)pentacarbonylchromium(0) (**28**) (0.36 g, 22%).

(e) Preparation of 26 from 28. A solution of **28** (0.2 g, 0.6 mmol) in hexane–THF (3:2, 25 mL) was cooled to −85 °C, and

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Table XII. Crystallographic Data for X-ray Diffraction Studies $[(CO)_5Cr\{SC(C_6H_4Ph\text{-}o)CHCMeNHCHMe_2\}]$ (18), $[(CO)_5W\{SC(NPh_2)CH_2NPh_2\}]$ (20), $[\eta^5\text{-}(MeCp)Mn(CO)_2\{SC(Ph)SCH_2C(S)NMe_2\}]$ (23)

	18	**20**	**23**
	A. Crystal Data		
formula	$CrC_{24}H_{21}NO_5S$	$WC_{31}H_{22}N_2O_5S$	$MnC_{19}H_{20}NO_2S_3$
M_r	487.49	718.41	445.49
cryst system	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a, Å	13.76 (1)	14.20 (2)	14.62 (1)
b, Å	20.14 (1)	10.48 (2)	11.56 (1)
c, Å	17.92 (1)	9.92 (2)	6.51 (1)
α, deg		97.6 (1)	91.6 (1)
β, deg	98.3 (1)	97.2 (1)	96.7 (1)
γ, deg		93.8 (1)	108.8 (1)
Z	8	2	2
U, Å^3	4916	1446	1032
D_{calcd}, g cm^{-3}	1.32	1.65	1.43
temp, ±5 °C	20	20	20
	B. Measurement of Intensity Data		
radiation		Mo Kα (0.7107 Å)	
cryst dimens, mm	0.20 × 0.15 × 0.10	0.63 × 0.20 × 0.25	0.15 × 0.10 × 0.15
μ, cm^{-1}	5.32	39.13	8.33
scan width, °θ	1.10	1.40	1.40
scan speed, °θ s^{-1}	0.04	0.05	0.05
reflctns measd	7177	3908	2867
total unique reflctns	3485	3585	2815
	C. Structure Refinement		
final residuals R	0.094	0.035	0.053
R_w	0.040	0.037	0.035

LiBu (0.78 mmol, 1.6 M) was added slowly, upon which the color of the reaction mixture changed immediately from yellow to dark brown. After the solution had been warmed to room temperature, the solvent was removed under vacuum. The oily brown residue was dissolved in CH_2Cl_2 the mixture cooled to −10 °C, and a small excess of $[Et_3O][BF_4]$ added. The product was purified as before to yield 0.019 g (10%) of **26**.

Crystallographic Analyses. Crystal data for compounds **18**, **20**, and **23** are given in Table XII. Orange crystals of $[(CO)_5Cr\{SC(C_6H_4Ph\text{-}o)CHCMeNHCHMe_2\}]$ (**18**) and $[(CO)_5W\{SC(NPh_2)CH_2NPh_2\}]$ (**20**) and black crystals of $[(\eta^5\text{-}MeCp)Mn(CO)_2\{SC(Ph)SCH_2C({=}S)NMe_2\}]$ (**23**) suitable for diffraction measurements were grown by slow crystallization from hexane–ether solutions, cooled to −20 °C. Unit cell constants were determined by least-squares analysis of the θ values for 25 reflections. Integrated intensities for independent reflections with $\theta < 23°$ were measured on a Philips PW 1100 diffractometer using graphite-monochromated Mo Kα radiation. Reflections with $I < 2\sigma_I$ were considered unobserved. No absorption corrections were applied. The structures were solved by the heavy-atom method and refined by full-matrix least squares, using the SHELX[38] series of crystallographic programs. The weights used were the quantities $1/\sigma_F^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions of **18** were calculated by assuming idealized geometrics [d(C–H) = 1.08 Å]. The phenyl hydrogen atoms of **20** were placed and refined in calculated positions. The remaining two hydrogen atoms could be located from a difference map, and their positions were refined independently from the atom to which they are bonded. The positions of all the hydrogen atoms of **23** could be located from difference maps. Final R values are listed in Table XII. The difference in R and weighted R values (0.094 and 0.040) for $CrC_{24}H_{21}NO_5S$ (**18**) is due to the large fraction (about 40%) of unobservable reflections measured for this set of data. This large percentage of weak reflections was caused by the small crystal used, but which made absorption corrections unnecessary.

Acknowledgment. We thank the C.S.I.R. for financial support and Mr. J. Albain of the C.S.I.R. for collection of the crystallographic data.

Registry No. **1**, 79953-58-5; **2**, 79953-59-6; **3**, 79970-16-4; **4**, 61642-90-8; **5**, 67126-37-8; **6**, 79953-60-9; **7**, 93756-26-4; **8**, 79953-61-0; **9**, 93756-27-5; **10**, 93859-90-6; **12**, 93756-28-6; **14**, 84749-54-2; **15**, 93756-29-7; **16**, 93756-30-0; **17**, 93756-31-1; **18**, 93756-32-2; **19**, 93756-33-3; **20**, 93756-34-4; **21**, 93756-36-6; **22**, 93756-37-7; **23**, 93756-38-8; **24**, 93781-77-2; **25**, 93756-39-9; **26**, 93756-40-2; **27**, 93756-41-3; **28** (X = N, Y = S), 33335-79-4; **28** (X = S, Y = N), 93756-42-4; Btz, 95-16-9; $Li\overline{CHS(CH_2)_3S}$, 36049-90-8; $[Cr(CO)_5\{C(OMe)Ph\}]$, 27436-93-7; $[W(CO)_5\{C(OEt)Ph\}]$, 36834-98-7; $Li\overline{CHSCH_2SCH_2S}$, 51102-72-8; $Li\overline{CHSCH_2NMeCH_2S}$, 61764-06-5; $Cr(CO)_6$, 13007-92-6; $[Cr(CO)_5\{C(OEt)Ph\}]$, 26160-57-6; 2-lithiobiphenyl, 55365-18-9; dimethylthioformamide, 758-16-7; *N,N*-diphenylthioformamide, 20979-96-8.

Supplementary Material Available: Physical and analytical data of new complexes (Tables A–D), spectroscopic data for the new complexes (Tables E–H), fractional coordinates of the hydrogen atoms for complexes **18** and **20** (Tables I and J), deviations of atoms from least-squares planes for complex **23** (Table K), thermal parameters for **18**, **20**, and **23** (Tables L–N), observed and calculated structure factors for **18**, **20**, and **23** (Tables O–Q) (51 pages). Ordering information is given on any current masthead page.

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