phenanthroline at the molybdenum. Either way solvation of the pyridine and the 1,10-phenanthroline will affect reactivities. What may provide a clue as to the mechanism operative is the observation that solvent effects on reactivity of $Mo(CO)_4(ROH)_2$ and of $Mo(CO)_4(py)(ROH)$, k_{2L} and k_{1L}, respectively, act in opposite directions. The modest increase in k_{1L} as the proportion of 1-butanol decreases (Table V) may be attributable to the corresponding increase in the chemical potential of the incoming ligand as its solvation decreases somewhat, with consequent increase in rate constant for associative attack. Thus, here we have associative displacement of ROH from $Mo(CO)_4(ROH)_2$ in contrast to dissociative loss of py from $Mo(CO)_4(py)(ROH)$, as indubitably from $Mo(CO)_4(py)_2$.

It is difficult to make a direct reactivity comparison for the rapid (k_1) step between the binary mixtures and the microemulsions, since the former show a first-order dependence on the concentration of the incoming ligand and the microemulsions a zero-order dependence. However, the k_{obsd} values for the microemulsions (Table IX) correspond to k_{obsd} for binary mixtures where incoming ligand concentrations are of the order of 5×10^{-3} M. This comparison may be giving a clue as to the effective concentration of phen or bpy in those regions of the microemulsions in close proximity to the molybdenum species. Indeed, it turns out that the small medium effects on reactivities, the probable inequivalence of second-order terms in mixed solvents and in microemulsions, and the lack of a probe for the possible effect of water on the charge-transfer spectra make comparisons of kinetic and spectroscopic results for the present compounds and reactions rather fruitless. Rather than conduct further investigations in this particular area, we feel it would be better to switch attention to other systems where greater contrasts between reactants, in terms of charges and hydrophobic or hydrophilic natures, would give greater reactivity contrasts. It would also be advantageous to use a substrate whose reactions were less complicated than those in Scheme I. In particular, a single leaving group would be desirable.

Solvolysis and substitution at *cis*-$Mo(CO)_4(py)_2$ have now been shown to follow an interesting and complicated pattern, with a rich diversity of reaction pathways. The kinetic situation in these alcohol-containing solvent media contrasts with the simple patterns encountered when, as has been usually the case, "innocent" solvents such as toluene or dichloromethane have been used. Our study of alcohol-containing solvents opens up new reaction pathways, involving a variety of reactive intermediates and new aspects of organometallic reactivity and mechanisms.

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Registry No. *cis*-$Mo(CO)_4(py)_2$, 16742-99-7; phen, 66-71-7; bpy, 366-18-7; dab, 5393-49-7; BuOH, 71-36-3; *i*-PrOH, 67-63-0.

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π-Arene Complexes. 3.[1] End-to-End Bridging Thiocarbonyl Complexes. Crystal and Molecular Structure of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$

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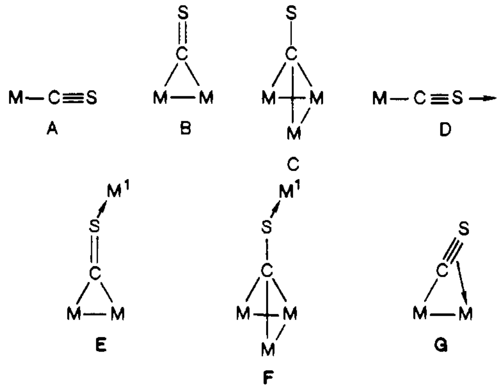
The dinuclear complexes $(\eta^6\text{-}C_6H_5R)(CO)_2CrCSCr(CO)_5$ (R = OMe, Me) and $(\eta^6\text{-}C_6H_3Me_3)(CO)_2CrCSCr(CO)_5$ containing a thiocarbonyl bridged in an end-to-end manner (via C and S) have been synthesized from the π-arene thiocarbonyl complexes and $Cr(CO)_5THF$. The X-ray structure of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (A) has been determined by single-crystal X-ray diffraction. Crystals of A ($Cr_2C_{15}H_8O_7S$) are triclinic, space group $P\bar{1}$, with a = 7.395 (1) Å, b = 10.373 (3) Å, c = 12.057 (1) Å, α = 77.72 (2)°, β = 79.91 (1)°, γ = 75.69 (2)°, and Z = 2. Although the Cr–C–S linkage is linear (angle 177.3 (3)°), the C–S–Cr linkage deviates greatly from linearity. The lowering of the C–S bond order on coordination through the sulfur atom is suggested by a C–S bond length of 1.604 (5) Å and $\nu(C{\equiv}S)$ absorption bands in the infrared region approximately 75 cm^{-1} lower than those observed for the parent thiocarbonyl complexes. The very long S–Cr distance of 2.486 (2) Å is indicative of a weak bond that is easily broken in polar solvents.

Introduction

Thiocarbonyl ligands have been found to coordinate to transition metals in different ways, and possible arrangements are shown (A–G).



A large number of transition-metal complexes with terminal and doubly bridged thiocarbonyls (A, B)[2,3] are known, and complexes with an additional coordination through the sulfur (D, E)[4,5] have also been reported. The complex $\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ is an example of a complex with a triply bridged thiocarbonyl (C) and $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]Cr(CO)_5$ the corresponding end-to-end-bonded compound (F).[6] To our knowledge no examples of complexes with thiocarbonyl ligands bonded sideways, as in arrangement G, exist.

It is known that the electrophilic character of the carbon of a thiocarbonyl is markedly greater compared to that of a carbonyl carbon and the sulfur is more basic than the oxygen.[7] Thiocarbonyl ligands therefore exhibit a much wider range of reactions toward nucleophiles and Lewis acids.[8,9] This explains why the

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(1) Lotz, S.; Schindehutte, M.; Van Dyk, M. M.; Van Rooyen, P. H.; Dillen, J. L. M. *J. Organomet. Chem.* **1985**, *295*, 51.
(2) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359.
(3) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.
(4) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2397.
(5) Kolb, O.; Werner, H. *Angew. Chem.* **1982**, *94*, 207.
(6) Werner, H.; Leonhard, K.; Kolb, O.; Rottinger, E.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 1654.
(7) Luttringhaus, A.; Grohman, J. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1955**, *10*, 365.

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thiocarbonyl ligand is capable of binding through the sulfur atom to another metal center (D–F). The first example of a complex with a terminal thiocarbonyl bonded to another metal in an end-to-end arrangement was $(diphos)_2(CO)WCSW(CO)_5$ (diphos = $Ph_2PCH_2CH_2PPh_2$).[10] This mode of coordination was also suggested, on the basis of spectroscopic evidence, for the unstable compound of formula $[(\eta^5\text{-}C_5H_5)Mn(CO)_2]_2CS$ formed during the reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_2THF$ with CS_2 in the absence of a sulfur acceptor.[11] $W(diphos)_2(CO)(CS)$ reacts with HgX_2 (X = Cl, I) to give the complexes $(diphos)_2(CO)WCSHgX_2$ and with $AgBF_4$ to give the ionic compound $[\{(diphos)_2(CO)WCS\}_2Ag]BF_4$.[4]

Single-crystal X-ray analysis were carried out for thiocarbonyl complexes of the above-mentioned bonding types with the exception of a structure of arrangement D. Thus, the fact that no further examples of terminal end-to-end-bonded species have recently been reported and our interest in the activation of thiocarbonyl and selenocarbonyl ligands as a result of this coordination mode led to this study. We wish to report the synthesis of end-to-end-bonded thiocarbonyl complexes and their structural features. The crystal and molecular structure determination of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ is the first example of a terminal thiocarbonyl bonded to another metal via the sulfur and thus acting as a bridge between the two metal units. Recently, it was found that an end-to-end-bridged CO complex, $(\eta^5\text{-}C_5Me_5)_2V(\mu\text{-}OC)V(CO)_5$, has a linear V–O–C–V bond.[12]

Experimental Section

General Procedures. All reactions and manipulations were carried out routinely under nitrogen and with solvents dried before use. Reagent grade chemicals were used without further purification and $Cr(\eta^6\text{-}C_6H_5Me)(CO)_3$, $Cr(\eta^6\text{-}C_6H_5Me)(CO)_2(CS)$, $Cr(\eta^6\text{-}C_6H_5OMe)(CO)_3$, $Cr(\eta^6\text{-}C_6H_3Me_3)(CO)_3$ prepared as reported previously.[13-15] Photolyses were run in Pyrex flasks with water-cooled jackets and a Philips medium-pressure mercury arc. Column chromatography on SiO_2 (0.063–0.200 mm) was performed on 2 cm × 40 cm columns that were cooled by circulating cold methanol (−10 °C) through the column jackets. Microanalyses were performed by F. Pascher and E. Pascher Microanalytical Laboratories, Bonn, West Germany. Infrared spectra were recorded on a Beckman IR4250 spectrometer and calibrated against polystyrene. Proton NMR spectra were recorded on a Bruker WP 80 MHz instrument and mass spectra on a Perkin-Elmer RMU-6H instrument operating at 70 eV. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

Synthesis. (i) Preparation of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (A). Solution A consists of $Cr(\eta^6\text{-}C_6H_5Me)(CO)_2CS$ (0.25 g, 1.00 mmol) dissolved in a mininum quantity of hexane.

Solution B, which consists of $Cr(CO)_6$ (0.22 g, 1 mmol), 4 cm^3 of THF, and 150 cm^3 of hexane, was irradiated for approximately 0.5 h at room temperature, whereafter the total volume of solvent was approximately halved under reduced pressure.

Solution B was added to solution A, and within 2 min an orange product started to precipitate. After 5 min the remaining yellow solution was decanted and the precipitate washed with 3 × 20 cm^3 hexane portions. The final product was recrystallized from CH_2Cl_2/hexane.

Yield: 80%. Mp: 84–86 °C. Mass spectrum: *m/e* 436 (M^+). Anal. Calcd for $Cr_2C_{15}H_8O_7S$: C, 41.29; H, 1.85; S, 7.35. Found: C, 41.83; H, 2.11; S, 7.98.

(ii) Preparation of $Cr(\eta^6\text{-}C_6H_5OMe)(CO)_2(CS)$. (Methoxybenzene)tricarbonylchromium(0) (0.5 g, 2.0 mmol) was dissolved in 80 cm^3 of benzene and placed in an irradiation vessel. Cyclooctene (5 cm^3) was added to this solution, which was irradiated for 20 min while N_2 was bubbled through it at room temperature. The resulting red solution was added to a mixture of triphenylphosphine (0.8 g, 3.0 mmol) and carbon disulfide (50 cm^3) and stirred overnight. The product was chromatographically purified (hexane/ether; 1/1) and recrystallized as yellow crystals from ether/hexane.

Table I. Experimental Data for X-ray Diffraction Study of A

formula	$Cr_2C_{15}H_8O_7S$
mol wt	436
space group	$P\bar{1}$
a, Å	7.395 (1)
b, Å	10.373 (3)
c, Å	12.057 (1)
α, deg	77.72 (2)
β, deg	79.91 (1)
γ, deg	75.69 (2)
V, Å^3	686
Z	2
d(calcd), g cm^{-3}	1.50
d(measd), g cm^{-3}	1.51
cryst size, mm	0.20 × 0.24 × 0.32
μ(Mo Kα), cm^{-1}	15.0
radiation (λ, Å)	Mo Kα (0.7107)
scan method	ω
scan speed, deg min^{-1}	var, max 3.30
octants; data collcn range, deg	$+h,\pm k,\pm l$; $3 \leq \theta \leq 25$
no. of data measd	3053
no. of unobsd data ($I \leq 2\sigma(I)$)	1127
no. of unique reflcns used	2520
no. of params refined	253
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.083
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.035

Yield: 70%. Mp: 48–49 °C. Mass spectrum: *m/e* 260 (M^+). Anal. Calcd for $CrC_{10}H_8O_3S$: C, 46.15; H, 3.10; S, 12.32. Found: C, 46.51; H, 3.27; S, 12.77.

(iii) Preparation of $(\eta^6\text{-}C_6H_5OMe)(CO)_2CrCSCr(CO)_5$. The same method as described under (i) was followed. Solution A consisted of 0.26 g (1.0 mmol) of $Cr(\eta^6\text{-}C_6H_5OMe)(CO)_2(CS)$ and B of 0.25 g (1.14 mmol) of $Cr(CO)_6$, 4 cm^3 of THF, and 60 cm^3 of hexane.

The final red product precipitated only after approximately 80% of the solvent was removed.

Yield: 85%. Mp: 45–46 °C. Mass spectrum: *m/e* 452 (M^+). Anal. Calcd for $Cr_2C_{15}H_8O_8S$: C, 39.83; H, 1.78; S, 7.09. Found: C, 40.27; H, 2.08; S, 7.74.

(iv) Preparation of $Cr\{\eta^6\text{-}(1,3,5\text{-}C_6H_3Me_3)\}(CO)_2(CS)$. (Mesitylene)tricarbonylchromium(0) (1.2 g, 4.7 mmol) was dissolved in benzene, 9 cm^3 cyclooctene was added, and the mixture was irradiated, as described under (ii), for 1 h. The resulting dark red solution was added to a mixture of triphenylphosphine (1.2 g, 4.6 mmol) and carbon disulfide (36 cm^3) and stirred overnight. Column chromatography of the reaction mixture with ether/hexane (1/3) as eluent yielded the desired thiocarbonyl complex, which was recrystallized from ether/hexane.

Yield: 82%. Mp: 126–128 °C. Mass spectrum: *m/e* 272 (M^+). Anal. Calcd for $CrC_{12}H_{12}O_2S$: C, 52.93; H, 4.44; S, 11.77. Found: C, 53.11; H, 4.52; S, 12.14.

(v) Preparation of $\{\eta^6\text{-}(1,3,5\text{-}C_6H_3Me_3)\}(CO)_2CrCSCr(CO)_5$. The same method as described under (iii) was used. Extended handling in vacuo leads to the decomposition of the title compound.

Yield: 79%. Mp: 140 °C dec. Mass spectrum: *m/e* 464 (M^+). Anal. Calcd for $Cr_2C_{17}H_{12}O_7S$: C, 43.97; H, 2.61; S, 6.9. Found: C, 44.47; H, 3.14; S, 7.52.

X-ray Analysis. All diffraction measurements were performed at room temperature on an Enraf-Nonius CAD-4F diffractometer using graphite-monochromatized Mo Kα radiation. The unit cell was determined from 25 randomly selected reflections by using the automatic search, index, and least-squares routines. The refined cell constants and other relevant crystal data for the orange crystal of A is presented in Table I, together with details of intensity measurements. All the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data by measuring the intensities of seven reflections with χ near 90° for different ψ values (0 ≤ ψ ≤ 360°, every 10°) and using the EAC program, from the Enraf-Nonius package. The maximum and minimum transmission factors were 1.00 and 0.95. Three standard reflections were used to check orientation and crystal stability at regular intervals, and the decay during data collection was less than 1%. The structures were solved by conventional Patterson and Fourier methods and refined by blocked-matrix least-squares techniques using SHELX.[16] The positions of all the hydrogen atoms were obtained from

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(8) Busetto, L.; Graziani, M.; Belluco, U. *Inorg. Chem.* **1971**, *10*, 78.

(9) Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. *J. Organomet. Chem.* **1976**, *114*, C49.

(10) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7568.

(11) Butler, I. S.; Coville, N. J.; Cozak, D. *J. Organomet. Chem.* **1977**, *133*, 59.

(12) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 6292.

(13) Rausch, M. D. *Pure Appl. Chem.* **1972**, *30*, 523.

(14) Jaouen, G.; Simonneaux, G. *Inorg. Synth.* **1979**, *19*, 197.

(15) Nicholls, B.; Whitting, M. C. *J. Chem. Soc.* **1959**, 551.

(16) Sheldrick, G. M. "SHELX-76 Programme System"; University of Cambridge, 1976.

a difference Fourier synthesis, and these were refined isotropically with a cmmon temperature factor (0.093 (7) Å^2). All the non-hydrogen atoms were refined anisotropically with $\sigma^{-2}(F)$ weights. Scattering factors for chromium(0) were taken from the literature.[17] The maximum noise level of the final difference electron density map was 0.52 e Å^{-3}.

Results and Discussion

Synthesis. Addition of saturated solutions of $Cr(\eta^6-C_6H_5R)(CO)_2(CS)$ and $Cr(CO)_5THF$ leads to the displacement of the weakly coordinated THF. The end-on-linked dinuclear complexes precipitate in near quantitative yields (eq 1). The

$$Cr(\pi\text{-arene})(CO)_2(CS) + Cr(CO)_5THF \xrightarrow[\text{hexane}]{} (\pi\text{-arene})(CO)_2CrCSCr(CO)_5 + THF \quad (1)$$

$$\pi\text{-arene} = C_6H_5R\ (R = H, Me, OMe),\ 1,3,5\text{-}C_6H_3Me_3$$

solubility of the product compared to those of the starting materials conveniently ensures a final product of high purity. Orange crystals were obtained from CH_2Cl_2/hexane mixtures. In the crystalline form these compounds are stable under nitrogen for months and can also be handled in air for short periods of time.

It must be remembered, however, that the linkage is weak and can easily be broken in polar solvents with coordinating properties. We found the best method for crystallization to be slow evaporation, in a nitrogen stream, of the more volatile CH_2Cl_2 from CH_2Cl_2/hexane mixtures. In contrast, attempts to recrystallize from ether/hexane mixtures led only to decomposition. In polar solvents the end-to-end-bridged thiocarbonyl adducts decompose rapidly (within minutes when open to air). The nature of the solvent therefore is not only important for the formation of the product but also for its isolation. The solubilities of the end-to-end-bridged thiocarbonyl complexes vary, and while the formation of these complexes with symmetrical π-arene ligands, e.g. C_6H_6, 1,3,5-$C_6H_3Me_3$, was found, their isolation and crystallization were more difficult.

Another aspect to be considered deals with the electron density on the thiocarbonyl ligand. Complexes with low $\nu(C{\equiv}S)$ absorptions in the infrared region are expected to form the most stable Lewis adducts. We ascribed our unsuccessful attempts to link $Mn(\eta^5-C_5H_5)(CO)_2(CS)$ and $Cr(CO)_5THF$ to the high $\nu(C{\equiv}S)$ absorption at 1266 cm^{-1}. Studies of the reactivities of thiocarbonyl ligands in tungsten complexes toward electrophiles required $\nu(C{\equiv}S)$ values below 1200 cm^{-1} for the formation of stable adducts.[4] In fact, we found values of 1230 cm^{-1} not too high for the formation of stable Cr–CS–Cr complexes (vide infra). However, the use of infrared thiocarbonyl frequencies as a general guideline for electronic effects is very useful.

We are presently looking into the possible influence of the configuration of the complex on the stability of end-to-end bridging thiocarbonyl compounds.[18]

Spectroscopic Studies. Proton NMR chemical shifts and infrared carbonyl and thiocarbonyl stretching frequencies of the π-arene thiocarbonyl complexes and end-to-end-bridged adducts are given in Table II.

Table II. Proton NMR Data and Infrared Frequencies in the $\nu(C{=}S)$ and $\nu(C{=}O)$ Regions of $Cr(\eta^6-C_6H_3R_3)(CO)_2(CS)$ and $(\eta^6-C_6H_3R_3)(CO)_2CrCSCr(CO)_5$

compd[a] R$_3$	^{1}H NMR chem shift,[b] δ π-arene	Me	IR,[c] cm^{-1} ν(CO)[d]	ν(CS)
H, H, Me	5.35–5.71 (m)	2.24 (s)	2070 (w), 1973 (vs), 1908 (vs), 1878 (s)	1156 (s)
	5.35–5.71 (m)	2.24 (s)	1950 (s), 1892 (s)	1205 (s)
			1986 (s), 1947 (s)	1230 (s)
H, H, OMe	5.01–5.79 (m)	2.17 (s)	2040 (w), 1980 (vs), 1933 (vs), 1880 (s)	1140 (s)
	5.00–5.78 (m)	2.17 (s)	1960 (s), 1920 (s)	1218 (s)
Me, Me, Me	5.09–5.44 (m)	2.22 (s)	2062 (w), 1945 (vs), 1905 (vs), 1873 (s)	1160 (s)
	5.08–5.44 (m)	2.22 (s)	1960 (s), 1920 (s)	1220 (s)

[a] Values for the starting thiocarbonyl complexes are given below those of the corresponding end-to-end-bridged thiocarbonyl complexes. [b] Measured in $CDCl_3$ relative to internal $SiMe_4$. The number of protons established by integration are in accord with the given structures: s = singlet, m = multiplet. [c] Measured in hexane for the starting thiocarbonyl complexes and as KBr disks for the end-to-end-bonded thiocarbonyl complexes. Two sets of values are given for $Cr(\eta^6-C_6H_5Me)(CO)_2(CS)$. The first are those obtained as KBr disks, and the second in a hexane solution: w = weak, s = strong, vs = very strong. [d] Broad poorly resolved bands due to overlapping for adducts.

The chemical shifts of the protons and substituents in the π-arene ring of the dinuclear thiocarbonyl complexes differ very little from those for their precursors. End-on coordination via the sulfur to a second metal center has little effect on the bonding properties of the π-arene ligand. Variation of L in $Cr(\eta^6-C_6H_5COOMe)(CO)_2L$ (L = CO, CNPh, $P(OPh)_3$, PPh_3, SPh_2, NC_5H_5) leads to considerable changes in the position of the chemical shifts of the π-arene protons.[19-21]

Unfortunately, the carbonyl absorption bands in the infrared region are broad, and the unambiguous assignment of values to the $Cr(\pi\text{-arene})(CO)_2$ part of the molecule is impossible due to some overlapping with the more intense absorptions of the $Cr(CO)_5$ moiety. Four poorly resolved bands are observed (see Table II)—the first three probably belong to $Cr(CO)_5$ moiety. It was not possible to measure these absorptions in solution due to excessive decomposition in polar solvents. Bands for $Cr(\eta^6\text{-arene})(CO)_2(CS)$ and $Cr(CO)_6$ were found in every instance.

End-on coordination of thiocarbonyl ligands of $(\eta^6-C_6H_5R)(CO)_2CrCSCr(CO)_5$ (R = Me, OMe) lowered the $\nu(C{\equiv}S)$ absorption bands by more than 75 cm^{-1} compared to the cases of their precursors. These differences are in good agreement with the values found for the complexes $(diphos)_2(CO)WCSHgX_2$.[4] This also supports the conclusions drawn of the estimated positions of the thiocarbonyl bands obscured by diphos ligand absorptions for these compounds. The lowering of the CS bond order on coordination to the second chromium is also supported by the lengthening of the C–S bond of A (vide infra).

Mass spectra were measured routinely (see Experimental Section). The absence of peaks for Cr_2CS^+ and for the ions corresponding to fragments whereby seven carbonyls are consecutively lost from the molecular ion peak $\{(\eta^6\text{-arene})(CO)_2CrCSCr(CO)_5\}^+$ is noteworthy. Instead, the principle ion peak corresponds to the fragment $\{Cr(\eta^6\text{-arene})(CO)_2(CS)\}^+$, whereafter different patterns in the order of fragmentation of the π-arene, the thiocarbonyl, and the carbonyls exist (*m/e* values for $\{Cr(\eta^6\text{-arene})\}^+$, $\{Cr(\eta^6\text{-arene})(CS)\}^+$, and $\{CrCS\}^+$ were observed).

Crystal and Molecular Structure of $(\eta^6-C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (A). The molecule A with the atomic numbering scheme used is shown in Figure 1, as well as the projection on the benzene plane showing the eclipsed conformation.

Fractional atomic coordinates, selected bond lengths (Å), and bond angles (deg) are shown in Tables III–V, respectively. The most striking features of the crystal structure determination of A are found in the bond lengths and angles in the CrCSCr moiety. The Cr(2)–S(1) bond distance of 2.486 (2) Å is slightly longer than the value of 2.458 (2) Å found for $Cr\{S(Et)CH_2Ph\}(CO)_5$ (see Figure 2) and not much shorter than the estimated covalent σ Cr–S distance of 2.52 Å.[22-24] The Cr(2)–S(1)–C(1) angle of 110.4 (2°) in A indicates a significant change of hybridization

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[17] (a) Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. (b) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[18] Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* **1982**, *82*, 499.

[19] Emanuel, R. V.; Randall, E. W. *J. Chem. Soc. A* **1969**, 3002.

[20] Deubzer, B.; Fritz, H. P.; Kreiter, G. C.; Öfele, K. *J. Organomet. Chem.* **1967**, *7*, 289.

[21] Lotz, S., unpublished results.

[22] Raubenheimer, H. G.; Boeyens, J. C. A.; Lotz, S. *J. Organomet. Chem.* **1976**, *112*, 145.

[23] Pauling L. *The Nature of the Chemical Bond*; Cornell University Publishers: New York, 1960.

[24] Cotton, F. A.; Richardson, D. C. *Inorg. Chem.* **1966**, *5*, 1851.

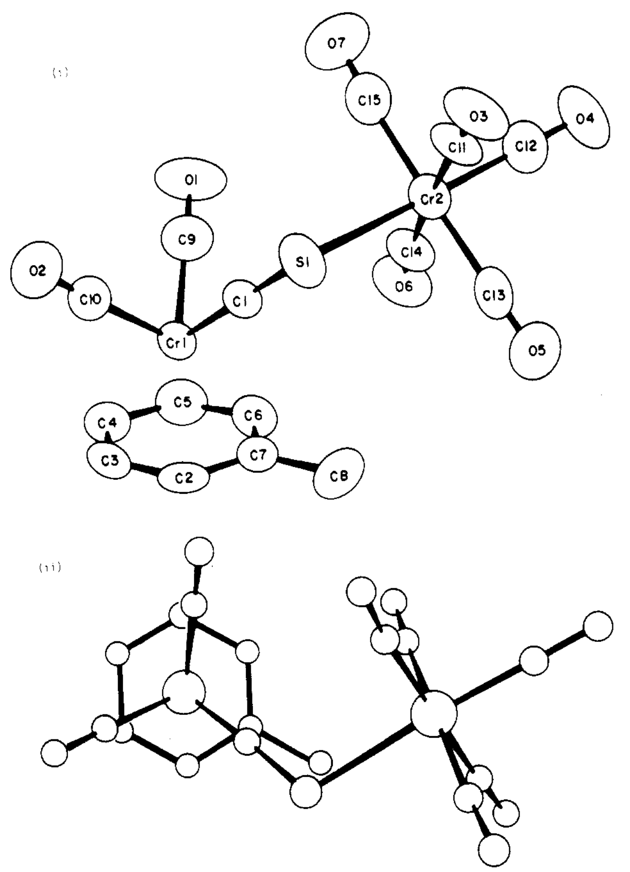


Figure 1. Two different views of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (A) (i) with anisotropically refined atoms showing the atomic numbering scheme used and (ii) a projection along the Cr–benzene bond.

Table III. Fractional Coordinates ($\times10^4$, $\times10^3$ for H) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$) for A

	x/a	*y/b*	*z/c*	*U*(eq)[a]
Cr(1)	5826 (1)	5437 (1)	7491 (1)	43 (1)
Cr(2)	3492 (1)	10205 (1)	7674 (1)	47 (1)
S(1)	3658 (2)	7950 (1)	8924 (1)	52 (1)
C(1)	4699 (7)	6773 (5)	8210 (4)	40 (3)
C(2)	8407 (7)	4591 (6)	8394 (5)	50 (4)
C(3)	7984 (8)	3552 (5)	7986 (6)	55 (4)
C(4)	7850 (8)	3662 (6)	6804 (6)	53 (4)
C(5)	8155 (8)	4856 (7)	6075 (5)	53 (4)
C(6)	8521 (7)	5913 (6)	6492 (5)	49 (4)
C(7)	8648 (7)	5796 (6)	7652 (6)	50 (4)
C(8)	9094 (9)	6900 (7)	8099 (6)	79 (5)
C(9)	4179 (8)	6244 (6)	6383 (5)	61 (4)
O(1)	3154 (6)	6725 (5)	5765 (3)	85 (3)
C(10)	4007 (8)	4539 (6)	8322 (5)	54 (4)
O(2)	2860 (6)	4027 (4)	8836 (4)	79 (3)
C(11)	1781 (8)	10938 (5)	8881 (5)	49 (4)
O(3)	815 (6)	11408 (4)	9585 (4)	68 (3)
C(12)	3254 (9)	11930 (6)	6829 (5)	57 (4)
O(4)	3114 (7)	12997 (4)	6290 (4)	77 (3)
C(13)	5499 (9)	10451 (6)	8329 (5)	55 (4)
O(5)	6717 (7)	10629 (5)	8686 (4)	83 (3)
C(14)	5327 (9)	9513 (6)	6482 (5)	52 (4)
O(6)	6425 (6)	9147 (4)	5777 (3)	71 (3)
C(15)	1457 (10)	9990 (7)	6961 (5)	66 (4)
O(7)	275 (7)	9955 (6)	6520 (5)	103 (4)
H(2)	859 (6)	452 (4)	929 (4)	93 (7)*
H(3)	760 (7)	271 (5)	864 (4)	93 (7)*
H(4)	751 (7)	283 (5)	639 (4)	93 (7)*
H(5)	788 (6)	484 (5)	522 (4)	93 (7)*
H(6)	885 (7)	684 (4)	591 (4)	93 (7)*
H(8A)	858 (7)	690 (5)	908 (4)	93 (7)*
H(8B)	840 (7)	765 (5)	798 (4)	93 (7)*
H(8C)	1016 (7)	680 (5)	823 (4)	93 (7)*

[a] Values marked with an asterisk denote isotropic temperature factors.

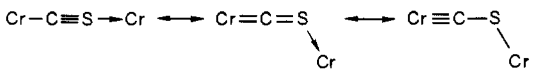
Table IV. Bond Lengths (Å) (Involving Non-H Atoms) for A

Cr(1)–C(1)	1.747 (5)	Cr(1)–C(2)	2.256 (6)
Cr(1)–C(3)	2.241 (5)	Cr(1)–C(4)	2.274 (6)
Cr(1)–C(5)	2.267 (5)	Cr(1)–C(6)	2.249 (5)
Cr(1)–C(7)	2.256 (6)	Cr(1)–C(9)	1.886 (6)
Cr(1)–C(10)	1.852 (6)	Cr(2)–S(1)	2.486 (2)
Cr(2)–C(11)	1.910 (6)	Cr(2)–C(12)	1.844 (6)
Cr(2)–C(13)	1.892 (7)	Cr(2)–C(14)	1.923 (6)
Cr(2)–C(15)	1.937 (8)	S(1)–C(1)	1.604 (5)
C(2)–C(3)	1.395 (10)	C(2)–C(7)	1.404 (8)
C(3)–C(4)	1.425 (10)	C(4)–C(5)	1.401 (9)
C(5)–C(6)	1.399 (10)	C(6)–C(7)	1.396 (9)
C(7)–C(8)	1.490 (11)	C(9)–O(1)	1.109 (7)
C(10)–O(2)	1.133 (7)	C(11)–O(3)	1.123 (7)
C(12)–O(4)	1.149 (7)	C(13)–O(5)	1.132 (9)
C(14)–O(6)	1.127 (7)	C(15)–O(7)	1.112 (10)

Table V. Bond Angles (deg) (Involving Non-H Atoms) for A

C(1)–Cr(1)–C(2)	100.8 (2)	C(1)–Cr(1)–C(3)	131.6 (2)
C(2)–Cr(1)–C(3)	36.1 (3)	C(1)–Cr(1)–C(4)	166.3 (3)
C(2)–Cr(1)–C(4)	65.7 (2)	C(3)–Cr(1)–C(4)	36.8 (2)
C(1)–Cr(1)–C(5)	142.4 (3)	C(2)–Cr(1)–C(5)	76.0 (2)
C(3)–Cr(1)–C(5)	64.7 (2)	C(4)–Cr(1)–C(5)	36.0 (2)
C(1)–Cr(1)–C(6)	108.2 (2)	C(2)–Cr(1)–C(6)	64.6 (2)
C(3)–Cr(1)–C(6)	76.7 (2)	C(4)–Cr(1)–C(6)	65.4 (2)
C(5)–Cr(1)–C(6)	36.1 (3)	C(1)–Cr(1)–C(7)	90.0 (2)
C(2)–Cr(1)–C(7)	36.3 (2)	C(3)–Cr(1)–C(7)	65.5 (2)
C(4)–Cr(1)–C(7)	77.9 (2)	C(5)–Cr(1)–C(7)	65.0 (2)
C(6)–Cr(1)–C(7)	36.1 (2)	C(1)–Cr(1)–C(9)	86.6 (2)
C(2)–Cr(1)–C(9)	163.9 (2)	C(3)–Cr(1)–C(9)	141.3 (3)
C(4)–Cr(1)–C(9)	106.1 (2)	C(5)–Cr(1)–C(9)	89.4 (2)
C(6)–Cr(1)–C(9)	99.6 (2)	C(7)–Cr(1)–C(9)	130.6 (2)
C(1)–Cr(1)–C(10)	86.4 (3)	C(2)–Cr(1)–C(10)	105.7 (2)
C(3)–Cr(1)–C(10)	87.8 (2)	C(4)–Cr(1)–C(10)	98.6 (2)
C(5)–Cr(1)–C(10)	130.9 (3)	C(6)–Cr(1)–C(10)	163.4 (2)
C(7)–Cr(1)–C(10)	140.0 (3)	C(9)–Cr(1)–C(10)	89.0 (3)
S(1)–Cr(2)–C(11)	87.2 (2)	S(1)–Cr(2)–C(12)	175.9 (2)
C(11)–Cr(2)–C(12)	88.7 (2)	S(1)–Cr(2)–C(13)	89.7 (2)
C(11)–Cr(2)–C(13)	88.8 (3)	C(12)–Cr(2)–C(13)	90.1 (3)
S(1)–Cr(2)–C(14)	93.8 (2)	C(11)–Cr(2)–C(14)	176.5 (3)
C(12)–Cr(2)–C(14)	90.3 (2)	C(13)–Cr(2)–C(14)	87.9 (3)
S(1)–Cr(2)–C(15)	91.8 (2)	C(11)–Cr(2)–C(15)	92.0 (3)
C(12)–Cr(2)–C(15)	88.4 (3)	C(13)–Cr(2)–C(15)	178.3 (3)
C(14)–Cr(2)–C(15)	91.3 (3)	Cr(2)–S(1)–C(1)	110.4 (2)
Cr(1)–C(1)–S(1)	177.3 (3)	Cr(1)–C(2)–C(3)	71.3 (3)
Cr(1)–C(2)–C(7)	71.9 (3)	C(3)–C(2)–C(7)	120.7 (6)
Cr(1)–C(3)–C(2)	72.5 (3)	Cr(1)–C(3)–C(4)	72.9 (3)
C(2)–C(3)–C(4)	121.1 (5)	Cr(1)–C(4)–C(3)	70.4 (3)
Cr(1)–C(4)–C(5)	71.7 (3)	C(3)–C(4)–C(5)	117.1 (6)
Cr(1)–C(5)–C(4)	72.3 (3)	Cr(1)–C(5)–C(6)	71.3 (3)
C(4)–C(5)–C(6)	121.7 (6)	Cr(1)–C(6)–C(5)	72.6 (3)
Cr(1)–C(6)–C(7)	72.2 (3)	C(5)–C(6)–C(7)	120.8 (5)
Cr(1)–C(7)–C(2)	71.9 (3)	Cr(1)–C(7)–C(6)	71.7 (4)
C(2)–C(7)–C(6)	118.6 (6)	Cr(1)–C(7)–C(8)	129.5 (4)
C(2)–C(7)–C(8)	120.2 (6)	C(6)–C(7)–C(8)	121.2 (5)
Cr(1)–C(9)–O(1)	177.2 (5)	Cr(1)–C(10)–O(2)	177.9 (5)
Cr(2)–C(11)–O(3)	177.2 (6)	Cr(2)–C(12)–O(4)	179.1 (5)
Cr(2)–C(13)–O(5)	177.5 (5)	Cr(2)–C(14)–O(6)	177.7 (6)
Cr(2)–C(15)–O(7)	175.4 (6)		

of the sulfur atom on coordination to the second chromium atom and cannot be rationalized in terms of canonical forms I or II.



I II III

In contrast, the Cr–S–C angles in Cr{S(Et)CH_2Ph}$(CO)_5$ of 112.0° and in Cr{$SCMe_2$}$(CO)_5$ of 120.3° with sp^3- and sp^2-hybridized sulfur atoms closely correlate with the ideal angle values of 109.4 and 120°.[22,25] The Cr(1)–C(1)–S(1) arrangement is essentially linear (177.3°), accentuating the angular end-on link of the sulfur with the second chromium atom. The end-on bridged

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(25) Karcher, B. A.; Jacobson, R. A. *J. Organomet. Chem.* **1977**, *132*, 387.

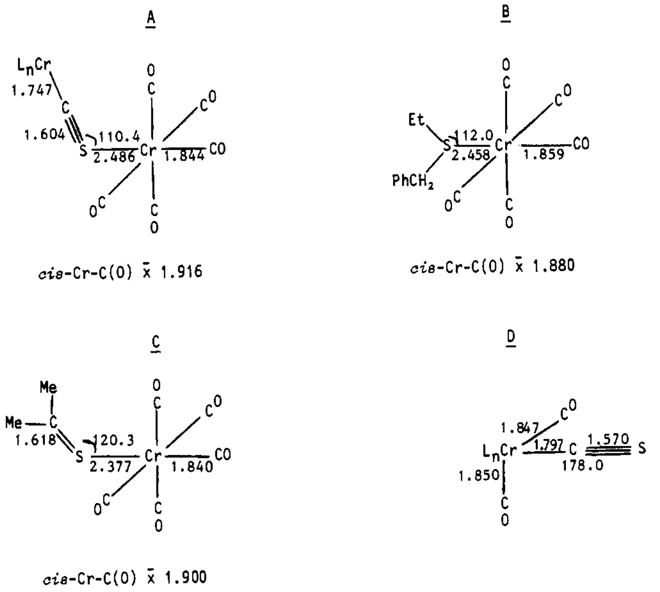

Figure 2. Structures related to A for comparison of relevant bond lengths (Å) and angles (deg) A, $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (this work); B, $Cr\{S(Et)CH_2Ph\}(CO)_5$;[18] C, $Cr\{SCMe_2\}(CO)_5$;[21] D, $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2(CS)$[23] ($L_n$ = π-arene).

carbonyl in the link V–O–C–V was found to be linear for $(\eta^5\text{-}C_5Me_5)_2VOCV(CO)_5$.[12]

The coordination of the sulfur atom to the second chromium center leads to a lengthening of the C(1)–S(1) distance. The value of 1.604 (5) Å is significantly longer than the expected distances of 1.51–1.54 Å for terminal thiocarbonyl ligands.[26] This distance is also comparable to 1.618 (8) Å in $Cr\{SCMe_2\}(CO)_5$ and 1.592 (8) and 1.587 (7) Å of the bridged thiocarbonyls of $\{Fe(\eta^5\text{-}C_5H_5)(CO)(CS)\}_2$.[9]

Compensation for this long C(1)–S(1) bond in A is found in a short Cr(1)–C(1) distance. The value of 1.747 (5) Å is significantly shorter than the corresponding distance of 1.797 (2) Å in $Cr(\eta^5\text{-}C_6H_5COOMe)(CO)_2(CS)$,[27] indicating a considerable degree of π-interaction between the chromium and thiocarbonyl carbon. The very short Cr(1)–C(1) distance warrants a comparison with the corresponding distances recorded for Fischer type carbenes (Cr═CR₂, i.e. II) and carbynes (Cr≡CR, i.e. III). The Cr–C(carbyne) distance of 1.69 (1) Å for $Cr(CO)_4(I)(CMe)$ is shorter and the Cr–C(carbene) distance of 2.04 (3) Å for $Cr(CO)_5\{C(OMe)Me\}$ significantly longer than the Cr(1)–C(1) bond length of 1.747 (5) Å for A.[28,29] The complexes $W(\eta^5\text{-}C_5H_5)(PPh_3)(CO)(CSPh)$ and $W\{HB(pz)_3\}(PPh_3)(CO)(CSPh)$ were previously described as having primarly carbyne form III.[30,31] The C–S bond length in A [C(1)–S(1) = 1.604 (5) Å] is shorter than that in $W(\eta^5\text{-}C_5H_5)(PPh_3)(CO)(CSPh)$ [WC–S = 1.716 (10) Å], and the angle at the sulfur is larger (110.4 (2)°) than 106.2 (5)°, suggesting less carbyne character in A as for the tungsten compound.[31]

Although significant differences exist in the Cr–C and C–S bond lengths of A and $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2(CS)$, the Cr- - -S distances are almost identical at 3.351 and 3.367 Å, respectively. Comparison of the Cr–C(1) and C–S distances of A with some of the shortest Cr–C(S) and longest C–S distances recorded for terminal thiocarbonyl complexes stresses the influence of end-on coordination on these distances. Bond lengths of 1.782 (9) and 1.75 (1) Å for Cr–C(S) and 1.585 (9) and 1.59 (1) Å for C–S for the complexes $Cr\{P(OMe)_3\}_3(CO)_2(CS)$ and $Cr(\eta^6\text{-}C_{10}H_{10}O)\{P(Ph)_3\}(CO)(CS)$, respectively, were reported.[32,33] The weak sulfur linkage leads to a short trans Cr–C(O) bond length of 1.844 (5) Å according to Table IV, which is significantly shorter than the mean of the cis Cr–C(O) value [1.916 (5) Å]. A similar trend for the bond lengths of A was also found for the V–O–C–V unit and its trans carbonyl.[12]

A shift to higher frequencies in the infrared spectrum of the ν(C═O) absorptions was observed for $(diphos)_2(CO)WCSHgX_2$.[4] This result points to less π-interaction between the chromium and carbonyl carbons on account of a lowering of electron density on the chromium due to the end-on coordination of the sulfur. It is expected that changes in ν(CO) of this magnitude would be reflected in C–O and M–C(O) bond lengths. Unfortunately, no conclusive evidence to this effect follows from the Cr–C(O) bond distances in A, and additional structural studies are needed. Nevertheless, when possible electronic effects as a result of ring substituents are ignored, bond lengthening due to end-on coordination seems probable as the Cr–C(O) distances of 1.886 (6) and 1.852 (6) Å in A are a little longer on average than the corresponding values of 1.850 and 1.847 Å in $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2(CS)$.[27] The effect of replacing an electron-withdrawing substituent (e.g., COOMe) in the arene ring by an electron-donating substituent (e.g., Me) leads to a shortening of the Cr–C(O) distances, as was found for $Cr(\eta^6\text{-}C_6H_5R)(CO)_3$ (R = Me, COOMe).[34,35]

A feature relating to the geometry of A is the eclipsed position of the tripod $Cr\{CSCr(CO)_5\}(CO)_2$ in relation to the arene carbon atoms (Figure 1). The bridging thiocarbonyl is found directly opposite the methyl substituent. A large number of studies related to different conformations due to variation in ring substituents have been reported.[36,37] By contrast, very little has been done by way of looking at positions taken up by ligands other than carbonyls with regard to arene ring substituents. There is only one short H- - -O distance (H(3)- - -O(5) = 2.39 (1) Å) in the structure of A.

Registry No. A, 103002-59-1; $Cr(\eta^6\text{-}C_6H_5OMe)(CO)_2(CS)$, 70140-18-0; $(\eta^6\text{-}C_6H_5OMe)(CO)_2CrCSCr(CO)_5$, 103002-60-4; $Cr\{\eta^6\text{-}(1,3,5\text{-}C_6H_3Me_3)\}(CO)_2(CS)$, 61483-88-3; $\{\eta^6\text{-}(1,3,5\text{-}C_6H_3Me_3)\}(CO)_2CrCSCr(CO)_5$, 103002-61-5; $Cr(\eta^6\text{-}C_6H_5Me)(CO)_2CS$, 70140-16-8; $Cr(CO)_5(THF)$, 15038-41-2; $Cr(\eta^6\text{-}C_6H_5OMe)(CO)_3$, 12116-44-8; $Cr\{\eta^6\text{-}(1,3,5\text{-}C_6H_3Me_3)\}(CO)_3$, 33435-43-7.

Supplementary Material Available: Tables of anisotropic thermal parameters for all non-hydrogen atoms with their esd's in parentheses and bond lengths and bond angles involving hydrogen atoms as well as an ORTEP plot of the unit cell contents (4 pages). Ordering information is given on any current masthead page.

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(26) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

(27) Saillard, J-Y.; Le Borgne, G.; Grandjean, D. *J. Organomet. Chem.* **1975**, *94*, 409.

(28) Huttner, G.; Lorenz, H.; Gartzke, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 609.

(29) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 642.

(30) Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983.

(31) Greaves, W. W.; Angelici, R. J.; Helland, B. J.; Klima, R.; Jacobson, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7618.

(32) Bird, P. H.; Ismail, A. A.; Butler, I. S. *Inorg. Chem.* **1985**, *24*, 2911.

(33) Korp, J. D.; Bernal, I. *Cryst. Struct. Commun.* **1980**, *9*, 821.

(34) Saillard, J-Y.; Grandjean, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 2285.

(35) Van Meurs, F.; Van Koningsveld, H. *J. Organomet. Chem.* **1977**, *131*, 423.

(36) Halet, J. F.; Saillard, J-Y.; Caro, B.; Le Bichan, J-Y.; Top, S.; Jaouen, G. *J. Organomet. Chem.* **1984**, *268*, C37.

(37) McGlinchey, M. J.; Fletcher, J. L.; Sayer, B. G.; Bougeard, P.; Faggiani, R.; Lock, C. J. L.; Bain, A. D.; Rodger, C.; Kundig, E. P.; Astruc, D.; Hamon, J-R.; Le Maux, P.; Top, S.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1983**, 634.