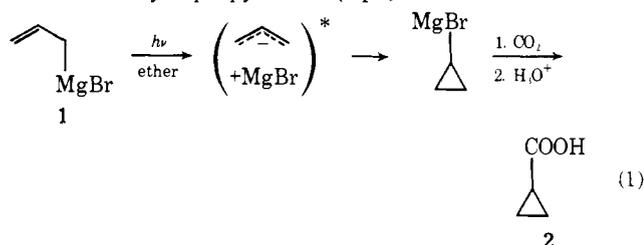


ucts are summarized in Table I. The cyclopropane derivatives were identified by comparison with authentic samples.⁹⁻¹¹

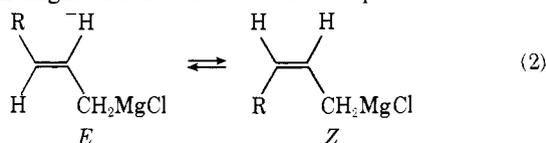
These allyl Grignard compounds did not undergo cyclization upon heating, but gave polymeric materials. Thus, several experiments were made in sealed evacuated tubes at 200 °C for different periods of time, 0.5–24 h, or upon heating in diglyme solution under reflux (165 °C).

We have measured the uv absorption spectra of allylmagnesium bromide (**1**) and of β -methylallylmagnesium chloride (**6**) in ether solutions (Table I). These, along with the known uv spectra of cinnamylmagnesium bromide,¹² show absorption maxima at longer wavelengths than the hydrocarbons from which they are derived. The uv spectra as well as other spectroscopic data (mainly NMR) indicate that the organomagnesium bonds in these systems are highly polarized, and exhibit ionic character with partial delocalization of the metal-carbon bond electron pair into the π electron system.⁴⁻⁶

The observed light-induced transformation may thus be visualized as ring closure of the electronically excited allyl anion to the cyclopropyl anion (eq 1).



Theoretical considerations suggest the disrotatory course¹ for such cyclization; however, the degree of stereoselectivity could not be established for these systems since the geometry of the anionic intermediates is not retained during the reactions. This behavior is likely to be due to: (a) inversion of the cyclopropyl anion to the preferred *trans* geometry and (b) the rapid rotation around the C-C bonds of the allyl anion.¹³ NMR studies established that allyl Grignard compounds exist in ether solutions as a rapidly equilibrating mixture of two isomers *E* and *Z* (**2**), the relative amounts of each isomer being determined by the nature of the substituent R.¹⁴ The *E* form is favored when R is bulky. The 1:1 formation of *trans*- and *cis*-1,2-dideuteriocyclopropane carboxylic acids and the predominant formation of the thermodynamically more stable *trans* cyclopropyl isomers **10** and **12** might be the result of these two phenomena.



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A Novel Tridentate Ligand Formed by the Condensation and Rearrangement of Three Ethoxycarbonyl Isothiocyanate Molecules in the Presence of $\text{RhCl}(\text{PPh}_3)_3$

Sir:

We wish to describe the preparation and characterization of a complex of Rh(III) in which a new tridentate ligand, formed by the condensation and rearrangement of three molecules of ethoxycarbonyl isothiocyanate in the presence of tris(triphenylphosphine)chlororhodium(I), is attached to the metal atom through two S linkages and one carbene C linkage.

A benzene solution of $\text{RhCl}(\text{PPh}_3)_3$ (0.432 mmol) and excess $\text{EtOCONCS} = \text{L}$ (3.66 mmol) was stirred at room temperature for 30 min and was then refluxed under Ar for an additional 2 h. After removal of the solvent under reduced pressure the residue was washed with *n*-hexane to yield a reddish orange powder. This crude product was redissolved in a minimal amount of acetone. Diethyl ether was added dropwise until crystals appeared. The mixture was kept at 5° overnight to yield reddish orange prisms. Analysis of the material is consistent with its formulation as $\text{RhCl}(\text{PPh}_3)_2\text{L}_3 \cdot (\text{CH}_3)_2\text{CO}$. Anal. Calcd: C, 54.96; H, 4.61; N, 3.77. Found: C, 54.94; H, 4.69; N, 3.78. The NMR spectrum of this complex dissolved in CDCl_3 shows two equivalent ethyl groups at τ 8.76 (t, 6 H, CH_3 ; $J = 7.5$ Hz) and 5.87 (q, 4 H, CH_2 ; $J = 7.5$ Hz) as well as a different ethyl group at τ 8.79 (t, 3 H, CH_3 ; $J = 6.8$ Hz) and 6.04 (q, 2 H, CH_2 ; $J = 6.8$ Hz). The acetone resonance at τ 7.95 (s, 6 H) is found to be consistent with one acetone molecule per molecule of complex. The ir (KBr disk) shows $\nu(\text{C}=\text{O})$ absorptions at 1785 (s), 1765 (s), and 1711 cm^{-1} (s) (acetone). A similar spectroscopic analysis indicates that when the material is recrystallized from a 1:1 acetone-diethyl ether solution the hemietherate is formed.

Previously we reported^{1,2} the unexpected product $\text{RhCl}(\text{PPh}_3)_2\text{L}'_2$, formed by the condensation of two molecules of $\text{L}' = \text{PhCONCS}$ with $\text{RhCl}(\text{PPh}_3)_3$. Even with a knowledge of the tridentate ligand in that complex we could not arrive at a satisfactory, unambiguous formulation for the present complex, $\text{RhCl}(\text{PPh}_3)_2\text{L}_3$. Accordingly, an x-ray diffraction study was undertaken.

The compound $\text{RhCl}(\text{PPh}_3)_2(\text{EtOCONCS})_3 \cdot (\text{CH}_3)_2\text{CO}$ crystallizes with four formula units in the triclinic space group $C_1^1-P\bar{1}$ in a cell of the following dimensions: $a = 15.214$ (6), $b = 27.571$ (9), $c = 12.857$ (6) Å; $\alpha = 103.12$ (2), $\beta = 90.24$ (2), $\gamma = 100.03$ (2)°; $V = 5166$ Å³; $d_{\text{calcd}} = 1.432$, $d_{\text{obsd}} = 1.35$ (3) g cm⁻³; μ (Cu $K\alpha$) = 53.56 cm⁻¹. Data were collected on a Picker x-ray diffractometer using Ni-filtered Cu $K\alpha$ radiation out to 2θ (Cu $K\alpha_1$) of 94°. A total of 7375 unique reflections having $F_o^2 > 3\sigma$ (F_o^2) was used in the ensuing calculations. The fact that the cell is indeed triclinic was established through extensive photographs, through a cell reduction, and by comparison of F_o^2 values of low-order planes. The presence of two formula units per asymmetric unit necessitates the location of 64 individual atoms and 12 rigid phenyl groups. Refinement of

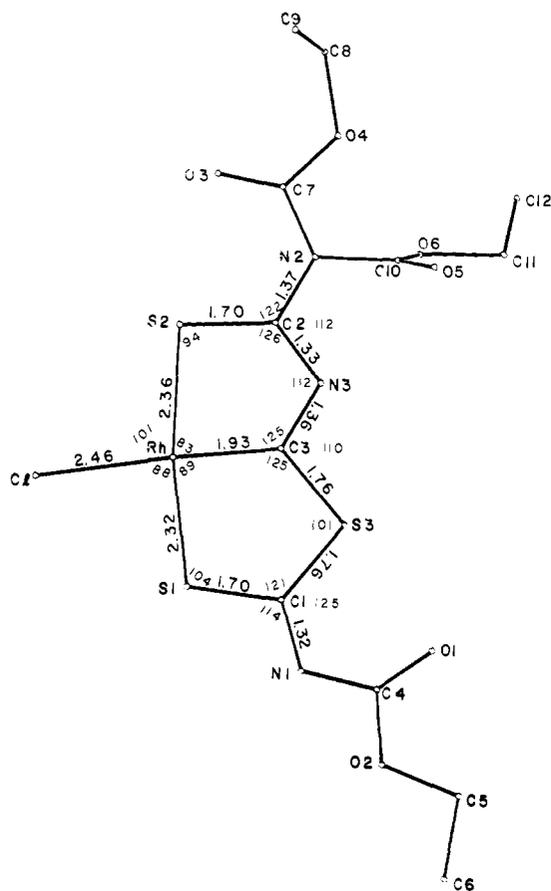


Figure 1. A drawing of molecule B of $\text{RhCl}(\text{PPh}_3)_2(\text{EtOCONCS})_3$, viewed in the isothiocyanate ligand plane. The PPh_3 groups approximately above and below the Rh atom have been omitted for the sake of clarity. As judged by agreement between the two independent molecules in the asymmetric unit, the estimated standard deviations on bond distances are 0.01–0.02 Å and on bond angles are 0.3–1.0°.

the resultant 401 variables (isotropic model) by full-matrix least-squares methods has converged to values of 0.072 and 0.091 for the conventional R and R_w indices, respectively. (See paragraph at end of paper regarding supplementary material.)

The two independent nonsolvent molecules in the asymmetric unit differ somewhat in conformations of their terminal groups; they are otherwise equivalent. In Figure 1 we show a projection of molecule B onto the ligand plane. The trans PPh_3 groups in axial positions, approximately above and below the Rh atom, have been omitted for the sake of clarity. The Rh atom has a slightly distorted octahedral coordination with trans PPh_3 groups. The four equatorial sites are occupied by the chloro ligand and by the tridentate ligand (EtOCONCS)₃. Two former EtOCONCS molecules can be thought of as $\text{C}(6)\text{--C}(5)\text{--O}(2)\text{--C}(4)\text{O}(1)\text{--N}(1)\text{--C}(1)\text{--S}(1)$ and $\text{C}(9)\text{--C}(8)\text{--O}(4)\text{--C}(7)\text{O}(3)\text{--N}(2)\text{--C}(2)\text{--S}(2)$; the two fragments of the third EtOCONCS molecule consist of $\text{C}(12)\text{--C}(11)\text{--O}(6)\text{--C}(10)\text{O}(5)$ attached to $\text{N}(2)$ and of $\text{N}(3)\text{--C}(3)\text{--S}(3)$ joining $\text{C}(2)$ and $\text{C}(1)$ to form a fused system of two five-membered rings. The tridentate ligand is attached to Rh through two S linkages ($\text{S}(1)$ and $\text{S}(2)$) and one carbene C linkage ($\text{C}(3)$). The fused ring system closely resembles that found earlier for $(\text{PhCONCS})_2$ attached to $\text{Rh}(\text{III})$,^{1,2} with the exception that an O atom in that system has been replaced by $\text{S}(2)$. With the exception of the geometrical changes brought about by this substitution, the geometries of the two ring systems are very similar. In particular, the present ring system is again essentially planar with some evidence for delo-

calization of bonding. The $\text{Rh}(\text{III})\text{--C}(3)$ (carbene) bond is again 1.93 Å, and the carbene again exerts a large trans influence on the trans chloro ligand.

Without mechanistic studies one can only speculate on the differing reactivity patterns of EtOCONCS and PhCONCS toward $\text{RhCl}(\text{PPh}_3)_3$. Presumably the reactions proceed along different but equally remarkable pathways, in part because of the differing basicities of R in the RCONCS groups.

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Supplementary Material Available: Atomic parameters (2 pages). Ordering information is given on any current masthead page.

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An Electron Spin Resonance Study of the Radical Anions Derived from Metal Carbene Complexes of Chromium, Molybdenum, and Tungsten

Sir:

A decade after the initial work by Fischer and Maasböl,¹ there still exists an active interest in transition metal carbene complexes,² particularly as regards their electronic structure, the mechanisms of their reactions, and their use in organic synthesis. ¹³C NMR³ and chemical studies⁴ have suggested an $\text{M}^{\ominus}\text{--C}^{\oplus}$ ylide nature for complexes of the type $(\text{CO})_5\text{MC}(\text{X})\text{Y}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in which the carbene carbon bound to the metal is best viewed as a carbocation stabilized by electron donation from the metal and from hetero substituents. Recent MO calculations⁵ validate this picture and reveal that the LUMO in a representative complex is localized primarily on the carbene atom and is considerably more stable than the next lowest unoccupied MO. By analogy with carbonium ions,⁶ these complexes should therefore readily undergo one-electron reduction to the corresponding carbon-centered radicals. We wish to report that a variety of reducing agents indeed produce such anionic organometallic radical species. We also present evidence suggesting that these novel species may be the reactive intermediates in the reactions of carbene complexes with strongly nucleophilic reagents via a single-electron transfer mechanism.

A dilute (~ 0.001 M) solution of (phenylmethoxycarbene)pentacarbonylchromium in THF/HMPA⁷ (2:1 v/v) treated briefly at -78° in an inert atmosphere with Na/K alloy dispersed in THF gives rise to an intense and highly resolved ESR spectrum (Figure 1) which persists indefinitely at low temperatures ($< -50^\circ$) but decays with increasing rates as the temperature is raised. A computer simulation