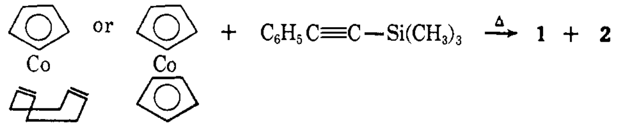
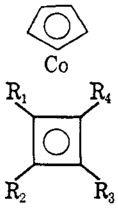
bearing unsubstituted positions on the cyclobutadiene ring.





1-11

1, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = Si(CH_3)_3$
2, $R_1 = R_2 = C_6H_5$; $R_3 = R_4 = Si(CH_3)_3$
3, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = Sn(C_6H_5)_3$
4, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = CH_3$
5, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = COCH_3$
6, $R_1 = R_2 = C_6H_5$; $R_3 = R_4 = COCH_3$
7, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = CHO$
8, $R_1 = R_2 = C_6H_5$; $R_3 = R_4 = CHO$
9, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = CF_3$
10, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = H$
11, $R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$

(Phenylethynyl)trimethylsilane and the cyclooctadiene complex in refluxing xylene gave a mixture of two isomers, **1** and **2**, in 59% yield. The ratio **1**:**2** was approximately 2:1. (Phenylethynyl)trimethylsilane and cobaltocene yielded the same mixture of isomers in refluxing diethylbenzene in 38% yield. (Phenylethynyl)-triphenyltin also reacts with the cyclooctadiene complex to produce **3** in 53% yield. The structure assigned seems reasonable on steric grounds. No cyclobutadiene complexes could be detected following the reaction of cobaltocene and the tin-substituted acetylene. Both the cyclooctadiene complex and cobaltocene reacted with phenylmethylacetylene, but for reasons which are not clear at present only a single cyclobutadiene complex, **4**, was isolated.

Arylacetylenes bearing electron-withdrawing substituents also yield cyclobutadiene complexes. Phenylacetylacetylene reacts with either the cyclooctadiene complex or cobaltocene to give the expected mixture of isomers **5** and **6**. Phenylpropargylaldehyde led only to a rather insoluble product which did not contain cyclobutadiene complexes and is believed to be polymeric. However, this difficulty may be circumvented by reaction of the cyclooctadiene complex with the diethyl acetal of phenylpropargylaldehyde. After hydrolysis of the reaction products, the corresponding isomeric aldehydes **7** and **8** may be isolated. Phenyltrifluoromethylacetylene[3] reacts with either the cyclooctadiene complex or cobaltocene to produce **9**. Chromatography gave evidence of a second complex, but too little was present to permit identification.

Compounds **1** and **3** react with HCl to give the same product, **10**. Compound **2** reacts with HCl to give the expected isomer, **11**. Compounds **10** and **11** are the first examples of the parent complex system which possess unsubstituted positions on the cyclobutadiene ring and present interesting possibilities for the study of competitive electrophilic substitution in four-, five-, and six-membered ring systems. The significance of the silyl derivatives as intermediates is evident from the fact that phenylacetylene has thus far formed no cyclobutadiene complexes with either the cyclooctadiene complex or cobaltocene but rather undergoes some trimerization.

The structures of the new cyclobutadiene complexes reported here are supported by elemental analyses, molecular weights (mass spectra), and nmr, ultraviolet and infrared spectra. The products may be isolated using column and thin layer chromatography. Most of them may be sublimed under reduced pressure at elevated temperatures. Although the stability limits of these compounds have not been fully defined, they are stable to air and water and seem to have good thermal stability. In the nmr spectra of these compounds in CCl_4 the position of absorption of the cyclopentadienyl protons varies from τ 5.02 (**9**) to 5.52 (**4**). The cyclobutadiene protons appear at τ 5.18 in **10** and at τ 5.70 in **11**. These spectra support the structures assigned to **10** and **11** since in **10** two flanking aryl groups would be expected to exert a greater deshielding effect on the cyclobutadiene protons than would a single flanking aryl group which would be the case in **11**. The mass spectra of these compounds always contain a peak at *m/e* 124 ($C_5H_5Co^+$). No peaks are found which can be ascribed to initial cleavage of C_5H_5. The other major peaks in the spectra may be rationalized in terms of degradation of the cyclobutadiene ring or substituent groups.

The reactions of the cyclooctadiene complex and cobaltocene with acetylenes are not completely general. Diiodoacetylene, for example, does not undergo complex formation. Neither does 3-phenylpropynamide. The results of the reactions reported here and a number of others which we have examined suggest that formation of cyclobutadiene complexes using these routes requires acetylenes bearing an aryl group conjugated with the triple bond. Even then cyclobutadiene complex formation may not occur if trimerization, more extensive polymerization, or other processes occur readily.

Our preliminary, independent investigation of substitution reactions of π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt(I) confirms the observations of Rausch and Genetti[1] that Friedel–Crafts acetylation occurs only in low yield and that metalation may be effected with *n*-butyllithium.[3a]

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[3] Phenyltrifluoromethylacetylene was prepared by sunlamp irrad ation of CF_3I and phenylacetylene followed by dehydrohalogenatic of the product by dropping it onto powdered KOH at 220°.

[3a] Note Added in Proof. A personal communication from M. D. Rausch and A. Siegel indicates that compounds **1** and **2** may also be made in high yield from cyclopentadienylcobalt dicarbonyl and phenyltrimethylsilylacetylene in refluxing xylene.

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[5] Postdoctoral research associate supported by the National Science Foundation Summer Research Participation Program for College Teachers.

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Two New Chromium–Carbonyl–Carbene Complexes

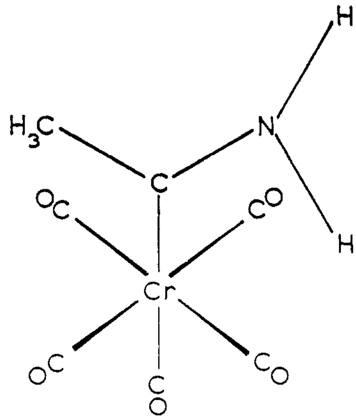
Sir:

When gaseous ammonia is passed through a benzene solution containing methylmethoxycarbenechromium pentacarbonyl,[1] an immediate color change occurs. Upon removal of the benzene by distillation under reduced pressure, pale yellow crystals form which can be recrystallized from a 9:1 hexane–ether mixture at −95°. The diamagnetic crystals melt at 76–77°. They are soluble in polar and nonpolar organic solvents and insoluble in water. In the absence of oxygen, the water-saturated ether solutions are remarkably stable. Total elemental analysis and molecular weight determination in benzene are in good agreement with the formation of $Cr(CO)_5CCH_3(NH_2)$. Gas chromatographic analysis of the solvent shows that methanol was the only other product.

Anal. Calcd for $C_7H_5CrNO_5$: C, 35.76; H, 2.12; Cr, 22.11; N, 5.96; O, 34.0. Found: C, 36.12; H, 2.08; Cr, 22.11; N, 5.91; O, 33.8.

The nmr spectrum of this complex in deuterated acetone exhibits a broad triplet centered at τ −0.25, J_{N-H} = 50 cps, as well as a singlet at τ 7.16 in the area ratio of 2:3, respectively. Upon addition of deuterium oxide, the broad triplet disappears and a band due to hydroxyl protons appears. This observation as well as the broadness of the band, which is due to the nuclear electric quadrupole of the nitrogen atom, suggests that the two hydrogen atoms are attached to the nitrogen atom. The triplet may then arise from the coupling of the nitrogen-14 with the protons attached to it. The singlet is attributed to the three CH_3 protons. This methyl group is not attached to the nitrogen atom; otherwise a multiplet due to spin–spin coupling with the NH_2 group should be observed.[2]

We believe, therefore, that the structure might be as shown below. In this structure the $Cr–CCH_3(NH_2)$ atoms define a plane, except for the CH_3 protons. In order to minimize steric interactions between the NH′ hydrogen atom and a *cis*-CO group, the plane might bisect the angle formed by two *cis*-CO groups and the Cr atom. This structure is then similar to that of the phenylmethoxycarbenechromium pentacarbonyl,[3] except that the C_6H_5 and OCH_3 groups have been replaced by the CH_3 and NH_2 groups.



A C_{4v} symmetry of the $Cr(CO)_5$ moiety is consistent with the four infrared CO stretching frequencies (hexane solution) at 2057, 1964, 1949, and 1941 cm⁻¹. Although it is predicted that only three bands should be observed,[4] other $M(CO)_5L$ molecules, where L represents a variety of ligands and M = Cr, Mo, and W, exhibit also four bands.[5,6]

The much slower reaction of $Cr(CO)_5CCH_3(OCH_3)$ with thiophenol yields methylthiophenoxycarbenechromium pentacarbonyl. The dark brown crystals have physical properties that are similar to the methylaminocarbene complex. The compound is monomeric in benzene and melts at 67–68°.

Anal. Calcd for $C_{13}H_8CrO_5S$: C, 47.56; H, 2.46; Cr, 15.84; O, 24.4; S, 9.8. Found: C, 47.62; H, 2.50; Cr, 15.99; O, 24.6; S, 9.2.

The nmr spectrum of this compound in deuteriobenzene exhibits lines at τ 3.10, 3.45, and 7.08 with relative intensities of 3:2:3, respectively. The two bands at τ 3.10 and 3.45 are assigned to the C_6H_5 protons; the line at τ 7.08 is due to the CH_3 protons. Only three CO stretching frequencies (hexane solution) are observed at 2064, 1986, and 1960 cm⁻¹. Both of these observations are consistent with a structure similar to that of $(CO)_5CrCCH_3(NH_2)$ except that an SC_6H_5 group is in the place of the NH_2 group.

The mass spectra of these new carbene complexes show a pattern similar to that of methylmethoxycarbenechromium pentacarbonyl.[7] This is additional proof for their structure. The complexes are therefore formed by replacement of the methoxy group by NH_2 or SC_6H_5 without any other rearrangements.

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[2] We thank Dr. E. Moser for the interpretation of the nmr spectrum.

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(7) We wish to thank Dr. J. Müller for this information in advance of publication and for his helpful discussions.

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The Circular Dichroism of L-Tryptophan by an Improved Dichrograph[1]

Sir:

The circular dichroism (CD) measurements of proteins and polypeptides have revealed the presence of well-defined ellipticity bands in the aromatic absorption region.[2-4] The origins of these bands have been associated with various aromatic amino acid side chains, although the specific information necessary for such correlation is rather limited, especially in those cases which exhibit poor signal-to-noise ratios due to either relatively high absorptivity, or to low rotatory strengths, or to both. Even in cases in which the signal-to-noise

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[1] This work was supported by research grants from the National Science Foundation (GB-6964) and the Research Foundation of the State University of New York.

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