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Carbene Derivatives of Molybdenum and Tungsten Containing Metal–Metal Bonds

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A series of compounds $C_5H_5M(CO)_2[M'(C_6H_5)_3]C(OR')R$ (M = Mo, W; M′ = Ge, Sn; R = CH_3, C_6H_5; R′ = CH_3, C_2H_5) have been prepared by the reaction of organolithium reagents with $C_5H_5M(CO)_3M'(C_6H_5)_3$ followed by alkylation. In these compounds the carbene and $M'(C_6H_5)_3$ ligands occupy mutually trans positions. The infrared spectra of these complexes show the presence of two conformers due to rotation about the metal–carbene bond; a study of the spectrum of a ^{13}CO-enriched complex indicates that both conformers are of C_s symmetry. The carbene complexes react with amines to form aminocarbene complexes; in the reaction with diethylamine, an ethyl group is cleaved from the amine. In some cases, compounds of formula $(C_6H_5)_3GeC_5H_4M(CO)_3R'$ are formed in the synthesis of the carbene complexes; in these species the $Ge(C_6H_5)_3$ group initially attached to the metal has been transferred to the cyclopentadienyl ring.

Introduction

A great many transition metal–carbene complexes have been studied in recent years, and this field of chemistry has been the subject of several reviews.[1–4]

As part of our interest in the chemistry of group 4–transition metal compounds, we have undertaken the preparation of carbene complexes which contain bonds between transition metals and silicon, germanium, and tin. The only such compounds which have been reported previously are $(C_6H_5)_3SnCo(CO)_3C(OC_2H_5)C_6H_5$,[5] $(C_6H_5)_3PbCo(CO)_3C(OC_2H_5)C_6H_5$,[5] and $(C_6H_5)_3GeMn(CO)_4C(OC_2H_5)CH_3$.[6] An account has been published previously of the reaction of the $[(C_6H_5)_3GeMn(CO)_4COCH_3]^-$ ion with H^+ to give cyclic germyloxycarbenes[6], and we were curious to determine whether such behavior would be observed for complexes of other metals.

This paper reports the preparation of a variety of carbene complexes from the compounds $C_5H_5M(CO)_3M'(C_6H_5)_3$ (M = Mo, W; M′ = Ge, Sn). In most cases the desired carbene complexes were obtained in a straightforward manner; however, this investigation did uncover some remarkable and unexpected reactions as well.

Experimental Section

All reactions were carried out under a nitrogen atmosphere; some representative preparations are described later in this section. Infrared spectra were recorded using a Perkin-Elmer Model 337 grating spectrophotometer with scale expansion and were calibrated against gaseous CO.[7] Proton NMR data were obtained using Varian A-60 or -56/60 instruments. Mass spectra were taken with an AEI-MS9 spectrometer. Microanalyses were performed by the University of Alberta microanalytical laboratory. Melting points were determined using a Gallenkamp apparatus and are uncorrected. Gas chromatographic analyses were performed using a Hewlett-Packard Model 5750 gas chromatograph equipped with a flame ionization detector.

Materials. 1,2-Dimethoxyethane (glyme) and tetrahydrofuran were distilled over calcium hydride before use; other solvents were used as obtained. $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$,[8] $C_5H_5Mo(CO)_3Sn(C_6H_5)_3$,[8] $C_5H_5W(CO)_3Ge(C_6H_5)_3$,[8] $C_5H_5W(CO)_3Sn(C_6H_5)_3$,[8] and $C_5H_5Mo(CO)_3H$[9] were prepared by published procedures. Organolithium reagents and trialkyloxonium salts were obtained from commercial sources; 95% ^{13}CO was obtained from Monsanto Research Corp.

Representative Reactions. I. Reactions of Starting Materials with Organolithium Reagents. A sample (1.00–4.00 g) of the appropriate starting material [$C_5H_5Mo(CO)_3Ge(C_6H_5)_3$, $C_5H_5Mo(CO)_3Sn(C_6H_5)_3$, $C_5H_5W(CO)_3Ge(C_6H_5)_3$, or $C_5H_5W(CO)_3Sn(C_6H_5)_3$] was dissolved in a minimum quantity of glyme (35–150 mL) and treated with a solution of organolithium reagent (phenyllithium in benzene–ether, methyllithium in ether, or *tert*-butyllithium in pentane). In general, the stoichiometric quantity of organolithium reagent was not sufficient to react completely with the starting material, and so the reagent was added in small portions until the infrared spectrum of the glyme solution showed the disappearance of all bands due to starting material.

II. Preparation of Phenylalkoxycarbenes. **$N(CH_3)_4\{C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(O)C_6H_5\}$.** A 1.50-g sample of $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ (2.73 mmol) was treated with phenyllithium as described above. The solvent was removed and the residue was dissolved in 150 mL of 50% methanol–water and filtered. After addition of an aqueous solution of tetramethylammonium bromide, the product separated as a yellow precipitate which was filtered and recrystallized from acetone–ether; yield 0.86 g of yellow crystals (1.23 mmol, 45%).

The compounds $N(CH_3)_4\{C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]C(O)C_6H_5\}$, $N(CH_3)_4\{C_5H_5W(CO)_2[Ge(C_6H_5)_3]C(O)C_6H_5\}$, and $N(CH_3)_4\{C_5H_5W(CO)_2[Sn(C_6H_5)_3]C(O)C_6H_5\}$ were prepared in the same way.

$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$. The reaction between 1.00 g of $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ (1.82 mmol) and phenyllithium in 35 mL of glyme was carried out as described above. The solvent was removed under vacuum and the residue was taken up in 100 mL of 50% methanol–water and filtered. A solution of excess $(C_2H_5)_3OBF_4$ in water was added and the product separated as a precipitate which was washed with water, filtered, and dried. The product was purified by chromatography over an alumina column, eluting as an orange band with 1:9 chloroform–hexane. The product was then recrystallized from dichloromethane–heptane; yield 0.52 g of orange crystals (0.79 mmol, 44%). Other phenylalkoxycarbene complexes were prepared in a similar manner; phenylmethoxycarbene complexes were prepared using a suspension of $(CH_3)_3OPF_6$ in water.

III. Preparation of Methylalkoxycarbenes. **$N(CH_3)_4\{C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(O)CH_3\}$.** A 2.00-g sample of $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ (3.65 mmol) was treated with methyllithium as described above. The solvent was removed and the residue was dissolved in water and filtered. On addition of a solution of $N(CH_3)_4Br$ the product separated and was filtered off and recrystallized from acetone–ether; yield 0.47 g of yellow crystals (0.74 mmol, 20%). $N(CH_3)_4\{C_5H_5W(CO)_2[Ge(C_6H_5)_3]C(O)CH_3\}$ was prepared in the same way.

$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)CH_3$. A 2.00-g sample of $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ (3.65 mmol) was treated with methyllithium in 75 mL of glyme; the solvent was removed, the residue was taken up in 50 mL of water, and a solution of excess $(C_2H_5)_3OBF_4$ in water was added. The product precipitated and was washed, filtered, dried, and purified by chromatography over an alumina column. It eluted as a light green band with 1:1 chloroform–hexane. The product was recrystallized from dichloromethane–heptane; yield 0.94 g of light green crystals (1.59 mmol, 44%). $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OCH_3)CH_3$ and $C_5H_5Fe(CO)[Ge(C_6H_5)_3]C(OCH_3)CH_3$ were prepared similarly.

$C_5H_5W(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)CH_3$ and $(C_6H_5)_3GeC_5H_4W(CO)_3C_2H_5$. A 2.50-g sample of $C_5H_5W(CO)_3Ge(C_6H_5)_3$ (3.92 mmol) was treated with methyllithium in 125 mL of glyme. The solvent was removed and the residue was taken up in 75 mL of water, filtered, and treated with excess $(C_2H_5)_3OBF_4$. The resulting precipitate was filtered, dried, and chromatographed over alumina. Chloroform–hexane (1:4) eluted a greenish yellow band of $(C_6H_5)_3GeC_5H_4W(CO)_3C_2H_5$, which was recrystallized from dichloromethane–heptane; yield 0.98 g of yellow-green crystals (1.47 mmol, 38%). A second greenish yellow band consisting of $C_5H_5W(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)CH_3$ was eluted with 1:1 chloroform–hexane and was recrystallized from dichloromethane–heptane; yield 0.45 g of olive

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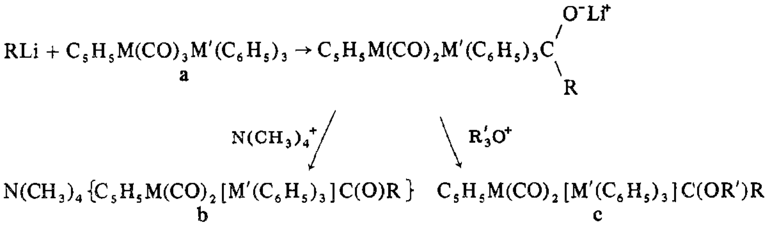
Scheme I



M = Mo, W; M' = Ge, R = CH_3, C_6H_5; M' = Sn, R = C_6H_5; R' = CH_3, C_2H_5

green crystals (0.66 mmol, 17%). $(C_6H_5)_3GeC_5H_4W(CO)_3CH_3$ and $C_5H_5W(CO)_2[Ge(C_6H_5)_3]C(OCH_3)CH_3$ were prepared similarly.

Reaction of Methyllithium with Triphenyltin Derivatives. A sample of $C_5H_5Mo(CO)_3Sn(C_6H_5)_3$ weighing 2.50 g (4.20 mmol) was treated with methyllithium in 100 mL of glyme; the solvent was removed and the residue was taken up in 50% methanol–water, filtered, and treated with excess aqueous $(C_2H_5)_3OBF_4$. The resulting precipitate was filtered, dried, and chromatographed over alumina. Chloroform–hexane (1:5) eluted first a greenish yellow band of $C_5H_5Mo(CO)_3C_2H_5$, identified by its infrared[10] and mass spectra; yield 0.130 g (0.474 mmol, 11%). A second, red-orange band of $C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]C(OC_2H_5)C_6H_5$ (identified by its infrared, NMR, and mass spectra) was eluted with the same solvent mixture; yield 0.363 g (0.518 mmol, 12%). Similarly, $C_5H_5Mo(CO)_3Sn(C_6H_5)_3$[9] treated with methyllithium and $(CH_3)_3OPF_6$ yielded $C_5H_5Mo(CO)_3CH_3$ (18%) and $C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]C(OCH_3)C_6H_5$ (12%); $C_5H_5W(CO)_3Sn(C_6H_5)_3$ yielded $C_5H_5W(CO)_3C_2H_5$[9] (16%) and $C_5H_5W(CO)_2[Sn(C_6H_5)_3]C(OC_2H_5)C_6H_5$ (10%) or $C_5H_5W(CO)_3CH_3$[9] (10%) and $C_5H_5W(CO)_2[Sn(C_6H_5)_3]C(OCH_3)C_6H_5$ (9%) when treated appropriately.

IV. Reactions with *tert*-Butyllithium. $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C(CH_3)_3$. A 3.00-g sample of $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ (5.47 mmol) was treated with *tert*-butyllithium in 100 mL of glyme, and the solvent was removed. The residue was taken up in 100 mL of water and filtered; the product was obtained by the addition of excess $(C_2H_5)_3OBF_4$. The product was chromatographed over alumina, eluting as a yellow band with 1:4 chloroform–hexane, and was recrystallized from dichloromethane–heptane; yield 0.193 g (0.304 mmol, 5.6%) of yellow crystals.

$(C_6H_5)_3GeC_5H_4Mo(CO)_3CH_3$. In another reaction, when a 3.00-g sample of $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ was reacted with *tert*-butyllithium as described above and the solution was treated with an aqueous suspension of $(CH_3)_3OPF_6$ and the resulting precipitate was chromatographed, the only product obtained was $(C_6H_5)_3GeC_5H_4Mo(CO)_3CH_3$; yield 0.153 g of yellow-brown crystals (0.272 mmol, 5.0%).

When $C_5H_5W(CO)_3Ge(C_6H_5)_3$ was treated with *tert*-butyllithium and the product was alkylated using $(C_2H_5)_3OBF_4$, the only product obtained was $(C_6H_5)_3GeC_5H_4W(CO)_3C_2H_5$ (40% yield).

V. Reactions of Phenylethoxycarbene Complexes with Amines. Synthesis of $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(NHC_2H_5)C_6H_5$. A 0.500-g sample of $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$ (0.76 mmol) was stirred in a pressure bottle with 50 mL of ethylamine. The mixture quickly (ca. 10 min) changed color from orange to very light yellow. After stirring of the mixture overnight the ethylamine was removed under vacuum and the product was recrystallized from dichloromethane–heptane; yield 0.490 g of fine yellow crystals (0.75 mmol, 98%).

Other aminocarbene complexes were prepared in the same manner. Ethylaminocarbene complexes could also be prepared (in yields of 74–96%) by reacting the phenylethoxycarbene complexes with diethylamine overnight under similar conditions; however these reactions proceeded much more slowly.

No reaction was observed between the phenylethoxycarbene complexes and ethanethiol.

VI. Preparation of ^{13}CO-Enriched Carbene Complexes. ^{13}CO-Enriched $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$. A 0.2062-g sample of $C_5H_5Mo(CO)_3H$ (0.840 mmol) was placed in a vessel of 192 mL volume. Using a specially designed vacuum line, 95% ^{13}CO was introduced to a pressure of 660 Torr (6.752 mmol of CO, calculated to yield a product containing 72.6% ^{13}CO at equilibrium). Then 30 mL of nitrogen-saturated hexane was introduced by injection through a rubber septum, and the solution was stirred vigorously overnight (although the infrared spectra of small aliquots removed periodically showed that exchange was essentially complete after 2 h). The gaseous CO was then removed using a Toepler pump on the same vacuum line and the solvent was removed under vacuum. The residue was dissolved in 10 mL of nitrogen-saturated tetrahydrofuran and stirred with a large excess of sodium sand for 1 h, which converted the $C_5H_5Mo(CO)_3H$ (as well as all of the $[C_5H_5Mo(CO)_3]_2$ resulting from air oxidation of the hydride) to $C_5H_5Mo(CO)_3Na$. The resulting solution was filtered into a small Schlenk tube containing 0.2980 g of $(C_6H_5)_3GeCl$ (0.882 mmol, 5% excess). This solution was stirred at room temperature for 48 h and then heated to 65 °C for 12 h, after which the reaction was complete. The solvent was removed, the residue was taken up in dichloromethane and filtered, and the product was precipitated by the addition of methanol; yield 0.3144 g (0.572 mmol, 60%).

^{13}Co-Enriched Carbene Complexes. Enriched $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ was converted to $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$ in 46% yield by the method already described, except that diethyl ether was used as the solvent for the reaction with phenyllithium.

Enriched $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$ (78% yield) was prepared by reacting ^{13}CO-enriched $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$ with dimethylamine as described previously.

Discussion

Syntheses of the Alkoxycarbene Complexes. Analytical, NMR, and infrared data for all complexes are presented in Tables I–III.

The alkoxycarbene complexes were generally synthesized straightforwardly by treatment of the appropriate starting materials first with an organolithium reagent and then with a trialkyloxonium salt, in the manner first described by Fischer.[11] The corresponding anionic acyl complexes could be isolated as tetraalkylammonium salts (see Scheme I).

The complex $C_5H_5Fe(CO)[Ge(C_6H_5)_3]C(OCH_3)CH_3$ was synthesized by an analogous reaction; however this complex was obtained in a very low yield and other similar iron complexes could not be isolated.

In some instances, however, the reaction was observed to take a different course. Treatment of triphenyltin–molybdenum or –tungsten complexes with methyllithium, followed by alkylation as above, yielded not the expected methylalkoxycarbene complexes (R = CH_3) but rather *phenyl*alkoxycarbene complexes (R = C_6H_5). As the triphenyltin ligand is the only source of phenyl groups in the system, it is presumed that this reaction proceeds via attack by methyllithium on the triphenyltin group on the starting material to yield phenyllithium, which then reacts with more starting material to yield phenylalkoxycarbene complexes in the normal fashion. Similar behavior has been reported for the reaction of $(C_6H_5)_3SbW(CO)_5$ with methyllithium;[12] here again, a phenylalkoxycarbene complex was obtained as the only product. Since tin and antimony are neighboring elements in the periodic table, it is perhaps not surprising that triphenyltin and triphenylantimony ligands behave similarly toward methyllithium.

The complexes $C_5H_5M(CO)_3R'$ (M = Mo, W; R' = CH_3, C_2H_5) were also obtained as by-products in these reactions. This probably indicates that some loss of the tin ligand occurs on reaction with methyllithium to give $C_5H_5M(CO)_3^-$, which

Table I. Analytical and Infrared Data

		Infrared spectra	
Compd	Analytical data[a]	$\nu(C\equiv O)^b$, cm^{-1}	$\nu(C=O)$ $\nu(C=N)^c$, cm^{-1}
	Alkoxycarbene Complexes		
$N(CH_3)_4\{C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]COCH_3\}$(**1**)	C-H-N, 20, Y, 215-218	1890 s, 1811 vs	1543 m
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OCH_3)CH_3$ (**2**)	C-H, 15, G, 173-174	1944 s, 1877 vs	
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)CH_3$ (**3**)	C-H, 44, G, 178-180	1943 s, 1875 vs	
$N(CH_3)_4\{C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]COC_6H_5\}$(**4**)	C-H-N, 45, Y, 212-215	1899 s, 1814 vs	1543 m
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OCH_3)C_6H_5$ (**5**)	C-H, 53, O, 188-189	1967 m, 1945 s, 1898 s, 1880 vs	
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$ (**6**)	C-H, 44, O, 187-189	1960 m, 1945 s, 1896 s, 1897 vs	
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C(CH_3)_3$ (**7**)	C-H, 5.6, Y, 176-178	1934 s, 1863 vs	
$N(CH_3)_4\{C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]COC_6H_5\}$(**8**)	C-H-N, 18, Y, 216-217	1892 s, 1811 vs	1515 m
$C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]C(OCH_3)C_6H_5$ (**9**)	C-H, 27, O, 159-160	1949 m, 1934 s, 1891 s, 1872 vs	
$C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]C(OC_2H_5)C_6H_5$ (**10**)	C-H, 28, O, 165-166	1950 m, 1934 s, 188 s, 1870 vs	
$N(CH_3)_4\{C_5H_5W(CO)_2[Ge(C_6H_5)_3]COCH_3\}$ (**11**)	C-H-N, 1.3, Y, 245-246	1892 s, 1811 s	1530 m
$C_5H_5W(CO)_2[Ge(C_6H_5)_3]C(OCH_3)CH_3$ (**12**)	C-H, 2.2, G, 186-187	1941 s, 1876 sh, 1872 vs	
$C_5H_5W(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)CH_3$ (**13**)	C-H, 17, Y-G, 199-200	1943 s, 1876 sh, 1871 vs	
$N(CH_3)_4\{C_5H_5W(CO)_2[Ge(C_6H_5)_3]COC_6H_5$ (**14**)	C-H-N, 22, Y, 258-260	1891 s, 1806 vs	1509 m
$C_5H_5W(CO)_2[Ge(C_6H_5)_3C(OCH_3)C_6H_5$ (**15**)	C-H, 3.1, O, 177-179	1959 m, 1942 s, 1893 s, 1873 vs	
$C_5H_5W(CO)_2[Ge(C_6H_5)_3C(OC_2H_5)C_6H_5$ (**16**)	C-H, 19, O, 196-198	1955 m, 1941 s, 1890 s, 1872 vs	
$N(CH_3)_4\{C_5H_5W(CO)_2[Sn(C_6H_5)_3COC_6H_5\}$ (**17**)	C-H-N, 25, Y, 144-145	1886 s, 1804 cs	1516 m
$C_5H_5W(CO)_2[Sn(C_6H_5)_3]C(OCH_3)C_6H_5$ (**18**)	C-H, 11, O, 185-186	1946 m, 1931 s, 1885 s, 1866 vs	
$C_5H_5W(CO)_2[Sn(C_6H_5)_3[C(OC_2H_5)C_6H_5$ (**19**)	C–H, 28, O, 164-165	1947 m, 1930 s, 1884 s, 1865 vs	
$C_5H_5Fe(CO)[Ge(C_6H_5)_3]C(OCH_3)CH_3$ (**20**)	C-H, 3.8, G, 132-135	1928 s	
	Aminocarbene Complexes		
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C[NH(C_2H_5)]C_6H_5$ (**21**)	C-H-N, 86, Y, 192-193	1929 s, 1861 vs	1500 m
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$ (**22**)	C-H-N, 83, Y, 214-215	1926 s, 1855 vs	1500 m
$C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]C[NH(C_2H_5)]C_6H_5$ (**23**)	C-H-N, 74, Y, 165-166	1919 s, 1855 vs	1500 m
$C_5H_5Mo(CO)_2[Sn(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$ (**24**)	C-H-N, 89, Y, 189-191	1917 s, 1849 vs	1500 m
$C_5H_5W(CO)_2[Ge(C_6H_5)_3]C[NH(C_2H_5)]C_6H_5$ (**25**)	C-H-N, 91, Y, 197-199	1927 s, 1856 vs	1498 m
$C_5H_5W(CO)_2[Ge(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$ (**26**)	C-H-N, 96, Y, 220-221	1923 s, 1850 vs	1500 m
$C_5H_5W(CO)_2[Sn(C_6H_5)_3]C[NH(C_2H_5)]C_6H_5$ (**27**)	C-H-N, 96, Y, 172-173	1916 s, 1846 vs	1498 m
$C_5H_5W(CO)_2[Sn(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$ (**28**)	C-H-N, 75, Y, 194-196	1912 s, 1843 vs	1500 m
	Other Complexes		
$(C_6H_5)_3GeC_5H_4Mo(CO)_3CH_3$ (**29**)	C-H, 5.0, Y, 148-150	2022 s, 1942 sh, 1936 vs	
$(C_6H_5)_3GeC_5H_4W(CO)_3CH_3$ (**30**)	C-H, 35, G, 158-160	2018 s, 1928 vs	
$(C_6H_5)_3GeC_5H_4W(CO)_3C_2H_5$ (**31**)	C-H, 38, Y, 122-123	2013 s, 1922 vs	

[a] The information given for each compound is as follows: elements for which satisfactory analyses were obtained, yield (%), color (Y = yellow, O = orange, G = light green), melting point (°C, uncorrected). Correct parent ion peaks were observed in the mass spectrum for all nonionic compounds. [b] Ionic compounds in tetrahydrofuran; nonionic compounds in *n*-heptane, except **20** in chloroform. [c] KBr disk.

is then alkylated by the trialkoxonium salt to yield the observed product.

Another unexpected reaction which was observed was the formation, in certain cases, of products of formula $(C_6H_5)_3GeC_5H_4M(CO)_3R'$ (M = Mo, R = CH_3; M = W, R' = CH_3, C_2H_5), in which the triphenylgermyl group had become detached from the metal center and had taken up a position on the cyclopentadienyl ring. Presumably this reaction proceeds through an intermediate in which the cyclopentadienyl ring has been lithiated (see Scheme II).

These products were not observed in all cases; their formation depended on the central metal (Mo or W) and on the organolithium reagent used, as shown in Table IV.

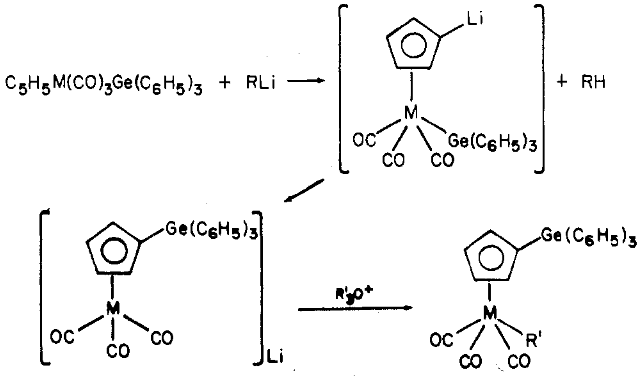
Thus the tendency to form ring-substituted products is seen to increase with the basicity of the organolithium reagent used. This is consistent with the mechanism proposed above, in that the more basic organolithium reagents would be expected to be more likely to metallate the cyclopentadienyl ring.

In addition *tert*-butylalkoxycarbene complexes are sterically disfavored due to the bulkiness of the *tert*-butyl group, and this would also tend to favor lithiation of the ring in preference to carbonyl group attack.

Also, tungsten complexes seem more prone to yield ring-substituted products than are those of molybdenum; whether this is because the cyclopentadienyl ring attached to tungsten is more susceptible to attack or because the carbonyl groups are less so is not clear.

It should be mentioned in passing that the product ratio between carbene and ring-substituted complexes was found to be somewhat variable. Also, there was a marked tendency to favor carbene products when $(C_2H_5)_3OBF_4$ was used as the alkylating agent and to favor ring-substituted products when $(CH_3)_3OPF_6$ was used. This was particularly striking in the case of the reaction of *tert*-butyllithium with $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$, where only $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C(CH_3)_3$ was obtained on treatment with $(C_2H_5)_3OBF_4$, whereas only $(C_6H_5)_3GeC_5H_4Mo(CO)_3CH_3$ was obtained on treatment with $(CH_3)_3OPF_6$. However, since ethoxycarbene products seemed in almost all cases to be more stable than and were obtained in higher yields than the corresponding methoxycarbene complexes, this effect would

Scheme II



(not isolated)

d

Table II. NMR Spectra[a]

Alkoxycarbene complexes	$\tau(C_5H_5)$[b]	$\tau(C\text{-}CH_3)$[b]	$\tau(O\text{-}CH_3)$[b] ($\tau(O\text{-}CH_2\text{-}CH_3)$[c])	$\tau(O\text{-}CH_2\text{-}CH_3)$[d]
1	5.17	7.55		
2	4.73	7.13	5.95	
3	4.74	7.12	(5.73)	8.62
4	5.08			
5	4.97		6.02	
6	5.00		(5.81)	8.70
7	4.68	8.77[f]	(5.91)	9.00
8	4.98			
9	4.92		5.90	
10	4.93		(5.69)	8.70
11	5.17	7.55		
12	4.68	7.19	6.02	
13	4.70	7.17	(5.78)	8.57
14	5.02			
15	4.88		6.10	
16	4.88		(5.91)	8.68
17	4.90			
18	4.80		6.00	
19	4.78		(5.73)	8.68
20	5.33	7.72	6.48	

Aminocarbene complexes	$\tau(C_5H_5)$[b]	$\tau(C\text{-}CH_3)$[b]	$\tau(N\text{-}CH_3)$[g] ($\tau(N\text{-}CH_2\text{-}CH_3)$[b]	$\tau(N\text{-}CH_2\text{-}CH_3)$[e]
21	5.32		(6.96)	8.67-9.17
22	5.37		6.83, 7.16	
23	5.25		(6.94)	8.67-9.17
24	5.26		6.68, 7.12	
25	5.22		(6.99)	8.67-9.17
26	5.25		6.75, 7.15	
27	5.32		(6.98)	8.67-9.17
28	5.18		6.63, 7.15	

Other compounds	$\tau(C_5H_5)$	τ(other)
29	4.68	9.82 ($\tau(MoCH_3)$)[b]
30	4.62	9.77 ($\tau(WCH_3)$)[b]
31	4.59	8.62 ($\tau(WC_2H_5)$) (all)[e]

[a] All values vs. TMS internal standard. Correct integrations were obtained for all spectra. Phenyl proton resonances were observed as broad multiplets in the range τ 2.1-3.3. $N(CH_3)_4^+$ proton resonances (where present) were observed as singlets in the range τ 6.67-6.83. [b] Singlet. [c] Quartet; $J_{CH_2\text{-}CH_3}$ = 7.0 Hz. [d] Triplet. [e] Multiplet. [f] Singlet; $C(CH_3)_3$ group protons. [g] Two singlets due to nonequivalent methyl groups. [h] Two overlapping quartets, $J_{CH_2\text{-}CH_3} = J_{HN\text{-}CH_2}$ = 7.0 Hz. (N-*H* proton resonance not observed.)

seem to be due largely to problems in the working up of the products, rather than to any actual participation of the trialkyloxonium salt in determining the course of the reaction.

Although a number of cyclopentadienylmetal complexes have been prepared having silyl,[13-21] germyl,[22] and stannyl[23] groups attached to the ring, we believe there is no precedent for their preparation by the type of reaction described here.

Synthesis of the Aminocarbene Complexes. The reaction between amines and alkoxycarbene complexes to yield aminocarbene complexes and alcohols is well-known.[24-25] When the phenylethoxycarbene complexes reported here were reacted with ethylamine or dimethylamine as solvent at room temperature for several hours, the corresponding ethylamino- or dimethylaminocarbene complexes were obtained in nearly quantitative yield.

$$C_5H_5M(CO)_2[M'(C_6H_5)_3]C(OC_2H_5)C_6H_5 + HNR^1R^2 \xrightarrow{25^\circ C} C_5H_5M(CO)_2[M'(C_6H_5)_3]C(NR^1R^2)C_6H_5 + C_2H_5OH$$

$$R^1 = R^2 = CH_3;\ R^1 = H,\ R^2 = C_2H_5$$

It was somewhat surprising, however, to find that when the phenylalkoxycarbene complexes were reacted with diethylamine at room temperature, the products obtained were *mono*ethylaminocarbene complexes, identical with those obtained from monoethylamine. The reactions in this case were much slower; nevertheless the yields obtained were high.

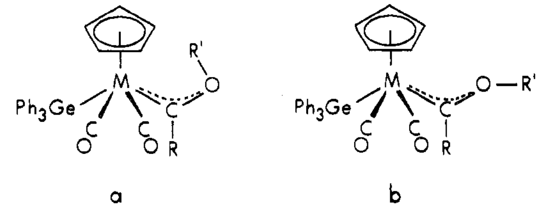


Figure 1. Possible isomerism about the (carbene)C–O bond in $C_5H_5M(CO)_2[M'(C_6H_5)_3]C(OR')R$ (**c**). (**a** is considered unlikely due to steric interaction between the C_5H_5 and OR′groups.)

The possibility that the observed products arose from the presence of ethylamine as an impurity in the diethylamine used was checked by gas chromatographic analysis of the diethylamine. No ethylamine was detected; thus an upper limit for the amount of ethylamine present in the diethylamine may be set at approximately 5 × 10^{-4} mol %. Since the reactions under discussion were observed up to the limit of solubility of the carbene complexes in diethylamine (about 0.4 mol %), this level of ethylamine as an impurity is insufficient to have formed the observed product.

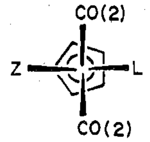
Apparently the observed products arise via the elimination of an ethyl group (presumably as C_2H_4) from diethylamine. This sort of behavior has also been observed in the reaction of diisopropylamine with $(OC)_5CrC(OCH_3)CH_3$, and the comparative instability of $(OC)_5CrC[N(C_2H_5)_2]CH_3$ has been noted.[27] A rationalization of this behavior in terms of the steric requirements of the aminocarbene ligand has been offered, and this would seem to receive support from the more ready elimination of an ethyl group in the cases reported here, in view of the large requirement of the cyclopentadienyl group in these complexes.

No reaction was observed between the phenylethoxycarbene complexes and ethanethiol under similar conditions.

Structure of the Carbene Complexes. The alkoxycarbene complexes described here, except for $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C(CH_3)_3$, all display infrared spectra which indicate the presence of two different species in heptane solution. This is particularly clear in the case of the phenylalkoxycarbene complexes, which show four clearly resolved C–O stretching frequencies. The same sort of spectra have been observed previously in the case of (arene)$Cr(CO)_2C(OCH_3)C_6H_5$ complexes[28] where the spectrum was interpreted as indicating the presence of two out of three possible conformers due to restricted rotation about the metal–carbene bond (vide infra).

In the case of the present compounds, the infrared spectra clearly indicate that the two species in solution are not cis–trans isomers; the fact that for both species the higher frequency, symmetric C–O stretching mode is less intense than the asymmetric stretching mode implies that in each species the two carbonyl groups occupy mutually trans positions.[29-31] Also, the two species do not appear to be due to restricted rotation about the (carbene)C–O bond (see Figure 1), as has been observed previously in the NMR spectra of some compounds;[32,33] only one set of peaks could be observed in the NMR spectrum of the present compounds down to −80 °C, far below the temperature (about −40 °C) at which this motion has previously been observed to freeze out.[32] In addition, inspection of scale molecular models suggests that only one of the two possible conformations about the (carbene)C–O bond is sterically allowed; the bulkiness of the cyclopentadienyl ring prevents the carbene ligand from assuming the config-

Table III. Observed[a] and Calculated Carbonyl Stretching Frequencies in ^{13}CO-Enriched Compounds[b]



Z = CO(1) or carbene
L = H or $Ge(C_6H_5)_3$

ν_{obsd}, cm^{-1}	ν_{calcd}, cm^{-1}	No. of ^{13}CO's (symmetry)	Mode
$C_5H_5Mo(CO)_3H$			
$k_1 = 16.171$; $k_2 = 15.529$; $k_{12} = 0.429$; $k_{22} = 0.240$ (mdyn/Å)			
2028.5	2027.9	0 (C_s)	A′
1949.0	1948.3		A′
1945.0	1945.6		A″
2004.0	2004.5	1 (C_s)	A′
1946.0	1945.6		A′
1926.0	1927.3		A″
c	2022.7	1 (C_1)	A
1948.0	1947.3		A
d	1908.4		A
2018.0	2017.0	2 (C_1)	A
c	1915.3		A
c	1902.5		A
c	1995.5	2 (C_s)	A′
c	1934.4		A′
d	1904.0		A″
1982.0	1982.9	3 (C_s)	A′
d	1905.0		A′
d	1902.5		A″
$C_5H_5Mo(CO)_3Ge(C_6H_5)_3$			
$k_1 = 15.789$; $k_2 = 15.385$; $k_{12} = 0.379$; $k_{22} = 0.403$ (mdyn/Å)			
2010.5	2010.5	0 (C_s)	A′
1943.5	1943.3		A′
1926.0	1926.0		A″
1995.0	1994.7	1 (C_s)	A′
c	1926.0		A′
c	1915.2		A″
2002.5	2002.8	1 (C_1)	A
1939.0	1939.0		A
c	1894.7		A
1983.0	1982.9	2 (C_1)	A
c	1917.8		A
c	1892.0		A
c	1994.8	2 (C_s)	A′
1915.5[c]	1915.2		A′
1883.0	1883.3		A″
1964.0[c]	1965.8	3 (C_s)	A′
c	1900.2		A′
1883.0[c]	1883.3		A″
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$			
Conformer A: $k_2 = 15.018$; $k_{22} = 0.501$ (mdyn/Å)			
Conformer B: $k_2 = 14.758$; $k_{22} = 0.513$ (mdyn/Å)			
Conformer A			
1960.0	1959.9	0 (C_s)	A′
1895.5	1895.5		A″
1945.0	1944.7	1 (C_1)	A
1869.0	1868.0		A
1916.0	1916.4	2 (C_s)	A′
1852.5	1853.5		A″
Conformer B			
1945.5	1944.5	0 (C_s)	A′
1878.0	1878.1		A″
1929.5	1929.2	1 (C_1)	A
1851.5	1851.0		A
1901.3	1901.3	2 (C_s)	A′
1836.4	1836.4		A″
$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$			
$k_2 = 14.438$; $k_{22} = 0.535$ (mdyn/Å)			
1926.0	1925.4	0 (C_s)	A′
1855.0	1855.4		A″
1910.5	1909.9	1 (C_1)	A
1829.5	1828.9		A
1881.5	1882.7	2 (C_s)	A′
1814.0	1814.2		A″

[a] Heptane solution. [b] See ref 38 for the numbering scheme for the CO groups given in this table. [c] Obscured or not observed. [d] Observed but not well resolved; not used in force constant calculation.

Table IV

RLi +	$C_5H_5M(CO)_3M'(C_6H_5)_3$ →	Products (on alkylation)
C_6H_5Li	M = Mo, W M′ = Ge, Sn	Carbene products (c) *only*
CH_3Li	M = Mo, M′ = Ge	c *only*
	M = W, M′ = Ge	c *and* ring substitution products (d)
$(CH_3)_3Li$	M = Mo, M′ = Ge	c and d
	M = W, M′ = Ge	d *only*

uration shown in Figure 1a. Consequently, we believe that the two species present in solutions of these carbene complexes are conformers due to restricted rotation about the metal–C(carbene) bond, as previously observed for the (arene)Cr$(CO)_2C(OCH_3)C_6H_5$ complexes. These conformers are shown as Newman projections, looking down the carbene–metal bond, in Figure 2.

Since only two of the three possible conformers are observed, it is obviously of interest to determine which two are present. This question has not been answered in the case of the (arene)Cr$(CO)_2C(OCH_3)C_6H_5$ complexes. In the case of the complexes discussed here, inspection of scale molecular models suggests that conformers such as that of Figure 2b are sterically less favorable than those of Figure 2a and c.

The answer to this problem can, in principle at least, be obtained by examination of the ^{13}CO satellite spectra in the C–O stretching region, as has been done for several other systems.[34-36] In the case of the conformers having C_s symmetry (Figure 2a and c), the stretching force constants for both carbonyl groups are identical (by symmetry), and there is no distinction between the two carbonyl groups with respect to substitution by ^{13}CO; thus both the all-^{12}CO spectrum and the mono-^{13}CO satellite spectrum will each consist of only two

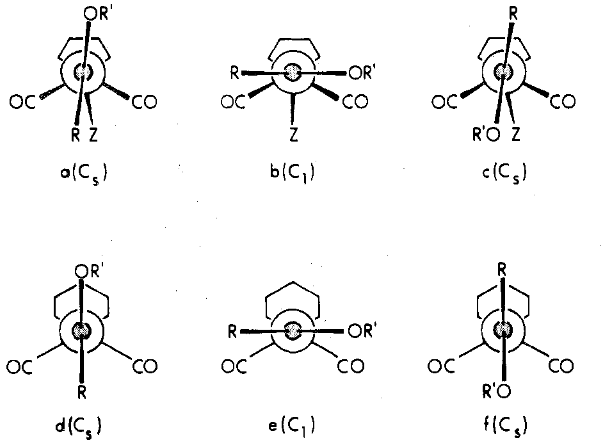


Figure 2. Possible conformers of $C_5H_5M(CO)_2[M'(C_6H_5)_3]C(OR')R$ ($Z = M'(C_6H_5)_3$) and $(arene(Cr(CO)_2C(OR')R$. (**b** and **e** each respresent one of a pair of enantiomers.)

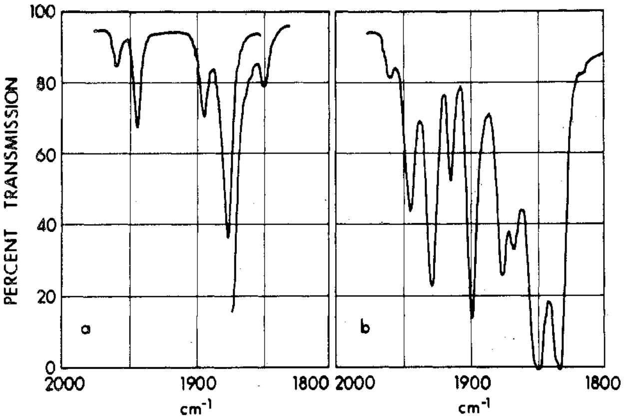


Figure 3. Infrared spectrum of $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$: a, 1% ^{13}CO (natural abundance); b, 70% ^{13}CO.

peaks.

However, in the case of the conformer of C_1 symmetry, the situation is different. Here the stretching force constants of the two carbonyl groups are not in general identical, and the two carbonyl groups are not equivalent with respect to substitution by ^{13}CO. Hence there will be two different ^{13}CO satellite spectra, depending on which of the two nonequivalent positions the single ^{13}CO molecule occupies, giving four satellite peaks in all. Since occupation of either position by a ^{13}CO molecule is equally likely, the satellite spectrum will consist of two pairs of peaks of equal intensity; the members of each pair may be expected to be separated by several wavenumbers.[34-36]

The infrared spectrum of $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$ is shown in Figure 3. The two conformers which are observed in this spectrum are designated as conformer A (peaks at 1960.0 and 1895.5 cm^{-1}) and conformer B (peaks at 1945.5 and 1878.0 cm^{-1}). Because of accidental overlap and the broadness of the peaks, only one ^{13}CO satellite peak can be clearly seen, at 1851.5 cm^{-1}; this is the satellite of the A″ mode conformer of B, identified on the basis of its intensity and position. This peak appears to be single, and thus conformer B may be assumed to be one of those of C_s symmetry (Figure 2a or c).

To observe the satellite peaks of conformer A, it was necessary to enrich the compound in ^{13}CO to the extent of approximately 70% ^{13}CO. (This degree of enrichment represents approximately the optimum in terms of the observability of the "satellite" peaks). This was done by synthesizing enriched $C_5H_5Mo(CO)_3H$ by direct exchange with gaseous

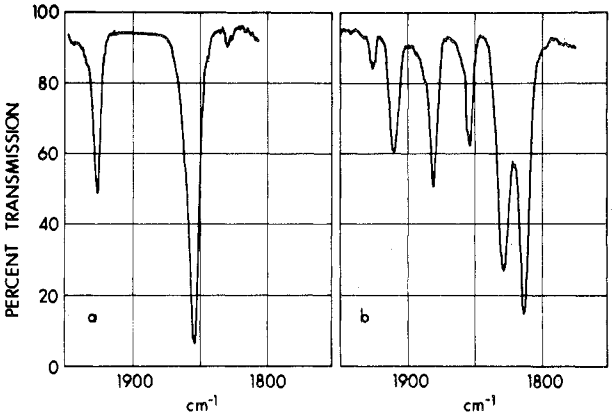


Figure 4. Infrared spectrum of $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$: a, 1% ^{13}CO (natural abundance); b, 70% ^{13}CO.

^{13}CO, and then preparing the carbene complex from the enriched hydride. The infrared spectrum of the enriched species (Figure 3b) is considerably complicated by the presence of bands due to molecules containing two ^{13}CO groups; however both the "satellite" bands of the conformer A (A′, 1945.0 cm^{-1}; A″, 1869.0 cm^{-1}) and one of the "satellite" bands of conformer B (A′, 1929.5 cm^{-1}; the A″ satellite overlaps with another peak) are distinct and well resolved. All of these peaks are single; therefore conformers A and B both appear to have C_s symmetry and thus correspond to Figures 2a and c. (The assignment of the peaks in the infrared spectrum, shown in Table III, was made with the aid of the computer program MOLVIBS, an energy-factored force constant evaluation program.[37])

If it is assumed that both conformers have the same molar absorption coefficient for their respective vibrational modes, it can be determined from the spectrum shown in Figure 3a that the conformers are present in the ratio of 3.14:1 at 25 °C. (The ratios calculated from the symmetric and asymmetric stretching peaks are 3.13:1 and 3.16:1, respectively; this close agreement strengthens our confidence in the aforementioned assumption.) This corresponds to an energy barrier of 2830 J/mol for rotation about the Mo–C bond. No values for the rotational barrier in $(arene)Cr(CO)_2C(OCH_3)C_6H_5$ complexes have been reported.

The observation of a trans configuration for these compounds is consistent with the rule proposed by Darensbourg and Darensbourg[5] to the effect that the carbonyl group with the highest stretching force constant is the one which is attacked by an organolithium reagent. The stretching force constants for $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$ (see Table III) are $k_1 = 15.789$ mdyn/Å and $k_2 = 15.385$ mdyn/Å.[38]

The aminocarbene complexes show only two carbonyl stretching peaks in their infrared spectrum (see, e.g., Figure 4a), indicating that only one of the three possible conformers is present. Again, the asymmetric stretching mode is more intense than the symmetric stretch, indicative of a trans configuration. The infrared spectrum of a 70% ^{13}CO-enriched $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C[N(CH_3)_2]C_6H_5$ (Figure 4b) shows that the conformer present is one of those of C_s symmetry, as the "satellite" peaks due to the singly enriched species at 1910.5 and 1829.5 cm^{-1} are single. There is nothing to indicate which of the two possible C_s conformers is present; examination of scale molecular models indicates that, due to the bulkiness of the dimethylamino group, neither conformer is sterically favored and no clear choice can be made on this basis.

The complex $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C(CH_3)_3$ also shows only two carbonyl stretching peaks, indicating the presence of only one conformer. Again, this is presumably due to the bulky *tert*-butyl group on the carbene ligand. It is not known which conformer is present, although presumably it is one of those of C_s symmetry; due to the difficulty of sythesizing this compound, no ^{13}CO-enrichment study was carried out.

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Registry No. **1**, 61813-06-7; **2**, 61813-04-5; **3**, 61813-03-4; **4**, 61813-02-3; **5**, 61813-00-1; **6**, 61202-80-0; **7**, 61846-65-9; **8**, 61812-99-5; **9**, 61812-97-3; **10**, 61966-53-8; **11**, 61812-96-2; **12**, 61846-67-1; **13**, 61812-94-0; **14**, 61812-93-9; **15**, 61812-91-7; **16**, 61812-90-6; **17**, 61812-89-3; **18**, 61812-87-1; **19**, 61812-86-0; **20**, 61812-85-9; **21**, 61812-84-8; **22**, 61812-83-7; **23**, 61812-82-6; **24**, 61812-81-5; **25**, 61812-80-4; **26**, 61812-79-1; **27**, 61812-78-0; **28**, 61812-77-9; **29**, 61812-76-8; **30**, 61812-75-7; **31**, 61812-74-6; $C_5H_5Mo(CO)_3H$, 12176-06-6; $C_5H_5Mo(CO)_3Ge(C_6H_5)_3$, 12100-83-3; $C_5H_5W(CO)_3Ge(C_6H_5)_3$, 12100-84-4; $C_5H_5Mo(CO)_3Sn(C_6H_5)_3$, 12100-85-5; $C_5H_5Mo(CO)_3C_2H_5$, 12083-68-0; $C_5H_5Mo(CO)_3CH_3$, 12082-25-6; $C_5H_5W(CO)_3C_2H_5$, 51232-59-8; $C_5H_5W(CO)_3CH_3$, 12082-27-8; $C_5H_5W(CO)_3Sn(C_6H_5)_3$, 12100-87-7; $(C_6H_5)_3GeCl$, 1626-24-0.

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Crystal and Molecular Structure of η^5-Cyclopentadienyl(triphenylgermyl)dicarbonyl[phenyl(ethoxy)carbene]molybdenum(II), π-$C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$, a Carbene Complex Containing a Metal–Metal Bond

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The structure of the carbene complex $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2H_5)C_6H_5$ has been determined by single-crystal x-ray techniques. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a unit cell of dimensions a = 10.611 (2), b = 21.247 (3), c = 13.040 (2) Å, and β = 96.32 (1)°. Full-matrix least-squares refinement of 2414 independent counter data yielded a final R factor of 0.056. The structural features of this molecule are compared with those of related compounds, and the stereochemical influences leading to the observed configuration of this complex are discussed.

Introduction

In a recent paper we have described the synthesis and reactions of a series of carbene complexes of general formula $C_5H_5M(CO)_2[M'(C_6H_5)_3]C(OR')R$ (M = Mo, W; M′ = Ge, Sn; R = CH_3, C_6H_5; R′ = CH_3, C_2H_5).[1] One of the interesting features of these compounds was the observation in their infrared spectra of two sets of peaks indicating the presence of two conformers in hydrocarbon solution. We presented evidence suggesting that these two conformers were due to restricted rotation about the metal–carbene bond, with both conformers having C_s symmetry and a trans configuration of ligands about the central metal (Mo or W).

In order to understand this system better and, in particular, to investigate the steric interactions within the molecule which determine the nature of the conformers observed, an x-ray

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