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.

References and Notes

(1) E. O. Fischer, *Rev. Pure Appl. Chem.*, **24**, 407 (1970).
(2) E. O. Fischer, *Pure Appl. Chem.*, **30**, 353 (1972).
(3) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
(4) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).
(5) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).
(6) M. J. Webb, R. P. Stewart, Jr., and W. A. G. Graham, *J. Organomet. Chem.*, **59**, C21 (1973).
(7) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).
(8) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).
(9) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, p 156.
(10) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
(11) R. Aumann and E. O. Fischer, *Angew. Chem.*, **79**, 900 (1967).
(12) E. O. Fischer and R. Aumann, *Chem. Ber.*, **102**, 1495 (1969).
(13) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954).

(14) M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).
(15) R. L. Schaaf, P. T. Kan, C. T. Lenk, and E. P. Deck, *J. Org. Chem.*, **25**, 1986 (1960).
(16) M. Kumada, T. Tsunemi, and S. Iwasaki, *J. Organomet. Chem.*, **10**, 111 (1967).
(17) G. P. Sollott and W. R. Peterson, Jr., *J. Am. Chem. Soc.*, **89**, 5054 (1967).
(18) A. F. Halasa and D. P. Tate, *J. Organomet. Chem.*, **24**, 769 (1970).
(19) E. B. Sokolova, S. M. Massarakaya, and N. A. Varfolomeeva, *Zh. Obshch. Khim.*, **40**, 1762 (1970).
(20) C. S. Kraihenzel and J. Conville, *J. Organomet. Chem.*, **23**, 357 (1970).
(21) E. W. Abel and S. Moorhouse, *J. Organomet. Chem.*, **28**, 211 (1971).
(22) D. Seyferth, H. P. Hoffmann, R. Burton, and J. F. Helling, *Inorg. Chem.*, **1**, 227 (1962).
(23) T. Dodo, H. Suzuki, and T. Takiguchi, *Bull. Chem. Soc. Jpn.*, **43**, 288 (1970).
(24) U. Klabunde and E. O. Fischer, *J. Am. Chem. Soc.*, **89**, 7141 (1967).
(25) E. Moser and E. O. Fischer, *J. Organomet. Chem.*, **16**, 275 (1969).
(26) E. O. Fischer and E. Offhaus, *Chem. Ber.*, **102**, 2449 (1969).
(27) J. A. Connor and E. O. Fischer, *J. Chem. Soc. A*, 578 (1969).
(28) H. J. Beck, E. O. Fischer, and C. G. Kreiter, *J. Organomet. Chem.*, **26**, C41 (1971).
(29) A. R. Manning, *J. Chem. Soc. A*, 1904 (1970).
(30) M. J. Mays and S. M. Pearson, *J. Chem. Soc. A*, 2291 (1968).
(31) F. A. Cotton and C. M. Lukehart, *J. Am. Chem. Soc.*, **93**, 2672 (1971).
(32) C. G. Kreiter and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **8**, 761 (1969).
(33) E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Moller, and R. D. Fischer, *J. Organomet. Chem.*, **28**, 237 (1971).
(34) J. Dalton, *Inorg. Chem.*, **10**, 1822 (1971).
(35) T. Sawai, Ph.D. Thesis, McGill University, Montreal, P.Q., Canada, 1972.
(36) E. Wood and W. A. G. Graham, unpublished results.
(37) R. S. Gay, Ph.D. Thesis, University of Alberta, Edmonton, Alberta, Canada, 1970.
(38) Our numbering of the force constants in these idealized square-pyramidal complexes follows the convention established in octahedral LM(CO)$_5$ complexes, where k_1 refers to the carbonyl trans to L. In the octahedral case, $k_1 < k_2$ in all known instances.^{39} For the square-pyramidal complexes investigated here, $k_1 > k_2$. It may be noted that a treatment of square-pyramidal tricarbonyl complexes involving an arbitrary relation between the interaction constants (made necessary by a lack of ^{13}CO information) has led to the opposite conclusion.^{40}
(39) R. S. Gay and W. A. G. Graham, *Inorg. Chem.*, **8**, 1561 (1969). Force constant values for Ph$_3$GeMn(CO)$_5$ and Ph$_3$SnMn(CO)$_5$ quoted by these authors are incorrect due to a wrong assignment. Correct values for Ph$_3$GeMn(CO)$_5$ are $k_1 = 16.40$ and $k_2 = 16.71$ mdyn/Å, while those for Ph$_3$SnMn(CO)$_5$ are 16.34 and 16.66 mdyn/Å.^{3} These compounds are thus *not* exceptions to the generalization that $k_1 < k_2$ in octahedral complexes.
(40) R. B. King and L. W. Houk, *Can. J. Chem.*, **47**, 2959 (1969).

Crystal and Molecular Structure of η^5-Cyclopentadienyl(triphenylgermyl)dicarbonyl[phenyl(ethoxy)carbene]molybdenum(II), π-C$_5$H$_5$Mo(CO)$_2$[Ge(C$_6$H$_5$)$_3$]C(OC$_2$H$_5$)C$_6$H$_5$, a Carbene Complex Containing a Metal–Metal Bond

L. Y. Y. CHAN, W. K. DEAN,* and W. A. G. GRAHAM

The structure of the carbene complex C$_5$H$_5$Mo(CO)$_2$[Ge(C$_6$H$_5$)$_3$]C(OC$_2$H$_5$)C$_6$H$_5$ 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 $\beta = 96.32$ (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$_5$H$_5$M(CO)$_2$[M'(C$_6$H$_5$)$_3$]C(OR')R (M = Mo, W; M' = Ge, Sn; R = CH$_3$, C$_6$H$_5$; R' = CH$_3$, C$_2$H$_5$).^{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

* To whom correspondence should be addressed at the Department of Chemistry, Emory University, Atlanta, Ga. 30222.

Table II

Final Atomic Parameters

Atom	x	y	z	B, Å^2
Mo	0.1715 (1)	0.1506 (1)	0.1236 (1)	a
Ge	0.2588 (1)	0.0654 (1)	0.2629 (1)	a
O(1)	0.4118 (8)	0.2038 (4)	0.2490 (6)	5.6 (2)
O(2)	0.2402 (7)	0.0283 (4)	0.0113 (6)	5.5 (2)
O(3)	0.1796 (14)	0.2293 (7)	−0.0651 (12)	4.1 (4)
O(3)′	0.2124 (14)	0.2536 (8)	−0.0208 (12)	4.3 (4)
C(1)	0.3259 (11)	0.1814 (5)	0.1987 (8)	4.0 (2)
C(2)	0.2202 (10)	0.0760 (6)	0.0542 (9)	4.4 (3)
C(3)	0.2540 (10)	0.1938 (5)	0.0061 (9)	4.3 (3)
C(4)	0.2354 (28)	0.2720 (14)	−0.1429 (26)	5.0 (6)
C(4)′	0.2713 (31)	0.3030 (18)	−0.0966 (27)	7.1 (9)
C(5)	0.2259 (29)	0.3347 (14)	−0.1165 (23)	6.7 (8)
C(5)′	0.2152 (35)	0.2662 (19)	−0.2020 (31)	9.8 (13)
C(1-1)^c	0.4439 (5)	0.0500 (3)	0.2708 (8)	3.6 (2)
C(1-2)	0.5078 (10)	0.0578 (3)	0.1832 (10)	4.0 (2)
C(1-3)	0.6361 (10)	0.0416 (3)	0.1868 (10)	4.8 (3)
C(1-4)	0.7006 (5)	0.0177 (3)	0.2780 (8)	5.3 (3)
C(1-5)	0.6367 (10)	0.0099 (3)	0.3655 (10)	6.0 (3)
C(1-6)	0.5084 (10)	0.0261 (3)	0.3619 (10)	4.7 (3)
C(2-1)	0.2241 (10)	0.0930 (3)	0.4021 (7)	3.4 (2)
C(2-2)	0.1140 (7)	0.0716 (3)	0.4412 (8)	3.8 (2)
C(2-3)	0.0857 (10)	0.0919 (3)	0.5383 (5)	4.0 (2)
C(2-4)	0.1675 (10)	0.1335 (3)	0.5962 (7)	5.2 (3)
C(2-5)	0.2775 (7)	0.1548 (3)	0.5571 (8)	5.7 (3)
C(2-6)	0.3058 (10)	0.1346 (3)	0.4601 (5)	4.2 (3)
C(3-1)	0.1782 (7)	−0.0195 (3)	0.2489 (5)	3.2 (2)
C(3-2)	0.0679 (7)	−0.0300 (3)	0.1818 (5)	4.1 (2)
C(3-3)	0.0144 (5)	−0.0903 (3)	0.1733 (3)	4.9 (3)
C(3-4)	0.0711 (7)	−0.1400 (3)	0.2319 (5)	4.6 (3)
C(3-5)	0.1814 (7)	−0.1294 (3)	0.2990 (5)	4.8 (3)
C(3-6)	0.2349 (5)	−0.0692 (4)	0.3075 (3)	4.2 (2)
C(4-1)	0.3809 (8)	0.1797 (4)	−0.0294 (6)	4.0 (2)
C(4-2)	0.3903 (8)	0.1336 (4)	−0.1049 (6)	5.5 (3)
C(4-3)	0.5090 (10)	0.1174 (3)	−0.1342 (6)	5.6 (3)
C(4-4)	0.6185 (8)	0.1473 (4)	−0.0881 (6)	6.1 (3)
C(4-5)	0.6091 (8)	0.1934 (4)	−0.0126 (6)	6.6 (3)
C(4-6)	0.4903 (10)	0.2096 (3)	0.0168 (6)	5.3 (3)
C(5-1)	−0.0527 (8)	0.1364 (3)	0.0936 (6)	4.5 (3)
C(5-2)	−0.0172 (8)	0.1363 (3)	0.2038 (7)	4.4 (3)
C(5-3)	0.0349 (8)	0.1975 (4)	0.2329 (5)	5.2 (3)
C(5-4)	0.0317 (8)	0.2354 (3)	0.1405 (7)	5.6 (3)
C(5-5)	−0.0225 (8)	0.1977 (4)	0.0544 (5)	5.1 (3)
H(1-2)	0.4651	0.0739	0.1212	
H(1-3)	0.6793	0.0468	0.1276	
H(1-4)	0.7864	0.0068	0.2808	
H(1-5)	0.6794	−0.0062	0.4276	
H(1-6)	0.4652	0.0209	0.4211	
H(2-2)	0.0593	0.0436	0.4017	
H(2-3)	0.0118	0.0078	0.5645	
H(2-4)	0.1483	0.1472	0.6620	
H(2-5)	0.3322	0.1829	0.5966	
H(2-6)	0.3797	0.1491	0.4338	
H(3-2)	0.0299	0.0037	0.1423	
H(3-3)	−0.0597	−0.0974	0.1282	
H(3-4)	0.0351	−0.1808	0.2263	
H(3-5)	0.2194	−0.1632	0.3385	
H(3-6)	0.3090	−0.0621	0.3526	
H(4-2)	0.3172	0.1133	−0.1362	
H(4-3)	0.5154	0.0861	−0.1854	
H(4-4)	0.6979	0.1363	−0.1080	
H(4-5)	0.6822	0.2137	0.0187	
H(4-6)	0.4839	0.2409	0.0680	
H(5-1)	−0.091 (4)	0.102 (2)	0.044 (3)	
H(5-2)	−0.026 (4)	0.102 (2)	0.244 (3)	
H(5-3)	0.068 (4)	0.213 (2)	0.296 (3)	
H(5-4)	0.062 (4)	0.281 (2)	0.129 (3)	
H(5-5)	−0.036 (4)	0.213 (2)	−0.027 (3)	

Anisotropic Temperature Factors^a

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Mo	625 (9)	180 (2)	615 (7)	58 (5)	212 (6)	35 (4)
Ge	681 (13)	177 (3)	527 (10)	0 (6)	194 (9)	12 (5)

Table II (*Continued*)

Group Parameters[b]

Group	x_c	y_c	z_c	δ	ϵ	η
C(1-1)–C(1-6)	0.5723	0.0339	0.2744	1.173	2.709	1.870
C(2-1)–C(2-6)	0.1958	0.1132	0.4992	2.737	2.200	−2.260
C(3-1)–C(3-6)	0.1247	−0.0797	0.2404	0.014	2.870	0.584
C(4-1)–C(4-6)	0.4997	0.1635	−0.0587	1.691	−3.123	0.791
C(5-1)–C(5-5)	−0.0052	0.1807	0.1450	2.649	2.617	−1.282
H(5-1)–H(5-5)	−0.0005	0.1822	0.1372	2.649	2.617	−1.282

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The individual atomic parameters for the phenyl and cyclopentadienyl group atoms are based on the refined rigid-body crystallographic coordinates for the groups which were based on the following models. The phenyl rings were presumed to have D_{6h} symmetry with a C–C bond length of 1.400 A and a C–H bond length of 0.95 A. The cyclopentadienyl carbon ring was presumed to have D_{5h} symmetry with a C–C bond length of 1.445 A, while the cyclopentadienyl hydrogen ring was allowed to refine semiindependently, being constrained to D_{5h} symmetry with an H···H distance of 2.62 A, and to lie parallel to the cyclopentadiene carbon ring; only the coordinates of the origin were allowed to vary. The origin of each ring was chosen at the center of the carbon framework. An isotropic temperature factor was allowed to vary for each carbon atom; for each hydrogen atom the isotropic temperature factor was fixed at 6.0 A². x_c, y_c, and z_c are the fractional coordinates of the group centroid; δ, ϵ, and η (in radians) are defined conventionally: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

crystal structure determination was undertaken on one member of the series, C₅H₅Mo(CO)₂[Ge(C₆H₅)₃]C(OC₂H₅)C₆H₅.

Experimental Section

Crystals of C₅H₅Mo(CO)₂[Ge(C₆H₅)₃]C(OC₂H₅)C₆H₅ were obtained in the form of orange prisms from heptane solution. Examination of Co Kα Weissenberg and Mo Kα precession photographs showed 2/m Laue symmetry, and the observed systematic absences (0k0 odd; h0l odd) indicated the monoclinic space group P2₁/n, a nonstandard setting of space group P2₁/c which was used throughout because of the near orthogonality of its axes. The general equivalent positions of space group P2₁/n are ±(x, y, z) and ±(¹/₂ − x, ¹/₂ + y, ¹/₂ − z).

A single crystal of approximate dimensions 0.24 × 0.06 × 0.08 mm between the centrosymmetric faces (001), (100); (011), (011); and (011), (011) was mounted about its longest dimension (corresponding to the a axis) on a glass fiber using Canada balsam. This crystal was used for accurate cell parameter measurements and intensity data collection on a Picker four-circle automated diffractometer (FACS I (DOS) system). Twelve high-angle reflections were centered accurately in 2θ using Ni-filtered Cu Kα radiation (λ 1.547 18 Å) and the approximate cell parameters were refined by the least-squares method to yield cell dimensions a = 10.611 (2), b = 21.247 (3), c = 13.040 (2) Å, and β = 96.32 (1)° at 20 °C. The calculated density of 1.47 g cm⁻³, based on four molecules per unit cell with molecular weight of 654.6 and a cell volume of 2944.9 Å³, agreed well with the value of 1.47 g cm⁻³ obtained experimentally by the flotation method in aqueous potassium iodide solution.

Intensity data were collected using the (θ–2θ) scan technique with stationary-crystal, stationary-counter background counts of 40 s taken at each scan limit. The scanning speed used was 1°/min with a base width of 2° (modified for dispersion effects of Cu Kα₁–Kα₂ radiation). Data were collected for 2θ < 120°. Three reference reflections were monitored every 100 reflections and showed no significant decay of the crystal throughout the data collection.

The intensity data were corrected for Lorentz and polarization effects and reduced to structure factor amplitudes F. The standard deviation σ(I) was estimated using the procedure of Doedens and Ibers[2] with an "ignorance" p factor of 0.03. A reflection was considered unobserved if the net intensity I was less than 3σ(I). This procedure resulted in 2414 observed reflections out of the total 4342 measured independent reflections. Only the observed reflections were used in subsequent computations, giving a final data-to-parameter ratio of ~19.5:1.

The data were also corrected for absorption. With μ = 52.6 cm⁻¹ for Cu Kα radiation, the range of the transmission factors was 0.73 for 0.85, which would cause a fluctuation of ±5.0% in the observed intensity data.

Structure Solution and Refinement. The solution of the structure, which required the location of one molecule as the independent unit, was accomplished by heavy-atom methods. The locations of the molybdenum and germanium atoms were obtained from the interpretation of a three-dimensional Patterson map. A Fourier synthesis phased on these atoms yielded initial coordinates for all remaining nonhydrogen atoms (although the subsequently discovered twofold disorder of the ethoxy group was not revealed).

Rigid-body parameters were then calculated for the four phenyl rings and for the cyclopentadienyl rings constraining these groups to

idealized geometries which were maintained throughout the least-squares refinement (see Table II, footnote b). Several cycles of least-squares refinement using isotropic thermal parameters for all atoms resulted in an R of 0.090. A difference map at this stage showed that the molybdenum and germanium atoms exhibited appreciable anisotropic thermal motion; the thermal parameters of these atoms were allowed to refine anisotropically, resulting in an R of 0.068. At this point the disordering of the ethoxy group was revealed by abnormally large thermal parameters for the ethoxy group atoms and by the presence of appreciable residual electron density in their vicinity. The introduction of a simple twofold disorder model resulted in a satisfactory solution for the oxygen atom, with the two half-atoms refining to nearly equal thermal parameters (~4.0 Å²) and occupancy factors (~0.5); accordingly the model adopted for the ethoxy group was limited to equal occupancy factors of 0.5 for the disordered positions. However, the carbon atoms of the ethoxy group were not sufficiently well resolved to refine to well-defined positions as shown by their rather large thermal parameters and by the bond lengths and angles involving these atoms. This may be partly due to the presence of the adjacent methyl and methylene hydrogen atoms. The inclusion of the simple twofold disorder model for the ethoxy group reduced R to 0.062.

Finally, the phenyl and cyclopentadienyl hydrogen atoms were included in the refinement. The phenyl hydrogen atoms were included as part of the appropriate rigid bodies, while the cyclopentadienyl hydrogen atoms were allowed to refine semiindependently as a separate rigid body. The discrepancy factors for the last cycle were R = 0.056 and R_w = 0.057 using individual weights $w_i = \sigma(F)^{-2}$. No parameter shifted by more than 0.1σ during the last cycle. A final three-dimensional Fourier difference map showed no residual electron density greater than 0.66 e Å⁻³ or less than −0.50 e Å⁻³.

All least-squares refinements were based on the minimization of $\sum w_i \|F_o| - |F_c\|^2$. The atomic scattering factors used for all calculations were taken from Cromer and Mann[3] for nonhydrogen atoms, with anomalous scattering of Mo and Ge atoms included,[4] and from Stewart et al.[5] for the hydrogen atoms.

The major computer programs used were PMMO (a local data reduction program), DATAP (absorption correction program by P. Coppens), BURP (a local modification by M. J. Bennett and W. Hutcheon of the least-squares refinement program SFLS5 by C. T. Prewitt), ORFFE (function and error program by W. A. Busing and H. A. Levy, locally modified to handle rigid bodies), ORTEP (molecular drawing program by C. K. Johnson), and FORDAP (Fourier map program by A. Zalkin).
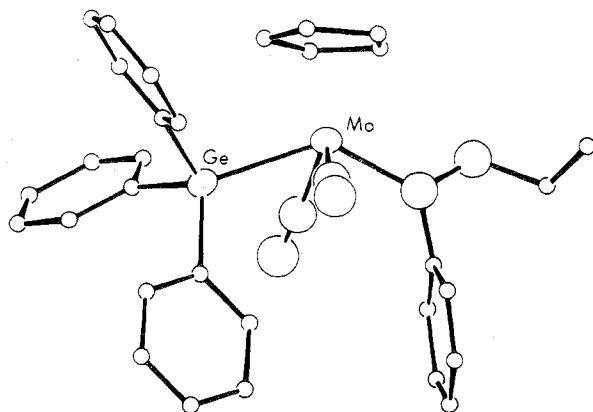
The values of |F_o| and |F_c| (in electrons × 10) obtained from the last cycle of least-squares refinement are presented in Table I. The positional and thermal parameters for all atoms are given in Table II. Interatomic distances and angles with estimated standard deviations are listed in Table III. Equations of least-squares plane and distances of selected atoms from these planes are given in Table IV.

Results and Discussion

General Description of the Molecular Structure. The compound C₅H₅Mo(CO)₂[Ge(C₆H₅)₃]C(OC₂H₅)C₆H₅ has the molecular structure shown in Figure 1 (side view) and Figure 2 (projection perpendicular to the plane of the cyclopentadienyl ring). These views clearly show that the molecule has a trans

Table III. Interatomic Distances and Bond Angles

A. Intramolecular Distances, Å

Bonding Distances

Mo–Ge	2.658 (2)	C(2)–O(2)	1.187 (12)
Mo–C(1)	1.928 (12)	C(3)–O(4-1)	1.502 (12)
Mo–C(2)	1.925 (12)	C(3)–O(3)	1.376 (17)
Mo–C(3)	2.062 (11)	C(3)–O(3)'	1.376 (17)
Mo–C(5-1)	2.387 (8)	O(3)–C(4)	1.529 (30)
Mo–C(5-2)	2.378 (8)	O(3)'–C(4)'	1.612 (34)
Mo–C(5-3)	2.361 (8)	C(4)–C(5)	1.381 (41)
Mo–C(5-4)	2.358 (8)	C(4)'–C(5)'	1.638 (48)
Mo–C(5-5)	2.374 (8)	C(5-1)–H(5-1)	1.033 (40)
Ge–C(1-1)	1.983 (5)	C(5-2)–H(5-2)	0.911 (41)
Ge–C(2-1)	1.981 (5)	C(5-3)–H(5-3)	0.919 (41)
Ge–C(3-1)	1.996 (5)	C(5-4)–H(5-4)	1.045 (40)
C(1)–O(1)	1.165 (12)	C(5-5)–H(5-5)	1.109 (42)

Nonbonding Distances

O(3)···O(3)'	0.823 (18)	O(3)···C(5-5)	2.867 (17)
C(4)···C(4)'	0.945 (37)	O(3)'···C(5-4)	3.022 (17)
C(5)···C(5)'	1.829 (48)	O(3)'···C(5-5)	3.020 (17)
O(3)···C(5-4)	3.256 (17)		

B. Intermolecular Distances Less Than 3.5 Å

O(1)···C(5)'	3.28 (4)	C(5)···C(1-4)	3.42 (3)
O(1)···C(3-4)	3.33 (1)	C(5)···C(1-5)	3.44 (3)
O(2)···C(1-3)	3.37 (1)		

C. Bond Angles, Deg

Ge–Mo–C(1)	70.8 (3)	Mo–C(1)–O(1)	173.4 (10)
Ge–Mo–C(2)	70.6 (3)	Mo–C(2)–O(2)	174.6 (10)
Ge–Mo–C(3)	131.8 (3)	Mo–C(3)–C(4-1)	127.5 (8)
C(1)–Mo–C(2)	105.1 (5)	Mo–C(3)–O(3)	119.1 (9)
C(1)–Mo–C(3)	79.6 (4)	Mo–C(3)–O(3)'	116.7 (9)
C(2)–Mo–C(3)	81.9 (5)	C(4-1)–C(3)–O(3)	111.6 (10)
C(1-1)–Ge–C(2-1)	106.5 (3)	C(4-1)–C(3)–O(3)'	112.3 (10)
C(1-1)–Ge–C(3-1)	105.5 (3)	C(3)–O(3)–C(4)	122.6 (16)
C(2-1)–Ge–C(3-1)	103.3 (3)	C(3)–O(3)'–C(4)'	128.3 (17)
Mo–Ge–C(1-1)	114.6 (2)	O(3)–C(4)–C(5)	111.0 (25)
Mo–Ge–C(2-1)	109.8 (2)	O(3)'–C(4)'–C(5)'	94.4 (25)
Mo–Ge–C(3-1)	116.1 (2)		

Table IV. Least-Squares Planes and Perpendicular Distances (Å) of Selected Atoms from These Planes[a]

1. Plane through C(1-1)–C(1-6)[b]

$$0.225X + 0.929Y + 0.294Z - 2.992 = 0$$

Ge	0.166 (1)

2. Plane through C(2-1)–C(2-6)[b]

$$0.464X - 0.775Y + 0.428Z - 1.536 = 0$$

Ge	0.055 (1)

3. Plane through C(3-1)–C(3-6)[b]

$$0.641X - 0.215Y - 0.737Z + 1.304 = 0$$

Ge	0.014 (1)

4. Plane through C(4-1)–C(4-6)[b]

$$0.021X - 0.704Y + 0.710Z + 2.873 = 0$$

C(3)	−0.085 (11)

5. Plane through C(5-1)–C(5-5)[b]

$$0.934X - 0.327Y - 0.143Z + 1.769 = 0$$

Mo	2.027 (1)

6. Plane through Mo, C(3), C(4-1), and a Point (X) Midway between O(3) and O(3)'

$$0.376X + 0.646Y + 0.664Z - 3.744 = 0$$

Mo	−0.005 (1)	O(3)	0.404 (16)
C(3)	0.019 (11)	O(3)'	0.418 (16)
C(4-1)	0.007 (8)	X	0.007

[a] The equations of the planes are given in an orthogonal angstrom coordinate system (X, Y, Z) which is related to the fractional coordinates (x, y, z) of the monoclinic unit cell: $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. Unit weights were used for all atoms. [b] These atoms were constrained to coplanarity during the least-squares refinement.

Figure 1. Molecular configuration of $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]$-$C(OC_2H_5)C_6H_5$.

Figure 2. Projection of the $C_5H_5Mo(CO)_2[Ge(C_6H_5)_3]C(OC_2$-$H_5)C_6H_5$ molecule down the Mo–(C_5H_5 ring center) vector.
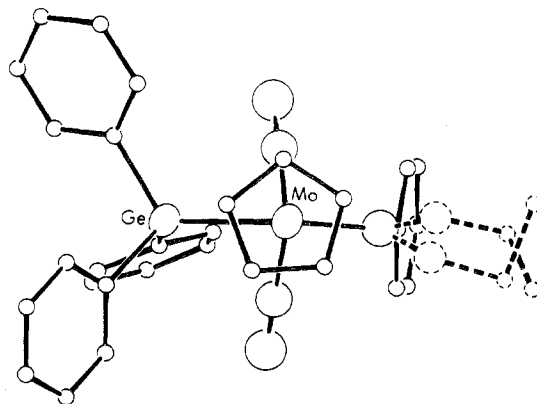
configuration of ligands about the molybdenum atom, confirming the earlier assignment of this geometry to the compound on the basis of its infrared spectrum.[1] The overall coordination geometry about the molybdenum atom is typical of such formally seven-coordinate cyclopentadienylmetal complexes, with the four basal ligands defining an approximate plane below the molybdenum atom and roughly parallel to the plane of the cyclopentadienyl ring.[6]

The molybdenum–germanium bond distance is 2.658 (2) Å; we believe this to be the first such distance to be reported. It is somewhat longer than the Ru–Ge distances reported for $Ru_3(CO)_9[Ge(CH_3)_2]_3$ (average value 2.493 Å[7]) and $C_6H_6Ru(CO)(GeCl_3)_2$ (2.408 (2) Å[8]). The Ge–C bond distances (average value 1.987 Å) are comparable to those found in tetraphenylgermane (1.954 (1) Å[9]), $Ru_3(C$-

$O)_9[Ge(CH_3)_2]_3$ (2.02 (7) Å[7]), and cis-$[(C_6H_5)_2GeOH]Pt$-$[P(C_2H_5)_3]_2C_6H_5$ (1.98 (1) Å[10]). The Mo–CO, Mo–C(cyclopentadienyl), and (carbonyl)C–O distances are of the expected lengths.

The Mo–C(carbene) distance of 2.062 (11) Å is intermediate between those reported for two other molybdenum carbene complexes, $C_5H_5Mo(CO)_2C(OH)C(CO_2C_2H_5)NNH$ (2.092 (12) Å[1]) and $[C_5H_5Mo(CO)_2C(OH)C(CO_2C_2H_5)$-$N(CH_3)N]PF_6$ (2.03 (3) Å[2]). It is shorter than the Mo–C-(sp^2) distance of 2.264 (14) Å observed in $C_5H_5Mo(CO)_2$ $[P(C_6H_5)_3]C(O)CH_3$,[13] indicating appreciable π interaction between the molybdenum atom and the carbene ligand, as expected for a carbene complex.[14]

The (carbene)C–O distances (i.e., the distances from the carbene carbon atom C(3) to the two disordered positions of

the ethoxy group oxygen atom, O(3) and O(3)' are both 1.376 (17) Å, comparable to those found in other alkoxy- and hydroxycarbene complexes. The (carbene)C–C(phenyl) distance of 1.502 (12) Å is not far from that expected for a C(sp^2)–C(sp^2) bond, about 1.48 Å. The (phenyl)C–C-(carbene)–O angles are experimentally equivalent at 111.6 (10) and 112.3 (10)°, are within the range of those observed in other oxycarbene complexes (104–120°), and are somewhat greater than the angle of 103° observed spectroscopically for singlet methylene.[15]

In other carbene complexes the carbenoid carbon and (at least) the three atoms to which it is attached are generally observed to be coplanar.[14] The planarity of the carbene ligand in the present complex is not easy to assess, owing to the disordering of the ethoxy group. However, as shown in Table IV, the Mo, C(3), and C(4-1) atoms and a point midway between the disordered positions of the oxygen atom (O(3) and O(3)') all lie within 0.02 Å of the mean least-squares plane through these four points. As can be seen in Figure 2, the planes of the carbene ligand (as defined above) and the phenyl group attached to it (C(4-1)–C(4-6)) are approximately perpendicular; the dihedral angle between these planes is 88.7°, indicating no π interaction between the phenyl group and the remainder of the carbene ligand. This situation has also been observed in the case of Cr(CO)$_5$C(OCH$_3$)C$_6$H$_5$.[16]

The crystal packing is determined primarily by van der Waals forces, as can be seen by an examination of the intermolecular distances, some of which are included in Table III.

Stereochemical Influences on the Observed Conformation of the C$_5$H$_5$Mo(CO)$_2$[Ge(C$_6$H$_5$)$_3$]C(OC$_2$H$_5$)C$_6$H$_5$ Molecule. The carbene ligand in C$_5$H$_5$Mo(CO)$_2$[Ge(C$_6$H$_5$)$_3$]C(OC$_2$H$_5$)C$_6$H$_5$ is oriented with the ethoxy group adjacent to the cyclopentadienyl ring, while the phenyl group is extended in the same direction as the carbonyl groups. This is in contrast to the situation observed in [N(CH$_3$)$_4$][C$_5$H$_5$Mn(CO)$_2$C(O)-C$_6$H$_5$], where the phenyl group is adjacent to the cyclopentadienyl ring.[17] The solid-state structure of the present compound corresponds approximately to one of the two conformers of C_s symmetry proposed on the basis of the observation of four C–O stretching frequencies in its infrared spectrum in heptane solution.[1] These frequencies are 1960 and 1896 cm^{-1} for one conformer (called conformer A) and 1945 and 1878 cm^{-1} for the other (conformer B).[1] On the basis of the solid-state spectrum of the complex (1937, 1862 cm^{-1}; Nujol mull) it seems probable that the conformation observed in this study for the solid state corresponds to conformer B. The positive frequency shifts on going from the solid state to solution spectra (8 and 16 cm^{-1} according to this assignment) are then within the range expected for metal carbonyl complexes.[18,19] The other possible conformation of C_s sym-

metry for this molecule (i.e., with the phenyl group, rather than the ethoxy group, adjacent to the cyclopentadienyl ring) would then correspond to conformer A. It may also be observed that conformer B is the more abundant species in solution (as indicated by the relative intensities of the peaks in the infrared spectrum[1]) and so presumably is energetically more stable.

The Mo–C(carbene)–O–ethyl linkage has a trans configuration, like that found in (C$_6$H$_5$)$_3$PCr(CO)$_4$C(OCH$_3$)CH$_3$[20] but unlike that in Cr(CO)$_5$C(OCH$_3$)C$_6$H$_5$ where a cis configuration is observed.[15] In the case of the present complex, a cis configuration would seem to be precluded by steric interactions between the cyclopentadienyl ring and the ethoxy group. The fairly close contacts between the ethoxy oxygen atom and the two closest cyclopentadienyl carbon atoms (2.87–3.26 Å) indicate considerable crowding in this part of the molecule; a cis configuration for the Mo–C–O–ethyl linkage would place the methylene carbon atom quite close to the cyclopentadienyl ring and result in considerable interference between the cyclopentadienyl and methylene carbon and hydrogen atoms. We believe that the evidence of this structure confirms our earlier conclusion, derived from inspection of molecular models, that cis–trans isomerism about the (carbene)C–O bond is unlikely in this complex.[1]

References and Notes
(1) W. K. Dean and W. A. G. Graham, *Inorg. Chem.*, preceding paper in this issue.
(2) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
(3) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(4) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(5) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(6) E. R. deGil and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 3751 (1969).
(7) J. Howard and P. Woodward, *J. Chem. Soc. A*, 3648 (1971).
(8) L. Y. Chan and W. A. G. Graham, *Inorg. Chem.*, **14**, 1778 (1975).
(9) P. C. Cheih, *J. Chem. Soc. A*, 3243 (1971).
(10) R. J. D. Gee and H. M. Powell, *J. Chem. Soc. A*, 1956 (1971).
(11) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1952 (1969).
(12) C. K. Prout, T. S. Cameron, and A. R. Gent, *Acta Crystallogr., Sect. B*, **28**, 32 (1972).
(13) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).
(14) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).
(15) G. Herzberg, *Proc. R. Soc. London, Ser. A*, **262**, 291 (1961).
(16) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 642 (1968).
(17) E. Hadicke and W. Hoppe, *Acta Crystallogr., Sect. B*, **27**, 760 (1971).
(18) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
(19) W. Beck and K. Lottes, *Z. Naturforsch., B*, **19**, 987 (1964).
(20) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 1274 (1969).