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THE CRYSTAL AND MOLECULAR STRUCTURE OF DIMETHYLPHENYLGERMANIUM ISOCYANIDE(PENTACARBONYL)-MOLYBDENUM(0)

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Summary

The compound $Mo(CO)_5CNGePhMe_2$ crystallizes in the monoclinic space group *Pc* with two molecules per unit cell of dimensions *a* 7.071(3), *b* 6.238(4), *c* 19.530(6) Å and *β* 91.426(2)°. X-ray diffraction data were collected by automated diffractometer methods. The molecular structure was determined by the heavy atom method phased on Mo and Ge and refined by full matrix isotropic/anisotropic least squares analysis from 1121 observed reflections to give discrepancy indices R_1 = 2.0 and R_2 = 2.7% The structure contains discrete molecular units with six ligand groups disposed at nearly octahedral positions around the molybdenum atom. Consideration of the thermal parameters for the isocyanide carbon and nitrogen confirms that the ligand is indeed an isocyanide and not a cyanide. Bond lengths in this complex are not unusual. ave. *d*(Mo—C) 2 05 Å for Mo—CO bonds; *d*(Mo—C) 2 150(8) Å for Mo—CNR bond; ave *d*(C—O) 1.13 Å, *d*(C—N) 1.159(8) Å, *d*(Ge—N) 1.897(6) Å.

Introduction

Syntheses of triorganosilyl and organogermyl isocyanide derivatives of Group VIB metal carbonyls are described in the preceding paper [1]. Herein we report the crystal and molecular structure for one of these compounds, $Mo(CO)_5CNGePhMe_2$.

Prior to this work, no structural data for complexes of silyl or germyl isocyanide ligands had been reported. We were interested in obtaining these data, first, to obtain a comparison of bond lengths between the free and complexed ligands and, second, to verify that the coordinated ligand was actually an isocyanide rather than a cyanide. Initially we attempted to determine the structure of $Mo(CO)_5CNGeMe_3$; this complex was chosen because of the availability of accurate structural data on the ligand obtained in a microwave spectral study [2]. Unfortunately, this effort met with experimental problems of twinning and disorder, so we then chose to look at $Mo(CO)_5CNGePhMe_2$ instead.

Experimental

Single crystal X-ray data Well-formed, colorless crystals of $Mo(CO)_5$-$CNGePhMe_2$ were grown at 0°C by slow evaporation of a butane solution of the compound to minimize decomposition. The crystal used, a parallelepiped with approximate dimensions 0.40 mm × 0.20 mm × 0.09 mm was mounted in a Lindemann glass capillary under notrigen, and placed on a Syntex $P\bar{1}$ four circle computercontrolled diffractometer equipped with a graphite monochromator and an LT-l gas-cooled low-temperature apparatus. The crystal was slowly cooled to —108°C (±5°) and after careful alignment, fifteen diffraction maximum were automatically centered in 2θ, χ, and ω. Mo-K_α radiation (λ 0.7107 Å) was used throughout the alignment and data collection procedures. The preliminary Syntex routines indicated a monoclinic unit cell which was verified by partial rotation axial photographs along each of the cell axes At —108° the cell constants chosen were a 7.071(3), b 6.238(4), c 19.530(6) Å, and β 91.426(2)°. The unit cell volume, 861.3(7) Å^3, yielded a calculated density of 1.703 g cm^{-3} for $M = 441.6$ and $Z = 2$, which agreed well with the measured density of 1.70(1), determined by flotation in aqueous zinc chloride (25°C). The total number of electrons per unit cell, $F(000)$ is 432.

Intensity data were collected by the $\theta - 2\theta$ scan technique with stationary counter background counts taken at the beginning and end of each scan. Variable scan rates (2—24 deg/min) were determined according to the intensity of the peak being measured. Backgrounds were counted for a total of 2/3 of the time used for the scan count. Two standard reflections (102) and (20$\bar{4}$) were monitored every 50 reflections as a check of crystal stability, and showed no significant deviation in intensity (±2.5%). A total of 1232 independent reflections were collected, distributed throughout the two octants hkl and $\bar{h}kl$, for which 2.0° $< 2\theta <$ 24.0°.

The data were corrected for Lorentz-polarization as previously described [3] and for absorption and then merged to give a total of 1121 reflections for which $I > 2\sigma(I)$. Transmission factors for the crystal varied from 0.62 to 0.79

The systematic absence $h0l$ for $l = 2n + 1$ is consistent with the space group $Pc(C_s^2)$ No. 7; or its centrosymmetric equivalent $P2/c$ (C_{2h}^4) No. 13 [4]. Due to the anticipated absence of any special symmetry within the molecule, the structural solution was attempted using the space group Pc, thus requiring the location of one molecule as the independent unit.

Solution and refinement of the structure. The solution of the structure was accomplished by the heavy atom method. The positions of the germanium and molybdenum atoms were obtained by a three-dimensional Patterson map. Three Fourier maps [5] revealed all but three carbon atoms, which subsequently were obtained from a difference map. Four cycles of full-matrix least squares refinements resulted in the discrepancy indices $R_1 = [\Sigma||F_0| - |F_c||/\Sigma|F_0|] \times 100 = 4.3$ and $R_2 = [\Sigma W_i(|F_0| - |F_c|)^2/\Sigma W_i|F_0|^2]^{1/2} \times 100 = 7.0$, using individual weights $w_i = 1/(\sigma(F_o))^2$ [3]. At this point, the enantiomorph compatible with the original choice was determined from the anomalous dispersion effects [6] of Mo and Ge.

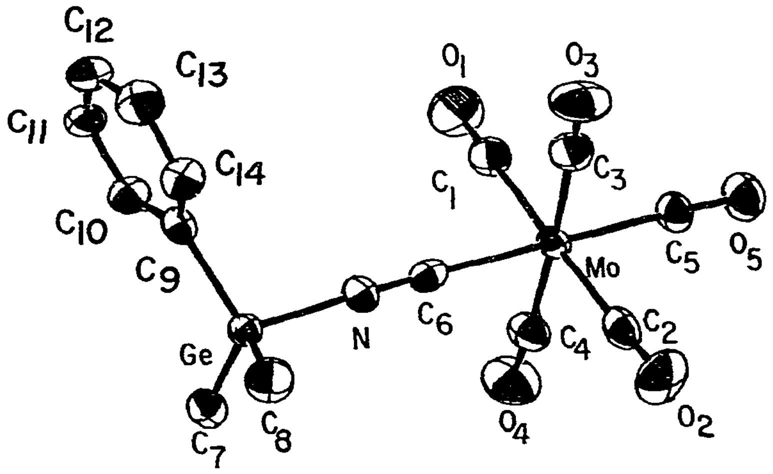

Fig 1 Molecular structure of $Mo(CO)_5CNGePhMe_2$

TABLE 1

FINAL ATOMIC POSITIONAL PARAMETERS FOR $Mo(CO)_5CNGePhMe_2$ (×10^4)

Atom	x	y	z
Mo	0	−1019 3(8)	0
Ge	−6609 0(10)	3131 3(10)	8016 7(4)
O(1)	−6129(8)	−3311(10)	−10360(3)
O(2)	−13938(8)	1330(10)	−9749(4)
O(3)	−8646(9)	2842(10)	−10930(3)
O(4)	−11018(8)	−4850(10)	−9003(3)
O(5)	−12137(8)	−3357(9)	−11215(3)
N	−7951(8)	1483(9)	−8685(3)
C(1)	−7481(10)	−2520(11)	−10227(3)
C(2)	−12521(10)	497(11)	−9823(3)
C(3)	−9179(10)	1466(11)	−10603(3)
C(4)	−10681(10)	−3476(12)	−9359(3)
C(5)	−11339(10)	−2526(11)	−10785(4)
C(6)	−8658(8)	596(11)	−9145(4)
C(7)	−8531(10)	4021(12)	−7402(4)
C(8)	−5536(10)	5418(12)	−8543(4)
C(9)	−4849(9)	1057(10)	−7622(3)
C(10)	−5399(9)	−2135(13)	−7081(3)
C(11)	−4227(11)	−1770(13)	−6819(4)
C(12)	−2454(11)	−2041(11)	−7073(4)
C(13)	−1877(9)	−757(11)	−7600(4)
C(14)	−3066(9)	776(10)	−7870(3)
H(7A)[a]	−9036	2785	−7143
H(7B)	−9609	4738	−7665
H(7C)	−7995	5111	−7063
H(8A)	−4540	4807	−8852
H(8B)	−4924	6491	−8231
H(8C)	−6537	6117	−8832
H(10)	−6695	−5	−6888
H(11)	−4668	−2689	−6427
H(12)	−1614	−3178	−6885
H(13)	−553	−884	−7768
H(14)	−2638	1691	−8262

[a] The hydrogen parameters are the idealized coordinates used for the final two least squares cycles.

Full matrix isotropic least squares refinement was then carried out to convergence at $R_1 = 3.86$ and $R_2 = 5\ 52$.

Interchanging the scattering factors for atoms C(6) and N (considering the complex to contain a coordinated cyanide) caused the thermal parameters for the now presumed carbon to enlarge and for the presumed nitrogen to shrink, indicating the original atom identifications were correct (vide infra). A difference map after isotropic convergence revealed 5 of the 11 hydrogen atoms and indicated high thermal anisotropy about the molybdenum, germanium and oxygen atoms. Thus, refinement was continued, allowing anisotropic thermal motion for non-hydrogen atoms. The refinement included idealized hydrogen atoms as fixed atom contributions, with all C—H distances set to 1.0 Å ($B_{iso} = 5.0$ Å^2). The phenyl hydrogen atoms were placed in the plane of the ring and those of the methyl groups were placed tetrahedrally about each carbon atom staggered with respect to each other. Anomalous dispersion corrections were included for molybdenum and germanium.

Full-matrix anisotropic least squares refinement for all non-hydrogen atoms converged with $R_1 = 2.0\%$ and $R_2 = 2.7\%$ No value of shift/error >0 07 was observed in the final cycle. The final data to parameter ratio was 5 6/1. The standard error in the observation of unit weight was 0 905.

All least squares refinements were based on the minimization of $\Sigma w_i ||F_o| - |F_c||^2$. The atomic scattering factors used for all non-hydrogen atoms were those compiled by Cromer and Mann [7]. The positional parameters for all atoms are given in Table 1 and the anisotropic thermal parameters in Table 2.

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (X10^4)^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	115 5(10)	129 1(14)	13 5(1)	−8 4(10)	−0 1(3)	−8 5(3)
Ge	113 8(13)	144 7(19)	14 4(2)	9 8(14)	3 7(3)	−8 7(5)
O(1)	172(12)	362(20)	45(2)	39(13)	25(4)	−19(5)
O(2)	151(12)	449(23)	46(2)	114(13)	1(4)	−41(5)
O(3)	338(17)	271(17)	28(2)	−57(14)	12(4)	25(5)
O(4)	245(13)	228(16)	45(2)	−5(11)	30(4)	39(6)
O(5)	234(12)	297(17)	25(2)	−12(11)	−15(3)	−33(5)
N	148(11)	156(16)	17(2)	1(11)	−6(4)	−1(4)
C(1)	143(16)	195(18)	21(2)	14(14)	5(4)	−10(4)
C(2)	195(18)	211(20)	18(2)	−39(16)	−10(4)	−18(5)
C(3)	200(16)	189(20)	15(2)	−20(15)	−3(4)	−4(5)
C(4)	146(15)	198(21)	24(2)	22(15)	7(4)	−12(6)
C(5)	146(14)	180(19)	16(2)	0(14)	0(4)	22(6)
C(6)	107(12)	164(20)	18(2)	26(12)	3(4)	6(5)
C(7)	180(16)	274(26)	28(2)	42(15)	6(5)	−25(6)
C(8)	174(15)	184(20)	26(2)	−31(14)	−11(5)	6(6)
C(9)	137(13)	162(18)	15(2)	−19(11)	−2(4)	−9(4)
C(10)	158(14)	254(21)	18(2)	1(15)	6(4)	8(6)
C(11)	227(19)	280(25)	18(2)	−7(17)	−2(5)	15(6)
C(12)	207(18)	176(20)	26(2)	27(15)	−12(5)	10(5)
C(13)	127(14)	186(20)	28(2)	14(13)	−1(4)	7(5)
C(14)	146(14)	179(18)	16(2)	2(12)	4(4)	11(4)

^{a} Anisotropic temperature factors are of the form exp $\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]\}$

TABLE 3

INTERATOMIC DISTANCES AND BOND ANGLES

A Bonding intramolecular distances (Å)

Metal—carbon bonds	Mo—C(1)	2.070(7)
	Mo—C(2)	2.055(8)
	Mo—C(3)	2.040(8)
	Mo—C(4)	2.044(8)
	Mo—C(5)	2.015(7)
	Mo—C(6)	2.150(8)
Germanium bonds	Ge—N	1.897(6)
	Ge—C(7)	1.918(7)
	Ge—C(8)	1.925(7)
	Ge—C(9)	1.942(6)
Carbonyl bonds	C(1)—O(1)	1.13(8)
	C(2)—O(2)	1.141(9)
	C(3)—O(3)	1.140(9)
	C(4)—O(4)	1.133(9)
	C(5)—O(5)	1.127(8)
Isocyanide bond	C(6)—N	1.159(8)
Ring bonds	C(9)—C(10)	1.385(10)
	C(10)—C(11)	1.373(11)
	C(11)—C(12)	1.376(10)
	C(12)—C(13)	1.374(11)
	C(13)—C(14)	1.370(9)
	C(14)—C(9)	1.373(10)

B. Intermolecular distances <3.9 Å

Ge···O(4)	3.837 [a]	O(5)···C(9)	3.605 [c]
O(4)···C(13)	3.809 [b]	N···O(4)	3.203 [a]

C Intramolecular angles (degree)

Angles centered on molybdenum			
C(1)—Mo—C(2)	177.3(3)	C(2)—Mo—C(6)	91.3(2)
C(1)—Mo—C(3)	87.8(3)	C(3)—Mo—C(4)	176.6(3)
C(1)—Mo—C(4)	90.5(3)	C(3)—Mo—C(5)	92.9(3)
C(1)—Mo—C(5)	90.9(3)	C(3)—Mo—C(6)	88.0(2)
C(1)—Mo—C(6)	90.7(2)	C(4)—Mo—C(5)	90.2(3)
C(2)—Mo—C(3)	90.4(3)	C(4)—Mo—C(6)	89.0(3)
C(2)—Mo—C(4)	91.4(3)	C(5)—Mo—C(6)	178.1(3)
C(2)—Mo—C(5)	87.1(3)		
Angles centered on germanium			
N—Ge—C(7)	103.7(3)	C(7)—Ge—C(8)	114.5(4)
N—Ge—C(8)	103.4(3)	C(8)—Ge—C(9)	116.6(3)
N—Ge—C(9)	102.5(2)	C(7)—Ge—C(9)	113.7(3)
ligand angles			
Ge—N—C(6)	172.5(5)	Mo—C(4)—O(4)	178.5(6)
Mo—C(6)—N	179.3(5)	Mo—C(3)—O(3)	177.1(6)
Mo—C(5)—O(5)	178.0(6)	Mo—C(2)—O(2)	177.6(6)
carbon angles			
Ge—C(9)—C(10)	119.7(5)	C(10)—C(11)—C(12)	119.5(7)
Ge—C(9)—C(14)	122.0(5)	C(11)—C(12)—C(13)	119.7(6)
C(10)—C(9)—C(14)	118.3(6)	C(12)—C(13)—C(14)	120.3(6)
C(9)—C(10)—C(11)	121.3(6)	C(13)—C(14)—C(9)	120.9(6)

The distances are given from the indicated atoms in one molecule to those in another molecule related by the symmetry operations a x, $1-y$, $1/2+z$; b $-1+x$, $-y$, $1/2+z$; c $1-x$, $-y$, $-1/2+z$

Interatomic bonding distances and bond angles, with estimated standard deviations calculated with the Busing—Martin—Levy function and error program from the full inverse matrix are presented in Table 3. The calculated and observed structure factor amplitudes obtained from the last cycle of the anisotropic least squares refinement are available *.

Discussion

The complex $Mo(CO)_5CNGePhMe_2$ consists of discrete molecules separated by normal Van der Waals distances. Its molecular structure is shown in Fig 1. The coordination about the molybdenum atom is octahedral, with the angles across the metal being only slightly different than 180°. The metal—CO and metal—CN units are linear. The angles about the germanium are approximately tetrahedral, the N—Ge—C(9) angle being the smallest at 102 5(2)°, with the phenyl ring tilted somewhat towards the nitrogen. The Mo—C(carbonyl) distances are 2.06 Å (av), consistent with earlier studies [8,9]. The carbonyl and phenyl ring distances are normal. Interestingly, the CN bond length 1.159(8) Å is the same as that reported for $GePhMe_2CN$ [2]. The molybdenum—isocyanide carbon bond length found here, 2 150(8) Å, compares favorably to molybdenum isocyanide carbon bond lengths in $Mo(CNMe)_4(CN)_4$ (2 148(8) Å) [10] but not in $[Mo(CNBu)_6I]I$ (2 06(2) and 2.12(2) Å) [11] In the latter complex, bond shortening is probably the result of π-bonding between metal and ligand

Initial evidence including infrared and ^{13}C NMR spectral data suggested that the $GePhMe_2NC$ ligand was an isocyanide rather than a cyanide. We sought to confirm this with the crystal structure data from an examination of the thermal parameters of the two atoms in question. Such an analysis has previously been used to distinguish nitrogen and carbon atoms in $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$ [8] and its linkage isomer [9]. Basically, if too much or too little electron density is assumed for the scattering atom, the thermal motion appears to either increase or decrease unrealistically.

Complete isotropic and anisotropic least squares refinements were undertaken for both the cyanide and the isocyanide isomers. In each study the thermal parameters were most consistent for the isocyanide configuration. In the isotropic refinement the temperature factors for the carbon and nitrogen atoms, assuming an isocyanide, were 1.93 and 2.52 Å^2, respectively, with R_1 = 3 86 and R_2 = 5 52 With the cyanide configuration, the thermal parameters diverged to 1 35 for carbon and 3.22 Å^2 for nitrogen and the converged R_1 and R_2 increased to 4.19 and 5 99. Similar results were obtained for the anisotropic refinement

For the cyanide possibility the larger nitrogen B_{iso} is due to an excess of electron density assumed for this atom, while for the carbon atom too little scattering power is allowed and the thermal parameter decreases. Naturally the least squares refinement alone cannot rule out the presence of a small percentage of the cyanide isomer, but together with the infrared spectrum, there is strong evi-

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* A table of structure factors has been deposited as NAPS Document No 03068 (8 pages) Order from ASIS/NAPS, c/o Microfiche Publications, P O. Box 3513 Grand Central Station, New York, N.Y. 10017 A copy may be secured by citing the document number, remitting $ 5 00 for photocopies or $ 3 00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

dence for the existence of only the isocyanide isomer. Application of Hamilton's R-ratio [12] test indicates the cyanide possibility can be eliminated at the 0.005 significance level

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References

1 P M Treichel and D B Shaw J Organometal Chem 139 (1977) 21
2 J R Durig Y S Li and J B Turner, Inorg Chem 13 (1974) 1495
3 T H Whitesides R W Slaven and J C Calabrese Inorg Chem , 13 (1974) 1895
4 International Tables for X-Ray Crystallography Vol. I 2nd ed The Kynoch Press Birmingham 1965 p 85 97
5 Programs used in the structure solution were written by J C Calabrese. In addition DEAR the J F Blount absorption correction program, ORFLS and ORFFE the Busing, Martin Levy least squares and error analysis program. ORTEP the Johnson thermal ellipsoid plotting program were used
6 D H Templeton in International Tables for X-Ray Crystallography Vo III. The Kynoch Press Birmingham, 1962, p 215
7 D T Cromer and J B Mann Acta Crystallogr , A. 24 (1968) 321
8 B C Wang W P Schaefer and R E Marsh Inorg Chem 10 (1971) 1492
9 R. Ronczek and W P Schaefer Inorg Chem , 13 (9174) 727
10 M Novotny D F. Lewis and S J Lippard J Amer Chem Soc 94 (1972) 6961
11 D F Lewis and S J Lippard Inorg Chem 11 (1972) 621.
12 International Tables for X-Ray Crystallography Vol IV The Kynoch Press Birmingham 1974 p 288