Of various η^1-CO_2 metal complexes reported so far,[34-41] $[W(CO)_5CO_2]^{2-}$ formed in the reaction of $[W(CO)_5]^{2-}$ with CO_2 at 195 K undergoes an oxide-transfer reaction with another CO_2 molecule to produce $[W(CO)_6]$ and CO_3^{2-} at room temperature.[34] Although $[Ru(bpy)_2(CO)(COO^-)]^+$ does not undergo such an oxide transfer reaction with another CO_2 molecule, it may easily be converted to $[Ru(bpy)_2(CO)_2]^{2+}$ via $[Ru(bpy)_2(CO)C(O)OH]^+$ in acidic conditions according to the equilibrium reactions shown in eq 5 and 6 and in Scheme I. Thus, the reduction of CO_2 conducted in acidic media produces only CO. On the other hand, in weak alkaline solutions such as pH 9.5, $[Ru(bpy)_2(CO)C(O)OH]^+$ (or $[Ru(bpy)_2(CO)(COO^-)]^+$) exists as a predominant species (Figure 7), which may undergo a two-electron reduction involving participation of one proton to give $HCOO^-$ with regeneration of the pentacoordinated ruthenium(0) complex $[Ru(bpy)_2(CO)]^0$. The evolution of CO as the same time may come from $[Ru(bpy)_2(CO)_2]^{2+}$ existing as a minor component (Figure 7) in the solution.

As described in a previous section, there is a close similarity between $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)Cl]^+$ as catalysts for the reduction of CO_2, suggesting that the two-electron reduction of $[Ru(bpy)_2(CO)Cl]^+$ results in the dissociation of Cl^- to afford the unstable pentacoordinated intermediate $[Ru(bpy)_2(CO)]^0$, which reacts with CO_2 to generate $[Ru(bpy)_2(CO)(COO^-)]^+$. Several attempts to identify the formation of $[Ru(bpy)_2(CO)(COO^-)]^+$ in an electrochemical two-electron reduction of $[Ru(bpy)_2(CO)Cl]^+$ at −1.40 to −1.50 V vs. SCE in CO_2-saturated anhydrous DMF, however, have given only an insoluble black precipitate. This may result from instability of $[Ru(bpy)_2(CO)(COO^-)]^+$ in anhydrous DMF at that potential. It is well-known that $[Ru(bpy)_2XY]^{n+}$ (X, Y = pyridine derivatives, halides, phosphines, and so on; n = 0–2) undergoes two successive one-electron reversible or quasireversible reductions[42] and the added electrons are considered to be localized mainly in π^*-orbitals of the bipyridine ligands.[43,44] A strong π-electron acceptor CO ligand may, however, resist such an electron localization in $[Ru(bpy)_2(CO)_2]^0$ and $[Ru(bpy)_2(CO)Cl]^-$. Thus, two-electron reductions of $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)Cl]^+$ may be followed by chemical reactions possibly to generate $[Ru(bpy)_2(CO)]^0$. The participation of $[Ru(bpy)_2(CO)]^0$ in the catalytic cycle of the present CO_2 reduction reasonably explains the formation of CO and $HCOO^-$ depending on pH of the solutions.

Registry No. CO_2, 124-38-9; CO, 630-08-0; HCO_2^-, 71-47-6; $[Ru(bpy)_2(CO)_2]^{2+}$, 105453-70-1; $[Ru(bpy)_2(CO)Cl]^+$, 86389-98-2; $[Ru(bpy)_2(CO)]^0$, 105399-80-2; $[Ru(bpy)_2(CO)(COO^-)]$, 86536-98-3; $[Ru(bpy)_2(CO)C(O)OH]^+$, 105373-59-9.

---

(34) (a) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982,** *104,* 6797. (b) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980,** *102,* 7604.

(35) (a) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982,** *104,* 5082. (b) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978,** *100,* 7405.

(36) Bianchini, C.; Meli, A. *J. Am. Chem. Soc.* **1984,** *106,* 2698.

(37) (a) Lee, G. R.; Cooper, N. J. *Organometallics* **1985,** *4,* 794. (b) Forshner, T.; Menard, K.; Culter, A. *J. Chem. Soc., Chem. Commun.* **1984,** 121. (c) Bodnar, T.; Coman, E.; Menard, K.; Culter, A. *Inorg. Chem.* **1982,** *21,* 1275.

(38) (a) Francis, B. R.; Green, M. L. H.; Luong-thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* **1976,** 1339. (b) Green, M. L. H.; Luong-thi, T.; Moser, G. A.; Packer, I.; Pettit, F.; Roe, D. M. *J. Chem. Soc., Dalton Trans.* **1976,** 1988. (c) Green, M. L. H.; Mackenzie, R. E.; Poland, J. S. *J. Chem. Soc., Dalton Trans.* **1976,** 1993.

(39) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984,** *23,* 2731.

(40) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983,** *105,* 5914.

(41) (a) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978,** *100,* 3941. (b) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979,** *101,* 1627.

(42) Sullivan, B. P.; Conrad, D.; Meyer, T. J. *Inorg. Chem.* **1985,** *24,* 3640.

(43) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984,** *23,* 1440.

(44) (a) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *J. Am. Chem. Soc.* **1983,** *105,* 3032. (b) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem.* **1983,** *149,* 115. (c) Ohsawa, Y.; DeAmond, M. K.; Hanck, K. W.; Morris, D. E.; Whitten, D. G.; Neveux, P. E., Jr. *J. Am. Chem. Soc.* **1983,** *105,* 6522.

MNDO Calculations for Compounds Containing Germanium[†1]

Michael J. S. Dewar,* Gilbert L. Grady,[‡] and Eamonn F. Healy

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received March 19, 1986

MNDO has been parametrized for germanium. Calculations are reported for a number of compounds of germanium. The results are comparable with those for the third-period elements.

Introduction

The MNDO method[2,3] is now established[4] as a practical procedure for studying behavior, giving results comparable[5] with those from quite good ab initio models (e.g., 4-31G) while requiring only one-thousandth as much computer time. Parameters are currently available for hydrogen,[3] for the second period elements beryllium,[6] boron,[7] carbon,[3] nitrogen,[3] oxygen,[3] and fluorine,[8] for the third-period elements aluminum,[9] silicon,[10] phosphorus,[11] sulfur,[12] and chlorine,[13] and for bromine,[14] iodine,[15] and tin.[16] Since d AOs are not currently included in MNDO, calculations are confined to compounds involving only normal group

---

[‡] Deceased January 28, 1986.

(1) (1) Part 73 of the series "Ground States of Molecules". For part 72 see: *Organometallics* **1985,** *4,* 1784.

(2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977,** *99,* 4899.

(3) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977,** *99,* 4907.

(4) For example, CA SEARCH list 148 citations of MNDO in the period since January, 1982, to be compared with 1073 for ab initio.

(5) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979,** *101,* 5558.

(6) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978,** *100,* 777.

(7) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977,** *99,* 5231.

(8) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978,** *100,* 58.

(9) Davis, L. P.; Guitry, R. M.; Williams, J. R.; Dewar, M. J. S. *J. Comput. Chem.* **1981,** *2,* 433.

© 1987 American Chemical Society

Table I. MNDO Parameters for Germanium

optimized parameters	value	derived parameters	value
U_{ss}/eV	−33.949 367	E_{heat}/kcal/mol	89.5
U_{pp}/eV	−27.425 105	E_{el}/eV	−76.248 944 0
ζ_s/au	1.293 180	D_1/au	1.255 609 1
ζ_p/au	2.020 564	D_2/au	1.049 865 5
β_s/eV	−4.516 479	AM/au	0.360 161 7
β_p/eV	−1.755 517	AD/au	0.364 372 2
α/Å^{-1}	1.978 498	AQ/au	0.434 733 7
G_{ss}/eV	9.800 000		
G_{pp}/eV	7.300 000		
G_{sp}/eV	8.300 000		
G_{p2}/eV	6.500 000		
H_{sp}/eV	1.300 000		

Table II. Calculated Heats of Formation (ΔH_f), First Ionization Energies (I_1), and Dipole Moments (μ)

	ΔH_f, kcal/mol		I_1, eV		μ, D	
compd	calcd	obsd	calcd	obsd	calcd	obsd
GeF	−16.4	−8[a]	6.0		1.42	
GeCl	17.4	37[a]	6.59		3.88	
GeBr	42.9	56.3[a]	6.74		4.28	
GeF_2	−124.5	−121[a]	8.95		2.66	2.61[b]
$GeCl_2$	−52.1	−42[a]	9.66		5.0	
$GeBr_2$	0.43	−15[a]	9.43		5.21	
GeI_2	67.4	11[a]	8.77		4.27	
GeH_4*	13.5	20.8[c]	12.07	11.31[d]		
$GeCl_4$*	−125.7	−118.5[a]	13.7	11.88[e]		
$GeBr_4$	−34.0	−71.7[a]	12.6			
GeI_4	57.6	−13.6[a]	11.26			
$GeCl(CH_3)_3$*	−62.1	−63.8[f]	11.77	10.5[g]	3.47	2.78[b]
$GeBr(CH_3)_3$*	−38.2	−53.1[f]	11.1	10.0[g]	3.45	2.84[b]
$Ge(CH_3)_4$	−32.8	−32.0[f]	11.8	9.29[h]		
$Ge(CH_3)_3$(*t*-Bu)	−39.0	−55.7[f]	10.64	8.98[h]		
$Ge(CH_3)_3NMe_2$*	−32.2	−29.1[f]	9.35		0.31	
$Ge(CH_3)_3OC_2H_5$*	−88.0	−87.8[f]	10.6		3.08	
$Ge(C_2H_5)_4$	−55.1	−39.7[i]	10.9		0.13	
$Ge(OCH_3)_4$	−230.7	−230.4[j]	11.07			
$[Ge(CH_3)_3]_2O$	−116.6	−127.0[f]	10.5			1.41[b]
$Ge_2(CH_3)_6$	−23.9	−62.5[h]	9.6	8.18[h]		
Ge_2H_6	46.9	38.8[a]	9.64			
Ge_3H_8	74.9	54.2[a]	9.14			
$Ge(CH_3)_3+$	162.7	165.0[f]				
$Ge(CH_3)_3$	−1.9	2.2[f]	8.02	8.0[f]	0.69	
$GeSn(CH_3)_6$	−29.4	−39.7[f]	9.86	8.20[f]	2.12	

[a] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schemm, R. H. *Natl. Bur. Std.* [*U.S.*] *Tech. Note* **1968**, *270*-3, 182. [b] McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1974; Vol. II. [c] Saalfeld, F. E.; Svec, H. J. *Inorg. Chem.* **1963**, *2*, 46. [d] Pullen, B. P.; Carlson, T. A.; Moddeman, W. E.; Schweitzer, G. K. *J. Chem. Phys.* **1970**, *53*, 768. [e] Basset, P. J.; Lloyd, D. R. *J. Chem. Soc. A* **1971**, 641. [f] Baldwin, J. C.; Lappert, M. F.; Pedley, J. B.; Poland, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 1943. [g] Drake, J. R.; Gorzelska, K. *J. Electron Spectrosc.* **1981**, *21*, 1981. [h] Lappert, M. F.; Pedley, J. B.; Simpson, B.; Spaulding, T. R. *J. Organomet. Chem.* **1971**, *29*, 195. [i] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970. [j] Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*; Sussex University: Brighton, U.K., 1977.

Table III. Calculated (Observed) Geometrical Parameters

molecule	bond lengths (Å) calcd (obsd)		bond angles (deg) calcd (obsd)		ref
GeH_4	GeH	1.482 (1.527)			*a*
$GeCl(CH_3)_3$	GeCl	2.257 (2.170)			*b*
	GeC	1.930 (1.940)	CGeCl	106.7 (106.6)	
$GeBr(CH_3)_3$	GeBr	2.373 (2.323)			*c*
	GeC	1.930 (1.936)	BrGeC	106.8 (106.3)	
$GeCl_4$	GeCl	2.225 (2.113)			*d*
$Ge(CH_3)_4$	GeC	1.939 (1.945)			*e*
	CH	1.11 (1.12)			
$Ge(CH_3)_2H_2$	GeH	1.486 (1.532)	HGeH	109.0 (108.7)	
	GeC	1.932 (1.950)	CGeC	111.0 (110)	*f*, *g*
$Ge(CH_3)_2Cl_2$	GeCl	2.243 (2.143)	ClGeCl	105.5 (108)	*h*
	GeC	1.928 (1.928)	CGeC	115.6 (121 ± 4)	
			CGeCl	108.7 (108)	
$Ge(CH_3)_2F_2$	GeF	1.743 (1.739)	FGeF	101.5 (105.4 ± 2)	*i*
	GeC	1.937 (1.928)	FGeC	109.7 (107.3)	
			CGeC	115.3 (121.0 ± 3.5)	
$Ge_2O(CH_3)_6$	GeC	1.945 (1.980)	GeOGe	161.3 (141)	*j*
	GeO	1.762 (1.770)	GeOC	107.6 (109)	

[a] Eades, R. A.; Dixon, D. A. *J. Chem. Phys.* **1980**, *72*, 3309. [b] Durig, J.; Hellams, K. L. *J. Mol. Struct.* **1975**, *29*, 349. [c] Li, Y. S.; Durig, J. *Inorg. Chem.* **1973**, *12*, 306. [d] Moreno, Y.; Nakamura, Y.; Iijima, T. *J. Chem. Phys.* **1960**, *32*, 643. [e] Hencher, J. L.; Mistoe, F. J. *Can. J. Chem.* **1975**, *53*, 3542. [f] Thomas, E. C.; Laurie, V. W. *J. Chem. Phys.* **1969**, *50*, 3512. [g] Durig, J.; Chen, M. M.; Li, Y. S. *J. Phys. Chem.* **1973**, *77*, 227. [h] Drake, J. E.; Hencher, H. L.; Shem, Q. *Can. J. Chem.* **1977**, *55*, 1104. [i] Drake, J. E.; Hemmings, R. T.; Hencher, J. L.; Mustoe, F. M.; Shem, Q. *J. Chem. Soc., Dalton Trans.* **1976**, 394. [j] Vilkov, L. V.; Tarensenko, N. A. *Zh. Strukt. Khim.* **1969**, *10*, 102.

valences. Thiel[17] has also parametrized lithium, and Schleyer et al.[18] have reported extensive MNDO calculations for compounds containing lithium, using these parameters. However, the parameters have not yet been published.

In our continuing program of improving and extending the scope of MNDO, the elements of group IVB (14[25]) were an obvious target. Recent work[19] here has shown that d AOs are not needed to explain the chemical behavior of silicon, suggesting that the standard form of MNDO, without d AOs, should be equally applicable to the other group IVB (14) elements. Apart from their chemical interest, availability of MNDO parameters should provide a good test of a recently developed[20] program for solid-state calculations, using MNDO, given that these elements include an insulator (diamond), two semiconductors (silicon and germanium), and two metals (tin and lead). Most of them also exist in different allotropic forms.

Here we report MNDO parameters for germanium and calculations for a number of germanium compounds. We decided on germanium as our next target for several reasons.

(a) While the chemistry of germanium is interesting and varied,[21] it has not yet been studied as fully as that of tin or silicon. Availability of MNDO parameters would enable us to make predictions regarding aspects of organogermanium chemistry which have not yet been investigated.

(b) Recent thermochemical data are available for a reasonable number of germanium compounds.

(c) The results for germanium would provide a further test of the applicability of the MNDO formalism to ele-

---

(10) Dewar, M. J. S.; Healy, E. F.; Stewart, J. J. P.; Friedheim, J. E.; Grady, G. L. *Organometallics* **1986**, *5*, 375.

(11) Dewar, M. J. S.; Rzepa, H. S.; McKee, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 3607.

(12) Dewar, M. J. S.; McKee, M. L. *J. Comput. Chem.* **1983**, *4*, 84.

(13) Dewar, M. J. S.; Rzepa, H. S. *J. Comput. Chem.* **1983**, *4*, 158.

(14) Dewar, M. J. S.; Healy, E. F. *J. Comput. Chem.* **1983**, *4*, 542.

(15) Dewar, M. J. S.; Healy, E. F.; Stewart, J. J. P. *J. Comput. Chem.* **1984**, *5*, 358.

(16) Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771.

(17) Personal communication from Professor W. Thiel.

(18) Schleyer, P. V. R.; Tidor, B.; Jemmis, E. D.; Chandrasekhar, J.; Worthwein, E.; Kos, A.; Luk, B. T.; Pople, T. A. *J. Am. Chem. Soc.* **1983**, *105*, 484.

(19) Dewar, M. J. S.; Healy, E. F. *Organometallics* **1982**, *1*, 1705.

(20) Dewar, M. J. S.; Stewart, J. J. P., to be submitted for publication.

(21) (a) Riviere, P.; Riviere-Baudet, M.; Satge, J. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: New York, 1982; Vol. 2. (b) Lesbre, M.; Mazerolles, P.; Satge, J. *The Organic Chemistry of Germanium*; New York, 1972.

Table IV. Calculated Heats of Formation, Geometries, and Vibrational Frequencies for Germylene and Selected Doubly Bonded Germanium Molecules

H_2Ge–X, X =	ΔH_f, kcal/mol	bond lengths (Å) calcd (obsd)		bond angles (deg) calcd (obsd)		vib freq, cm^{-1}	
(germylene)	51.4	Ge–H	1.471 (1.580)[a]	HGeH	96.0 (93.0)[a]		
GeH_2 (D_{2h})	96.6	Ge–Ge	2.259 (2.300)[a]			GeGe	286
		Ge–H	1.489 (1.580)[a]				
CH_2 (D_{2h})	54.6	Ge–C	1.717 (1.779)[b]	HGeC	121.5 (123.0)[b]	GeC	854 (906)[c]
		Ge–H	1.490 (1.542)[b]	HCGe	125.0 (122.0)[b]		(847)[d]
		C–H	1.089 (1.085)[b]				
NH (D_{2h})	66.4	Ge–N	1.647 (1.695)[b]	HGeN	117.9 (118.1)[b]	GeN	978 (994)[c]
		Ge–H	1.497 (1.552)[b]		122.8 (128.8)[b]		(854)[d]
			1.500 (1.538)[b]	HNGe	135.5 (122.8)[b]		
		N–H	0.977 (1.022)[d]				
O (D_{2h})	14.4	Ge–O	1.611 (1.634)[b]	HGeO	119.4 (124.0)[b]	GeO	980 (1036)[c]
		Ge–H	1.499 (1.547)[b]				(881)[d]

[a] Fjeldberg, T.; Haaland, A.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1407. [b] Trinquier, G.; Barthelat, J.-C.; Satge, J. *J. Am. Chem. Soc.* **1982**, *104*, 5931. [c] Reference *b*, SCF calculated value. [d] Reference *b*, CI calculated value.

ments of later periods. Reassurance concerning this is important in view of our plans to extend MNDO to additional elements, in particular transition metals.

Procedure

The sum of squares of the differences between the calculated values for the properties and the reference values were used to define the error function SSQ. These properties included heats of formation, ionization energies, dipole moments, and geometries. The first derivatives of the heat of formation and ionization energies with respect to the various parameters were calculated analytically. The derivatives of the dipole moments were evaluated by finite difference, and the derivative of the energy with respect to geometry was used as a measure of the deviation of the calculated geometry from the experimental. A knowledge of these derivatives allowed the calculation of the derivative of the SSQ with respect to the various parameters. A line search along the search direction yielded the optimum step size, and this information was used to update the Hessian matrix. When this procedure was repeated, an optimum set of parameters was obtained. The algorithm used was a modification of the Davidon–Fletcher–Powell (DFP) procedure.[22]

Results and Discussion

Table I shows the final parameters for germanium, in the notation used previously.[2-16]

Table II shows the heats of formation (ΔH_f), first ionization energies (I_1; derived by using Koopmans' theorem) and dipole moments (μ), for 26 germanium-containing molecules, including several interesting diatomic ones. Molecules included in the basis set for parametrization are indicated by asterisks. Experimental values are included for comparison whenever they are available.

The mean absolute error in ΔH_f is 15.4 kcal/mol with a few molecules accounting for a large part of it. The results for germanium are thus about the same as those[10-14] for compounds of the third-period elements. The values for compounds containing more electronegative atoms are systematically too positive, while those for compounds containing less electronegative atoms are too negative. The largest error is for the tetraiodide, as was also the case for tin.[16] If the tetraiodide and diiodide are omitted, the average error in ΔH_f falls to 11.1 kcal/mol. It should be noted that heats of formation have been measured for only a small number of germanium compounds and even these may be subject to considerable experimental error.[23] Measurements of heats of combustion in particular are likely to suffer from problems similar to those encountered[10] in analogous silicon compounds. Here, as elsewhere, the lack of accurate thermochemical data is not only deplorable in itself but also a serious obstacle to any kind of theoretical calculation. The only way to assess the value of *any* current procedure, ab initio or semiempirical, is by comparison with experiment.

The calculated ionization energies are systematically too large. The mean error in I_1 for the nine molecules in Table II for which there are experimental data is 1.3 eV. A similar error was found in MNDO calculations for compounds of the third-period elements, in particular chlorine,[13] and was attributed to neglect of interactions between the inner electrons and valence electrons in MNDO, due to use of the core approximation.

Very few measurements of dipole moments seem to have been reported for compounds of germanium (Table II). The agreement with the MNDO values is, as usual, reasonable.

Table III compares the calculated geometries with experiment. Bond angles involving germanium are reproduced fairly well. The errors in the corresponding bond lengths are comparable with those for bonds involving third-period elements,[9-13] being likewise greater than for the "organic" elements C, H, N, and O.[3] Calculated Ge–H bond lengths are generally too small and germanium–halogen ones too large by ca. 0.1 while the values for Ge–C bonds are close to those observed. While the errors are larger numerically than for the "organic" elements, the chemical consequences should not be serious because the bonds are so long. Furthermore, the larger errors are for bonds to univalent elements, errors which should not greatly alter the geometry of the rest of the molecule. The only large error in a bond angle is for the Ge–O–Ge angle in hexamethyldigermoxane, where the calculated value (161°) is too large by 20°.

Germanium is predicted to have a large positive formal charge in the compounds studied here, ranging from +1.5 in alkylgermanes to +2.2 in $Ge(OCH_3)_4$. The calculated charge distributions are not reported because they showed no unexpected features.

Due to the recent interest in multiply bonded group IVB (14) compounds we have calculated selected properties of some doubly bonded species and compared the values with high level ab initio results (Table IV). All the $H_2Ge{=}X$ molecules are predicted to be planar D_{2h} structures. In the case of germaethylene ($H_2Ge{=}CH_2$), germamimine ($H_2Ge{=}NH$), and germanone ($H_2Ge{=}O$) this is also what is found by using pseudopotential ab initio methods (footnote *b*, Table IV). As can be seen from Table IV both

---

(22) Fletcher, R.; Powell, J. D. *Comput. J.* **1963**, *6*, 163. Davidon, W. C. *Comput. J.* **1968**, *10*, 406.

(23) (a) Pilcher, G., *Int. Rev. Sci. Phys. Chem. Ser. Two* **1975**, *10*, 45. (b) O'Neal, H. E.; Ring, M. A. *Inorg. Chem.* **1966**, *5*, 437.

methods give a bond length ordering of $Ge{=}O < Ge{=}N < Ge{=}C$, with a concomitant decrease in the stretching vibrational frequencies. The MNDO frequencies are in better agreement with the ab initio SCF values than with the CI results.

For digermene (Ge_2H_4) the situation is different. While MNDO gives a planar structure, ab initio MO calculations yield a nonplanar, trans-folded structure with the angle θ between the Ge–Ge bond and the GeC_2 plane being 40°. This latter result agrees with the X-ray structure of Ge_2R_4, $[R{=}CH(Si(Me_3)_2]$[24] which has a fold angle of 32°. The analogous Sn structure has a fold angle of 41°,[24] indicating an even weaker M–M bond.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. AFOSR 86-0022), the Robert A. Welch Foundation (Grant No. F-126), and the National Science Foundation (Contract CHE82-17948). The calculations were carried out by using a Digital VAX 11/780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. GeF, 14929-46-5; GeCl, 21110-21-4; GeBr, 25884-11-1; GeF_2, 13940-63-1; $GeCl_2$, 10060-11-4; $GeBr_2$, 24415-00-7; GeI_2, 13573-08-5; GeH_4, 7782-65-2; $GeCl_4$, 10038-98-9; $GeBr_4$, 13450-92-5; GeI_4, 13450-95-8; $GeCl(CH_3)_3$, 1529-47-1; $GeBr(CH_3)_3$, 1066-37-1; $Ge(CH_3)_4$, 865-52-1; $Ge(CH_3)_3$(*t*-Bu), 1184-91-4; $Ge(CH_3)_3NMe_2$, 13361-67-6; $Ge(CH_3)_3OC_2H_5$, 4848-66-2; $Ge(C_2H_5)_4$, 597-63-7; $Ge(OCH_3)_4$, 992-91-6; $[Ge(CH_3)_3]_2O$, 2237-93-6; $Ge_2(CH_3)_6$, 993-52-2; Ge_2H_6, 13818-89-8; Ge_3H_8, 14691-44-2; $Ge(CH_3)_3^+$, 76568-90-6; $Ge(CH_3)_3$, 21941-60-6; $GeSn(CH_3)_6$, 16393-89-8; $Ge(CH_3)_2F_2$, 811-70-1; GeH_2, 24968-55-6; H_2GeGeH_2, 82323-93-1; H_2GeCH_2, 60188-36-5; H_2GeNH, 83025-94-9; H_2GeO, 78812-54-1; $Ge(CH_3)_2H_2$, 1449-64-5; $Ge(CH_3)_2Cl_2$, 1529-48-2; Ge, 7440-56-4.

---

[24] Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480.

[25] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Communications

A Vanadium–Phosphinidene Complex Exhibiting Vanadium–Phosphorus Multiple Bonding

Atta M. Arif, Alan H. Cowley,* and Marek Pakulski

Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Nicholas C. Norman

Department of Inorganic Chemistry
University of Newcastle upon Tyne
Newcastle upon Tyne NE1 7RU, U.K.

A. Guy Orpen

Department of Inorganic Chemistry, University of Bristol
Cantocks Close, Bristol BS8 1TS, U.K.

Received August 12, 1986

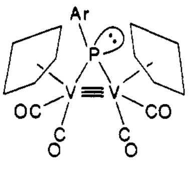
Summary: The reaction of (2,4,6-*t*-$Bu_3C_6H_2$)PCl_2 with $Na_2[(\eta\text{-}C_5H_5)V(CO)_3]$ affords the bridging phosphinidene complex $[V_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}P(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}]$ (**1**). The nature of the bonding in **1** is discussed on the basis of spectroscopic and X-ray crystallographic data and preliminary EHMO calculations. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.954 (2) Å, b = 11.562 (2) Å, c = 14.362 (3) Å, α = 109.82 (2)°, β = 94.09 (2)°, and γ = 100.85 (2)°.

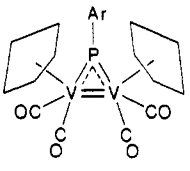
Phosphinidene (phosphanediyl) complexes of the type $RP(ML_n)_2$ are attracting significant recent attention. The known complexes feature either 16- or 15-electron fragments with transition metals from groups 6–8.[1] We report (i) the first group 5 phosphinidene complex and (ii) the first example of a phosphinidene moiety bonded to a *14*-electron organometallic fragment.

Equimolar quantities of $ArPCl_2$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$) and $Na_2[(\eta\text{-}C_5H_5)V(CO)_3]$[2] were allowed to react in THF solution at 25 °C. After removal of the THF, the resulting dark brown residue was extracted with *n*-hexane and purified by column chromatography (Florisil/*n*-hexane). This afforded $[(\eta\text{-}C_5H_5V(CO)_4]$ and a dark green solution from which crystals were obtained at −20 °C, corresponding to the composition $[V_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}PAr)$ (1), 28% yield.

The diamagnetism of 1 was established by the observability of (noncontact shifted) ^1H and ^{13}C NMR spectra which exhibited peaks corresponding to C_5H_5 and 2,4,6-*t*-$Bu_3C_6H_2$ groups.[3] No metal hydride resonances were detected within the range +10 to −20 ppm. The 121.5-MHz $^{31}P\{^1H\}$ spectrum comprised a broad singlet at δ +670 which is in the region characteristic of μ-phosphinidine complexes,[1,4] while the IR spectrum of 1 was indicative of the presence of four CO ligands.[3]

If each vanadium is to achieve an 18 electron configuration, two valence isomers, A and B, are possible. The


A


B

---

[1] (a) For a recent review of phosphinidenes bonded to 16e organometallic fragments, see; Huttner, G. *Pure Appl. Chem.* **1986**, *58*, 585. See also; Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460. (b) For phosphinidenes bonded to 15e organometallic fragments: Arif, A. M.; Cowley, A. H.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1707.

[2] The salt $Na_2[(\eta\text{-}C_5H_5)V(CO)_3]$ was prepared from $(\eta\text{-}C_5H_5)V(CO)_4$ and sodium amalgam in THF following the procedure of Fischer and Schneider (Fischer, E. O.; Schneider, R. J. J. *Chem. Ber.* **1970**, *103*, 3684).

[3] NMR data for 1 in C_6D_6 (25 °C): ^1H 8.08 (d, 2H,C_6H_2, $^4J_{PH}$ = 2.5Hz), 5.36 (s, 5H, C_5H_5), 1.62 (s, 9H p-$C(CH_3)_3$), 1.48 (s, 18H, o-$C(CH_3)_3$). $^{13}C\{^1H\}$ 124.3 (d,m-C_6H_2, $^3J_{PC}$ = 8Hz), 99.5 (s, C_5H_5), 34.1 (s, p-$C(CH_3)_3$), 32.1 (s, o-$C(CH_3)_3$). The carbonyl carbons were not detected, presumably because coupling to ^{51}V and long relaxation times. IR: $\nu_{C{=}O}$ (*n*-hexane) 1985(m), 1930(s), 1855(m)cm^{-1}.

0276-7333/87/2306-0189$01.50/0 © 1987 American Chemical Society