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Supplementary Material Available: A listing of observed and calculated structure factors and tables of anisotropic thermal parameters, complete bond angles and bond lengths, and hydrogen atom coordinates (49 pages). Ordering information is given on any current masthead page.

Electronic Structure of Group 14 (η^4-Metallole)tricarbonyliron Complexes[†,‡]

C. Guimon and G. Pfister-Guillouzo

Laboratoire de Physico-Chimie Moléculaire—ERA 895, IURS, 64000 Pau, France

J. Dubac,* A. Laporterie, G. Manuel, and H. Iloughmane

Laboratoire des Organométalliques—ERA 829, Université Paul-Sabatier, 31062 Toulouse Cédex, France

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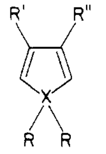
Some methyl derivatives of metalloles $R_2XC_4H_4$ (X = C, Si, Ge) and their tricarbonyliron complexes have been prepared in order to study the influence of both the group 14 elements and complexation effects on the electronic structure of the diene ring using photoelectron spectroscopy (UPS, He I, He II). Strong electron donation from iron to the metallole ligand has been demonstrated. This transfer, which is the result of participation of the lowest vacant orbital of the ring ($3b_1$) in the highest occupied orbital (HOMO) of the complex, shows that these compounds have a certain aromatic character.

A few of the numerous studies on the electronic structures of metal–diene complexes are devoted to tricarbonyliron compounds. Most of the research has been limited to the butadiene ligand itself and to its substituted derivatives,[1-5] to cyclobutadiene,[5-7] 1,3-cyclohexadiene,[4,5] and *trans*-1,3-pentadiene.[1,5,8] As far as we know, no systematic studies have been undertaken on tricarbonyliron complexes of cyclopentadienes and, a fortiori, on silicon and germanium analogues.

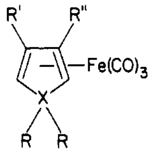
A comprehensive analysis of the electronic features of (5,5-dimethylcyclopentadiene)tricarbonyliron and those of several (methylsilole) and (methylgermole)tricarbonyliron complexes is presented in this paper. We have extended the synthesis used for methylsiloles[9,10] to methylgermoles. Photoelectron spectroscopy is a very suitable technique to evaluate metal–ligand interactions or electronic modifications arising from the substitution of a carbon atom by a silicon or a germanium atom.

Synthesis and Identification of Group 14 (η^4-Metalloles)tricarbonyliron Complexes

5,5-Dimethylcyclopentadiene (2) was prepared from β,β-dimethylglutaric acid by the method of Rouse and Tyler.[11] Reaction of 2 with $Fe_2(CO)_9$ led to the corresponding tricarbonyliron complex 8.[12-14] Preparation of complexes 9–11 has been described previously.[9] The method of synthesis of 1,1,3,4-tetramethylsilole (4)[9b] was applied to the two methylgermole derivatives 6 and 7, which were obtained pure and were uncontaminated with the transoid isomer.[15]

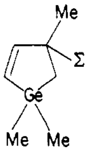


	X	R	R'	R''
1	C	H	H	H
2	C	Me	H	H
3	Si	Me	H	H
4	Si	Me	Me	Me
5	Ge	Me	H	H
6	Ge	Me	H	Me
7	Ge	Me	Me	Me

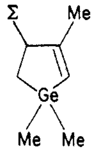


	X	R	R'	R''
8	C	Me	H	H
9	Si	Me	H	H
10	Si	Me	Me	Me
11	Ge	Me	H	H
12	Ge	Me	H	Me
13	Ge	Me	Me	Me

The *N*-phenylcarbamates corresponding to alcohols 14 and 16 (prepared by photooxygenation–reduction of



14, Σ=OH
15, Σ=OCONHPh



16, Σ=OH
17, Σ=OCONHPh

[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

[‡] Part 22 of "Application of Photoelectron Spectroscopy to Molecular Properties". Part 21: C. Guimon, G. Pfister-Guillouzo, P. Meunier, B. Gautheron, G. Tainturier, and S. Pouly, to be submitted for publication.

(1) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, 50, 654.

(2) Worley, S. D. *J. Chem. Soc., Chem. Commun.* **1970**, 980.

(3) Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *28*, 1193.

(4) Green, J. C.; Powell, P.; Van Tilborg, J. *J. Chem. Soc., Dalton Trans.* **1976**, 1974.

(5) Worley, S. D.; Webb, T. R.; Gibson, D. H.; Ong, T. S. J. Electron Spect., 1980, *18*, 189. Worley, S. D.; Webb, T. R.; You, T. *Ibid.* **1982**, *28*, 129.

(6) Hall, M. B.; Hillier, I. H.; Connor, J. A.; Guest, M. F.; Lloyd, D. R. *Mol. Phys.* **1975**, *30*, 839.

(7) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760. Kostic, N. M.; Fenske, R. F. *Chem. Phys. Lett.* **1982**, *90*, 306.

(8) (a) Derrick, P. J.; Asbrink, L.; Edquist, O.; Jonsson, B. O.; Lindholm, E. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *6*, 203. (b) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

(9) (a) Laporterie, A.; Iloughmane, H.; Dubac, J. *J. Organomet. Chem.* **1983**, *244*, C12. (b) *Tetrahedron Lett.* **1983**, 3521.

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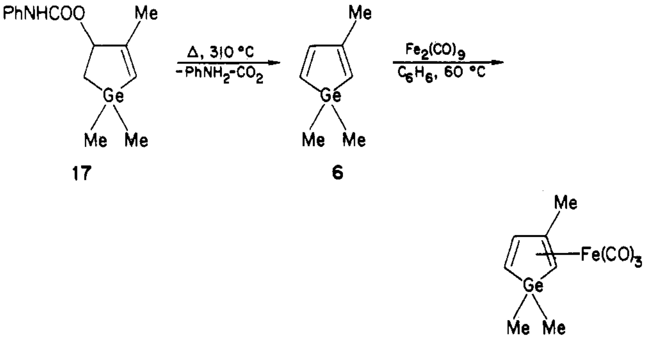
Table I. Nuclear Magnetic Resonance Spectra (^{1}H) of Germoles 5-7 and the Corresponding Tricarbonyliron Complexes

compd	δ(GeMe)^b	δ(C(2)H)	δ(C(3)H)	δ(C(4)H)	δ(C(5)H)	δ(CMe)	*J*, Hz
5^{37}	0.38 (s)	6.20 (m)	6.70 (m)	6.70 (m)	6.20 (m)		*c*
6	0.35 (s)	5.66 (m)		6.65 (s)	6.20 (m)	1.97 (d)	^3J(C(4)H/C(5)H) = 10, ^4J(C(2)H/C(4)H) = 2, ^4J(C(2)H/C(3)CH$_3$) = 2^d
7	0.30 (s)	5.71 (s)			5.71 (s)	1.97 (s)	
11	−0.14 (s) 0.58 (s)	1.72 (m)	5.22 (m)	5.22 (m)	5.22 (m)	1.72 (m)	*c*
12	0.01 (s) 0.71 (s)	1.90 (m)		5.38 (m)	1.77 (d)	1.99 (s)	^3J(C(4)H/C(5)H) = 5.7, ^4J(C(2)H/C(4)H) = 1.3, ^5J(C(2)H/C(5)H) = 1.9, J(C(2)H/C(3)CH$_3$) = 0^d
13	0.00 (s) 0.63 (s)	1.86 (s)			1.86 (s)	2.30 (s)	

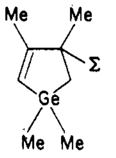
^{a} Solvent CCl$_4$ (**5-7, 13**) or C$_6$D$_6$ (**11, 12**). ^{b} Complexes **11-13**: high-field signal Ge-Me corresponds to *exo* Ge-Me; low-field signal to endo Ge-Me. ^{c} Ethylenic protons: degenerate AA′XX′ system; for such systems in π-complexes, see ref 12-14 and 35. ^{d} Systems analyzed by double resonance.

1,1,3-trimethylgermacyclopent-3-ene)[16] were obtained by reaction of phenyl isocyanate with the mixture of **14** and **16** (68/32 ratio) in boiling pentane. The tertiary carbamate **15** was first decomposed into 1,1,3-trimethylgermole (**6**). This germole was not thermally stable as the monomer and was polymerized. Thermolysis of the pure secondary carbamate **17** in a regiospecific reaction gave germole **6** which could be trapped at −78 °C. The subsequent immediate reaction of **6** with Fe$_2$(CO)$_9$ in benzene at 60 °C led to the tricarbonyliron complex **12**.

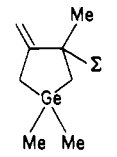


17 **6** **12**

Tertiary carbamates **19** and **21** (45/55), stable in refluxing pentane, were prepared from the mixture of alcohols **18** and **20** (43/57 ratio) by the same procedure and isolated by fractional crystallization.[18]

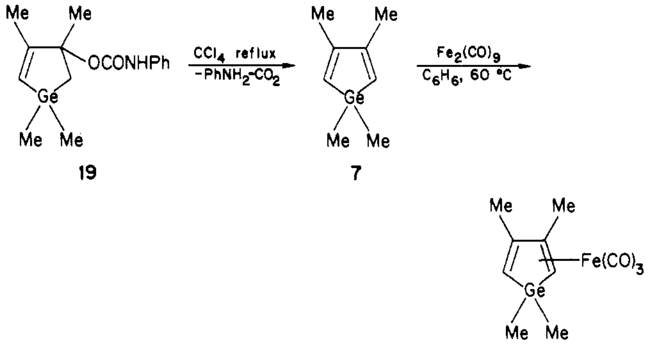


18, Σ = OH
19, Σ = OCONHPh



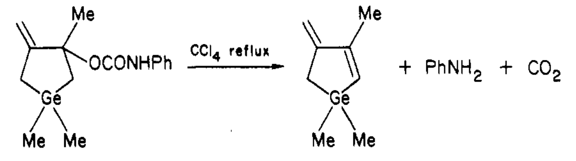
20, Σ = OH
21, Σ = OCONHPh

When carbamate **19** was heated in refluxing carbon tetrachloride, the stable 1,1,3,4-tetramethylgermole (**7**) was formed. Reaction of **7** with Fe$_2$(CO)$_9$ gave the Fe(CO)$_3$ complex **13**.



19 **7** **13**

Under the same conditions, decomposition of the isomeric carbamate **21** led to the known 1,1,3-trimethyl-4-methylenegermacyclopent-2-ene (**22**).



21 **22**

Spectroscopic Identification of Complexes 11-13

The principal characteristics of the ^{1}H NMR spectra of the tricarbonyl iron–germole complexes **11**, **12**, and **13** and those of complexes **8**,[12-14] **9**, and **10**[9] are similar (Table I). Two X–CH$_3$ signals (exo and endo), the very strong shielding (~4 ppm) of C(2)H and C(5)H protons, and a lowering of vicinal coupling constants $^{2,3}J_{\mathrm{HH}}$ and $^{4,5}J_{\mathrm{HH}}$ in comparaison with those of the noncomplexed metalloles may be noted. The equivalence of the two ethylenic protons and the two C–CH$_3$ methyl groups in **13** (as in **10**)[9b] would indicate that the plane of symmetry of the metallole is also present for LFe(CO)$_3$ complexes.

In the mass spectrum, a successive decarbonylation process leads to fragment ions quite similar to those obtained from carbonyl diene π-complexes and organometallic group 14 diene complexes.[20,21] The base peak in the mass spectra of compounds **9** and **11-13** corresponds

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(10) Iloughmane, H. Thèse de 3ème cycle, Université Paul-Sabatier, Toulouse, 1983, No. 2843.

(11) Rouse, R. S.; Tyler, W. E., III *J. Org. Chem.* **1961**, *26*, 3525.

(12) Muller, H.; Herberich, G. E. *Chem. Ber.* **1971**, *104*, 2772.

(13) Eilbracht, P.; Dahler, P.; Totzauer, W. *Tetrahedron Lett.* **1976**, 2225.

(14) Eilbracht, P.; Mayser, U. *J. Organomet. Chem.* **1977**, *135*, C23.

(15) Catalytic dehydration of alcohols **14** + **16** or **18** + **20** leads to mixture of germoles **6** or **7** and transoid isomers as **22**.[16] Analogous silicon alcohols give same results. C-methylated group 14 metalloles are isomerized into transoid dienes on Al$_2$O$_3$ or ThO$_2$.[10,17] Such an isomerization may be avoided by the *N*-phenylcarbamate[9b] thermolysis method presented in this paper.

(16) Laporterie, A.; Manuel, G.; Dubac, J.; Mazerolles, P. *Nouv. J. Chim.* **1982**, *6*, 67.

(17) Laporterie, A.; Manuel, G.; Iloughmane, H.; Dubac, J. *Nouv. J. Chim.* **1984**, *8*, 437.

(18) Alcohol **18** was obtained recently in a pure isomeric state by one of us.[19] Thus, carbamate **19** can be prepared by an unequivocal reaction.

(19) Manuel, G.; Bertrand, G.; El Anba, F. *Organometallics* **1983**, *2*, 391.

(20) (a) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1977**, *128*, 57. (b) Jutzi, P.; Karl, A.; Burschka, C. *Ibid.* **1981**, *215*, 27.

(21) McMahon, R. J. *Coord. Chem. Rev.* **1982**, *47*, 1 and references therein.

Table II. Vertical Ionization Potentials of Analogues of Cyclopentadienes and the Corresponding Tricarbonyliron Complexes

compd	d_{Fe}		$\pi(a_2)$	$\pi(b_1)$	$\sigma(b_2)$	$\sigma(a_1)$	$\pi(b_1)$	σ
1[a]			8.55	10.7	12.2	12.6	14.8	13.5
2			8.45	10.55	11.3	11.6	12.5	12.6
4			8.20	9.8	10.15[b]	10.15[b]	11.15	11.45
7			8.20	9.55	9.85	10	11	11.45
8	7.9	8.45	9.50	11	12.1			
9	7.8	8.40	9.50	10.4[b]	10.6[b]	10.6[b]	11.35	11.75
10	7.55	8.25	9.20	10[b]	10.2[b]	10.3[b]	11.2	11.2
11	7.75	8.40	9.35	10.15[b]	10.3[b]	10.3	11.2	11.9
12	7.50	8.20	9.25	10[b]	10.1[b]	10.25	11.2	
13	7.45	8.20	9.1	9.75[b]	9.9[b]	10.1[b]	11.1	11.95

[a] Reference 22. [b] Approximate values (overlapping of corresponding bands).

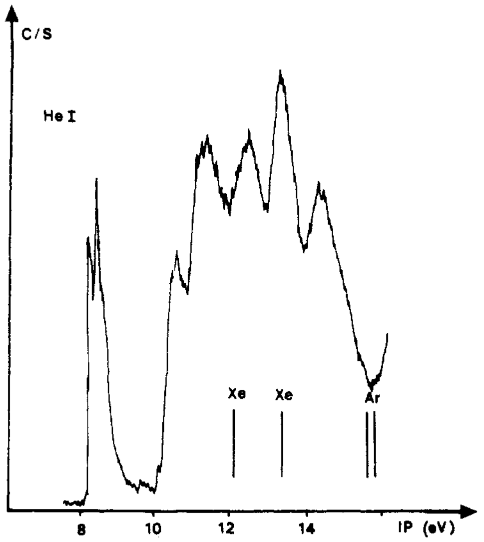

Figure 1. Photoelectron spectrum (He I) of 5,5-dimethylcyclopentadiene.

to the $[M - 3CO]^+ = LFe^+$ fragment.

Photoelectron Spectra of Group 14 Metalloles and Corresponding Complexes

Group 14 Metalloles. The electronic structure of cyclopentadiene itself is well-defined. Its photoelectron spectrum (8,25) and those of its monosubstituted derivatives RC_5H_5 (R = 1-Me, 2-Me, 5-SiH_3) have been studied.[22,23] A clear destabilization of molecular orbitals more particularly associated to bonding orbitals of the tetracoordinated center is induced when substitution by a *gem*-dimethyl group occurs. Signals between 12 and 14 eV (Figure 1) for the nonsubstituted derivative are more clearly resolved. Three bands are observed at 11.3, 12.5, and 13.5 eV. The first two at 8.45 and 10.55 eV are assigned to ionization of electrons of the π a_2 and π b_1 orbitals of the dienic system. A slight shift of these two ionization potentials toward low energy is observed by comparison to that of cyclopentadiene itself. Ionization of bonding σ orbitals with b_2 and a_1 symmetry corresponds to the observed band around 11.5 eV. It seems logical to associate ionization of the π-orbital with b_1 symmetry and ionization of the σ orbital to the band observed at 12.5 eV. The C–H (methyl group) antisymmetric combination effectively interacts with the b_1 orbital of the dienic system, and the resulting totally symmetrical orbital is the most perturbed by methylation (14.8 eV for cyclopentadiene, 13.4 eV for 5-methylcyclopentadiene, and 12.5 eV for 5,5-dimethylcyclopentadiene). The 13.5-eV band is associated with the ionization of σ-bonding electrons.

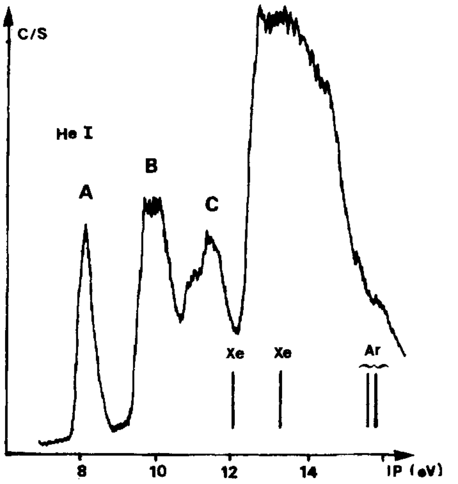

Figure 2. Photoelectron spectrum (He I) of 1,1,3,4-tetramethylsilole.

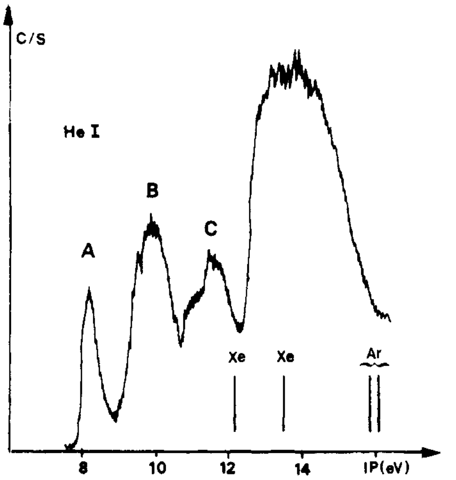

Figure 3. Photoelectron spectrum (He I) of 1,1,3,4-tetramethylgermole.

The photoelectron spectra of group 14 metalloles show three bands between 8 and 12 eV. The first band at 8.20 eV corresponds to ionization of the π a_2 orbital (Table II) (those orbitals possessing a node on the Si or Ge atom). The ionization potential is slightly shifted toward lower energy in comparison with 5,5-dimethylcyclopentadiene, in agreement with the inductive effect of the Si or Ge and, for the major part, with the effect of two methyl groups in the 3- and 4-positions. The associated ionization of the

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(22) Cradock, S.; Findlay, R. H.; Palmer, M. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1650.

(23) Distefano, G.; Pignataro, S.; Innorta, G.; Fringelli, F.; Marino, G.; Taticchi, A. *Chem. Phys. Lett.* **1973**, *22*, 132.

(24) Koopmans, T. *Physica (Amsterdam)* **1934**, *1*, 104.

(25) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899 and 4907.

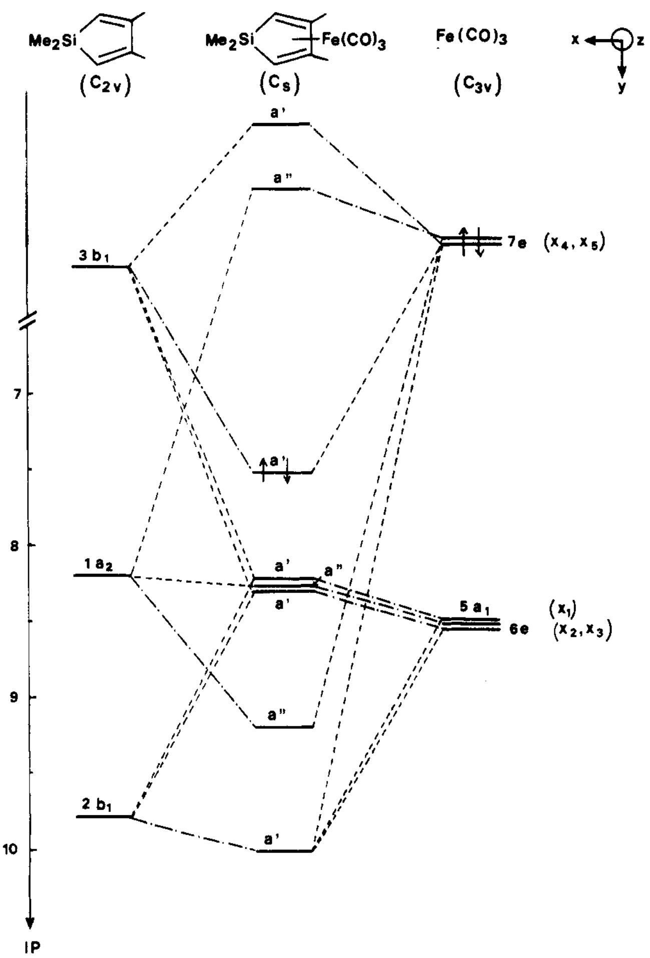

Figure 4. Correlation diagram between frontier molecular orbitals of 1,1,3,4-tetramethylsilole, its corresponding complex, and Fe-$(CO)_3$ fragment: (–•–) most important participation; (- - -) lowest participation.

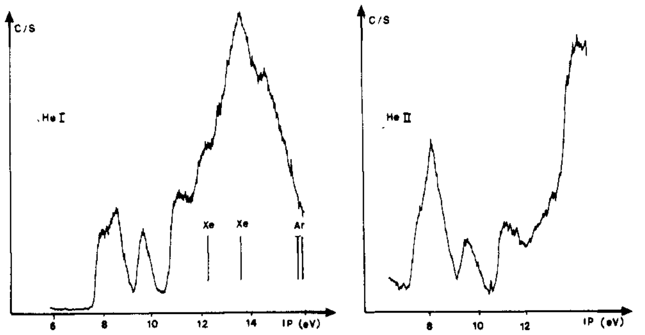

Figure 5. Photoelectron spectra (He I, He II) of (5,5-dimethylcyclopentadiene)tricarbonyliron complex.

π b_1 orbitals appears at a significantly lower potential in comparison with cyclopentadiene: 9.8 eV for the silicon derivative and 9.55 eV for the germanium derivative. This destabilization is due to the fact that this orbital is localized on the metal (Ge is less electronegative than Si). For the same reason, the σ b_2 and σ a_1 orbitals corresponding to X–C bands appear in the same area, at 10.15 and 9.85 eV, respectively (11.3 eV for 5,5-dimethylcyclopentadiene). The third band includes, in fact, two partially overlapping bands due to an ionization of the b_1 orbital and the σ orbital.

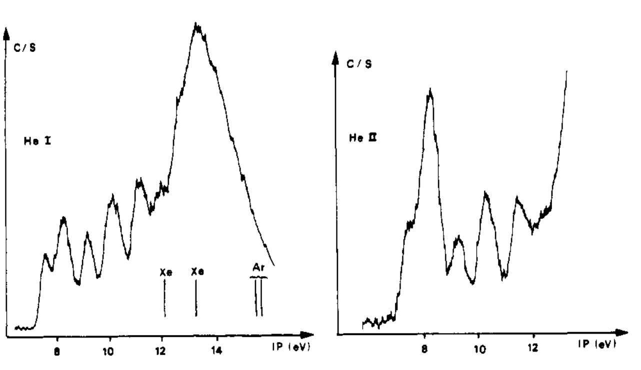

Figure 6. Photoelectron spectra (He I, He II) of (1,1,3,4-tetramethylsilole)tricarbonyliron complex.

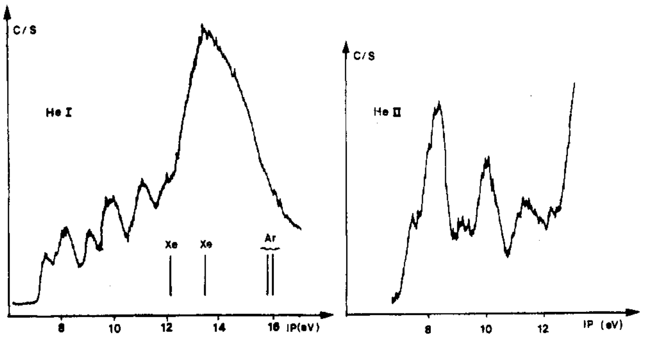

Figure 7. Photoelectron spectra (He I, He II) of (1,1,3,4-tetramethylgermole)tricarbonyliron complex.

Complexes. The electronic structure of the d_8 $Fe(CO)_3$ fragment with C_{3v} symmetry is well-known.[26] This structure is deduced from that of iron in an octahedral surrounding and from the $Mn(CO)_3^+$ ion.[26–29] The lowering of symmetry induces a partial splitting of the t_{2g} orbitals into an a_1 orbital and two degenerate orbitals of e symmetry.[30] The $Fe(CO)_3$ fragment possesses two electrons in degenerate 7e orbitals. So, it is possible to explain the preference of $Fe(CO)_3$ for conjugated olefins considering the donor–acceptor properties of these ligands and also the splitting of the e level. The result of the interaction between the conjugated diene and $Fe(CO)_3$ appears in a clear electron transfer from iron to ligand. This system may be compared to an aromatic π-system; the metal aromaticity concept has been called upon to explain chemical behavior of such complexes.[7] It is of importance to note, in the case of studied complexes, that the geometrical structure of the ligand is modified and the ring presents an envelope shape with a dihedral angle closed to 30°.[20b,31] This deformation may indicate the tendency of the system to be stabilized by a metal–ligand interaction including $2n + 2$ electrons but may come from a simple steric effect. The interactions occurring are represented in Figure 4. As has been already mentioned,

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[26] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

[27] Orgel, L. E. *J. Inorg. Nucl. Chem.* **1956**, *2*, 315.

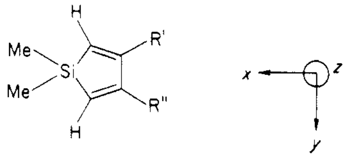
[28] Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

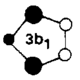
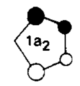
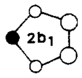
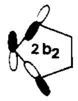
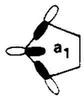
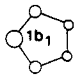
[29] Guimon, C.; Pfister-Guillouzo, G.; Mathey, F. *Nouv. J. Chim.* **1979**, *3*, 725 and references therein.

[30] Except for the $5a_1$ MO which is associated at d_{z^2} AO, the 6e and 7e MO's are linear combinations of both the four other d(Fe) AO's and the orbitals localized on the CO groups (although with a lesser weight). In the octahedral symmetry, the five combinations are $\chi_1 = d_{z^2}$ ($5\ a_1$), $\chi_2 = (2/3)^{1/2}d_{xy} - (1/3)^{1/2}d_{yz}$ and $\chi_3 = (2/3)^{1/2}d_{x^2-y^2} + (1/3)^{1/2}d_{xz}$ (6e), and $\chi_4 = (2/3)^{1/2}d_{yz} + (1/3)^{1/2}d_{xy}$ and $\chi_5 = (2/3)^{1/2}d_{xz} - (1/3)^{1/2}d_{x^2-y^2}$ (7e). Nevertheless the presence of the CO groups, the 4s(Fe) and 4p(Fe) AO's modify these coefficients. Thus an EHT calculation gives a localization rate for the 6e OM's: $C^2_{d_{xy}}/C^2_{d_{yz}} = C^2_{d_{x2-y2}}/C^2_{d_{xz}} = 2.62$ (instead of 2). This mixing is less important for the vacant 7e MO's ($C^2_{d_{yz}}/C^2_{d_{xy}} = C^2_{d_{xz}}/C^2_{d_{x2-y2}} = 7.72$) on account of the secondary interactions (principally with 4p(Fe) AO's) which vary with the form of the 3d MO's and their energy.

[31] Muir, K.; Walker, R.; Abel, E. W.; Blackmore, T.; Whiteley, R. J. *J. Chem. Soc., Chem. Commun.* **1975**, 698.

Table III. Calculated Ionization Potentials ($-\epsilon_i$ for Occupied Orbitals) by the MNDO[25] Method According to Koopman's Theorem[24] and the Shape of the Corresponding Molecular Orbitals[a]



						
R' = R'' = H		9.28	10.98	11.51	11.73	13.43
R' = R'' = Me		9.13	10.41	11.07	11.09	12.00

[a] LUMO is the $3b_1$ orbital. Si—C(Me) = 1.86 Å, Si—CH = 1.82 Å, and C=C = 1.35 Å.[31]

the most important interactions exist between the X_4 and $^1a_2$ orbitals[30] and the X_5 and $3b_1$ orbitals. The last interaction gives rise to the highest occupied molecular orbital (HOMO). Due to its low overlap with the π-orbitals of the ring, $5a_1$ and 6e orbitals, close in energy, these are slightly modified. On the other hand, the $2b_1$ orbital, with only a slight overlap with the d_{z^2} (X_1) and d_{xy} (X_5 and X_3) orbitals, is poorly stabilized compared with the $1a_2$ orbital.

Worley[5] observed such a difference of stabilization on complexation of a 4π-electron dienic system. These observations are corroborated by analysis of the photoelectron spectra of complexes of cyclopentadiene and group 14 metalloles (Figures 5–7). Table II indicates the variation of ionization potential values depending on H and Me substituents on the ring. Also, the band intensities change with photon energy (He I, 21.21 eV; He II, 40.81 eV).

Band intensities are proportional to the cross sections and depend on two factors: the nature of the ionized orbitals and the energy of the ionizing photons. Qualitative rules were proposed.[32,33] Bands associated with molecular orbitals with large d contributions increase in intensity when He II instead of He I photons are used. Furthermore, bands associated with molecular orbitals localized on third or fourth period atoms (Si and Ge in this paper) are slowly decreased when He I is replaced by He II in comparison with more localized orbitals in a second period atom (carbon).

In the three spectra (Figures 5 –7), the second band is considerably increased in intensity compared to the other bands when the spectra are recorded with He II. This increase evidently comes from ionization of partially degenerate 3d orbitals. The first band shows an intensity change which is smaller for the second band but larger than the rest. This fact confirms a strong mixing between 7e (d_{xz}) iron orbital and the $3b_1$ vacant orbitals of ligand HOMO orbital of the complex. The next bands are associated with extension of electron essentially localized on the ring and belonging to orbitals stabilized by complexation. This complexation is more important for $1a_2$ orbital (Table II, 0.9–1 eV) than for $2b_1$ orbital (0.2–0.4 eV).

The substitution of methyl groups in silicon derivatives agrees with this finding. Thus, on one hand, the most sensitive band to the methylation effect is the band associated to the π b_1 orbital, and on the other, the destabilization of 0.25 eV for the HOMO is only explained by an important contribution of the vacant $3b_1$ orbitals of the ligand to this occupied molecular orbital (in the complex). This variation is identical with those observed passing from 1,1,3,4-tetramethylgermacyclopentadiene to 1,1,3-trimethylgermacyclopentadiene (Table II).

Finally, the fifth band in the spectra of complexes of metalloles (around 11.2 eV) decreases in relative intensity from silicon to germanium analogue derivatives. This fact may be related to the ionization of the b_1 orbital localized on Si and Ge atoms (Table III).

To conclude, electronic structures of studied complexes reveal some metal aromaticity features. Important localization of HOMO $3b_1$ orbital on the ligand predicts an interesting reactivity of such complexes with both hard and soft electrophilic reagents. High charge density on C_α, due to metal–ligand transfer (revealed by the high deshielding effect in the ^{1}H NMR), may induce versatile electrophilic reactions.

Experimental Section

General Data. All melting and boiling points reported in this section are uncorrected. The ^{1}H NMR spectra were obtained on either a Varian Associates EM 360 A 60-MHz or a CAMECA 250-MHz spectrometer. Chemical shifts are reported in units parts by million (ppm) downfield from internal tetramethylsilane. Photoelectron spectra were recorded on a photoelectron spectrometer 0078 of "Photoelectron Laboratories". The excitation sources were He I and He II resonance lines argon and xenon signals were used as internal calibrants (Xe, $^2p_{1/2}$, 12.126 eV, $^2p_{3/2}$, 13.443 eV; Ar, $^2p_{1/2}$, 15.755 eV, $^2p_{3/2}$, 15.93 eV).

All starting materials were purchased unless other wise indicated. Germacyclopentenols **14**, **16**, **18**, and **20** were prepared from the corresponding germacyclopentenes.[16]

1,1,4-Trimethyl-3-(phenylcarbamoyl)-1-germacyclopent-4-ene (17). A mixture of alcohols **14** and **16** (68/32 ratio) (10.3 g, 55 mmol) and phenyl isocyanate (6.57 g, 55 mmol) was refluxed for 10 h in 100 mL of pentane. A small quantity of *N*,*N*′-diphenylurea was separated by filtration, and the solvent was removed. The residue gave on distillation 4.75 g of carbamate **17** (88% yield calculated from **16**): bp 163–165 °C (0.3 mm); ^{1}H NMR (60 MHz, CCl_4) δ 0.30 (s, 3 H, $GeCH_3$), 0.37 (s, 3 H, $GeCH_3$), 0.43–1.67 (m, 2 H, C(2)H), 1.87 (d, J = 0.5 Hz, 3 H, C(4)–CH_3), 5.9 (m, 2 H, C(3)H and C(5)H), 6.9–7.6 (m, 5 H, C_6H_5). Anal. Calcd for $C_{14}H_{19}O_2NGe$: C, 54.96; H, 6.27. Found: C, 55.06; H, 6.30.

1,1,3,4-Tetramethyl-3-(phenylcarbamoyl)-1-germacyclopent-4-ene (19) and 1,1,3-Trimethyl-4-methylene-(3-phenylcarbomyl)-1-germacyclopentane (21). A mixture of alcohols **18** and **20** (43/57 ratio) (14.2 g, 71 mmol) and phenyl isocyanate (8.42 g, 71 mmol) was refluxed for 6 h in pentane. After the solution was cooled, a white powder corresponding to equimolar quantities of carbamates **19** and **21** was isolated by filtration. Pure carbamate **21** (3.9 g, 30% yield) was separated by fractional crystallization from pentane–chloroform: mp 110 °C dec; ^{1}H NMR (60 MHz, CD_3COCD_3) **19** δ 0.32 (s, 3 H, $GeCH_3$), 0.36 (s, 3 H, $GeCH_3$), 1.6 (m, overlapped by C(3)–CH_3 and C(4)–CH_3 systems,

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(32) Schweig, A.; Thiel, W. *J. Electron Spectrosc.* **1974**, *3*, 27 and references therein.

(33) Tseng, H. K.; Pratt, R. H.; Yu, S.; Ron, A. *Phys. Rev.* **1978**, *17*, 1061.

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1 H, C(2)H), 1.43 (s, 3 H, C(3)–CH_3), 1.67 (d, *J* ≃ 1 Hz, 3 H, C(4)–CH_3), 5.77 (m, 1 H, C(5)H), 8.17 (s, 1 H, NH), 6.93–7.77 (m, 5 H, C_6H_5), **21** δ 0.37 (s, 3 H, $GeCH_3$), 0.42 (s, 3 H, $GeCH_3$), 0.97–1.97 (m, 4 H, C(2)H and C(5)H), 1.77 (s, 3 H, C(3)–CH_3), 4.80 and 5.00 (2m, 2 H, CH_2═C), 8.50 (s, 1 H, NH), 6.98–7.80 (m, 5 H, C_6H_5). Anal. Calcd for $C_{15}H_{21}O_2N$ Ge: C, 56.31; H, 6.62. Found: C, 56.36 (**19**), 56.29 (**21**); H, 6.60 (**19**), 6.64 (**21**).

1,1,3-Trimethylgermole (6) and the Corresponding Tricarbonyliron Complex (12). The pyrolysis was conducted in a 25 × 1.4 cm vertical Pyrex tube enclosed in a thermoregulated electric tube furnace. Half of the column was filled with Pyrex chips heated to 310 °C. The carbamate **17** (1.10 g, 3.6 mmol) in 6 mL of pentane was mechanically added at a rate of 60 mL/h simultaneous with an argon flow of 10 mL/min. The pyrolyzate was collected in a liquid-nitrogen trap. Aniline and germole **6** were identified by ^1H NMR. Germole **6** was stable as the monomer at low temperature, and no transoid isomer **22**[16] was detected in the NMR spectrum (Table I). Like 1,1-dimethylgermole,[34] pure 1,1,3-trimethylgermole polymerized within 2–3 h at 20 °C.

The pyrolyzate resulting from carbamate **17** (1.10 g) was warmed from −78 up to 20 °C and immediately poured into a flask containing $Fe_2(CO)_9$ (1.30 g, 3.6 mmol) in benzene (30 mL) preheated to 60 °C. The mixture was magnetically stirred at 60 °C for 6 h. After filtration, the solvent was removed under vacuum (40 mmHg). Purification was accomplished by column chromatography (SiO_2, Merck 60) using hexane-benzene (80/20 ratio) as eluting solvent. A yellow liquid was isolated and identified as complex **12** (0.30 g, 27% yield). IR (liquid film, cm^{-1}) ν(CO) 1975, 2050; mass spectrum (70 eV), M^+ 210 (20), $[M - CO]^+$ 282 (54), $[M - 2CO]^+$ 254 (79), $[M - 3CO]^+$ 226 (100%), 210 (82), 208 (46), 196 (127), 168 (17), 170 (13), 153 (89). Anal. Calcd for $C_{10}H_{12}O_3FeGe$: C, 38.91; H, 3.92. Found: C, 38.96; H, 4.06.

1,1,3,4-Tetramethylgermole (7) and the Corresponding Tricarbonyliron Complex 13. Carbamate **19** (1.8 g, 6 mmol) was refluxed for 10 h in 40 mL of CCl_4. The solvent was removed under vacuum (50 mmHg), and distillation of the residue gave 0.9 g of germole **7** (85% yield): bp 75 °C (30 mm); ^1H NMR, see Table I. Anal. Calcd. for $C_6H_{14}Ge$: C, 45.40; H, 8.89. Found: C, 45.42, H, 8.87.

Germole **7** (1.03 g, 6.5 mmol) and $Fe_2(CO)_9$ (2.40 g, 6.5 mmol) in benzene were stirred at 60 °C for 3 h. A yellow liquid, identified as complex **13** (1.44 g, 65% yield), was isolated by column chromatography using hexane–benzene (80/20 ratio) as eluting solvent: ^1H NMR, see Table I; IR (cm^{-1}, liquid film) ν(CO) 1970, 2040; mass spectrum (70 eV), M^+ 324 (11), $[M - CO]^+$ 296 (43), $[M - 2CO]^+$ 268 (60), $[M - 3CO]^+$ 240 (100%), 224 (60), 222 (83), 210 (37), 167 (74). Anal. Calcd for $C_{11}H_{14}O_3FeGe$: C, 40.94; H, 4.37. Found: C, 40.91; H, 4.40.

Registry No. **2**, 4125-18-2; **3**, 18135-88-1; **4**, 82763-95-9; **5**, 78750-31-9; **6**, 82763-92-6; **7**, 82763-96-0; **8**, 42535-31-9; **9**, 85944-69-0; **10**, 87965-49-9; **11**, 85944-70-3; **12**, 94890-84-3; **13**, 94890-85-4; **14**, 82763-86-8; **16**, 82764-03-2; **17**, 94890-81-0; **18**, 82763-89-1; **19**, 94890-82-1; **20**, 82763-91-5; **21**, 94890-83-2; $Fe_2(CO)_9$, 15321-51-4; phenyl isocyanate, 103-71-9.

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[34] Laporterie, A.; Manuel, G.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *210*, C33.

[35] Maddox, M. L.; Stafford, S. L.; Kaesz, H. D. *Adv. Organomet. Chem.* **1965**, *3*, 1.

A Ring-Opening Reaction of 1-Siloxy-1-alkoxycyclopropanes. Preparation of Main-Group Metal Homoenolates of Alkyl Propionate

Eiichi Nakamura,* Jun-ich Shimada, and Isao Kuwajima*

Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

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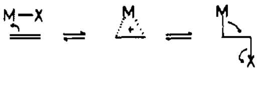
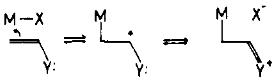
1-(Trimethylsiloxy)-1-alkoxycyclopropanes (**1**) react with a variety of main-group metal halides (Table III) to give the corresponding 3-metalated alkyl propionates (the metal homoenolates of propionates). Spectral properties (Tables I and II) indicate that these homoenolates generally possess a chelate structure (e.g., **3** and **4**), which endows a particular stability to the complex. The reaction mechanism is also discussed.

Heterometalation of olefins is an established method for the synthesis of organometallics yet is very limited in its scope.[1] The reaction as schematized in eq 1 involves development of electron deficiency on the carbon adjacent to the one forming the carbon–metal bond. In this case, it is well-known that the reverse reaction is overwhelmingly favored unless the carbon–metal bond is strong enough or the incipient cation is stable enough to favor the forward reaction. The picture shown in eq 2 illustrates the latter possibility[2] and, in fact, has been exploited in halostannylation of enol silyl ethers by $SnCl_4$.[3]



(1)



(2)

An exact parallel of eq 1 is seen with the heterometalation of cyclopropanes, for which the reverse reaction has ample precedent (eq 3).[4] A protocol (eq 4) to facilitate this reaction by a scheme similar to eq 2, however, does not work so well. Hydroxylated and siloxylated cyclopropane derivatives react with Hg(II) much faster than the unsubstituted ones,[5] but they still do not react well with other metals.[6]

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[1] Negishi, E. "Organometallic in Organic Synthesis"; Wiley: New York, 1980; Vol. 1, p 48. Matteson, D. S. "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974; Chapter 4.

[2] House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514.

[3] Nakamura, E.; Kuwajima, I. *Chem. Lett.* **1983**, 59.

[4] Cf. Sommer, L. H.; Van Strien, R. E.; Whitmore, F. C. *J. Am. Chem. Soc.* **1949**, *71*, 3056. Hawthorne, M. F.; Dupont, J. A. *J. Am. Chem. Soc.* **1958**, *80*, 5830. Kuivila, H. G.; Scarpa, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 6990.

[5] Gibson, D. H.; DePuy, C. H. *Chem. Rev.* **1974**, *74*, 605.

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