Direct Synthesis and Structure of η^4-1-Functionally Substituted 2,3,4,5-Tetraphenyl-1-Silacyclopenta-2,4-diene Complexes of Irontricarbonyl

Wan-Chul Joo*, Hong Lae Sohn, Jang Hwan Hong, Young Kun Kong†, and P. Singh‡

Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746
†Department of Chemistry, Kyunggi University, Suwon 440-270
‡Department of Chemistry, North Carolina State University, Releigh, NC 27695-8204, U.S.A. *Received January 14, 1989*

We obtained the new complexes, Fe[η^4-R,R'-TPSCp](CO)$_3$(R,R'-TPSCp = 1,1-disubstituted 2,3,4,5-Tetraphenyl-1-Silacyclopenta-2,4-diene; R = Ph, R' = Cl, R = R' = Cl) from the reaction of the corresponding R,R'-TPSCp with ironpentacarbonyl under reflux in toluene. Also, the analogous complexes with R = R' = Me and R = Me,R' = Cl were obtained in an identical manner. We have determined the crystal structure of Fe[Ph(Cl)-TPSCp](CO)$_3$ by using Mo ka, λ = 0.71069Å, where the unit cell was found to be monocline with a = 9.042 (6)Å, b = 19.870 (9)Å, c = 17.426 (9)Å and β = 96.28(4)°. The butadiene moiety of TPSCp ring is planar and the dihederal angle of the butadiene plane and C4-Si-C25 plane was opened up to 41.8°. The C-C distances in the butadiene moiety were found to be 1.4346, 1.462, and 1.440 Å, respectively. it may be said that the four π – electrons are delocalized over the four carbons in five membered ring through coordination with ironcarbonyl. In this complex Fe is either in distorted tetrahedron environment with the centroid of the four C-atom butadiene moiety and three carbons of the three carbonyls or in distorted square-pyramidal environment with two midpoints of double bonds of the butadiene moiety and two carbons of carbonyl defining the base of the pyramid and the carbon of remaining carbonyl the apex.

Introduction

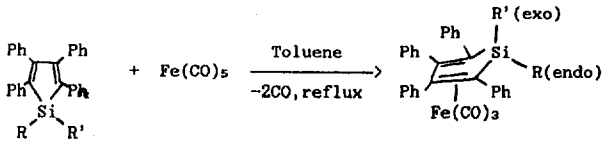
The reaction of 1-silacyclopenta-2,4-diene with transition metal carbonyls is of our interest because it gives η^4-silacyclopenta-2,4-diene complexes which may be converted to η^5-silacyclopentadienyl complexes. Metal carbonyl complexes of 1,1-diorgano-2,5-diphenyl[1-5] and 1,1-diorgano-3,4-dimethyl-1-silacyclopenta-2,4-diene[6-8] have been studied rather extensively, whereas studies for the metal carbonyl complexes of 1-functionally substituted 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene(RR'-TPSCp) are scarce in literature[9, 10]. In this report we describe the direct synthesis of Fe[RR'-TPSCp](CO)$_3$(R = Ph, R' = Cl:R = R' = Cl) and the crystal structure of Fe[Ph(Cl)-TPSCp](CO)$_3$.

Results and Discussion

Most of the η^4-complexes of 1,1-diorgano TPSCp were synthesized from the reactions of the corresponding TPSCp with diironnonacarbonyl or triirondodecacarbonyl in benzene or toluene at 60-100 °C, whereas with ironpentacarbonyl the synthesis was reported to be successful only under the extreme reaction conditions such as at 180-200 °C in benzene (sealed tube), but unsuccessful at temperature below 150 °C.[9] In contrast to TPSCp, it was reported that 1,1-diorgano-2,5-diphenyl-1-silacyclopenta-2,4-diene irontricarbonyls[1] were obtained in the reactions with diironnonacarbonyl or triirondodecacarbonyl in benzene at 40-80 °C, and also with ironpentacarbonyl in benzene at 130-140 °C. Therefore, it was believed that TPSCp was too inert to form complexes directly with ironpentacarbonyl under mild reaction conditions.[1] There have been a few iron-carbonyl complexes of TPSCp which were prepared either indirectly through stepwise substitution at silicon by using 1,1-diorgano TPSCp irontricarbonyls[11] or photochemically from the corresponding TPSCp with ironpentacarbonyl.[12]

However, it is known that the crystal structures of 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene[13] and 1,1-dimethyl-TPSCp[14] are almost planar. Therefore, it is somewhat unexpected that the TPSCp is inert in reactivity toward η^4-complex formation with transition metal carbonyls.

In fact, our investigation provides that 1,1-disubstituted TPSCp are not inert, but rather active enough to form η^4-complexes directly with ironpentacarbonyl under reflux in toluene. We could synthesize the new complexes of Fe[RR'-TPSCp](CO)$_3$ (R = Ph, R' = Cl and R = R' = Cl) in good yield. The known complexes with R = R' = Me and R = Me, R' = Cl were also obtained in an identical manner in this study, although it was reported[1,9] that these compounds could be unable to be obtained under this reaction conditions.



I

a R=Cl, R'=Ph

b R=R'=Cl

c R=R'=CH_3

d R=CH_3, R'=Cl

II

a R=Cl, R'=Ph

b R=R'=Cl

c R=R'=CH_3

d R=CH_3, R'=Cl

d' R=Cl, R'=CH_3

Although the reaction products IIc and IId, IId' isomers could be identified by the known chemical shifts in ^{1}H-NMR, it was impossible to identify the configuration of IIa in an identical manner. Thus, the crystal structure of IIa was determined, and it was found that the bulky phenyl group at silicon was in an exo position as expected.

We now present the crystal data of IIa. X-ray data were collected on a Nicolet R3m/μ four-circle automatic diffractometer equipped with a pulse-height analyzer and a graphite

Table 1. Crystal Data

formula	$C_{37}H_{25}O_3ClSiFe$
mo. wt, g mol^{-1}	637.00
crystal size, mm	(0.42 × 0.33 × 0.30)mm
λ(MoK$_\alpha$), Å	0.71069
a, Å	9.042(6)
b, Å	19.870(9)
c, Å	17.426(9)
β, deg	96.28(4)
V, Å^3	3112(3)
space group	$P2_1/n$
Z	4
D_{calc}, g cm^{-3}	1.36
F(000), e$^-$	1312
temp, K	297
scan type	$\theta/2\theta$
scan range	2° + dispersion
scan speed, deg min^{-1}	variable between 4 and 29.3
2θ range, deg	$3 \leq 2\theta \leq 45$
background	measured for 1.2 the scan time each at the beginning and end of a scan
octants measured	hkl and hki$^-$
standards	2 after 48 reflections
no. measured	4559
no. used, NO$\leq 2\sigma$(I)	3265
μ, cm^{-1}	6.4
R^a	0.043
$R_w{}^b$	0.050
goodness of fit, S^c	1.60
max shift/ σ	0.08
no variables, NV	389
difference peak excursion, eÅ^{-3}	+0.42, −0.32

$^aR = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^bR_w = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$. $^cS = [\Sigma w(|F_o| - |F_c)^2/(NO-NV)]^{1/2}$.

monochromator. Cell constants were obtrained from a least-squares refinement of the setting angles of 20 reflections with 2θ-values between 15° and 30°. The intensity data were collected using the values summarized in Table 1. The raw data were corrected for background and for Lorentz and polarization effects but for absorption. The position of Fe, Cl and Si atoms were determined by direct methods and the rest of the nonhydrogen atoms by the difference Fourier technique. The structure was refined by the block-diagonal least-squares technique by assigning anisotropic thermal parameters to the nonhydrogen atoms. The hydrogen atoms were placed in theoretical positions at a later stage of refinement with a C-H distance of 0.96 Å and a fixed isotropic thermal parameter 1.2 times the equivalent isotropic thermal parameter of the attached nonhydrogen atom. The function minimized with $\Sigma w(||F_o| - |F_c||)^2$, where w is the weight of an observation F, and is given by $w = 1/(\sigma^2(F) + 0.00033F^2)$. The experimental conditions and the results of the refinement are summarized in Table 1.

The X-ray atomic scattering factors and corrections for the anomalous dispersion by Fe and Cl atoms for Mo Ka radiation were taken from the *International Tables for X-ray Crystallography*[15]. All computations were performed on a Data General Microeclipse Computer with the crystallographic program package SHELXTL supplied by the Nicolet Corporation.[16]

Table 2. Fractional Coordinates *X, Y, Z*, and Thermal Parameters, *U*

	X	*Y*	*Z*	*U**
Fe	4108(1)	3009(1)	1792(1)	43(1)
Cl	4163(1)	2132(1)	3817(1)	67(1)
Si	5647(1)	2249(1)	3037(1)	41(1)
C(1)	2856(4)	2738(2)	982(3)	60(2)
O(1)	2010(3)	2573(2)	493(2)	97(1)
C(2)	3952(4)	3848(2)	1429(3)	62(2)
O(2)	3769(4)	4378(2)	1184(2)	102(2)
C(3)	2726(4)	3078(2)	2450(2)	59(2)
O(3)	1800(4)	3151(2)	2834(2)	99(2)
C(4)	4929(4)	2029(2)	2041(2)	40(1)
C(5)	4159(4)	1375(2)	1836(2)	44(1)
C(6)	4889(5)	827(2)	1583(2)	66(2)
C(7)	4165(5)	212(2)	1460(3)	83(2)
C(8)	2749(5)	140(2)	1606(3)	88(2)
C(9)	2021(5)	671(2)	1854(3)	100(2)
C(10)	2706(5)	1287(2)	1971(3)	81(2)
C(11)	5870(4)	2392(2)	1569(2)	41(1)
C(12)	6459(4)	2107(2)	876(2)	45(1)
C(13)	7965(4)	1954(2)	941(2)	58(2)
C(14)	8591(5)	1638(2)	356(2)	67(2)
C(15)	7728(5)	1467(2)	−306(2)	71(2)
C(16)	6243(5)	1604(2)	−378(2)	73(2)
C(17)	5600(5)	1920(2)	207(2)	60(1)
C(18)	6429(4)	3022(2)	1924(2)	40(1)
C(19)	7444(4)	3468(2)	1537(2)	43(1)
C(20)	8719(4)	3711(2)	1954(2)	53(1)
C(21)	9716(4)	4106(2)	1606(3)	69(2)
C(22)	9469(5)	4255(2)	836(3)	75(2)
C(23)	8205(5)	4014(2)	414(2)	68(2)
C(24)	7188(4)	3632(2)	758(2)	55(1)
C(25)	5985(4)	3112(2)	2684(2)	39(1)
C(26)	6313(3)	3714(2)	3181(2)	41(1)
C(27)	6287(4)	4375(2)	2913(2)	56(1)
C(28)	6635(4)	4906(2)	3419(3)	71(2)
C(29)	7003(5)	4786(3)	4194(3)	79(2)
C(30)	7035(5)	4148(2)	4467(3)	76(2)
C(31)	6679(4)	3620(2)	3962(2)	55(1)
C(32)	7312(4)	1756(2)	3415(2)	46(1)
C(33)	8727(4)	2000(2)	3390(3)	72(2)
C(34)	9966(5)	1614(3)	3604(3)	94(2)
C(35)	9806(5)	977(3)	3838(3)	93(2)
C(36)	8449(6)	715(2)	3872(3)	106(3)
C(37)	7206(5)	1105(2)	3669(3)	85(2)

*Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

The final positional and equivalent isotropic thermal parameters for the nonhydrogen atoms are given in Table 2. The atomic numbering scheme is shown in Figure 1.

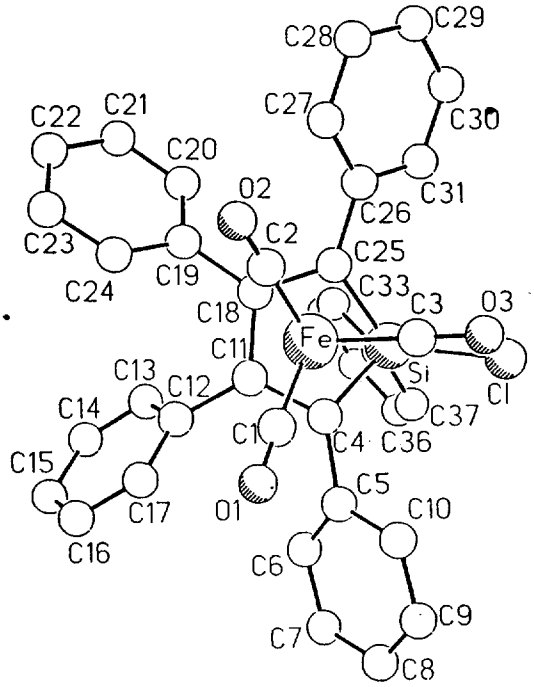


Figure 1. View of the complex looking down the normal to the four-atom diene plane and showing the atom numbering system. Carbon atoms 34,35 and 38 are not labeled due to crowding. Hydrogen atoms are omitted for clarity and others are drawn as circles of arbitrary size. Heteroatoms are shaded.

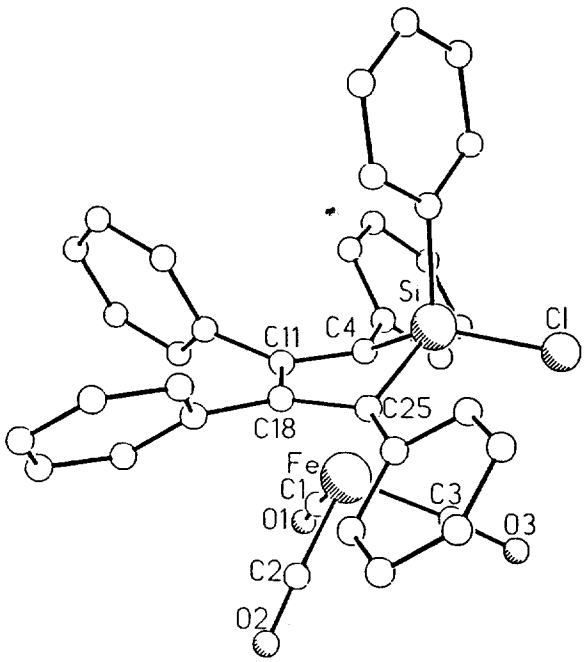


Figure 2. View of the complex showing the orientations of the substituents on the central five-membered ring. Hydrogen atoms are not shown.

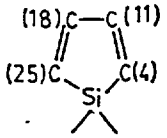
The four carbon atoms C4, C11, C18 and C25 constituting the diene portion of the five-membered ring containing the silicon atom are coplanar with deviations of −0.011, 0.019, −0.019 and 0.011 Å, respectively. The angles around the C11 and C18 are 358.9° and 359.9°, whereas the C4 and C25 353.0° and 356.0°, respectively. The C4 SiC25-butadiene dihedral angle has opened up to 41.8°, so that the silicon atom is out of the diene plane by 0.827 Å. The five-membered ring is, therefore, in an envelope configuration. The phenyl substituent on silicon is in an axial orientation. There are some interesting observations in interatomic distances and angles, a selected list of which is given in Table 3.

Table 3. Selected Distances (Å) and Angles (°) and their *esd*'s

Bond distances		Bond angles	
Fe-C4	2.112(3)	C1-Fe-C2	89.0(2)
Fe-C11	2.081(3)	C1-Fe-C3	95.9(2)
Fe-C18	2.086(3)	C2-Fe-C3	97.0(2)
Fe-C25	2.182(3)	Fe-C1-O1	176.6(4)
Fe-C1	1.792(4)	Fe-C2-O2	176.1(4)
Fe-C2	1.783(4)	Fe-C3-O3	175.5(4)
Fe-C3	1.792(4)	C4-Si-C25	87.7(1)
C1-O1	1.130(5)	Si-C4-C5	122.6(2)
C2-O2	1.141(5)	Si-C4-C11	104.5(2)
C3-O3	1.137(5)	C5-C4-C11	125.9(3)
Si-C4	1.839(3)	C4-C11-C12	124.1(3)
Si-C25	1.859(3)	C4-C11-C18	112.6(3)
Si-C32	1.856(3)	C12-C11-C18	122.2(3)
Si-Cl	2.025(2)	C11-C18-C19	121.3(2)
C4-C11	1.440(5)	C11-C18-C25	112.3(3)
C11-C18	1.462(5)	C19-C18-C25	126.3(3)
C18-C25	1.436(5)	Si-C25-C18	105.3(2)
		Si-C25-C26	125.3(2)
		C18-C25-C26	125.4(3)

For example, the carbon-carbon distances in the five-membered ring show considerable conjugation, the formally single C-C bond (1.462(5)Å) being only slightly longer than the formally double C = C bonds (1.440(5) and 1.436(5)Å), respectively. The Fe-C4 and Fe-C25 distances (2.112 and 2.172 Å, respectively) are longer than Fe-C11 and Fe-C18 distances (2.081 and 2.086 Å, respectively). This is consistent with a similar observation of Mills and Robinson[17] that the distances between Fe and the terminal carbon atoms in 1,3-butadiene, in the crystal structure of the π-complex, Fe(η^4-1,3-butadiene)$(CO)_3$, are slightly longer (2.14 Å) than those between Fe and the central carbon atoms (2.06 Å). In addition, the Fe-C4 and Fe-C25 distances themselves are unequal due, probably, to the unsymmetrical substitution at the silicon atom. The coordination geometry at the iron atom is not clear-cut. If the centroid of the four-atom diene moiety is taken as the fourth ligand site for the Fe atom, the other three sites being the carbons of the three carbonyls, a distorted tetrahedron seems to be an appropriate description, the three CO-Fe-CO angles lying between 89 and 97°, and the other three angles at Fe, *i.e.*, those substended by the diene centroid and the three carbonyl carbons C1, C2 and C3, being 123.4, 121.9 and 121.8°, respectively. The distance between Fe and the diene centroid is 1.716 Å, which is similar to the distances between Fe and the carbonyl carbons, C1, C2 and C3 (Table 3). On the other hand the coordination can also be described as a distorted square pyramid with atoms C1, C2 and the midpoints of the two double bonds, C4 = C11 (L1) and C18 = C25 (L2), defining the base of the pyramid and C3 the apex. A least-squares plane through the four sites C1, C2, L1 and L2 shows that they deviate by −0.063, +0.060,

Table 4. The Bond Distances and Angles of 1-Silacyclopentadienes and Related Complexes



Compound	M-C(4) [M-C(25)]	M-C(11) [M-C(18)]	C(4)-C(11) [C(18)-C(25)	C(11)-C(18)	Si-C(4) [Si-C(25)]	around C(4),C(11) C(18),C(25)	dihedral angle pl.C(4),Si,C(25) pl.C(4),C(11),C(18),C(25)	ref.
$Fe(C_4Ph_4SiPhCl)(CO)_3$	2.112(3)	2.081(3)	1.440(5)	1.462(5)	1.839(3)	353.0° 358.9°	41.8 °C	This
	[2.182(3)]	[2.086(3)]	[1.436(5)]		[1.859(3)]	359.9° 356.0°		work
$Ru(C_4Ph_2H_2SiMe_2)(CO)_3$	2.293(4)	2.189(3)	1.453(4)	1.406(7)	1.880(7)		32°	13
$[Co(C_8H_{14}Si)(PMe_3)_3]BPh_4$	2.316(8)	2.062(6)	1.382(10)	1.472(11)	1.854(5)	359.6°	41.3°	
	[2.197(7)]	[2.274(7)]	[1.403(9)]		[1.875(7)]	349.9°		8
$C_4Ph_4SiMe_2$			1.358(2)	1.511(2)	1.868(3)	359.5° 360.0°		
						360.0° 359.7°	~0°	14
$C_4Ph_2H_2SiMe_2$			1.345(4)	1.466(6)	1.878(3)		3.0°	13

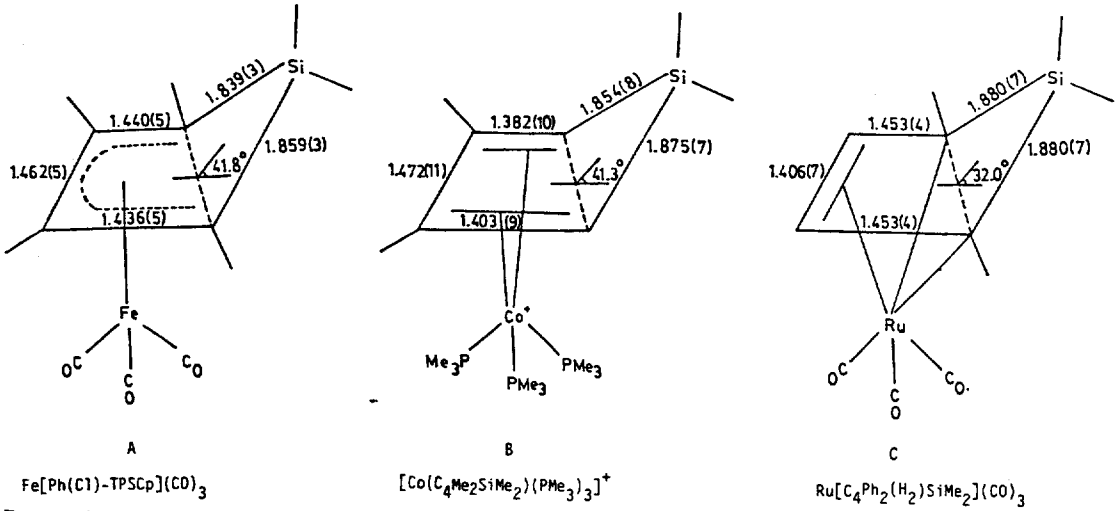


Figure 3. Perspective views of A = Fe[Ph(Cl)-TPSCp](CO)$_3$, B = [Co($C_4Me_2SiMe_2$)(PMe_3)$_3$]$^+$, C = Ru[$C_4Ph_2(H_2)SiMe_2$](CO)$_3$.

+0.078 and −0.078 Å, respectively; the iron atom is out of this plane by −0.510 Å. The apical atom C3 is at a distance of −2.243 Å from this plane. It is clear, therefore, that the coordination polyhedron around the iron atom, whether it is the tetrahedron with the fourth ligating site at the centroid of the four-atom diene moiety, or the square pyramid with the fourth and fifth sites being at the centers of the two ethylenic double bonds, is quite distorted. It may be pointed out that the three carbonyl moieties bonded to the iron atom are located in slightly different environments as shown in Figure 1. C1 ≡ O1 straddles the diene bond, C4 = C11, the C1---C4 and C1---C11 distances being 2.854 and 2.887 Å, respectively. C2 = O2, however, is closer to C18 than to C25, the C2---C18 and C2---C25 distances being 2.834 and 3.069 Å, respectively. The third carbonyl C3 ≡ O3 and the Si-Cl moiety almost eclipse each other, and are tilted in the opposite directions from the four-atom diene plane.

Atom C3, however, makes close contacts with the following atoms; (van der Waals distances[18] are given in parentheses) C4, 3.022(3.40); C25, 2.931(3.40); Si, 3.185(3.80); Cl, 3.197 Å(3.45 Å).

We compared this structure (IIa) with those of Ru[$C_4Ph_2H_2SiMe_2$](CO)$_3$[13] and [Co($C_4Me_2H_2SiMe_2$)(PMe_3)$_3$]$^+$[8], Table 4 shows structural data of IIa and the related complexes.

It is very interesting to know the following characteristics. First, the bond distances of C4-C11, C18-C25 and C11-C18 are almost same for Fe[Ph(Cl)-TPSCp](CO)$_3$, whereas in [Co($C_4Me_2H_2SiMe_2$)(PMe_3)$_3$]$^+$, the C4-C11 and C18-C25 are significantly shorter than C11-C18, while in Ru[$C_4Ph_2H_2SiMe_2$](CO)$_3$, C4-C11 and C18-C25 are remarkably longer than the C11-C18. Secondly, the dihedral angles of Fe- and Co$^+$-complexes are 41.8 and 41.3°, respectively, whereas of Ru-complex 32.0°. Finally, the environment of central metal is a distorted Td/SP for Fe-complex, a ditorted SP for Co$^+$-complex and a distorted Oh for Ru-complex.

Accordingly, it may be said that in Fe-complex, the coordination of TPSCp occurs through the π-electrons being delocalized over the four carbon atoms, whereas it was proposed[14] that in Co$^+$-complex, 1-silacyclopentadiene ring maintains the butadiene fragment, and that in Ru-complex, there are two σ-bonds and one π-bond between 1-silacyclopentadiene ring and Ru. These relations are visualized in Figure 3.

In Co$^+$-complex, the positive charge causes stronger interaction towards the butadiene moiety, leading to reduce the electron density, whereas the +*I*-effect of the two methyl groups may compensate the reduced electron density in the butadiene moiety. Thus the butadiene fragment in ligand re-

Table 5. Spectral Data of Tricarbonyl [1,1-R,R'-TPSCp] Iron

	Compound		^{1}H-NMR(ppm)	Mass	I.R.(cm^{-1})
	R	R'			
II-a	Ph	Cl	δ(Si-Ph) 7.23-7.82(m,5H)	636(M^+,5), 608(M^+-CO,18), 580(M^+-2CO,3)	ν_{CO} = 2050(s), 1990(s)
			δ(C-Ph) 6.70-7.23(m,20H)	552(M^+-3CO,100), 496(Ligand,5)	1975(s,b)
II-b	Cl	Cl	δ(C-Ph) 6.96-7.23(m)	594(M^+,12), 566(M^+-Co,30), 538(M^+-2CO,4)	ν_{CO} = 2070(s), 1995(s,b)
				510(M^+-3CO,100), 434(Ligand,2)	
II-c	Me	Me	δ(CH_3) 0.28(s,3H,exo)	554(M^+,3), 526(M^+-CO,6)	ν_{CO} = 2040(s), 1970(s)
			δ(CH_3) 0.85(s,3H,endo)	470(M^+-3CO,46)	δ_{Si-CH_3} = 1245(m), 1255(m)
			δ(C-Ph) 6.76-7.23(m,20H)	414(Ligand, 100)	
II-d	Me	Cl	δ(CH_3) 0.69(s,1H,exo)	574(M^+,9), 546(M^+-CO,11)	ν_{CO} = 2040(s), 1985(s)
			δ(CH_3) 1.21(s,2H,endo)	518(M^+-2CO,13)	δ_{Si-CH_3} = 1245(w), 1255(w)
			δ(C-Ph) 6.82-7.23(m,20H)	490(M^+-3CO,82), 434(Ligand, 100)	

mains and serves as a 2-and 2-electron system.

In Ru-complex, one may attribute the resulted butene moiety to the effect that 4*d*-orbitals of Ru extend farther into space and thus interact most strongly with the butadiene moiety. On the other hand, in Fe-complex there is neither such a strong interaction between ligand and central metal atom as in Co^+ and Ru-complex, nor such a +*I*-effect as in Co^+-complex. This will be responsible for the π-electrons delocalized system of Fe-complex. The spectral data of the Fe[RR'-TPSCp]$(CO)_3$ complexes are given in Table 5.

Experiments

Elemental analyses were performed by Yanaco, MT-2 Elemental Analyzer at the Chemical Analytic Center of the College of Engineering, Seoul National University. ^{1}H-NMR-spectra were obtained on Bruker WP 80 SY, 80 MHz FT-NMR, Mass spectra on Jeol Gas-chromatography and Mass Spectrometer DMX 300, IR as KBr-Pellet on Shimazu IR-440 and Melting point on Wagner & Münz. Co., Capillary Type.

R,R'-TPSCp(R = R' = CH_3, R = CH_3/R' = Cl, R = Ph/R' = Cl and R = R' = Cl). These compound were prepared according to the procedure being improved by us.[19] Tricarbonyl (η^4-1-phenyl-1-chloro-TPSCp) iron (IIa).

A mixture of 0.496g (1.0 mmole) of 1-phenyl-1-chloro-TPSCp and 0.27 m*l* (0.39g, 2.0 mmole) of $Fe(CO)_5$ in 50 m*l* of toluene was refluxed with stirring for 20 hours. The greenish-yellow solution was changed to red, dark-green and finally black. After the solvent and excess $Fe(CO)_5$ were distilled off in vacuum following by washing with 50 m*l* of n-pentane, 60 m*l* of *n*-hexane were given to the residue. When the dark suspension was stirred for 10 minutes and allowed to stand for 20 hours at room temperature, the orange solution together with black precipitate was obtained. After separation of the precipitate by decantation, the solution was condensed to a half and kept at room temperature for 40 hours, then orange solid was obtained. Recrystallization from *n*-hexane two or three times gave 0.42g of orange crystal (IIa, 70%).

Anal. Calcd. for $C_{37}H_{25}O_3ClSiFe$: C, 69.77; H, 3.96%. Found: C, 70.00; H, 3.97%.

Tricarbonyl(η^4-1,1-dichloro-TPSCp) iron(IIb), Tricarbonyl(η^4-1,1-dimethyl-TPSCp) iron(IIc) and Tricarbonyl(η^4-1-methyl-1-chloro-TPSCp) iron(IId + IId') were prepared with 1.0 mmole of the corresponding RR'-TPSCp with 2.0 mmoles of $Fe(CO)_5$ principally in identical manner as described in the preparation of (IIa).

IIb: yellow crystal (75%), mp 118-120 °C; Anal. Calcd for $C_{31}H_{20}O_3Cl_2$ SiFe; C, 62.54; H, 3.39%. Found: C, 62.51; H, 3.91%. IIc: orange crystal (70%), mp 144-145 °C; Anal. Calcd for $C_{33}H_{26}O_3SiFe$: C, 71.48; H, 4.73%. Found: C, 71.25; H, 5.02%. IId + IId': orange crystal (75%), mp 165-167 °C; Anal. Calcd for $C_{32}H_{23}O_3ClSiFe$: C, 66.85; H, 4.03%. Found: C, 65.07; H, 4.32%.

Acknowledgement. Financial support of this work by the basic science research institute program of Ministry of Education, Korea is greatefully acknowledged. The authours wish to express their gratitude to the National Science Foundation (CHE/8307022) for providing funds towards upgrading X-ray diffractometer at the North Carolina State University.

Supplementary Material Available. Table of anisotropic thermal parameters (1 page); table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

References

1. W. Fink, *Helv. Chim. Acta,* **57,** 167 (1974).
2. Edward W. Abel, T. Blackmore, Robert J. Whitley, *J. Chem. Soc.,* Dalton, 2484 (1976).
3. Robert J. McMahon, *Coordination Chem. Rev.,* **47,** 1 (1982).
4. F. Carre, E. Colomer, J. Y. Corey, R. J. Corriiu, C. Guerin, B. J. L. Henner, B. Kolani and W. W. Choy, W. C. Man, *Organometallics,* **5,** 910 (1986).
5. R. J. P. Corriu, C. Guerrin, B. J. L. Henner, W. W. Choy and W. C. Man, *J. Organomet. Chem.,* **320,** C1 (1987).
6. J. Dubac, A. Laporterie and H. Iloughmane, *J. Organomet. Chem.,* **293,** 295 (1985).
7. G. T. Burns, E. Colomer, R. J. P. Corriu and M. Lheureux, *Organometallics,* **6,** 1398 (1987).
8. L. C. Ananias de Carvakho, M. Daartiguenave, F. Dahan and Dartiguenave, *Organometallics,* **5,** 2205 (1986).
9. J. C. Burnet, B. Resibois and J. Bertrand, *Bull. Soc. Chim. Fr.,* 3424 (1969).
10. H. Sakuri, and J. Hayashi, *J. Organomet. Chem.,* **63,** C10 (1973).
11. H. Sakurai, J. Hayashi and T. Kobayashi, *J. Organomet.*

Chem., **110**, 303 (1976).
12. P. Jutzi and A. Karl, *J. Organomet. Chem.*, **128**, 57 (1977).
13. K. W. Muir and R. Walker, *J. Chem. Soc., Chem. Commun.*, 698 (1975).
14. Laszlo, Parknyi, *J. Organomet. Chem.*, **216**, 9 (1981)
15. International Tables for X-ray Crystallography, Vol. IV. Kynoch Press, Birmingham, England, 1974, pp. 71-102 and 148-151.
16. SHELXTL, 1983, Nicolet X-ray Instruments, Madison, WI 53711.
17. O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963).
18. A. J. Bondi, *Phys. Chem.*, **68**, 441 (1964).
19. W. C. Joo, Y. C. Park, S. K. Kang, J. H. Hong and Y. K. Kong, *Bull. Kor. Chem. Soc.*, **8**, 270 (1987).

Gas Chromatography / Mass Spectrometry and Gas Chromatography / Tandem Mass Spectrometry of some *s*-Triazine Pesticides

Yoo Joong Kim and Myung Soo Kim*

Department of Chemistry, Seoul National University, Seoul 151-742. *Received January 30, 1988*

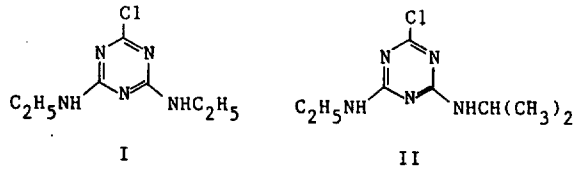
Some *s*-triazine herbicides, namely simazine, atrazine, and propazine present as trace components in a complex mixture were analyzed by GC/MS and GC/MS/MS methods. Even though monitoring the molecular ions was the best in terms of sensitivity, adequate analysis could not be done when interfering species were present. When doubly charged ions which appeared at characteristic *m/z* values were monitored, chromatograms were rather free from interference. More importantly, selected reaction monitoring was found to provide a selective means of detection with general applicability.

Introduction

Mass spectrometry is one of the most useful instrumental methods for the identification and structure determination of various compounds.[1,2] When coupled with gas or liquid chromatography, the resulting instrumental methods commonly called GC/MS[3,4] and LC/MS[5], respectively, become powerful techniques for the qualitative and quantitative analyses of trace components in complex mixtures. For the screening and quantitation of a trace component, one or several different ions generated upon ionization of the compound are selectively recorded.[6] This technique is usually called selected ion monitoring (SIM) or selected ion recording (SIR). Since the mass spectrometer spends most of its time to detect only a few different ions, effective time constant for each channel in SIM becomes enormously larger than for scanning-type GC/MS, enabling parts per billion (ppb) analysis.[7] GC/MS analysis of trace components in a very complex mixture is often hampered by the presence of interfering components. Hence, a thorough and time-consuming pretreatment of a sample is usually needed in such a case.

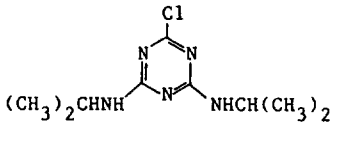
Tandem mass spectrometry or mass spectrometry/mass spectrometry (MS/MS)[8-10] has been proposed as an alternative to GC/MS for mixture analysis.[11-13] In this technique a mixture is introduced to the ion source of a mass spectrometer. A characteristic ion produced from the analyte of interest is separated by the first stage mass spectrometer. Dissociation of this selected ion as monitored by the second stage mass spectrometer provides a means to identify and quantitate the analyte of interest. This technique is often called selected reaction monitoring (SRM) to distinguish it from selected ion monitoring (SIM) described above, Since the separation and detection are all done in a mass spectrometer, analysis can be done faster than in GC/MS. MS/MS can also be utilized for detection of components separated by GC.[12,14] Excellent selectivity of this technique often enables the analysis of trace components which are difficult to analyze with GC/MS. Alternatively, extensive pretreatment of a sample can often be avoided with GC/MS/MS.

s-Triazines are widely used as pre-emergence selective herbicides, simazine (2-chloro-4,6-bis(ethylamino)-*s*-triazine, I), atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine, II), propazine (2-chloro-4,6-bis(isopropylamino-*s*-triazine, III) being the most important. Recently, we have carried out an investigation on the mass spectral fragmentations of these compounds and 2-amino-4-chloro-6-ethylamino-*s*-triazine (IV) utilizing MS/MS and high resolution mass spectrometry.[15] As an extension of this work, GC/MS and GC/MS/MS analysis of *s*-triazine herbicides have been performed and reported here.

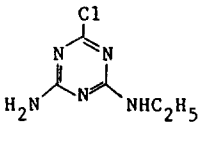


I

II



III



IV

Experimental

The instrument used in this work was a double focusing mass spectrometer with reversed geometry (VG ZAB-E) coupled to a gas chromatograph (HP model 5890). A schematic diagram for the instrument is shown in Figure 1. A fus-