Table II. Functions of the Augmented STO-3G+ and 3-21+G Basis Sets of Silicon and MO Expansion Coefficients of the Highest Doubly Occupied MO (B$_{2g}$) and the SOMO (A$_{2u}$) in Si$_4$H$_8$·⁻

basis functions (exponents)	STO-3G+		3-21+G		
	3p		3pI	3pO	
	1.479		1.079		
	0.412	p	0.302	0.093	p
	0.161	0.033			0.033
B$_{2g}$	0.386	0.125	0.248	0.212	−0.006
A$_{2u}$	0.174	−0.336	0.091	0.565	−0.169

coupling constants has been determined for the former radical by EPR (the ^{29}Si hyperfine coupling constant is not known),[9,11] accurate data for the latter radical have been measured by ENDOR spectroscopy.[12] Moreover, relative signs of the hyperfine couplings were determined by general TRIPLE resonance.[12] Since it seems to be reasonable to assume a positive sign for the large methyl ^{13}C coupling constant, this choice of signs has been adopted in Table I.

A comparison with the calculated data reveals an unexpected good agreement. The important general features are reproduced correctly, namely, a large (positive) ^{13}C coupling constant, a fairly small (positive) ^{29}Si coupling constant, and a small proton coupling constant. Perhaps more importantly, the calculation predicts that the electron spin density is located mainly in diffuse orbitals, particularly in Rydberg-type Si pπ orbitals which contribute almost 100% to the total Si value. This result is in excellent agreement with the conclusions drawn from ENDOR relaxation studies for the various nuclei, demonstrating that anisotropic hyperfine interactions are negligibly small [Tr(A′$_{Si}^2$) ≈ 30–100 MHz^2], implying essentially isotropic electron spin distributions around the ^{29}Si and ^{13}C nuclei.

The diffuse character of the SOMO is not an artefact of the limited valence basis (STO-3G) where electron density could be forced into the diffuse orbitals. An improved basis set (3-21G) for the unsubstituted species Si$_4$H$_8$·⁻ also rules out a valencelike SOMO. Additional diffuse functions on silicon, labeled as s and p, exhibit only small contributions to valence orbitals such as the highest doubly occupied MO (B$_{2g}$). In contrast, the expansion coefficients of the diffuse functions are increased by a factor of 30 in the SOMO (A$_{2u}$) of Si$_4$H$_8$·⁻. According to Table II the MO expansion coefficients of the inner (3pI) and the outer (3pO) basis functions also indicate unequivocally an increased size of the SOMO compared with valencelike orbitals. The sizes of the inner and the outer "valence" basis functions, i.e. the orbital radii, differ by a factor of 2. The importance of Rydberg orbitals especially for the photochemistry of polysilanes is extensively described in the literature.[15]

Thus, the experiment as well as the calculations would rule out a SOMO constructed from valence-type Si 3pπ atomic orbitals. The present calculations provide a satisfactory picture of the electron spin density distribution in cyclopolysilane radical anions, rendering obsolete any previous speculations invoking the participation of hybrid orbitals or of Si 3d orbitals.

(15) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1975; Vols. 1–3. Bock, H.; Wittel, K.; Veith, M.; Wiberg, N. *J. Am. Chem. Soc.* 1976, *98*, 109. Halevi, E. A.; Winkelhofer, G.; Meisl, M.; Janoschek, R. *J. Organomet. Chem.* 1985, *294*, 151. Experimental and calculated electronic transitions of Si$_4$Me$_8$ are reported in ref 5.

Migration of the Phosphorus Ligand from Iron to the Cyclopentadienyl Ring in Complexes of the Type (η5-C5H5)(CO)LFe{P(O)YZ}

**Hiroshi Nakazawa,* Makoto Sone, and Katsuhiko Miyoshi***

Department of Chemistry, Faculty of Science
Hiroshima University, Hiroshima 730, Japan

Summary: Reaction of (η5-C5H5)(CO)LFe{P(O)YZ} (L = CO, Y = Z = OEt; L = CO, Y = OMe, Z = NEt2; L = P(OMe)Ph2, Y = Z = Ph) with lithium diisopropylamide (LDA) results in a migration of the P(O)YZ group from iron to the cyclopentadienyl ring. The resulting (η5-C5H4{P-(O)YZ})(CO)LFe⁻ anion reacts with MeI to give (η5-C5H4-{P(O)YZ})(CO)LFeMe.

Transition-metal complexes containing a η5-cyclopentadienyl group (Cp) and three monodentate ligands, which are referred to as piano-stool complexes because of their molecular shape, are well-known. Recently reactions

(1)
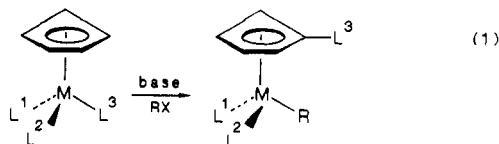
of cyclopentadienyl complexes have been reported in which one of the monodentate ligands on the transition metal undergoes base-induced migration to the Cp ring: silyl from iron[1] and rhenium,[2] acyl from iron[3] and rhenium,[4] alkoxycarbonyl from iron,[3c] formyl from rhenium,[4b] hydride from rhenium,[5] and germyl from molybdenum and tungsten.[6] Some related reactions also have been reported.[7] However, migration of a phosphorus substituent on a transition metal to a Cp bonded to the same metal atom has not been reported thus far. We report here the first example of such phosphorus substituent migration from a transition metal to the Cp ring (eq 2).

In a typical reaction, 298 mg (0.95 mmol) of (η5-C5H5)(CO)2Fe{P(O)(OEt)2} in 10 mL of THF was treated with 2 equiv of freshly prepared lithium diisopropylamide (LDA) in THF at −78 °C. The initially yellow solution immediately became dark brown. After the mixture had been stirred for 10 min at −78 °C, 118 μL (269 mg, 1.90 mmol) of MeI was added, and the mixture was allowed to warm gradually to room temperature. The solvent was

(1) (a) Berryhill, S. R.; Sharenow, B. *J. Organomet. Chem.* 1981, *221*, 143. (b) Thum, G.; Ries, W.; Greissinger, D.; Malisch, W. *J. Organomet. Chem.* 1983, *252*, C67. (c) Berryhill, S. R.; Clevenger, G. L.; Burdurlu, F. Y. *Organometallics* 1985, *4*, 1509. (d) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* 1986, *5*, 1056.
(2) (a) Pasman, P.; Snel, J. J. M. *J. Organomet. Chem.* 1986, *301*, 329. (b) Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* 1988, *7*, 2158.
(3) (a) Liebeskind, L. S.; Welker, M. E. *Organometallics* 1983, *2*, 194. (b) Brinkman, K.; Helquist, P. *Tetrahedron Lett.* 1985, *26*, 2845. (c) Abbott, S.; Baird, G. J.; Davies, S. G.; Dordor-Hedgecock, I. M.; Maberly, T. R.; Walker, J. C.; Warner, P. *J. Organomet. Chem.* 1985, *289*, C13.
(4) (a) Heah, P. C.; Gladysz, J. A. *J. Am. Chem. Soc.* 1984, *106*, 7636. (b) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* 1986, *108*, 1185.
(5) (a) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* 1985, 283. (b) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* 1988, *110*, 6110.
(6) Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* 1977, *16*, 1061.
(7) (a) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* 1974, 516. (b) Werner, H.; Hofmann, W. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 464. (c) Hubbard, J. L.; McVicar, W. K. *J. Am. Chem. Soc.* 1986, *108*, 6422. (d) Pannell, K. H.; Vincenti, S. P.; Scott III, R. C. *Organometallics* 1987, *6*, 1593.

(2)

1a	L = CO, Y = Z = OEt	**1b**
2a	L = CO, Y = OMe, Z = NEt₂	**2b**
3a	L = P(OMe)Ph₂, Y = Z = Ph	**3b**
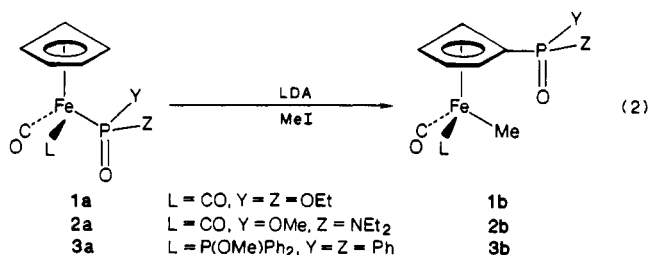
removed from the resulting orange solution under reduced pressure, and the residue was loaded on a silica gel column and eluted with dichloromethane/acetone (10/1). A yellow band was collected, and the solvent was removed to give 310 mg (0.94 mmol) of $(\eta^5\text{-}C_5H_4\{P(O)(OEt)_2\})(CO)_2FeMe$ (**1b**) (99% yield).[8] An identical result was obtained on using *n*-BuLi in place of LDA.

Spectroscopic data for the starting complexes[9] and the products are summarized in Table I. For the following reasons, we conclude that migration products of a phosphorus ligand to a cyclopentadienyl ligand were obtained. (i) The $^{31}P\{^1H\}$ NMR spectra exhibit a singlet for **1a** and **2a** and a doublet for **3a** at about 100 ppm, whereas a singlet in the spectra of the products at about 20 ppm, which is very close to that for O=PPh₃ (23.0 ppm) and O=P(OEt)₂Ph (16.9 ppm).[11] (ii) In the $^{31}P\{^1H\}$ NMR spectrum, a coupling between two phosphorus atoms is observed for **3a**, but it disappears for **3b**. (iii) The ^1H NMR spectra show a multiplet due to the Cp ring at about 4.6–5.2 ppm for the products but a singlet for the Cp ring protons of the starting complexes. (iv) In the ^1H NMR spectra, a singlet assigned to the methyl protons was observed for **1b** and **2b** and a doublet was observed in the spectrum of **3b**, indicating that the methyl group is bonded to the iron atom.

(3)
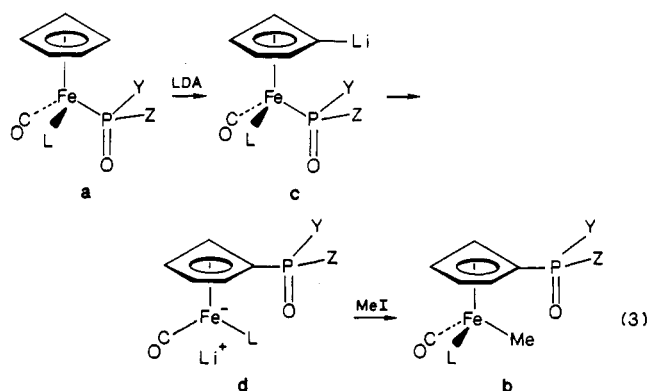
The migration reaction may proceed as shown in eq 3. That is, a proton is initially abstracted from the cyclopentadienyl ligand of **a** to give $(\eta^5\text{-}C_5H_4Li)(CO)LFe\{P(O)YZ\}$ (**c**), followed by migration of the P(O)YZ group from iron to the Cp ring to afford $(\eta^5\text{-}C_5H_4\{P(O)YZ\})$-

---

Table I. Spectroscopic Data

complex	IR, ν_C, cm⁻¹	^1H NMR δ (in acetone-d_6)	$^{31}P\{^1H\}$ NMR δ (in CH₂Cl₂)
1a	2035, 1983	1.22 (t, J = 6.8 Hz, 6 H), 3.97 (m, 4 H), 5.20 (s, 5 H)	89.9 (s)ᵃ
2a	2028, 1975	1.11 (t, J = 7.4 Hz, 6 H), 3.35 (d, J = 11.1 Hz, 3 H), 3.10 (m, 4 H), 5.07 (s, 5 H)	103.3 (s)
3a	1938	2.98 (d, J = 11.4 Hz), 4.41 (s, 5 H), 6.98–7.78 (m, 20 H)	91.6 (d, J = 73.5 Hz), 170.5 (d, J = 73.5 Hz)
1b	2016, 1959	0.34 (s, 3 H),ᵇ 1.35 (t, J = 7.0 Hz, 6 H), 4.08 (d, quar, J = 7.0, 14.0 Hz, 4 H), 4.83 (m, 2 H), 5.10 (m, 2 H)	21.7 (s)
2b	2012, 1958	0.28 (s, 3 H), 1.07 (t, J = 7.0 Hz, 6 H), 3.11 (m, 4 H), 3.58 (d, J = 11.0 Hz, 3 H), 5.01 (m, 2 H), 5.17 (m, 2 H)	18.9 (s)
3b	1931	-0.37 (d, J = 5.0 Hz, 3 H), 3.50 (d, J = 11.6 Hz, 3 H), 4.10 (m, 1 H), 4.37 (m, 1 H), 4.62 (m, 1 H), 4.83 (m, 1 H), 7.23–7.69 (m, 20 H)	20.5 (s), 181.7 (s)

ᵃ In acetone. ᵇ In CDCl₃.

$(CO)LFe^-Li^+$ (**d**). This then reacts with MeI to give the final product **b**. The reaction mixture of **1a** and LDA showed IR (ν_{CO}) absorptions at 1889 and 1822 cm⁻¹ in THF and a $^{31}P\{^1H\}$ NMR resonance at 27.8 ppm in THF, indicating the formation of $(\eta^5\text{-}C_5H_4\{P(O)(OEt)_2\})$-$(CO)_2Fe^-Li^+$ (**1d**), which is stable in THF even at room temperature. Similar reaction sequences were proposed for silyl,[1a,c,2] acyl,[3c,4] alkoxycarbonyl,[3c] hydride,[5] and germyl[6] migration from a transition metal to the Cp ring.

The Fe–P bond in **1a** is not cleaved by Lewis acids[10] but is readily activated by the deprotonated cyclopentadienyl ring formed in the reaction with a strong base. Complex **3a** has two types of Fe–P bonds: a covalent bond in Fe–P(O)Ph₂ and a dative bond in Fe–P(OMe)Ph₂. In the reaction with a Lewis base, the former covalent bond is cleaved selectively with the dative bond remaining intact; i.e., only the P(O)Ph₂ group can migrate to the Cp ring.

The P(O)YZ group migration from an iron atom to the Cp ring seems to take place irrespective of the substituents on the phosphorus, Y and Z. Gladysz et al. reported that a phosphido ligand on a transition metal shows no tendency to migrate to a Cp ring.[5b,12] Therefore, it can be said that a pentavalent tetracoordinated phosphorus atom

(8) Yellow oil. Anal. Found (Calcd): C, 43.61 (43.93); H, 5.68 (5.22). Yield and analytical data on the other new complexes. Complex **2b**: yellow oil (66.4% yield). Anal. Found (Calcd): C, 45.88 (45.77); H, 5.99 (5.91); N, 3.93 (4.11). Complex **3b**: yellow powder (83.0% yield). Anal. Found (Calcd): C, 66.52 (66.22); H, 5.17 (5.21).

(9) Preparative methods for **1a**: ref 10. Haines, R. J.; DuPreez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28*, 405. Haines, R. J.; DuPreez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1970**, *24*, C26. For **2a**: Nakazawa, H.; Kadoi, Y.; Miyoshi, K., manuscript in preparation. For **3a**: Nakazawa, H.; Yamaguchi, M.; Miyoshi, K., manuscript in preparation.

(10) Nakazawa, H.; Morimasa, K.; Kushi, Y.; Yoneda, H. *Organometallics* **1988**, *7*, 458.

(11) Moedritzer, K.; Maier, L.; Groenaeghe, L. C. D. *J. Chem. Eng. Data* **1962**, *7*, 307.

(12) Zwick, B. D.; Arif, A. M.; Patton, A. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 910.

directly bonded to a transition metal (M–P(E)YZ) can migrate to a Cp ring, whereas a trivalent tricoordinated phosphorus on a transition metal (M–PYZ) cannot migrate, though both of the M–P(E)YZ and M–PYZ bonds are formally covalent in nature. Further studies of the phosphorus migration process are in progress.

Group V Metallacyclopropenes in Synthesis. An Efficient Route to Polyfunctional Ring Systems via the Cocyclization of Diynes with Substituted Monoacetylenes[1]

Andrew C. Williams, Pamela Sheffels,[†] Derek Sheehan,[‡] and Tom Livinghouse*,[2]

Department of Chemistry, Montana State University Bozeman, Montana 59717

Received January 11, 1989

Summary: A variety of monosubstituted alkynes have been shown to undergo facile trimerization to the corresponding arenes in the presence of the CpNbCl₄/Mg catalyst system. A novel benzocycle annulation procedure (e.g., 1 → 3) is described that relies on the use of the above low-valent organoniobium species.

Zirconocene–alkyne complexes have recently emerged as an important new class of synthetic intermediates.[3–5] Despite the intense interest which has been shown in the alkyne complexes of group IV metals, relatively few synthetic applications of group V–alkyne complexes have been recorded.[6,7] In this communication we wish to report the first examples of benzocycle annulation (e.g., 1 → 3) via
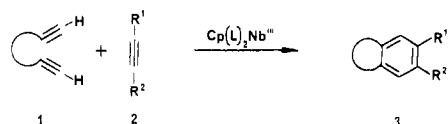
the cocyclization of diynes and monoacetylenes on low-valent group V metal centers. Curtis and Real have recently described the direct synthesis of several thermally stable cyclopentadienylniobium(III)–alkyne complexes from *diarylacetylenes*.[7a] The possibility that related group V metallacyclopropenes might serve as versatile synthetic intermediates prompted us to investigate the preparation

---

[†] Montana State University Undergraduate Dissertation Fellow, 1987–1989.

[‡] Montana State University Summer Undergraduate Fellow, 1988.

(1) Part 1 in a series on the synthetic applications of group V metallacyclopropenes.

(2) Fellow of the Alfred P. Sloan Foundation, 1989–1991.

(3) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137.

(4) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(5) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahasi, T. *Tetrahedron Lett.* **1987**, *28*, 917.

(6) For recent publications involving the synthetic applications of low-valent niobium–imine complexes see: (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551. (b) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 3152.

(7) (a) Curtis, M. D.; Real, J. *Organometallics* **1985**, *4*, 940. (b) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668.

Table I. Catalytic Trimerization of Alkynes by CpNbCl₄/Mg
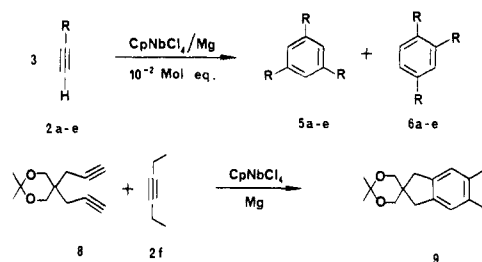
RC≡CH	yield 5 + 6, %	ratio 5/6
2a: R = Ph	90	7
2b: R = n-C₄H₉	91	1.22
2c: R = (CH₂)₃OSi-t-BuMe₂	95	1.17
2d: R = (CH₂)₂OCO-i-Bu	83	1.16
2e: R = SiMe₃	0	...

and reactivity of these species.

The reactive metallacyclopropenes utilized in this study were generated by the reduction of CpNbCl₄[8] with Mg⁰ (100 mesh) under argon in the presence of the appropriate alkyne in THF at 0 °C. Complexation of phenylethyne (2a) in the above manner gave a solution of the corresponding metallacycle 4a that underwent slow decomposition at 25 °C with concomitant formation of a mixture of the isomeric triphenylbenzenes 5a and 6a (5a/6a = 7) that could be isolated in 83% yield. Evidence for the intermediacy of 4a was provided by its interception with PhNCO and subsequent hydrolysis to furnish *N*-phenylcinnamide (7) in 55% yield.[9,10]   The analogous
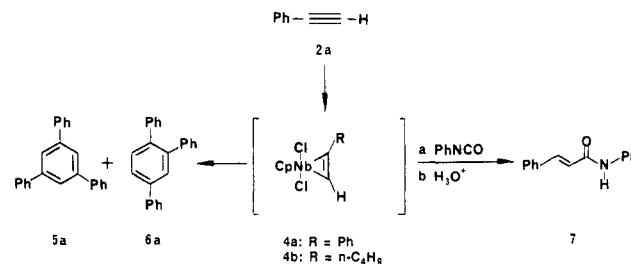
CpNbCl₂-1-hexyne complex 4b was found to be consid-

---

(8) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc. Dalton Trans.* **1980**, *7*, 1156.

(9) The scope and limitations of trapping reactions involving the functionalization of group V metallacyclopropenes with carbon-based electrophiles is under current investigation.

(10) A representative experimental procedure is as follows: An oven-dried 12-cm Pyrex test tube equipped with a rubber septum, magnetic stirring bar, and argon inlet was charged with 100 mesh magnesium powder (24 mg, 1 mg-atom) and cyclopentadienylniobium tetrachloride (300 mg, 1 mmol). The tube was purged with argon and cooled to 0 °C whereupon phenylethyne (102 mg, 1 mmol) and dry THF (4 mL) were added by syringe. The reaction mixture was then stirred at 0 °C for 1 h at which time all of the magnesium had dissolved and a homogeneous dark red solution of the metallocyclopropene 4a had been formed. A solution of phenyl isocyanate (119 mg, 1 mmol) in dry THF (1 mL) was then added, and the resultant solution was stirred at 50 °C for 12 h. The reaction mixture was cooled to 25 °C, and saturated aqueous NH₄Cl (1 mL) was added. After being stirred for 30 min, the mixture was diluted with ether (15 mL) and the organic layer was separated and then dried with brine (10 mL). The mixture was filtered through Florisil, and the solvents were removed in vacuo. The residue was then subjected to chromatography (20% ethyl acetate–hexane for elution) to afford 123 mg (55%) of *N*-phenylcinnamide (7) as a white solid: mp 154–157 °C (authentic 156–158 °C); ¹H NMR (300 MHz, CDCl₃) δ 8.16 (br s, 1 H, N*H*), 7.73 (d, 1 H, *J* = 15.6 Hz PhC*H*=CHCONHPh), 7.60 (d, 2 H, *J* = 7.8 Hz, ArH), 7.36–7.24 (m, 5 H, ArH), 7.10 (d, 1 H, *J* = 7.4 Hz, ArH), 6.65 (d, 1 H, *J* = 15.6 Hz, PhCH=C*H*CONHPh); IR (CHCl₃) 3684, 3620, 3429, 3319, 3027, 2977, 2895, 1679, 1632, 1597, 1578, 1439, 1380, 1336, 1285 cm⁻¹. Efforts to isolate the metallocyclopropene 4a by removal of the THF at 20 °C resulted in the rapid decomplexation–cyclotrimerization of the phenylethyne to give the triphenylbenzenes 5a and 6a (5a/6a = 7).