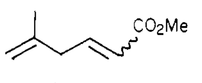
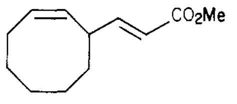


9a (*trans*)
9b (*cis*)



10

of **1b** *and* 1,4- and 1,3-cod (Figure 1).[24] Isomerization of **1b** to the thermodynamically less favored **2a,b** is not observed under the reaction conditions used. Noteworthy is the fact that the codimerization of a 1:1 (w/w) mixture of 1,5-cod and methyl acrylate gives rise to **10**, isomers of cod, and only trace amounts of **1b**.[25] The isomerization of 1,5-cod may proceed through reaction paths involving successive addition and elimination of **8** to one double bond of 1,5- and 1,4-cod. However, the mechanism of the palladium-catalyzed isomerization of olefins is still unclear since allylhydridopalladium[26] or cationic allylpalladium[27] species may also act as intermediates. Very few cationic hydridopalladium complexes have been isolated and characterized. They are stabilized by combinations of basic phosphines (e.g., $P(i\text{-}Pr)_3$) and chelating diphosphines (e.g., $Ph_2PCH_2CH_2PPh_2$).[28] Addition of the latter ligand during the course of the catalytic acrylate dimerization stops catalysis, but workup of the reaction mixture cannot afford a complex like **8** where $L_n = Ph_2PCH_2CH_2PPh_2$. Further studies directed toward the mechanism of this reaction that may be different from those of the reactions reported in the literature[7,10,11,27] are in progress.

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[24] **5a** (0.2 mM) and **5b** (0.2 mM) are dissolved in 1,2-dichloroethane (2 mL). *n*-Octane (internal standard) and methyl acrylate (2 mL) are added. Aliquots of this solution are placed in Carius tubes and heated to 60 ± 0.1 °C. Every 30 min one tube is cooled down, 2 equiv of PBu_3 are added in order to quench the catalyst, and the mixture is analyzed by GC. The results are reported in Figure 1.

[25] Methyl acrylate (11 mM) and cyclo-1,5-octadiene (8.6 mM) are added to a mixture of **5a** (0.2 mM) and **5b** (0.2 mM). The solution is heated at 80 °C for 31 h. Two fractions are collected from distillation: fraction 1 comprises 1,5-, 1,4-, and 1,3-cyclooctadienes (0.5 g, respectively 58, 7, and 35%); fraction 2 (0.78 g) corresponds to **10** [m/z 194; ^1H NMR ($CDCl_3$) δ 1.60 (8 H, br m), 2.15 (2 H, br m), 3.33 (1 H, m), 3.72 (3 H, s), 5.33 (1 H, dd, $J = 11, 8$ Hz), 5.72 (1 H, dt, $J = 11, 7$ Hz), 5.82 (1 H, d, $J = 16$ Hz), 7.00 (1 H, dd, $J = 16, 7$ Hz).

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A Twisted P–C Double Bond: Synthesis and Structure of a [(Methylene)phosphine]iron Tetracarbonyl Complex

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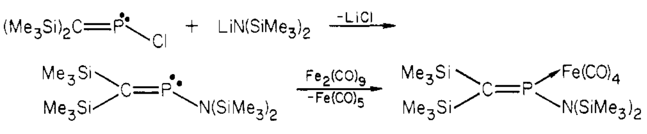
Summary: The reaction of $(Me_3Si)_2C{=}PCl$ with $LiN(SiMe_3)_2$ affords the tetrasilylated amino(methylene)phosphine **1** which reacts smoothly with $Fe_2(CO)_9$ yielding the η^1 complex $(Me_3Si)_2C{=}P[Fe(CO)_4]N(SiMe_3)_2$ (**2**). X-ray crystallographic analysis of **2** reveals an unusual coordination of the phosphine ligand in an equatorial position as well as a short (1.657 Å), but severely twisted (30.3°), P–C double bond.

The high level of current interest in unusually-hybridized phosphorus compounds has been stimulated, in part, by their potential as new types of ligands in organometallic chemistry. Among the (methylene)phosphines, $RP{=}CR_2$, for example, both σ (η^1) and π (η^2) complexes of the $-P{=}C<$ moiety are now known.[1,2] With two exceptions,[2] however, all of the (methylene)phosphine complexes have contained the same ligand, $MesP{=}CPh_2$, first reported by Bickelhaupt.[3] In order to extend these studies to the use of other ligands, we have begun an investigation of the coordination chemistry of our recently prepared amino(methylene)phosphines.[4] We report here the synthesis of the new (methylene)phosphine $(Me_3Si)_2NP{=}C(SiMe_3)_2$ and its iron tetracarbonyl complex that is found to have an unusually twisted phosphorus–carbon double bond.

Treatment of lithium bis(trimethylsilyl)amide (68 mmol) in Et_2O (250 mL) at 0 °C with chloro[bis(trimethylsilyl)methylene]phosphine[5] (68 mmol) afforded the tetrasilylated amino(methylene)phosphine **1** as a distillable yellow liquid [bp 61–63 °C (0.01 mm)] in 59% yield. A purified sample of **1** (ca. 5 mmol) was then allowed to react with 1 equiv of $Fe_2(CO)_9$ in pentane (25 mL) at room temperature with stirring for 18 h. Quantitative formation of the (phosphine)iron tetracarbonyl complex was shown by ^{31}P NMR spectroscopy, and **2** was isolated as dark orange crystals (mp 153–155 °C) by slow evaporation of the solvent. In addition to NMR spectroscopy (Table I), compounds **1** and **2** were characterized by satisfactory elemental analysis.[6]



Several aspects of the NMR spectra of **1** and **2** are structurally diagnostic. First, the low-field ^{31}P and ^{13}C chemical shifts in both compounds are indicative of sp^2 hybridization and strongly suggest η^1-coordination to $Fe(CO)_4$ via the phosphorus lone pair. Second, nonequivalence of the C-bonded Me_3Si groups due to hindered rotation about the P=C double bond is seen in the ^1H, ^{13}C, and ^{29}Si NMR spectra. Third, there is a substantial coupling ($^2J_{PC} = 18.6$ Hz) between phosphorus and the carbonyl carbons of the $Fe(CO)_4$ group, indicating that **2** does not undergo the rapid intermolecular exchange of CO as observed for the analogous complexes of the isoelectronic aminophosphenium ions.[7]

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[1] See, for example: (a) Klebach, Th. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; van Helrk, A. *J. Organomet. Chem.* **1981**, *210*, 211. (b) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. W. *Polyhedron* **1982**, *1*, 89. (c) Al-Resayes, S.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 930.

[2] (a) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3737. (b) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mischler, A. *Ibid.* **1984**, *106*, 826.

[3] Klebach, Th. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4886.

[4] (a) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679. (b) Thoma, R. J. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984.

[5] Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159.

[6] Compound **1**: Anal. Calcd for $C_{13}H_{36}NPSi_4$: C, 44.64; H, 10.37. Found: C, 44.37; H, 10.58. Compound **2**: Anal. Calcd for $C_{17}H_{36}FeNO_4PSi_4$: C, 39.45; H, 7.01. Found: C, 39.17; H, 7.00.

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Table I. NMR Spectroscopic Data[a]

	1	2
$\delta(^{31}P)$	383.1	311.4
$\delta(^{1}H)$ (J_{PH})		
$N(SiMe_3)_2$	0.16 (0.5)	0.32
$C(SiMe_3)_2$[b]	0.12 (2.1)	0.15
	0.15	0.25
$\delta(^{13}C)$ (J_{PC})		
$N(SiMe_3)_2$	3.90 (1.9)	2.99 (2.0)
$C(SiMe_3)_2$[b]	3.05 (7.8)	−0.10 (14.6)
	3.64	2.26 (4.9)
P=C	187.5 (96.7)	162.1 (12.6)
CO		213.6 (18.6)
$\delta(^{29}Si)$ (J_{PSi})		
$N(SiMe_3)_2$	1.42	7.90 (5.0)
$C(SiMe_3)_2$[b]	−4.60 (39.3)	−5.30 (15.8)
	−9.84 (10.7)	−8.00 (19.4)

[a] Chemical shifts downfield from Me_4Si for ^1H, ^{13}C, and ^{29}Si and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C, ^{31}P, and ^{29}Si, $CDCl_3$.
[b] Nonequivalent Me_3Si groups due to hindered P=C bond rotation.

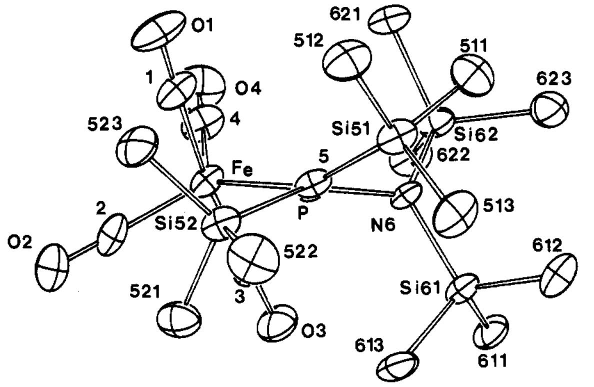

Figure 1. ORTEP drawing of 2 viewed down the C(5)=P bond. Thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (deg): P-Fe = 2.208 (2); Fe-C(1) = 1.795 (4); Fe-C(2) = 1.794 (2); Fe-C(3) = 1.787 (4); Fe-C(4) = 1.768 (7); P=C = 1.657 (5); P-N = 1.681 (4); N-Si = 1.788 (4), 1.790 (4); C(5)-Si = 1.884 (7), 1.890 (6); Fe-P-C(5) = 128.0 (2); Fe-P-N = 116.8 (2); N-P-C(5) = 115.2 (8); P-C(5)-Si(51) = 135.0 (7); P-C(5)-Si(52) = 118.7 (3).

The X-ray crystallographic analysis[8] of 2 (Figure 1) confirms the η^1-coordination mode of the (methylene)phosphine and reveals some unexpected features. Most significant is the severe twist about the P=C bond of 30.3 (6)°; however, the P—C bond distance of 1.657 (5) Å is significantly shorter than the 1.68–1.72 Å range reported by Appel[9] for a series of planar P=C π-systems. The distance is equivalent to the 1.647 (9) and 1.657 (4) Å values reported recently for some three-coordinate (methylene)phosphoranes.[10,11] Steric interactions between the bulky substituents are relieved by a rotation about the P=C bond. Although the P=C bond is considerably longer than a C=C bond, the present structure is indicative of the interactions that would exist in tri- and tetraisobutylethylenes.

In contrast to most simple (phosphine)iron tetracarbonyl complexes,[12,13] the ligand is coordinated at an equatorial site in a slightly distorted trigonal-bipyramidal geometry around the iron. The Fe, P, C(2), and C(4) atoms are coplanar with a maximum deviation from the plane of 0.001 Å. In the trigonal plane, the P–Fe–C angles are 124.1 (3) and 125.5 (3)° while the C–Fe–C angle is compressed to 110.4 (3)°. The two axial ligands make a C–Fe–C angle of 173.1 (4)° and are bent toward the phosphine ligand which, to our knowledge, is unprecedented. The angles between axial and equatorial ligands range from 86.8 (2) to 94.7 (3)°. All three atoms in the N—P=C linkage have trigonal-planar geometries with the Si_2N and Si_2C planes being nearly orthogonal. The NPC plane lies between the axial and equatorial planes of the $Fe(CO)_4$ moiety, probably to further minimize steric interactions.

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Supplementary Material Available: Tables of atomic positional parameters and U_{eq} values, hydrogen atom positions and isotropic U values, anisotropic thermal parameters, interatomic distances, valence angles, and observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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(7) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* 1981, *20*, 4289.

(8) Crystal of dimensions 0.17 × 0.34 × 0.41 mm, triclinic space group $P\bar{1}$ with $a = 10.567$ (3) Å, $b = 15.129$ (7) Å, $c = 10.562$ (3) Å, $\alpha = 97.44$ (3)°, $\beta = 115.50$ (2)°, $\gamma = 106.08$ (3)°, V = 1403 (1) Å^3, $Z = 2$, μ(calcd) = 1.225 g cm^{-3}, $F(000) = 548$, and λ (Cu Kα) = 66.5 cm^{-1}. A total of 3831 independent reflections were collected by θ–2θ scan technique on Syntex $P2_1$ diffractometer; 3036 were considered observed ($I > 3\sigma(I)$) (lorentz and polarization corrections, but no absorption corrections). Anisotropic refinement (H atom positions fixed, thermal parameters isotropic) led to $R = 0.051$ and $R_w = 0.062$ where $w = 1/\sigma^2\ (F_o)$. Scattering factors and real and imaginary anomalous dispersion corrections; Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* 1968, *A24*, 321. Atomic coordinates, thermal parameters, bond lengths, and valence angles are listed in supplementary Tables 1–5. Lists of structure factors are also available.

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(10) Appel, R.; Knoch, F.; Kunze, H. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 157.

(11) Caira, M.; Neilson, R. H.; Watson, W. H.; Wisian-Neilson, P.; Xie, Z.-M. *J. Chem. Soc., Chem. Commun.*, in press.

(12) Axial substitution is very common for (phosphine)iron tetracarbonyl complexes. For example, see the following and references cited therein. Keiter, R. L.; Rheingold, A. L.; Hamerski, J. J.; Castle, C. K. *Organometallics* 1983, *2*, 1635.

(13) Equatorial substitution is quite unusual for (phosphine)iron tetracarbonyl complexes. Three examples, with confirmation by X-ray crystallography, have been reported: (a) Sheldrick, W. S.; Morton, S.; Stelzer, O. *Z. Anorg. Allg. Chem.* 1981, *475*, 232. (b) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* 1983, *105*, 2085. (c) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Ibid.* 1983, *105*, 7751.

Kinetic Deuterium Isotope Effects in the Reaction of Vaska's Compound $(Ph_3P)_2Ir(CO)Cl$ with CH_3I and $CH_3OSO_2CF_3$

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Summary: The k_H/k_{D_3} values of 0.94 and 1.13 were observed, respectively, for the reaction of $(Ph_3P)_2Ir(CO)Cl$ with CH_3I and $CH_3OSO_2CF_3$ at 35 °C in toluene, consistent with a Menschutkin-type S_N2 displacement process.

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