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.

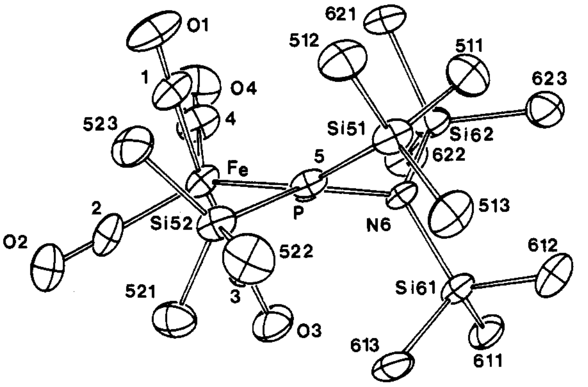

Figure 1. ORTEP drawing of **2** viewed down the C(5)=P bond. Thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (deg): P–Fe = 2.208 (2); Fe–C(1) = 1.795 (4); Fe–C(2) = 1.794 (2); Fe–C(3) = 1.787 (4); Fe–C(4) = 1.768 (7); P=C = 1.657 (5); P–N = 1.681 (4); 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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[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, α = 97.44 (3)°, β = 115.50 (2)°, γ = 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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[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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Table I. Kinetic and Isotope Effect Data for Reaction of $(Ph_3P)_2Ir(CO)Cl$ with CH_3X and CD_3X

compd	temp, °C	solv[a]	10^2k_2,[b] M^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_H/k_D
$CH_3OSO_2CF_3$	25.0 ± 0.1	T	3.11 ± 0.09 (6)[c]	11.2	−28.1	1.13 ± 0.02
	35.1 ± 0.2	T	5.95 ± 0.05 (5)			1.17 ± 0.02
$CD_3OSO_2CF_3$	25.0 ± 0.1	T	2.75 ± 0.04 (4)	10.5	−30.6	
	35.1 ± 0.2	T	5.10 ± 0.06 (3)			
CH_3I	25.0 ± 0.1	A	2.29 ± 0.08 (7)	7.30	−41.7	1.00 ± 0.02
	35.1 ± 0.2	A	3.53 ± 0.03 (3)			0.94 ± 0.02
	45.0 ± 0.2	T	5.60 ± 0.27 (3)	21.7	−6.55	1.00 ± 0.02
	55.3 ± 0.2	T	9.18 ± 0.10 (3)			0.94 ± 0.02
CD_3I	25.0 ± 0.1	A	2.28 ± 0.05 (7)	8.53	−37.6	
	35.1 ± 0.2	A	3.76 ± 0.03 (3)			
	45.0 ± 0.2	T	5.61 ± 0.03 (3)	21.8	−6.26	
	55.3 ± 0.2	T	9.81 ± 0.12 (3)			

[a] T = toluene; A = acetonitrile. [b] Second order rate constant. [c] Number of determinations.

One of the most ubiquitous organometallic reactions is oxidative addition.[1] A typical and classical example is the interaction of Vaska's complex $(Ph_3P)_2Ir(CO)Cl$ with methyl halides. Although this reaction has been extensively investigated[2] since the original studies of Chock and Halpern,[3] there are still unanswered questions on the exact mechanism of this process. Kinetic data unambigiously indicate a bimolecular pathway but do not distinguish between (a) radical (one-electron transfer), (b) S_N2, or (c) three-center ("front-side insertion") additions, although the preponderance of evidence, involving solvent effects, trapping studies, and stereochemical investigations, is most consistent with a concerted S_N2-like pathway.[1,2]

A widely employed and useful tool for mechanistic investigations is kinetic deuterium isotope effects.[4] Surprisingly, to our knowledge, this technique has not been applied to the above reaction. Hence we wish to report our investigation on the secondary kinetic deuterium isotope effects in the reaction of Vaska's compound with methyl iodide and methyl triflate and their deuterio analogues.

All reactions were carried out in carefully degassed, freshly distilled solvents, with repurified commercial reagents. Rates were measured by standard spectrophotometric techniques, by following the disappearance of Vaska's compound at 387 nm. Excellent pseudo-first-order rates were observed for 90% reaction with a concentration of 1.5×10^{-4} M in Vaska's complex and a concentration range of 7.3×10^{-3} to 8.2×10^{-3} M in either CH_3X or CD_3X. For minimization of errors, the rates of the hydrogen and deuterium compounds were measured simultaneously side by side with the identical stock solution of Vaska's compound. The data are summarized in Table I.

Perusal of the data in Table I reveals a number of interesting facts. Neither the absolute rate constants nor the isotope effects are significantly affected by solvent polarity in the reaction of methyl iodide. Reaction of the sulfonate ester is not significantly different than reaction of the halide. Since sulfonate esters generally do not react by electron-transfer processes, this observation mitigates against such a process in this reaction.

Most revealing are the deuterium isotope effect data. The small inverse and unity k_H/k_{D_3} for reaction of CH_3I are consistent with an S_N2-like transition state. It is well-known that S_N2 reactions generally have small inverse to very small positive secondary kinetic deuterium isotope effects.[4] In particular, in the extensively investigated Menschutkin reaction the k_H/k_{D_3} ranges from 0.93 to 1.11 for reaction of methyl halides with a wide variety of nucleophiles.[5] The positive isotope effect of 1.13 for reaction of the triflate ester is also consistent with such a process. The superior leaving ability[6] of the triflate ($CF_3SO_3^-/I^- = 1.5 \times 10^6$) results in a less tightly bound transition state giving rise to a larger (i.e., positive) deuterium isotope effect. Such a trend from inverse to positive kinetic isotope effects as a function of the variation of the transition-state structure has recently been observed by Ando and coworkers[7] in the reaction of benzyl arenesulfonates with a variety of nucleophiles.

In summary, the observed secondary kinetic deuterium isotope effects of 0.94 and 1.13 for the reaction of Vaska's compound with CH_3I and CH_3OTf are consistent with an S_N2-type pathway and provide further support for such a mechanism for this classical oxidative addition process.

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Registry No. $(Ph_3P)_2Ir(CO)Cl$, 14871-41-1; CH_3I, 74-88-4; CH_3OTf, 333-27-7; D_2, 7782-39-0.

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