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How To Insulate a Reactive Site from a Perfluoroalkyl Group: Photoelectron Spectroscopy, Calorimetric, and Computational Studies of Long-Range Electronic Effects in Fluorous Phosphines $P((CH_2)_m(CF_2)_7CF_3)_3$

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Abstract: This study advances strategy and design in catalysts and reagents for fluorous and supercritical CO_2 chemistry by defining the structural requirements for insulating a typical active site from a perfluoroalkyl segment. The vertical ionization potentials of the phosphines $P((CH_2)_mR_{f8})_3$ ($m = 2$ (**2**) to 5 (**5**)) are measured by photoelectron spectroscopy, and the enthalpies of protonation by calorimetry (CF_3SO_3H, $CF_3C_6H_5$). They undergo progressively more facile (energetically) ionization and protonation ($P(CH_2CH_3)_3$ > **5** > **4** ≈ $P(CH_3)_3$ > **3** > **2**), as expected from inductive effects. Equilibrations of *trans*-Rh(CO)(Cl)(L)$_2$ complexes (L = **2**, **3**) establish analogous Lewis basicities. Density functional theory is used to calculate the structures, energies, ionization potentials, and gas-phase proton affinities (PA) of the model phosphines $P((CH_2)_mCF_3)_3$ (**2′**−**9′**). The ionization potentials of **2′**−**5′** are in good agreement with those of **2**−**5**, and together with PA values and analyses of homodesmotic relationships are used to address the title question. Between 8 and 10 methylene groups are needed to effectively insulate a perfluoroalkyl segment from a phosphorus lone pair, depending upon the criterion employed. Computations also show that the first carbon of a perfluoroalkyl segment exhibits a much greater inductive effect than the second, and that ionization potentials of nonfluorinated phosphines $P((CH_2)_mCH_3)_3$ reach a limit at approximately nine carbons ($m = 8$).

Introduction

The design and synthesis of compounds that have high affinities for fluorine-rich solvents[1−3] and/or supercritical CO_2[4,5] have seen exponential growth and development over the past few years. One driving force has been the new technique of fluorous biphase chemistry or catalysis.[1−3] Fluorous compounds are intended to be separable or recoverable with fluorous solvents—such as perfluorocarbons and perfluoroethers—or fluorous stationary phases.[6] Toward this end, they are derivatized with varying numbers of fluorine-containing "ponytails" of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$ (abbreviated $(CH_2)_mR_{fn}$), with *n* typically 6, 8, or 10. These provide a "like dissolves like" driving force. Applications of fluorous compounds have ranged from recoverable reagents and transition metal catalysts[1,2] to strategic separations and liquid-phase combinatorial or parallel syntheses.[7] The "ponytails" also provide high solubilities in supercritical CO_2, although shorter R_{fn} segments are usually sufficient.[4,5]

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(1) (a) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72−75. (b) Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641−650.
(2) Review literature since 1999: (a) de Wolf, E.; van Koten, G.; Deelman, B.-J. *Chem. Soc. Rev.* **1999**, *28*, 37−41. (b) Fish, R. H. *Chem. Eur. J.* **1999**, *5*, 1677−1680. (c) Cavazzini, M.; Montanari, F.; Pozzi, G.; Quici, S. *J. Fluorine Chem.* **1999**, *94*, 183−193. (d) Diederichsen, U. *Nachr. Chem. Technol. Lab.* **1999**, *47*, 805−809. (e) Hope, E. G.; Stuart, A. M. *J. Fluorine Chem.* **1999**, *100*, 75−83. (f) Hope, E. G.; Stuart, A. M. In *Advanced Inorganic Fluorides*; Nakajima, T., Zemva, B., Tressaud, A. Eds.; Elsevier: Amsterdam, 2000; Chapter 13, pp 403−436. (g) Endres, A.; Maas, G. *Chem. Unserer Zeit* **2000**, *34*, 382−393.
(3) Survey of practical considerations and underlying physical principles: Barthel-Rosa, L. P.; Gladysz, J. A. *Coord. Chem. Rev.* **1999**, *190*−*192*, 587−605.
(4) (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475−493. (b) Wells, S. L.; DeSimone, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 518−527; *Angew. Chem.* **2001**, *113*, 534−544.
(5) Representative recent literature: (a) Kainz, S.; Koch, D.; Leitner, W. In *Stereoselective Reactions of Metal-Activated Molecules*; Werner, H., Schreier, W., Eds.; Vieweg: Wiesbaden, Germany, 1998; pp 151−156. (b) Kainz, S.; Brinkmann, A.; Leitner, W.; Pfaltz, A. *J. Am. Chem. Soc.* **1999**, *121*, 6421−6429. (c) Caroll, M. A.; Holmes, A. B. *Chem. Commun.* **1998**, 1395−1396. (d) Morita, D. K.; Pesiri, D. R.; David, S. A.; Glaze, W. H.; Tumas, W. *Chem. Commun.* **1998**, 1397−1398. (e) Shezad, N.; Oakes, R. S.; Clifford, A. A.; Rayner, C. M. *Tetrahedron Lett.* **1999**, *40*, 2221−2224. (f) Carter, C. A. G.; Baker, R. T.; Nolan, S. P.; Tumas, W. *Chem. Commun.* **2000**, 347−348. (g) Palo, D. R.; Erkey, C. *Organometallics* **2000**, *19*, 81−86, and references therein. (h) Banat Osuna, A. M.; Chen, W.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Stuart, A. M.; Xiao, J.; Xu, L. *J. Chem. Soc., Dalton Trans.* **2000**, 4052−4055. (j) Kläui, W.; Bongards, J.; Reiss, G. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3894−3895; *Angew. Chem.* **2000**, *112*, 4077−4079. (k) Osswald, T.; Schneider, S.; Wang, S.; Bannwarth, W. *Tetrahedron Lett.* **2001**, *42*, 2965−2967.
(6) Typical examples: (a) Curran, D. P.; Luo, Z. *J. Am. Chem. Soc.* **1999**, *121*, 9069−9072. (b) Zhang, Q.; Luo, Z.; Curran, D. P. *J. Org. Chem.* **2000**, *65*, 8866−8873.
(7) Curran, D. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1174−1196; *Angew. Chem.* **1998**, *110*, 1230−1255.

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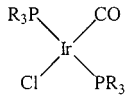
Table 1. IR Data for Fluorous Phosphine Analogues of Vaska's Complex



R	IR ν_{CO} (cm^{-1})	medium
(CH$_2$)$_2$R$_{f6}$	1973.6[a]	C$_6$H$_5$CF$_3$
(CH$_2$)$_2$R$_{f8}$ (**2**)[c]	1973.9[a]	C$_6$H$_5$CF$_3$
(CH$_2$)$_3$R$_{f8}$ (**3**)[c]	1956.7[a]	C$_6$H$_5$CF$_3$
(CH$_2$)$_4$R$_{f8}$ (**4**)[c]	1949.2[a]	C$_6$H$_5$CF$_3$
(CH$_2$)$_5$R$_{f8}$ (**5**)[c]	1946.1[a]	C$_6$H$_5$CF$_3$
(CH$_2$)$_7$CH$_3$	1942.3[a]	C$_6$H$_5$CF$_3$
p-C$_6$H$_4$(CH$_2$)$_3$R$_{f8}$	1958[b]	Nujol
C$_6$H$_5$	1952[b]	Nujol

[a] Reference 9b. [b] Reference 10. [c] Phosphine number.

The solubility properties of such molecules are easy to quantify, and many "partition coefficients" involving solvent mixtures such as perfluoro(methylcyclohexane)/toluene (CF$_3$C$_6$F$_{11}$/CH$_3$C$_6$H$_5$) have been tabulated.[3,8] However, quantitative data on electronic properties are scarce. The methylene or (CH$_2$)$_m$ segment of a ponytail can be regarded as a "tuning element". At some limiting "high *m* value", the active site of the reagent or catalyst would be analogous to that of a nonfluorous analogue bearing protons or *n*-alkyl groups in the same positions. Short of this limit, the highly electronegative R$_{fn}$ groups will render the active site more Lewis acidic—a possible advantage or disadvantage. Thus, there is a distinct need for data that bear upon this point. Chemists with experience in this field develop an intuitive feel or bias for such issues, but unambiguous experimental calibration is ultimately required.

One relevant and surprising set of data features fluorous trialkylphosphines of the formula P((CH$_2$)$_m$R$_{f8}$)$_3$ (m = 2−5, compounds **2**−**5**) and the iridium carbonyl adducts shown in Table 1.[9,10] A complex of tri(*n*-octyl)phosphine, P((CH$_2$)$_7$CH$_3$)$_3$, which lacks fluorine atoms, was prepared for reference. As the number of methylene groups (m) was extended from two to five, the IR ν_{CO} values decreased from 1973.9 to 1946.1 cm^{-1}. However, they did not reach the limit of the nonfluorinated phosphine (1942.3 cm^{-1}), or otherwise converge. This shows that the electron-withdrawing effect of the perfluoroalkyl groups is still felt through five methylene groups (and, in this case, the intervening phosphorus−iridium and iridium−CO bonds). Graphical analyses suggest that seven to eight methylene groups are required for essentially complete insulation (limiting value 1943.7 cm^{-1}).[9b] Note that the IR data reflect the combined effect of six ponytails, thereby affording more resolution than experiments involving compounds with only one ponytail. Two triarylphosphine complexes that illustrate a long-range effect are also included in Table 1.

To more precisely define the electronic properties of a typical series of fluorous compounds with different m values, we designed the three-part study presented below. First, photoelectron spectroscopy is used to determine gas-phase vertical ionization potentials (VIP) of the phosphines **2**−**5**. A vertical ionization potential represents the energy difference between a molecule and a radical cation (M$^{\bullet+}$) that has the same geometry as the ground state, and is one of the most common gas-phase measures of substituent effects upon lone pairs.[11] Second, as a probe of condensed-phase properties, calorimetric and equilibrium measurements are used to assay Brønsted and Lewis basicities. Third, density functional theory (DFT) is employed to independently calculate VIP values, predict gas-phase proton affinities (PA), and further characterize the asymptotic limits associated with the (CH$_2$)$_m$ and R$_{fn}$ segment lengths.[12] Some computational data for fluorous phosphines and primary amines of varying (CH$_2$)$_m$ lengths have been reported earlier,[13] but as secondary parts of studies primarily concerned with synthesis or catalysis.

Results

Ionization Data. The photoelectron spectra of fluorous phosphines **2**−**5** were determined as described in the Experimental Section, and are depicted in Figure 1. The lowest energy ionizations of phosphines are nearly always associated with the phosphorus lone pair,[11b] and the VIP values for these bands exhibited a monotonic decrease from 9.22 to 8.49 eV (±0.03 eV). This indicates a progressively more facile ionization, as would be intuitively expected from the increasing number of methylene groups between phosphorus and the perfluoroalkyl segments. Experimental VIP values of other phosphines are given in Table 2,[14] together with computational data described below. That of **4** (8.59 eV) is close to P(CH$_3$)$_3$ (8.58 eV), whereas **5** (8.49 eV) is less readily ionized than P(CH$_2$CH$_3$)$_3$ (8.34−8.28 eV) and P((CH$_2$)$_3$CH$_3$)$_3$ (8.14−8.00 eV). Both **2** and **3** (9.22 and 8.85 eV) are much less readily ionized than any simple trialkylphosphine, with the former between PH(CH$_3$)$_2$ and PH$_2$CH$_3$ (9.08 and 9.70 eV). Most triarylphosphines with strongly electron-withdrawing substituents are also much more readily ionized (P(*p*-C$_6$H$_4$CF$_3$)$_3$, 8.65 eV).[15]

The condensed-phase counterpart of the lowest ionization potential is the oxidation potential. However, cyclic voltammograms of **2**−**5** in CH$_2$Cl$_2$ showed only irreversible oxidations, so no thermodynamically meaningful data could be acquired. The E(p,a) values were ca. +1.10 V on a scale where ferrocene is oxidized at +0.46 V. Repeated cycling appeared to coat the electrode.

(8) The partition coefficient data in ref 3 has been updated on the following Web page: http://www.organik.uni-erlangen.de/gladysz/research/gifs/fluorous/partition.html.

(9) (a) Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. A. *J. Org. Chem.* **1998**, *63*, 6302−6308. (b) Alvey, L. J.; Meier, R.; Soós, T.; Bernatis, P.; Gladysz, J. A. *Eur. J. Inorg. Chem.* **2000**, 1975−1983. (c) See also Wende, M.; Meier, R.; Gladysz, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 11490−11491.

(10) Soós, T.; Bennett, B. L.; Rutherford, D.; Barthel-Rosa, L. P.; Gladysz, J. A. *Organometallics* **2001**, *20*, 3079−3086.

(11) (a) H. Bock, *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 613−637; *Angew. Chem.* **1977**, *89*, 631−655. (b) Szepes, L.; Nagy, A.; Zanathy, L. In *The Chemistry of Organic Arsenic, Antimony, and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; Chapter 7.

(12) Given the hypothetically infinite resolution of computational chemistry, there is the opportunity to quantify long-range effects that are not (at least today) experimentally observable or measurable. The asymptotic limits relevant to this study are those associated with negligible differences in reactivity or equilibria ($\Delta\Delta G^{\ddagger}_{298}$ or $\Delta\Delta G_{298}$ < 0.1 kcal/mol), or commonly utilized spectroscopic observables.

(13) (a) Horváth, I. T.; Kiss, G.; Cook, R. A.; Bond, J. E.; Stevens, P. A.; Rábai, J.; Mozeleski, E. J. *J. Am. Chem. Soc.* **1998**, *120*, 3133−3143. (b) Szlávik, Z.; Tárkányi, G.; Gömöry, Á.; Tarczay, G.; Rábai, J. *J. Fluorine Chem.* **2001**, *108*, 7−14.

(14) (a) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1972**, 711−719. (b) Lappert, M. F.; Pedley, J. B.; Wilkins, B. T.; Stelzer, O. Unger, E. *J. Chem. Soc., Dalton Trans*. **1975**, 1207−1217. (c) Cradock, S.; Rankin, D. W. H. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 940−946. (d) Cowley, A. H. *Inorg. Chem.* **1982**, *21*, 85−88. (e) Elbel, S.; Dieck, H. T. *Z. Naturforsch.* **1976**, *31b*, 178−189. (f) Schmidt, H.; Schweig, A.; Mathey, F.; Müller, G. *Tetrahedron* **1975**, *31*, 1287−1294. (g) Distefano, G.; Innorta, G.; Pignataro, S.; Foffani, A. *J. Organomet. Chem.* **1968**, *14*, 165−172.

(15) Wilson, M. R.; Woska, D. C.; Giering, W. P. *Organometallics* **1993**, *12*, 1742−1752, and references therein.

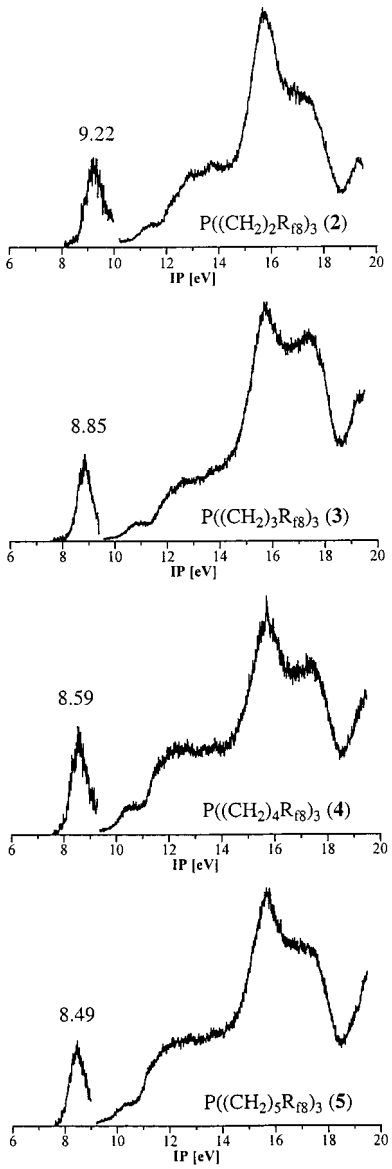


Figure 1. Photoelectron spectra.

Calorimetry and Equilibria. Complementary equilibrium data were sought. Angelici has previously measured the enthalpies of many reactions of amines and phosphines with triflic acid (CF_3SO_3H) in dichloromethane.[16] The values correlate well with Brønsted basicities, and analogous data were sought for **2**−**5**. Due to their sparing solubilities in dichloromethane, trifluoromethylbenzene ($CF_3C_6H_5$)[17] was employed. The resulting enthalpies of protonation are summarized in Scheme 1. The reactions become more exothermic with increasing numbers of methylene groups, in accord with the VIP values.

For calibration, the enthalpy of protonation of the triarylphosphine P(*p*-$C_6H_4CF_3)_3$ was similarly measured. The value compared very well with that obtained by Angelici in dichloromethane (−13.0(7) vs −13.6(2) kcal/mol).[16] Thus, both solvents appear to give similar results. On this basis (and neglecting standard deviations), the enthalpy of protonation of **2** (−25.5(5) kcal/mol) is between that of $P(CH_3)(C_6H_5)_2$ and $P(CH_3)_2(C_6H_5)$ (−24.7(0) and −28.4(2) kcal/mol).[16] The enthalpies of protonation of **4** and **5** (−31.9(6) and −32.0(3) kcal/mol) are between those of $P(CH_3)_3$ and $P(CH_2CH_3)_3$ (−31.6(2) and −33.7(3) kcal/mol). The pK_a(BH^+,H_2O) values of **2**−**5** can also be extrapolated from calibration graphs (5.05, 8.08, 8.57, 8.63).[16] That of **5** is close to $P(CH_2CH_3)_3$ (8.69).

Reactions of **2**−**4** or closely related phosphines with the dirhodium bridging chloride complex $[Rh(CO)_2(Cl)]_2$ have been previously described.[9b,19] Rhodium bis(phosphine) complexes analogous to the iridium complexes in Table 1 can be isolated in high yields. Calorimetric measurements proved problematic, so attempts were made to assay the direction of the equilibrium shown in Scheme 2—an undertaking complicated by the probable intermediacy of a rhodium complex with one ligand of **2** and one ligand of **3**. One NMR tube was charged with a solution of *trans*-$Rh(CO)(Cl)(P((CH_2)_2R_{f8})_3)_2$ and **3** (0.0086 and 0.0275 mmol in 0.7 mL of $CF_3C_6H_5$), and another was charged

Table 2. Calculated and Observed Vertical Ionization Potentials (VIP, eV) for Non-Fluorous Phosphines

	VIP(calc)[a]	VIP(expt)
$P(CH_3)_3$, C_{3v}	8.57	8.58[d]
	8.43[b]	
	8.43[c]	
PH_3, C_{3v}	10.56	10.85[e]
PF_3, C_{3v}	12.58	12.23[f]
$PF(CH_3)_2$, C_S	9.41	9.37[e]
$PH(CH_3)_2$, C_S	9.04	9.08[e]
PH_2CH_3, C_S	9.69	9.70[g]
PF_2CH_3, C_S	10.53	10.34[e]
$P(C(CH_3)_3)_3$, C_3	7.51	7.70,[e] 7.72[h]
$P(CH_2CH_3)_3$, C_3	8.27[c]	8.28,[i] 8.34[h]
$P((CH_2)_2CH_3)_3$, C_3	8.16[c]	
$P((CH_2)_3CH_3)_3$, C_3	8.08[c]	8.00,[j,k] 8.14[h]
$P((CH_2)_4CH_3)_3$, C_3	8.04[c]	
$P((CH_2)_5CH_3)_3$, C_3	8.03[c]	
$P((CH_2)_6CH_3)_3$, C_3	8.01[c]	
$P((CH_2)_7CH_3)_3$, C_3	8.00[c]	
$P((CH_2)_8CH_3)_3$, C_3	7.98[c]	
$P((CH_2)_9CH_3)_3$, C_3	7.98[c]	

[a] At (U)B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p). [b] At (U)B3LYP/6-31G(d)//B3LYP/6-31G(d). [c] At (U)B3LYP/6-311+(d,p)//B3LYP/6-31G(d). [d] Reference 14a. [e] Reference 14b. [f] Reference 14c. [g] Reference 14d. [h] New measurements in this work. [i] Reference 14e. [j] Reference 14f. [k] Reference 14g.

Scheme 1. Enthalpies of Protonation of Fluorous Phosphines

$$P((CH_2)_mR_{f8})_3 + CF_3SO_3H \xrightarrow[30\ ^\circ C]{CF_3C_6H_5} [HP((CH_2)_mR_{f8})_3]^+ CF_3SO_3^-$$

ΔH_p (kcal/mol)

2, -25.5±0.5
3, -31.0±0.3
4, -31.9±0.6
5, -32.0±0.3

(16) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51−60.
(17) Ohrenberg, C.; Geiger, W. E. *Inorg. Chem.* **2000**, *39*, 2948−2950.

(18) (a) A reviewer has emphasized that this bracketing, which we offer as a simple statement of fact, does not hold for the VIP values, which are 8.45 eV for $(P(CH_3)_2(C_6H_5)$, 8.28 eV for $P(CH_3)(C_6H_5)_2$, and 7.92 eV for $P(C_6H_5)_3$.[15] (b) The same is true for the IR ν_{CO} values of rhodium carbonyl complexes *trans*-$Rh(CO)(Cl)(L)_2$, which are 1987 (L = **2**, $CF_3C_6H_5$), 1968 ($P(CH_3)_2(C_6H_5)$, THF),[19] and 1974 ($P(CH_3)(C_6H_5)_2$, THF)[19] cm^{-1}. An identical relationship holds for the corresponding iridium complexes (1974 cm^{-1}, $CF_3C_6H_5$;[9a,20] 1955 cm^{-1}, KBr;[21] 1950 cm^{-1}, KBr[21]). (c) It is to be expected that various physical and chemical probes of fluorous phosphines will give different matches with respect to non-fluorous phosphines. Enthalpies of protonation, for example, will not be directly affected by the phosphine π-acceptor strengths.
(19) Li, C.; Nolan, S. P.; Horváth, I. T. *Organometallics* **1998**, *17*, 452−456.

Scheme 2. Relative Lewis Basicities of **2** and **3**

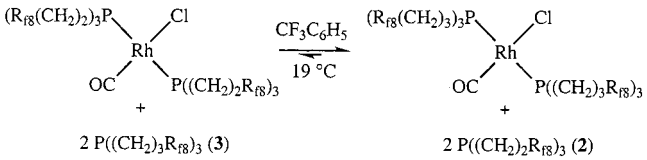


Table 3. Calculated and Observed Gas-Phase Proton Affinities (PA, kcal/mol)

	PA(calc)[a]	PA(calc)[b]	PA(expt)[c]
PH_2CH_3	202.4	206.0	206.9
$PH(CH_3)_2$	215.5	217.9	218.9
$P(CH_3)_3$	226.0	227.4	228.0

[a] At B3LYP/6-311+G(d,p) + ΔZPE (HF/6-31G(d)). [b] At CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) + ΔZPE (HF/6-31G(d)). [c] Reference 22.

with an analogous solution of *trans*-$Rh(CO)(Cl)(P((CH_2)_3R_{f8})_3)_2$ and **2**. In both cases, only broad signals for the rhodium-bound phosphines were observed, and the samples became heterogeneous when cooled. However, the first tube gave a 66:34 **2**/**3** mixture (note a 1.6-fold excess of **3** was utilized), whereas the second gave a 90:10 **2**/**3** mixture (a 1.6-fold excess of **2** was utilized). This clearly shows **3** to have a higher Lewis basicity than **2**, in accord with the other data above.

Computations: Reference Phosphines. To better analyze and extend the preceding data to other phosphines, high-level density functional computations were carried out. The methods were first optimized and calibrated. As summarized in Table 2, the VIP value of $P(CH_3)_3$ was calculated by three protocols. At the B3LYP/6-31(d) level, it was 8.43 or 0.15 eV lower than experiment. However, the larger 6-311+G(d,p) basis set gave nearly perfect agreement. Similar computations were conducted for other reference phosphines (Table 2, first eight compounds). The calculated and experimental values were quite close, with PF_3 giving the largest deviation (0.35 eV or 2.8%).

Gas-phase proton affinities (PA) were computed. These have a sign convention opposite that of the enthalpies of protonation in Scheme 1—i.e., the standard enthalpy change for the reaction $BH^+ \rightarrow B + H^+$. Table 3 gives the PA values calculated for PH_2CH_3, $PH(CH_3)_2$, and $P(CH_3)_3$ at the B3LYP/6-311+G(d,p) level, including the ZPE correction (HF/6-31G(d) level). Although the data are close to the experimental results,[22] PH_2CH_3 showed a deviation of 4.5 kcal/mol (2.2%).

To probe this discrepancy, highly correlated computations were conducted. These used the coupled cluster method, with single, double, and optional triplet substitutions (CCSD(T)) and the B3LYP/6-311+G(d,p) geometry. As shown in Table 3, at the CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) + ΔZPE (HF/6-31G(d)) level, the PA values are in very good agreement with experiment, with a maximum deviation of 1.0 kcal/mol. However, the CCSD(T) method is much more time-intensive and costly than the B3LYP method. Since full optimization at the B3LYP/6-311+G(d,p) level would be prohibitively expensive for large fluorous phosphines, the VIP and PA data below were obtained from single-point B3LYP/6-311+G(d,p) calculations using the B3LYP/6-31G(d) geometries.

(20) Guillevic, M.-A.; Rocaboy, C.; Arif, A. M.; Horváth, I. T.; Gladysz, J. A. *Organometallics* **1998**, *17*, 707−717.
(21) Lawson, H. J.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 6223−6227.
(22) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 6252−6259.

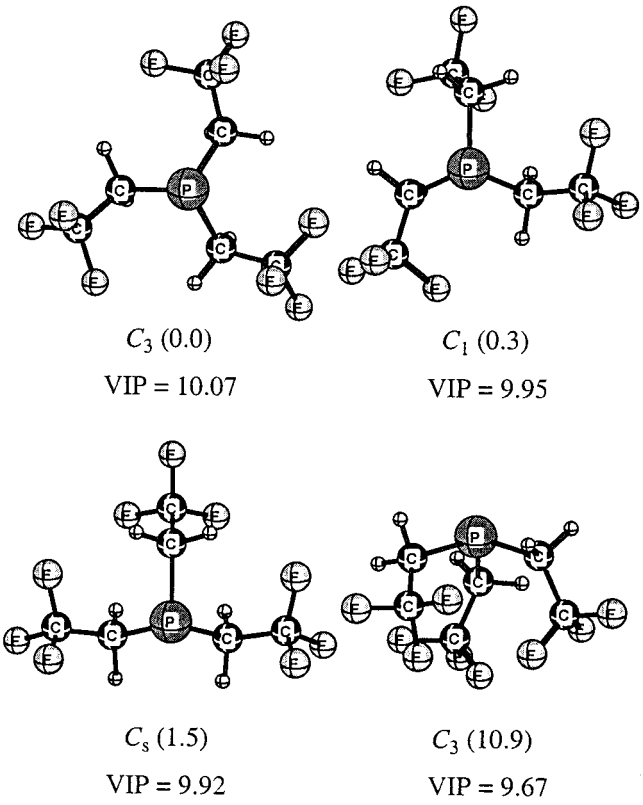


Figure 2. Computed conformational energy minima (kcal/mol) and VIP values (eV) for $P(CH_2CF_3)_3$ ($P(CH_2R_{f1})_3$ or **1′**).

In contrast to $P(CH_3)_3$, which has only one conformational energy minimum, longer chain trialkylphosphines have numerous local minima. Each will have a discrete first ionization potential, complicating comparisons. Thus, all local minima of $P(CH_2CF_3)_3$ or $P(CH_2R_{f1})_3$ were located, as shown in Figure 2. The global energy minimum has C_3 symmetry, with all methyl groups gauche to the phosphorus lone pair. The least stable local minimum (+10.9 kcal/mol) also has C_3 symmetry, with all methyl groups nearly anti to the lone pair. The other two structures are only slightly higher in energy than the global minimum. The global minimum has the largest VIP value and the least stable minimum the smallest.

Next, the structures of tri(*n*-alkyl)phosphines through *n*-decyl were optimized in C_3 symmetry. On the basis of the results in Figure 2, these were presumed to yield the global energy minima. The corresponding VIP values were calculated and are summarized in Table 2. They show a significant effect of chain length through *n*-pentyl or $P((CH_2)_4CH_3)_3$. Past this stage, successive increments in the VIP values are only 0.02−0.01 eV, with "saturation" effectively reached at *n*-nonyl or $P((CH_2)_8CH_3)_3$ (<0.01 eV or <0.23 kcal/mol difference versus *n*-decyl).[12]

Computations: Fluorous Phosphines. The structures of various fluorous phosphines $P((CH_2)_mR_{fn})_3$ ($m = 0-9$; $n = 1-3$) were optimized in C_3 symmetry. The VIP and PA values were calculated, and the results are summarized in Table 4.

An important issue not represented in the above experimental data was analyzed. Namely, how long must the R_{fn} segment be in order to exert a maximum or "saturation" effect upon phosphorus lone pair properties? The phosphines $P(CH_2R_{f1})_3$ (**1′**), $P(CH_2R_{f2})_3$ (**1″**), and $P(CH_2R_{f3})_3$ (**1‴**), each with a spacer of one methylene group, were compared. The VIP and PA values

Table 4. Computed VIP (eV) and PA (kcal/mol) Values for Fluorous Phosphines $P((CH_2)_mR_{fn})_3$

	VIP[a]	PA[b]
$P(R_{f1})_3$, C_3 (**0′**)	11.67	160.0
$P(R_{f2})_3$, C_3 (**0″**)	11.37	164.7
$P(CH_2R_{f1})_3$, C_3 (**1′**)	10.07	194.7
$P((CH_2)_2R_{f1})_3$, C_3 (**2′**)	9.38	207.2
$P((CH_2)_3R_{f1})_3$, C_3 (**3′**)	8.92	217.5
$P((CH_2)_4R_{f1})_3$, C_3 (**4′**)	8.67	222.2
$P((CH_2)_5R_{f1})_3$, C_3 (**5′**)	8.48	226.5
$P((CH_2)_6R_{f1})_3$, C_3 (**6′**)	8.38	229.0
$P((CH_2)_7R_{f1})_3$, C_3 (**7′**)	8.28	231.2
$P((CH_2)_8R_{f1})_3$, C_3 (**8′**)	8.22	
$P((CH_2)_9R_{f1})_3$, C_3 (**9′**)	8.17	
$P(CH_2R_{f2})_3$, C_3 (**1″**)	10.02	195.7
$P(CH_2R_{f3})_3$, C_3 (**1‴**)	10.01	196.2
$P((CH_2)_2R_{f2})_3$, C_3 (**2″**)	9.39	207.8

[a] At (U)B3LYP/6-311+G(d,p)//B3LYP/6-31G(d). [b] At (U)B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) + ΔZPE (HF/6-31G(d)).

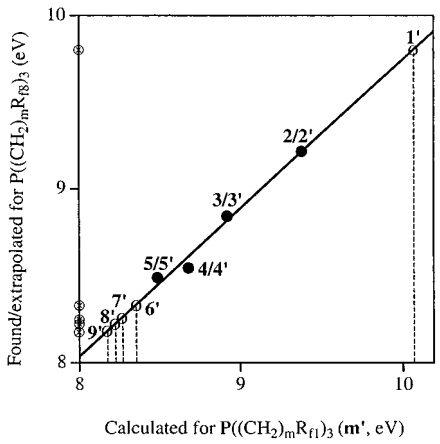


Figure 3. Comparison of calculated and experimental VIP values.

of the last two (Table 4) show only a small difference, indicating that saturation is nearly complete at R_{f2} in this series. The phosphines $P((CH_2)_2R_{f1})_3$ (**2′**) and $P((CH_2)_2R_{f2})_3$ (**2″**), each with a spacer of two methylene groups, were also compared. The VIP and PA values show an even smaller difference.[23] Hence, phosphines of the formulas $P((CH_2)_mR_{f1})_3$ (designated henceforth as ***m′***) were taken as models for **2**−**5**. The use of R_{f2} segments would have greatly increased the computational expense.

The computed VIP values for model compounds **2′**−**5′** (Table 4) agree very well with those of **2**−**5** (Figure 1), and are plotted against each other in Figure 3. The linear relationship (R = 0.98) allows the values computed for the higher model compounds **6′**−**9′** to be confidently extrapolated to those of the presently unknown fluorous phosphines **6**−**9** (predicted, eV: **6**, 8.35; **7**, 8.27; **8**, 8.21; **9**, 8.17). The values computed for **1″** and **1‴** (10.02−10.01 eV) can similarly be extrapolated to the unknown fluorous phosphine with a single methylene spacer,

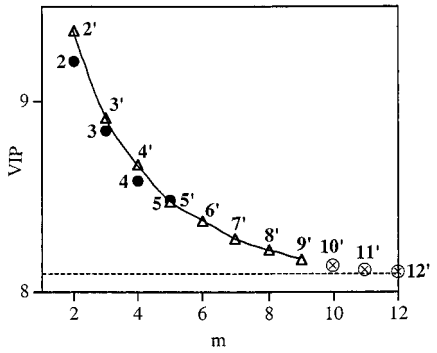


Figure 4. Relationship between VIP (eV) and m for $P((CH_2)_mR_{f8})_3$ (**2**−**5**, ●) and $P((CH_2)_mR_{f1})_3$ (**2′**−**9′**, △) as well as extrapolated values for **10′**−**12′** (⊗).

$P(CH_2R_{f8})_3$ (**1**). The predicted VIP (9.73 eV) is somewhat lower, reflecting a trend to slightly higher computational vs experimental values as m decreases (see also Figure 4).

At this stage, the issue of the number of methylene groups needed to insulate a phosphorus lone pair from a perfluoroalkyl group remains.[12] The data for $P((CH_2)_mR_{f1})_3$ in Table 4 show VIP differences of 0.06 and 0.05 eV between m = 7 (**7′**), 8 (**8′**), and 9 (**9′**). These are larger than those between $P((CH_2)_6CH_3)_3$, $P((CH_2)_7CH_3)_3$, and $P((CH_2)_8CH_3)_3$, which have the same number of nonfluorinated carbons (0.02 and 0.01 eV; Table 2). This is consistent with a residual inductive effect of the fluorinated segment. The graphical analysis in Figure 4 suggests that an effective limit is almost reached with m = 10 (8.14 eV), with further incremental decreases for m = 11 and 12 to a limit of ca. 8.12−8.11 eV.[24] However, note that the nonfluorinated phosphines in Table 2 converge to a still lower limit (7.98 eV). That in Figure 4 is between the computed VIP values of $P(CH_2)_2CH_3)_3$ and $P(CH_2)_3CH_3)_3$ (8.16 and 8.08 eV).

The apparent difference in limiting VIP values crystallizes the question as to what constitutes the best reference molecule for fluorous phosphines $P(CH_2)_mR_{fn}$ in which the perfluoroalkyl group is "completely" insulated from phosphorus. It is possible to sidestep this issue with an alternative probe of the asymptotic limit, which makes use of homodesmotic exchange reactions.[25] Two series are given in Scheme 3. The left side of each equation features a molecule with CH_3 and CF_3 end groups that are separated by m methylene groups. The right side of each equation features a molecule with phosphorus atoms and CF_3 end groups that are separated by m methylene groups. The other molecules in the equilibria remain constant. The enthalpies will approach a limiting value as m becomes large enough to block out end group−end group interactions.

The enthalpies of the homodesmotic equations in Scheme 3 were computed at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) + ZPE (RHF/6-31G(d)) level. Both $P(CH_2CH_3)_3$ and $P((CH_2)_2CH_3)_3$ give convergence to a "high m value" limit of seven. Continuing to eight methylene groups would make a difference of at most 0.1 kcal/mol (0.0043 eV), a quantity that

(23) Although the difference is small, **2″** is computed to be thermodynamically more difficult to ionize than **2′**, consistent with a slightly greater electron-withdrawing effect of R_{f2} vs R_{f1}. In contrast, for the series **1′**, **1″**, **1‴** as well as **0′**, **0″**, ionizations become more facile upon going from R_{f1} to R_{f2} to R_{f3}. Although these interesting trends deserve additional scrutiny, they are beyond the scope of this study. A possible explanation involves lone pair/F^- or R_{fn}^- hyperconjugative effects that are blocked or greatly attenuated at $m \geq 2$. For related phenomena with fluorine-containing carbanions, see: (a) Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 396−397. (b) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141−1150. (c) Raabe, G.; Gais, H.-J.; Fleischhauer, J. *J. Am. Chem. Soc.* **1996**, *118*, 4622−4630, and references cited therein.

(24) Computational resources were not sufficient to calculate the PA values of **8′** and **9′**, but they can be roughly estimated from the changes in VIP values. A reasonable estimate for the asymptotic limit would be 234 kcal/mol.

(25) Georg, P.; Trachtman, M.; Bock, C. W.; Bret, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222−1227. The term homodesmotic denotes reactions in which there are equal numbers of (1) each type of bond in reactants and products and (2) each type of atom with the same connections in reactants and products.

Scheme 3. Homodesmotic Exchange Reactions

$$P(CH_2CH_3)_3 + 3\,H_3C(CH_2)_mCF_3 = P((CH_2)_mCF_3)_3 + 3\,CH_3CH_2CH_3 \quad \text{Eq. 1}$$

ΔH = 7.1 kcal/mol (m = 1)

ΔH = 1.7 kcal/mol (m = 2)

ΔH = 0.9 kcal/mol (m = 3)

ΔH = 0.0 kcal/mol (m = 4)

ΔH = -0.5 kcal/mol (m = 5)

ΔH = -0.5 kcal/mol (m = 6)

ΔH = -0.6 kcal/mol (m = 7)

$$P((CH_2)_2CH_3)_3 + 3\,H_3C(CH_2)_mCF_3 = P((CH_2)_mCF_3)_3 + 3\,CH_3CH_2CH_2CH_3 \quad \text{Eq. 2}$$

ΔH = 7.4 kcal/mol (m = 1)

ΔH = 2.0 kcal/mol (m = 2)

ΔH = 1.2 kcal/mol (m = 3)

ΔH = 0.3 kcal/mol (m = 4)

ΔH = -0.2 kcal/mol (m = 5)

ΔH = -0.3 kcal/mol (m = 6)

ΔH = -0.5 kcal/mol (m = 7)

has a small effect upon equilibrium constants at room temperature.[12] The limiting enthalpies are close to zero, and would be expected to become even closer to zero as the *n*-alkyl group of the phosphine utilized is lengthened.

Discussion

The above data provide a clear answer to the question—or perhaps more exactly the challenge—posed in the title, "how to insulate a reactive site from a perfluoroalkyl group". Even upon going from a spacer of four methylene groups to five methylene groups between a phosphorus and a perfluoroalkyl segment, changes in experimental properties are easily detectable (Table 1, Figure 1, Scheme 1). All experimental measures carry error limits, and in this regard theory is able to play an important defining role—especially since the issue is not an absolute value, but the attenuation of an effect or a relative value. The computational data in Scheme 3 indicate that the asymptotic limit is reached with seven to eight methylene groups, in accord with earlier estimates from the IR data in Table 1.[9b] The VIP data in Figure 4 suggest a somewhat higher limit, in the range of 10 methylene groups.[12]

This represents a remarkable long-range electronic effect that to our knowledge has never been documented with any other type of conformationally unrestrained bifunctional molecule.[26] Since the PES and computational data provide gas-phase values, speculative "nonclassical" transmission mechanisms—such as a non-through-bond or non-field process operative in a special microenvironment such as a micelle—can be excluded. Polar effects can be magnified in the gas phase due to the absence of dampening solvent interactions, and this may be a factor in the higher limit or degree of transmission evident in the VIP data in Figure 4. However, the IR data clearly show long-range transmission in solution (Table 1).

The calorimetry and equilibrium measurements were also conducted in solution (Schemes 1 and 2). Care was taken to analyze pure samples, replicate values, and avoid sources of error. However, sample quantities were not sufficient to study concentration effects, such that values could be extrapolated to infinite dilution. Compare the enthalpies of protonation of **2**−**5** in Scheme 1 with the PA values of **2′**−**5′** in Table 4. Both indicate monotonically increasing basicities. The gas-phase data (207.2, 217.5, 222.2, 226.5 kcal/mol) are still removed from an asymptotic limit (ca. 234 kcal/mol).[24] In contrast, when standard deviations are neglected, the solution phase data seem to be converging (−25.5, −31.0, −31.9, −32.0 kcal/mol), consistent with a dampening effect.

Scheme 2 establishes that the Lewis basicities of **2** and **3** parallel the enthalpies of protonation and Brønsted basicities. However, the rhodium in Scheme 2 is capable of π backbonding, and this interaction will be stronger with **2**. Hence, a linear correlation with Brønsted basicities is not expected. The enthalpies of reactions of rhodium and ruthenium complexes with a lower R_{fn} homologue of **2**, $P((CH_2)_2R_{f6})_3$, have also been measured.[19,27] The data, obtained in THF, show that $P((CH_2)_2R_{f6})_3$ has electronic properties similar to those of $P(CH_3)_2(C_6H_5)$, and steric properties similar to those of $P(CH_2CH_3)_3$, with respect to the rhodium and ruthenium fragments employed. It can be safely assumed that **2** is similar. However, as emphasized above,[18] the non-fluorous phosphine that provides the best match is very much a function of the physical or chemical probe.

A related family of fluorous tri(*n*-alkyl)amines, $N((CH_2)_mR_{f8})_3$, has been synthesized with *m* ranging from 3 to 5.[28] Even with five methylene groups, there is a detectable diminution of Brønsted basicity in $CDCl_3$ as compared to model compounds such as tri(*n*-dodecyl)amine.[28] The equilibrium in eq 1 shows a significant basicity increase upon lengthening the $(CH_2)_m$ segment from $m = 4$ to 5.

$$^{+}HN((CH_2)_4R_{f8})_3\ CF_3CO_2^{-} + {:}N((CH_2)_5R_{f8})_3 \rightleftharpoons {:}N((CH_2)_4R_{f8})_3 + {}^{+}HN((CH_2)_5R_{f8})_3\ CF_3CO_2^{-} \quad K_{eq} = 11\text{–}5 \quad (1)$$

DFT calculations have been reported for two related primary fluorous amines, $NH_2((CH_2)_4R_{f2})$ and $NH_2((CH_2)_5R_{f2})$ (as well as lower homologues), and the corresponding PA values are 214.1 and 215.8 kcal/mol.[13b] Interestingly, this ΔPA is approximately one-third that for **4′** and **5′** (Table 4), which feature three ponytails per heteroatom. On the basis of these and other data,[29] there is every reason to believe that the long-range effects documented with **2**−**5** and **2′**−**9′** should be general for many classes of Lewis and Brønsted bases.

Aggregative phenomena always constitute a potential complication in solution. We have previously shown a nonlinear

(26) For an interesting computational study of long-range electronic effects in monofunctional $X(CH_2)_mCH_3$ compounds ($m = 4, 5, 11$; X = F, CF_3, and other groups), see: Nolan, E. M.; Linck, R. G. *J. Phys. Chem. A* **2001**, *105*, 7297−7307. There is a clear influence on properties such as atomic charge polarizations, carbon 1s orbital energies, and atomic dipole vectors over the entire carbon chain.[12]

(27) Other relevant calorimetric data: (a) Smith, D. C., Jr.; Stevens, E. D.; Nolan, S. P. *Inorg. Chem.* **1999**, *38*, 5277−5281. (b) Smith, D. C.; Klaman, A. L.; Cadoret, J.; Nolan, S. P. *Inorg. Chim. Acta* **2000**, *300*−*302*, 987−991.

(28) Rocaboy, C.; Bauer, W.; Gladysz, J. A. *Eur. J. Org. Chem.* **2000**, 2621−2628.

(29) Schlosser, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1496−1513; *Angew. Chem.* **1998**, *110*, 1538−1556.

NMR response as tri(*n*-dodecyl)amine is titrated with CF_3CO_2H in $CDCl_3$.[28] Any added stability associated with a protonated phosphine, such as micelle formation, will lead to a more exothermic protonation. Any added stability associated with an unprotonated phosphine will lead to a less exothermic protonation. With regard to the latter, we find that **2** is an effective gelator for hexane at very low concentrations.[30] Hence, it is prudent to treat all calorimetric data for fluorous compounds that have not been extrapolated to infinite dilution with caution.

Two other types of long-range electronic effects are implicit in the phosphines analyzed above. The first is the intrinsic influence of a progressively longer $(CH_2)_m$ segment, be it in the fluorous phosphines **2**−**5** and **2′**−**9′** (Table 4) or the tri(*n*-alkyl)phosphines $P((CH_2)_mCH_3)_3$ (Table 2). To our knowledge, there have been no attempts to determine the "high *m* value" limit or saturation point in the latter series, in either gas or condensed phases, or with related amines. Our results indicate a value of 8 (*n*-nonyl). In the fluorinated series, this independent effect of the $(CH_2)_m$ segment must play a role in the *m* value at which insulation is complete. The second type of long-range effect concerns the length of the R_{fn} segment. Here, the computational data showing that the second perfluorinated carbon has a much smaller inductive effect than the first (e.g., **2″** vs **2′**) is in line with many experimental observations. For example, the Hammett σ constants associated with CF_3, CF_2CF_3, and $CF_2CF_2CF_2CF_3$ groups are all very close (σ_p 0.53−0.54, 0.52, 0.52; σ_m 0.43−0.46, 0.47−0.50, 0.47−0.52).[31]

Looking ahead, the preceding data pose a number of interesting issues for further research. What are the transmission properties of other types of spacers or insulating segments, which might for example contain oxygen or silicon[32] atoms? What are the asymptotic limits associated with aromatic fluorous assemblies such as $:DC_6H_4(CH_2)_mR_{fn}$, where :D is a donor atom? The two iridium triarylphosphine complexes in Table 1 demonstrate a distinct long-range effect. While this study was being reviewed, a parametrized approach, the QALE model, has been applied to these and many other of the above questions.[33]

In summary, this study has advanced strategy and design in catalysts and reagents for fluorous and supercritical CO_2 chemistry by clearly identifying the methylene spacer lengths needed for the effective[12] insulation of a typical active site (phosphorus) from a perfluoroalkyl chain. The surprisingly long-range electronic effects have not been anticipated by most researchers in these fields. To our knowledge, such effects have not previously been demonstrated, either experimentally or computationally, in other series of acyclic or conformationally unrestrained bifunctional organic compounds.[26] However, they are certain to have counterparts that will manifest themselves in important chemical contexts. Finally, the electronic properties of **2**−**5** have been calibrated, in both gas and condensed phases, versus those of well-studied nonfluorinated phosphines. By every measure, **4** is similar to $P(CH_3)_3$, but **5** remains less electron-rich than $P(CH_2CH_3)_3$. The best reference compound for the most widely utilized of these phosphines, **2**, depends on the property. Ionization is much less thermodynamically favorable than with any tri(*n*-alkyl)phosphine, or triphenylphosphine bearing electron-withdrawing para substituents. However, the Brønsted basicity in nonaqueous solvents is between those of $P(CH_3)(C_6H_5)_2$ and $P(CH_3)_2(C_6H_5)$.[18b,c]

Experimental Section

The title phosphines[9] and rhodium complexes[9b,20] were prepared as described earlier or in the Supporting Information, and checked for purity by ^1H and ^{31}P NMR. $CF_3C_6H_5$ (Aldrich or ABCR) was dried with P_2O_5 and distilled under argon, and CF_3SO_3H (Aldrich) was used as received.

Measurements. Photoelectron spectra (PES) were measured on a Leybold-Heraeus UPG200 instrument equipped with a He(I) radiation source (21.21 eV).[34] Samples were evaporated directly into the target chamber at 300−350 °C to achieve sufficient vapor pressure. The energy scale was calibrated with xenon (12.130, 13.436 eV) and argon (15.759, 15.937 eV) lines. The accuracy was approximately ±0.03 eV. Cyclic voltammograms were recorded as detailed previously.[35]

Calorimetry was performed under argon using standard high vacuum or Schlenk techniques or in a MBraun glovebox containing less than 1 ppm oxygen and water. The mixing vessels of the Setaram C-80 were cleaned, oven-dried at 120 °C, and taken into the glovebox. A sample of $P((CH_2)_mR_{f8})_3$ (0.010−0.015 g) was transferred into a 2 mL volumetric flask and accurately weighed on a high precision balance. Dry $CF_3C_6H_5$ was added to make a 2 mL solution, which was syringed into the inner compartment of the calorimetric cell. Next, CF_3SO_3H (5 equiv) was dissolved in enough $CF_3C_6H_5$ to make a 10 mL stock solution, 2 mL of which was syringed into the outer compartment of the cell. The vessel was closed, taken out of the glovebox, and inserted in the calorimeter. The reference cell was loaded in the same fashion, except that the inner compartment contained neat solvent. After the calorimeter had reached equilibrium at 30.0 °C (ca. 2 h), reaction was initiated by inverting the calorimeter. At the end of the reaction, the vessels were transferred to the glovebox, opened, and analyzed by ^{31}P and ^1H NMR. Conversions to $H[P((CH_2)_mR_{f8})_3)]^+CF_3SO_3^-$ were quantitative. The enthalpy values represent the average of five determinations.

NMR spectra were recorded on a JEOL-EX400 spectrometer. A 5 mm NMR tube was charged with *trans*-$Rh(CO)(Cl)(P((CH_2)_2R_{f8})_3)_2$ (0.0250 g, 0.0086 mmol), **3** (0.0389 g, 0.0275 mmol), and $CF_3C_6H_5$ (0.7 mL) in a glovebox. The tube was transferred to the NMR probe, and ^{31}P spectra (inverse gated) were recorded at 19 °C. An identical experiment was conducted with *trans*-$Rh(CO)(Cl)(P((CH_2)_3R_{f8})_3)_2$ (0.0250 g, 0.0084 mmol), **2** (0.0367 g, 0.0267 mmol), and $CF_3C_6H_5$ (0.7 mL). For data, see the text.

Computations. Geometries were optimized at the density functional B3LYP/6-31G(d) level and characterized as energy minima at the HF/6-31G(d) level by frequency calculations which provide the zero-point energies (ZPE).[36] Selected optimizations (see text) were carried out at the B3LYP/6-311+G(d,p) level. Unless otherwise noted, single-point energies were calculated at the B3LYP/6-311+G(d,p) level using the B3LYP/6-31G(d) geometries. The total electronic energies (au) and ZPE data (kcal/mol) for all compounds are given in the Supporting Information. All calculations were done with the Gaussian 98 program.[37] The ZPE difference between B and BH^+ (HF/6-31(d) level) was taken

(30) (a) Wende, M. Unpublished results, University of Erlangen−Nürnberg. (b) For some other fluorous gelators, see: van Esch, J. H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263−2266; *Angew. Chem.* **2000**, *112*, 2351−2354.
(31) Exner, O. In *Correlation Analysis in Chemistry*, Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 10.
(32) Richter, B.; Spek, A. L.; van Koten, G.; Deelman, B.-J. *J. Am. Chem. Soc.* **2000**, *122*, 3945−3951.
(33) Fernandez, A. L.; Wilson, M. R.; Prock, A.; Giering, W. P. *J. Am. Chem. Soc.* **2001**, *123*, 3429−3435.
(34) For additional details, see: Rademacher, P.; Kowski, K.; Hermann, H.; Lüttke, W. *Eur. J. Org. Chem.* **1999**, 3191−3197.
(35) (a) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775−788. (b) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810−822.
(36) For theoretical methods and applications: Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

into account in all PA calculations. Since this was nearly constant for $P((CH_2)_mR_{f1})_3$ compounds with $m = 1-5$, the same value was used for homologues with $m = 6-7$.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A. 5; Gaussian, Inc.: Pittsburgh, PA, 1998.

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Supporting Information Available: The synthesis and characterization of *trans*-$Rh(CO)(Cl)[P((CH_2)_2R_{f8})_3]_2$ by a method previously reported for related compounds,[9b,20] and total electronic energies calculated at various levels of theory for phosphines and related reference molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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