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Convenient Modular Syntheses of Fluorous Secondary Phosphines and Selected Derivatives

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Abstract: Reactions of the fluorous primary phosphines $R_{fn}(CH_2)_2PH_2$ [$R_{fn} = (CF_2)_{n-1}CF_3$; n = 6, 8, 10] and $R_{fn'}CH{=}CH_2$ [(n′ = 6, 8, 10) (1:1; THF, reflux) in the presence of AIBN give the title compounds [$R_{fn}(CH_2)_2$][$R_{fn'}(CH_2)_2$]PH [n/n′ = 6/6 (**4**, 55%), 8/8 (**5**, 58%), 10/10 (**6**, 53%), 8/6 (**7**, 52%), 10/8 (**8**, 51%)] as low-melting white solids on up to 10-g scales. The chiral tertiary phosphine [$R_{f6}(CH_2)_2$][$R_{f8}(CH_2)_2$][$R_{f10}(CH_2)_2$]P (**9**) is similarly prepared from **7** and $R_{f10}CH{=}CH_2$ in the presence of VAZO (neat, 100 °C; 67%). The reaction of **5** and THF·BH_3 yields the phosphine borane **5**·BH_3 (95%). Additions of triphosgene [$(CCl_3O)_2CO$] to **5** or $R_{f8}(CH_2)_2PH_2$ give [$R_{f8}(CH_2)_2]_2PCl$ or $R_{f8}(CH_2)_2PCl_2$, which are characterized *in situ*. The $CF_3C_6F_{11}$/toluene partition coefficients of **4**–**9** increase with the number and lengths of the R_{fn} segments.

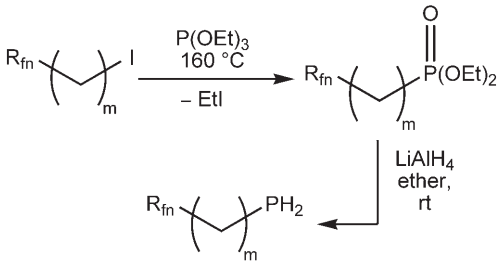
Keywords: fluorous; partition coefficients; phosphines; phosphine-boranes; radical additions

Introduction

Since fluorous catalysis was first reported in 1994,[1] numerous processes have been developed.[2,3] A variety have employed fluorous phosphines,[4] either as metal complexes[5,6] or as independently competent Lewis base catalysts.[7] Applications of the latter type fall under the rubric of "organocatalysis,"[8,9] a field that is growing extremely rapidly. These developments have prompted intense interest in efficient syntheses of fluorous phosphines.[4,10] Both trialkyl and triaryl systems have been extensively studied, and a good selection of ditertiary diphosphines are available.

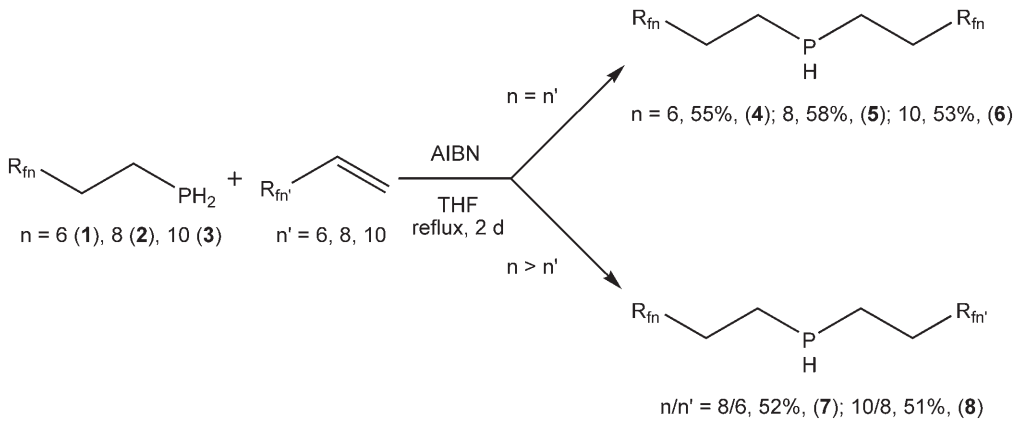
Many syntheses of fluorous aliphatic phosphines utilize free-radical chain additions of phosphorus-hydrogen bonded species $R_{3-x}PH_x$ to fluorous terminal alkenes $R_{fn}(CH_2)_{m'}CH{=}CH_2$ [$R_{fn} = CF_3(CF_2)_{n-1}$].[1,11] These are ideal from the criterion of atom economy, but there are important limitations in the case of PH_3 (x = 3). First, PH_3 is a toxic, expensive gas.[12] It often contains traces of P_2H_4, which promotes spontaneous ignition in air. Second, additions to alkenes must be carried out under pressure in autoclaves. Third, it has not proved possible to effect single or double additions with good selectivities. Hence, primary and secondary phosphines cannot be accessed in high yields.

We have sought to develop convenient, modular syntheses of fluorous primary, secondary, and tertiary aliphatic phosphines that (1) avoid the use of PH_3, (2) can be conducted on large scales, and (3) allow access to chiral-at-phosphorus species. For fluorous secondary and tertiary phosphines, primary phosphines represent attractive building blocks. Accordingly, we recently reported facile syntheses from fluorous primary alkyl iodides $R_{fn}(CH_2)_mI$ as shown in Scheme 1.[13] This sequence exploits the unique status of $P(OEt)_3$ as an inexpensive, readily available *mono*-functionalizable "aufbau unit" for the synthesis of organophosphorus com-



n/m	$R_{fn}(CH_2)_mPH_2$	overall yield
6/2	78% (**1**)	44%
8/2	71% (**2**)	40%
8/3	66%	38%
10/2	62% (**3**)	37%

Scheme 1. Syntheses of fluorous primary phosphines.



Scheme 2. Syntheses of fluorous secondary phosphines.

Table 1. Physical data for fluorous phosphines.

Fluorous Phosphine	Mp [°C] (DSC)	Bp [°C] (Torr)	Solubilities			
			toluene	$CF_3C_6F_{11}$	THF	$CF_3C_6H_5$
4	29.7	135 (0.034)	sol	sol	sol	sol
7	50.4	150 (0.0075)	moderate sol	sol	sol	sol
5	79.7	165 (0.044)	poorly sol	sol	moderate sol	sol
8	89.9	205 (0.20)	poorly sol	sol	poorly sol	sol
6	116.7	210 (0.027)	very poorly sol	moderate sol	poorly sol	sol
9	43.4	215 (0.0090)	very poorly sol	moderate sol	very poorly sol	sol

pounds *via* the Arbuzov reaction.[14] Reductions of the intermediate fluorous primary phosphonates with $LiAlH_4$ afford fluorous primary phosphines in reasonable yields on > 10-g scales.

We set out to further develop the chemistry of these compounds, and report herein free-radical additions that give achiral and chiral fluorous secondary phosphines $[R_{fn}(CH_2)_2][R_{fn'}(CH_2)_2]PH$ in good selectivities. These are of interest both as precursors to other phosphines – such as pincer[15] ligands – and as potential organocatalysts.[9] Representative derivatives are also described, including a chiral tertiary phosphine and a phosphine borane. This work provides alternatives to novel methodology recently reported by Horváth for achiral and chiral fluorous tertiary phosphines.[10c] Taken together with other data summarized in the discussion section, convenient routes to unbranched fluorous aliphatic phosphines of every conceivable substitution pattern are now available.

Results

Syntheses of Fluorous Secondary Phosphines

As shown in Scheme 2, the fluorous primary phosphines $R_{fn}(CH_2)_2PH_2$ [n = 6 (**1**), 8 (**2**), 10 (**3**)][13] and commercial terminal alkenes $R_{fn'}CH{=}CH_2$ (n′ = 6, 8, 10) were combined in a 1:1 ratio in the presence of the initiator AIBN.[16] After 2 days in refluxing THF, work-up gave the achiral symmetrically-substituted and chiral unsymmetrically-substituted secondary phosphines $[R_{fn}(CH_2)_2][R_{fn'}(CH_2)_2]PH$ [n/n′ = 6/6 (**4**), 8/8 (**5**), 10/10 (**6**), 8/6 (**7**), 10/8 (**8**)] in 51–58% yields. The crude reaction mixtures contained some unreacted primary phosphine and small amounts of tertiary phosphine. Since the boiling points increase with the number and lengths of the perfluoroalkyl segments, these were easily separated by vacuum distillation. When the solvent was omitted, much more tertiary phosphine formed.

The phosphines **4**–**8** were isolated as low-melting white solids that gave good microanalyses (Experimental Section). As summarized in Table 1, the melting points increased with the lengths of the perfluoroalkyl chains. No other phase transitions were evident by DSC. The solids could be kept under air for several days. However, care had to be taken with **4**, which melted below body temperature, becoming more air sensitive.

The solubilities of **4**–**8** were probed in representative solvents at room temperature. As indicated in Table 1, they decreased with the lengths of the perfluoroalkyl chains, but noticeably increased at elevated temperatures. Similar trends have been observed with many other fluorous molecules.[17] Solubilities also decreased in

Table 2. Summary of partition coefficients.

Entry	Analyte	$CF_3C_6F_{11}$/toluene
1	$R_{f6}(CH_2)_2PH_2$ (**1**)	53 : 47[a, b]
2	$R_{f8}(CH_2)_2PH_2$ (**2**)	64 : 36[b, c]
3	$R_{f10}(CH_2)_2PH_2$ (**3**)	74 : 26[b, c]
4	$[R_{f6}(CH_2)_2]_2PH$ (**4**)	91.9 : 8.1[a, d]
5	$[R_{f6}(CH_2)_2)(R_{f8}(CH_2)_2]PH$ (**7**)	96.8 : 3.2[d, e]
6	$[R_{f8}(CH_2)_2]_2PH$ (**5**)	99.5 : 0.5[d, e]
7	$[R_{f8}(CH_2)_2)(R_{f10}(CH_2)_2]PH$ (**8**)	$>99.7 : <0.3$[a, d]
8	$[R_{f10}(CH_2)_2]_2PH$ (**6**)	$>99.7 : <0.3$[a, d]
9	$[R_{f6}(CH_2)_2]_3P$	98.8 : 1.2[c, d,f]
10	$[R_{f8}(CH_2)_2]_3P$	$>99.7 : <0.3$[c, d,f]
11	$[R_{f10}(CH_2)_2]_3P$	$>99.7 : <0.3$[c, d,f]
12	$[R_{f6}(CH_2)_2)(R_{f8}(CH_2)_2][R_{f10}(CH_2)_2]P$ (**9**)	$>99.7 : <0.3$[a, d]

[a] Data at 25 °C.
[b] Determined by ^1H NMR, ref.[13]
[c] Data at 27 °C.
[d] Determined by GC.
[e] Data at 24 °C.
[f] Ref.[11a]

the solvent sequence $CF_3C_6H_5 \geq CF_3C_6F_{11} > THF >$ toluene. Since **6** is poorly soluble in THF, but not the precursor **3**, it can also be purified by extraction. Similarly, **5** is moderately soluble in THF, but the tertiary phosphine by-product $[R_{f8}(CH_2)_2]_3P$[11a] is very poorly soluble.

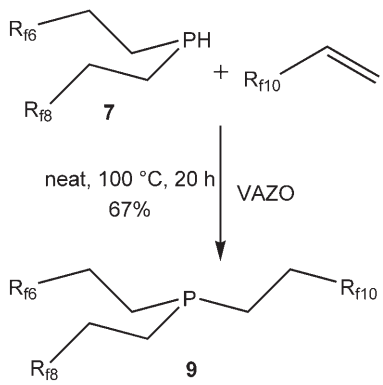
The phosphines **4**–**8** were further characterized by NMR and IR spectroscopy and mass spectrometry, as detailed in the Experimental Section. The NMR properties were similar, despite the fact that spectra of the R_{f10} species **6** and **8** were acquired in fluorous solvents. The ^{31}P NMR signals were as expected coupled to hydrogen ($\delta = -66.9$ to -67.4, d, $^1J_{PH} = 191-198$ Hz). The $^{13}C\{^1H\}$ spectra showed PCH_2 signals that were coupled to phosphorus but not, within detection limits, to fluorine ($\delta = 11.4$ to 9.8, d, $^1J_{CP} = 13$ Hz). The PCH_2CH_2 signals were further downfield ($\delta = 30.7$ to 29.6, dt, $^2J_{CP} = 14-15$ Hz, $^2J_{CF} = 22-24$ Hz) and strongly coupled to both phosphorus and fluorine. Mass spectra showed molecular ions as well as peaks for the corresponding oxides.

In order to quantify the fluorous-phase affinities of **4**–**8**, the $CF_3C_6F_{11}$/toluene partition coefficients were measured by GC as described in the Experimental Section. The results are summarized in Table 2. Previously reported values for reference compounds are also given. These data are analyzed in the Discussion section.

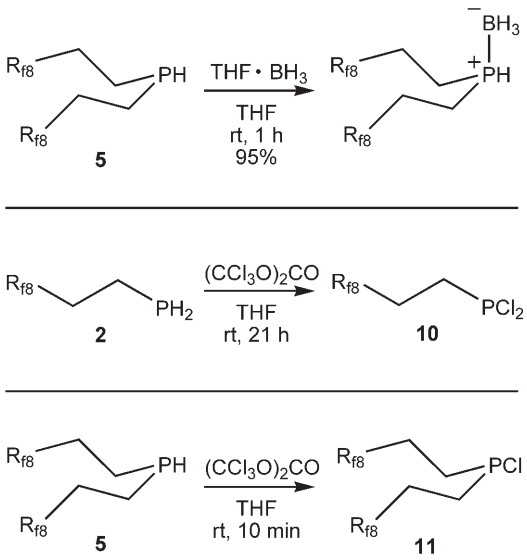
For purposes of initial characterization, the preceding syntheses were conducted on 0.5–1.1-g scales. However, some were subsequently conducted on 10-g scales. In the most efficient protocols, the reductions of the phosphonates $R_{fn}(CH_2)_2P(O)(OC_2H_5)_2$ (Scheme 1) were carried out in THF, such that the resulting THF solutions of **1**–**3** could be used directly in Scheme 2. A typical procedure that provided **5** in 61% overall yield and > 97% purity is given in the Experimental Section.

Derivatives and Related Chemistry

We sought to demonstrate representative applications of the preceding compounds. The synthesis of a chiral fluorous tertiary phosphine was targeted first. Thus, the unsymmetrically-substituted secondary phosphine **7** and $R_{f10}CH{=}CH_2$ were combined (1:2) without solvent in the presence of the initiator VAZO.[16] As shown in Scheme 3, after 20 h at 100 °C, work-up gave the target molecule $[R_{f6}(CH_2)_2][R_{f8}(CH_2)_2][R_{f10}(CH_2)_2]P$ (**9**) in 67% yield. The air-stable low-melting white solid was characterized analogously to the other new phosphines above (Tables 1, 2, and Experimental Section). The ^{31}P NMR signal ($\delta = -25.3$) was downfield from that of the precursor **7** ($\delta = -67.4$). Despite the asymmetry, the PCH_2CH_2 units exhibited identical ^1H and ^{13}C NMR signals. Trends in the chemical shifts and coupling constants are analyzed elsewhere.[18]



Scheme 3. Synthesis of an asymmetric fluorous tertiary phosphine.



Scheme 4. Additional derivatives of primary and secondary phosphines.

Phosphine boranes play important roles in the synthesis of organophosphorus compounds.[19] However, fluorous phosphines are normally much less basic than non-fluorous analogues,[20] and only a few borane adducts are known.[21] Thus, as shown in Scheme 4 (*top*), **5** and THF·BH_3 were combined in THF. Work-up gave the target compound **5**·BH_3 as an analytically pure white powder in 95% yield, which was characterized in the same manner as the other new compounds. The ^{31}P NMR signal ($\delta = -5.4$) was downfield from that of the precursor **5** ($\delta = -67.4$), consistent with other phosphine boranes.[19b] Also, the ^{1}H NMR spectrum showed a *ca.* 1.5 ppm upfield shift of the PH signal. Further reactions of **5**·BH_3 have recently been reported.[22]

Phosphorus-chlorine bonds are very useful for the elaboration of organophosphorus compounds. Triphosgene or $(CCl_3O)_2CO$, a crystalline substitute for toxic phosgene,[23] has been shown to efficiently transform primary phosphines to the dichlorides $RPCl_2$ and secondary phosphines to the chlorides RR′PCl.[24] Accordingly, the primary phosphine **2** and the secondary phosphine **5** were treated with triphosgene in THF as shown in Scheme 4 (*middle*, *bottom*). Vigorous gas evolution occurred. The target molecules $R_{f8}(CH_2)_2PCl_2$ (**10**) and $[R_{f8}(CH_2)_2]_2PCl$ (**11**) cleanly and rapidly formed, as assayed by ^{31}P NMR.

Work-up of the first reaction gave **10** as a colorless oil that was pure by ^{1}H, ^{13}C, and ^{31}P NMR. THF and $CF_3C_6F_{11}$ solutions did not show any decomposition over the course of 2 d under argon. When **10** was allowed to partition between equal volumes of THF and $CF_3C_6F_{11}$, significant quantities remained in THF, reflecting diminished fluorophilicity as compared to the compounds in Table 2 with two perfluoroalkyl segments. As expected, the ^{31}P NMR signal ($\delta = 185.1-189.1$) was far downfield of that of the precursor **2** ($\delta = -138.1$), and other NMR trends are analyzed elsewhere.[18]

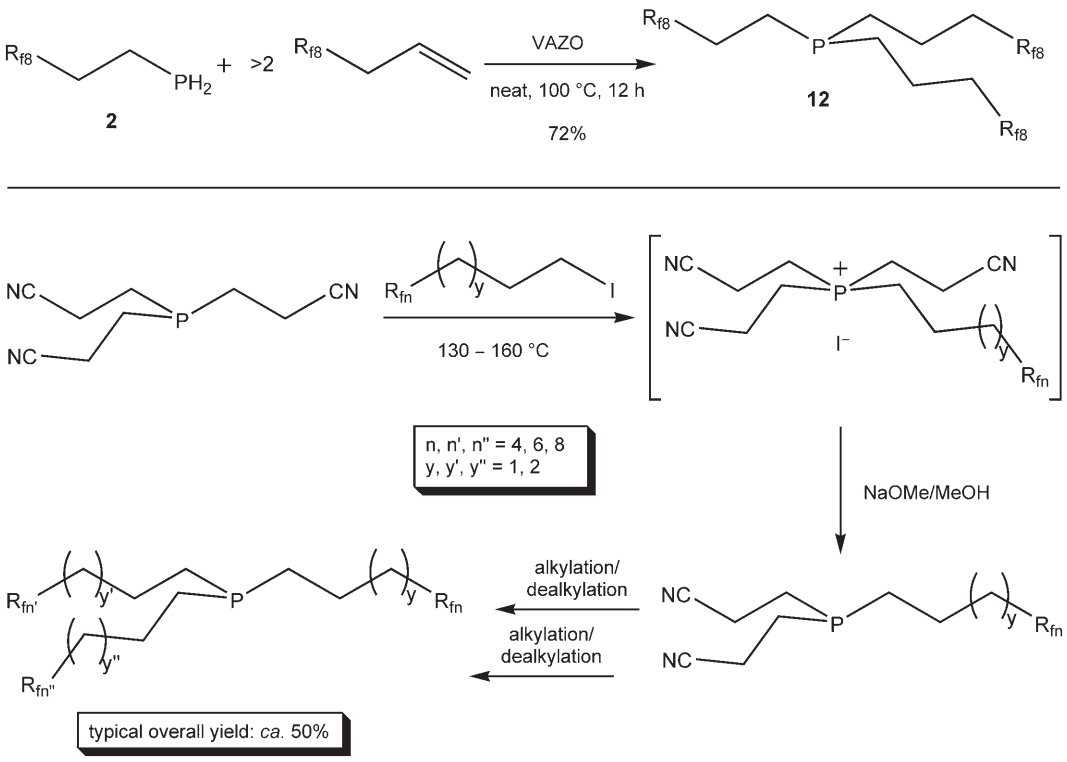
In contrast, THF solutions of **11** decomposed within 1 h under argon, giving voluminous white precipitates. When the THF was quickly removed at room temperature, a very sensitive white solid was obtained that was soluble in $CF_3C_6F_{11}$. Alternatively, when equimolar volumes of $CF_3C_6F_{11}$ were added to THF solutions of **11**, complete extraction occurred. The $CF_3C_6F_{11}$ solutions of **11** were stable for 4 d under argon at room temperature.

Discussion

The new syntheses of fluorous secondary and chiral-at-phosphorus tertiary phosphines described above nicely complement other methodologies reported earlier. First, as shown in Scheme 5 (*top*), the fluorous primary phosphine **2** has previously been reacted with an excess of the fluorous alkene $R_{f8}CH_2CH{=}CH_2$ under conditions similar to those in Schemes 2 and 3.[11b] This afforded the achiral tertiary phosphine $[R_{f8}(CH_2)_2][R_{f8}(CH_2)_3]_2P$ (**12**, 72%), in which two of the phosphorus substituents contain *three* methylene groups. Similar reactions were conducted with the related primary phosphines $R_{f8}(CH_2)_mPH_2$ and alkenes $R_{f8}(CH_2)_{m'}CH{=}CH_2$ (m/m′ = 3/0, 3/2, 4/1), giving other tertiary phosphines in comparable yields.

Analogous reactions of PH_3 with excesses of fluorous alkenes $R_{f8}(CH_2)_{m'}CH{=}CH_2$ (m′ = 0–3) afford the symmetrical tertiary phosphines $[R_{fn}(CH_2)_m]_3P$ (m = 2–5).[11a, b] These results indicate that it should be possible to employ fluorous alkenes with methylene spacer segments (m′ = 1–3) in Schemes 2 and 3. Single and twofold additions of *non-fluorous* primary phosphines to fluorous alkenes have also been described.[11c,22] Hence, analogous additions of fluorous primary phosphines with three or more methylene groups, which are readily available *via* Scheme 1 and other methods,[11b,13] are certain to be successful.

Horváth has recently reported a complementary modular approach to fluorous tertiary phosphines, including chiral-at-phosphorus species.[10c] His protocol starts from commercially available $P(CH_2CH_2CN)_3$ and features three consecutive alkylation/dealkylation sequences. As depicted in Scheme 5 (*bottom*), reactions with fluorous primary iodides with three or more methylene groups at elevated temperatures give phosphonium salts; additions of NaOMe then afford 3-methoxypropionitrile and regenerate tertiary phosphines. Fluorous primary iodides with two methylene groups are much weaker alkylating agents, and any limitations here would prevent access to targets of the type **9**. However, this might be circumvented with more electrophilic $R_{fn}(CH_2)_2X$ species.



Scheme 5. Other modular syntheses of tertiary phosphines.

Another advantage of the phosphine syntheses in Schemes 2 and 3 is their perfect atom economy. However, the yields, while good, are admittedly not quantitative. In this context, fluorous chemistry is often complicated by work-up and separation issues that have no counterpart in non-fluorous chemistry. On a laboratory scale, it is much more important that the by-products be easy to remove. In Scheme 2, the key to success is their substantially different volatilities. In some of the syntheses, differential solubilities can also be exploited.

As summarized in Table 2, the $CF_3C_6F_{11}$/toluene partition coefficients of the new phosphines show the expected dependencies upon the numbers and lengths of the ponytails.[25] Those of the R_{f6}/R_{f8} secondary phosphines **4**, **5**, and **7** (91.9:8.1 to 99.5:0.5; entries 4–6) are intermediate between those of the corresponding primary phosphines (53:47 to 64:36; entries 1 and 2) and tertiary phosphines (98.8:1.2 to $>$99.7:$<$0.3; entries 9 and 10). The partition coefficient of **5** is also quite close to that of the related thioether, $[R_{f8}(CH_2)_2]_2S$ (99.5:0.5 *vs.* 98.7:1.3).[25,26] With the R_{f8}/R_{f10} fluorous secondary phosphines **8** and **6**, the quantities remaining in the toluene phase can no longer be detected by GC ($>$99.7:$<$0.3; entries 7 and 8). The tertiary phosphine **9** (entry 12) behaves similarly. Thus, the fluorous phase affinities – as well as the absolute solubilities – of the title compounds can be fine-tuned, which augers well for applications in catalysis.

Conclusion

Convenient, general, and easily scalable syntheses of fluorous secondary phosphines $[R_{fn}(CH_2)_2][R_{fn'}(CH_2)_2]PH$ from fluorous primary phosphines and terminal alkenes have been developed. The secondary phosphines can be elaborated to chiral-at-phosphorus tertiary phosphines, phosphine boranes, and other derivatives. These sequences are especially attractive in view of a new route to fluorous primary phosphines that avoids the use PH_3.[13] Taken together with other literature procedures,[10c,11] convenient syntheses of unbranched fluorous aliphatic phosphines $[R_{fn}(CH_2)_m][R_{fn'}(CH_2)_{m'}][R_{fn''}(CH_2)_{m''}]$ of every conceivable substitution pattern (n = or ≠ n′ = or ≠ n″, etc.) are now available, with the proviso that the insulating spacers consist of at least two methylene groups (m, m′, m″ $\geq$ 2). Applications of the new phosphines in the synthesis of pincer ligands[22] and achiral and chiral fluorous phosphonium salts[18,27] will be reported in the near future.

Experimental Section

General

Reactions were conducted under N_2 atmospheres unless noted. Chemicals were treated as follows: THF and toluene, distilled

from Na/benzophenone; $CF_3C_6H_5$ (ABCR, 99%), distilled and freeze/pump/thaw degassed (3 ×); $CF_3C_6F_{11}$ (ABCR, 90%), distilled from CaH_2; $CDCl_3$ (Deutero GmbH, 99.8%), DMSO-d_6 (Deutero GmbH, 99.0%), THF-d_8 (Acros, 99.5%), C_6F_6 (Aldrich, 99.5+%), AIBN (Merck, >98%), VAZO (Fluka, ⩾97%), $R_{fn}CH{=}CH_2$ (Lancaster or Apollo, 97–99%), $(CCl_3O)_2CO$ (Aldrich, 98%), $LiAlH_4$ (Acros, 95%) and $THF \cdot BH_3$ (Aldrich, 1.0 M in THF), used as received.

NMR spectra were recorded on standard 300/400 MHz spectrometers at 27.0 °C and referenced as follows: ^1H, residual internal $CHCl_3$ (δ = 7.24), THF-d_7 (δ = 3.58), or DMSO-d_5 (δ = 2.49); ^{13}C, internal $CDCl_3$ (δ = 77.0), THF-d_8 (δ = 25.5), or DMSO-d_6 (δ = 39.7); ^{31}P, external H_3PO_4 (δ = 0.00); ^{19}F, internal C_6F_6 (δ = −162.0). The extensively coupled ^{13}C signals of the fluorinated carbons are not listed below. IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. DSC data were recorded with a Mettler-Toledo DSC821 apparatus and treated by standard methods.[28] Gas chromatography was conducted on a ThermoQuest Trace GC 2000 instrument. Elemental analyses were conducted on a Carlo Erba EA1110 instrument.

$[R_{f6}(CH_2)_2]_2PH$ (4)

A round-bottom flask was fitted with an N_2 inlet and a condenser and charged with $R_{f6}(CH_2)_2PH_2$ (**1**;[13] 0.500 g, 1.32 mmol), $R_{f6}CH{=}CH_2$ (0.455 g, 1.32 mmol), AIBN (0.026 g, 0.16 mmol), and THF (6.0 mL). The mixture was refluxed for 2 d, and allowed to cool. The solvent was removed under reduced pressure and the colorless oily residue distilled (Kugelrohr). Compound **4** was collected as a white solid; yield: 0.529 g (0.729 mmol, 55%); mp 32 °C (capillary), 29.7 °C (DSC, T_e); bp 135 °C/0.034 Torr; anal. calcd. for $C_{16}H_9F_{26}P$: C 26.46, H 1.25; found: C 26.21, H, 1.37; IR (powder film): ν = 2279 (w), 1208 (s), 1140 cm^{-1} (s); ^1H NMR (THF-d_8): δ = 3.30 (d of pseudoquint, $^1J_{HP}$ = 198 Hz, 1H, P*H*), 2.53–2.23 (m, 4H, C$H_2$$CF_2$), 2.09–1.75 (dm, 4H, PC$H_2$); $^{13}C\{^1H\}$ NMR (THF-d_8): δ = 30.7 (dt, $^2J_{CP}$ = 14 Hz, $^2J_{CF}$ = 22 Hz, *C*$H_2$$CF_2$), 11.4 (d, $^1J_{CP}$ = 13 Hz, P*C*H_2); ^{31}P NMR (THF-d_8): δ = −67.3 (d, $^1J_{PH}$ = 198 Hz); ^{19}F NMR (THF-d_8): δ = −77.2 (t, $^4J_{FF}$ = 10 Hz, 6F, C*F*$_3$),[29] −110.7 (pseudoquint, 4F), −117.8 (m, 4F), −118.8 (m, 4F), −119.3 (m, 4F), −122.2 (m, 4F); MS (positive FAB, 3-NBA): *m*/*z* = 743 ($[M+H+O]^+$, 100%), 727 ($[M+H]^+$, 21%).

$[R_{f8}(CH_2)_2]_2PH$ (5)

Method A: The phosphine $R_{f8}(CH_2)_2PH_2$ (**2**;[13] 1.000 g, 2.083 mmol), $R_{f8}CH{=}CH_2$ (0.929 g, 2.08 mmol), AIBN (0.041 g, 0.25 mmol), and THF (10.0 mL) were combined in a procedure analogous to that for **4**. An identical work-up gave **5** as a white solid; yield: 1.119 g (1.208 mmol, 58%); mp 97 °C (capillary), 79.7 °C (DSC, T_e); bp 165 °C/0.044 Torr; anal. calcd. for $C_{20}H_9F_{34}P$: C 25.94, H 0.98; found: C 26.00, H 0.81; IR (powder film): ν = 2277 (w), 1197 (s), 1146 cm^{-1} (s); ^1H NMR (THF-d_8): δ = 3.31 (d of pseudoquint, $^1J_{HP}$ = 198 Hz, 1H, P*H*), 2.47–2.30 (m, 2H, C$H_2$$CF_2$), 2.05–1.75 (dm, 4H, PC$H_2$); $^{13}C\{^1H\}$ NMR (THF-d_8): δ = 30.7 (dt, $^2J_{CP}$ = 14 Hz, $^2J_{CF}$ = 22 Hz, *C*$H_2$$CF_2$), 11.4 (d, $^1J_{CP}$ = 13 Hz, P*C*H_2); ^{31}P NMR (THF-d_8): δ = −67.4 (d, $^1J_{PH}$ = 198 Hz); ^{19}F NMR (THF-d_8): δ = −77.2 (t, $^4J_{FF}$ = 10 Hz, 6F, C*F*$_3$),[29] −110.7 (pseudoquint, 4F), −117.8 (m, 12F), −118.6 (m, 4F), −119.2 (m, 4F), −122.2 (m, 4F); MS (positive FAB, 3-NBA): *m*/*z* = 942 ($[M+O]^+$, 100%), 926 ($[M]^+$, 3%).

Method B (representative large-scale synthesis): A Schlenk flask was charged with $R_{f8}(CH_2)_2P(O)(OC_2H_5)_2$ (10.405 g, 17.812 mmol)[13] and THF (300 mL), and cooled to 0 °C. Solid $LiAlH_4$ (1.040 g, 27.39 mmol) was added in three portions with stirring. The mixture was stirred at room temperature for 16 h, and cooled again to 0 °C. Water was slowly added with stirring until a white precipitate had formed. The THF layer was separated, and the precipitate was extracted with THF (3 × 30 mL). The combined THF layers were dried ($MgSO_4$) and filtered. The filtrate was distilled under oil pump vacuum to give a colorless THF solution of **2**. Then $R_{f8}CH{=}CH_2$ (7.217 g, 16.16 mmol) and AIBN (0.735 g, 4.48 mmol) were added. The mixture was placed in an 80 °C bath. After 16 h (reflux with stirring), the mixture was cooled. A ^{31}P NMR spectrum showed a 55% conversion of **2** to **5** and the tertiary phosphine $[R_{f8}(CH_2)_2]_3P$ (*ca.* 44:53:3). The solvent and unreacted **2** were removed under reduced pressure to give **5** (7.120 g, 7.688 mmol, 43%) as a white solid. Then $R_{f8}CH{=}CH_2$ (3.600 g, 8.060 mmol) and AIBN (0.410 g, 2.50 mmol) were added to the distillate. The mixture was placed in an 80 °C bath. After 16 h (reflux with stirring), the mixture was cooled. A ^{31}P NMR spectrum showed a 78% conversion of **2**. The solvent and unreacted **2** were removed under reduced pressure to give **5** (3.020 g, 3.261 mmol, 18%) as a white solid (total for two crops: 10.140 g, 10.949 mmol, 61% containing traces of **2** and *ca.* 2% of the tertiary phosphine).

$[R_{f10}(CH_2)_2]_2PH$ (6)

The phosphine $R_{f10}(CH_2)_2PH_2$ (**3**;[13] 0.553 g, 0.953 mmol), $R_{f10}CH{=}CH_2$ (0.520 g, 0.952 mmol), AIBN (0.019 g, 0.12 mmol), and THF (8.0 mL) were combined in a procedure analogous to that for **4**. An identical work-up gave **6** as a white solid; yield: 0.567 g (0.504 mmol, 53%); mp 123 °C (capillary), 116.7 °C (DSC, T_e); bp 210 °C/0.027 Torr; anal. calcd. for $C_{24}H_9F_{42}P$: C 25.60, H 0.81; found: C 25.24, H, 0.70; IR (powder film): ν = 2285 (w), 1200 (s), 1146 cm^{-1} (s); ^1H NMR ($CF_3C_6F_{11}+CDCl_3$ capillary): δ = 3.11 (d of pseudoquint, $^1J_{HP}$ = 191 Hz, 1H, P*H*), 2.25–1.99 (m, 4H, C$H_2$$CF_2$), 1.93–1.54 (dm, 4H, PC$H_2$); $^{13}C\{^1H\}$ NMR ($CF_3C_6F_{11}+CDCl_3$ capillary): δ = 29.6 (dt, $^2J_{CP}$ = 14 Hz, $^2J_{CF}$ = 24 Hz, *C*$H_2$$CF_2$), 9.8 (d, $^1J_{CP}$ = 13 Hz, P*C*H_2); ^{31}P NMR ($CF_3C_6F_{11}+CDCl_3$ capillary): δ = −66.9 (d, $^1J_{PH}$ = 191 Hz); ^{19}F NMR [$CF_3C_6H_5+CDCl_3$ (3 drops)]: δ = −77.4 (t, $^4J_{FF}$ = 10 Hz, 6F, C*F*$_3$),[29] −111.0 (pseudoquint, 4F), −117.8 (m, 20 F), −118.8 (m, 4F), −119.4 (m, 4F), −122.3 (m, 4F); MS (positive FAB, 3-NBA, peaks > 700): *m*/*z* = 1143 ($[M+H+O]^+$, 100%), 1127 ($[M+H]^+$, 81%).

$[R_{f6}(CH_2)_2][R_{f8}(CH_2)_2]PH$ (7)

The phosphine **2** (1.000 g, 2.083 mmol),[13] $R_{f6}CH{=}CH_2$ (0.721 g, 2.08 mmol), AIBN (0.041 g, 0.25 mmol), and THF (22.0 mL) were combined in a procedure analogous to that for **4**. An identical work-up gave **7** as a white solid; yield: 0.897 g (1.09 mmol, 52%); mp 73 °C (capillary), 50.4 °C (DSC, T_e); bp 150 °C/0.0075 Torr; anal. calcd. for $C_{18}H_9F_{30}P$: C 26.17, H 1.10; found: C 26.03, H 1.06; IR (powder film): ν = 2275 (w), 1194 (s), 1142 cm^{-1} (s); ^1H NMR (THF-d_8): δ = 3.31 (d of pseudoquint,

$^1J_{HP}$ = 198 Hz, 1H, P*H*), 2.48–2.27 (m, 4H, CH_2CF$_2$), 2.06–1.73 (dm, 4 H, PCH_2); ^{13}C{^{1}H} NMR (THF-d_8): δ = 30.7 (dt, $^2J_{CP}$ = 14 Hz, $^2J_{CF}$ = 23 Hz, *C*H$_2$CF$_2$), 11.4 (d, $^1J_{CP}$ = 13 Hz, P*C*H$_2$); ^{31}P NMR (THF-d_8): δ = −67.4 (d, $^1J_{PH}$ = 198 Hz); ^{19}F NMR (THF-d_8): δ = −77.2 (t, $^4J_{FF}$ = 10 Hz, 6F, C*F*$_3$),[29] −110.8 (m, 4F), −117.8 (m, 8F), −118.8 (m, 4F), −119.2 (m, 4F), −122.2 (m, 4F); MS (positive FAB, 3-NBA, peaks > 600): *m/z* = 843 ([M + H + O]$^+$, 51%), 827 ([M + H]$^+$, 16%).

[$R_{f8}(CH_2)_2$][$R_{f10}(CH_2)_2$]PH (8)

The phosphine **3** (0.500 g, 0.862 mmol),[13] R_{f8}CH=CH$_2$ (0.384 g, 0.861 mmol), AIBN (0.017 g, 0.10 mmol), and THF (14.0 mL) were combined in a procedure analogous to that for **4**. An identical work-up gave **8** as a white solid; yield: 0.447 g (0.436 mmol, 51%); mp 101 °C (capillary), 89.9 °C (DSC, T_e); bp 205 °C/0.20 Torr; anal. calcd. for $C_{22}H_9F_{38}P$: C 25.75, H 0.88; found: C 25.77, H 0.95; IR (powder film): ν = 2286 (w), 1198 (s), 1146 cm^{-1} (s); ^{1}H NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): δ = 3.11 (d of pseudoquint, $^1J_{HP}$ = 191 Hz, 1H, P*H*), 2.23–1.95 (m, 4H, CH_2CF$_2$), 1.92–1.55 (dm, 4H, PCH_2); ^{13}C{^{1}H} NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): δ = 29.6 (dt, $^2J_{CP}$ = 15 Hz, $^2J_{CF}$ = 24 Hz, *C*H$_2$CF$_2$), 9.8 (d, $^1J_{CP}$ = 13 Hz, P*C*H$_2$); ^{31}P NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): δ = −67.0 (d, $^1J_{PH}$ = 191 Hz); ^{19}F NMR [$CF_3C_6H_5$ + $CDCl_3$ (3 drops)]: δ = −77.4 (t, $^4J_{FF}$ = 9 Hz, 6F, C*F*$_3$),[29] −111.0 (m, 4F), −117.8 and −117.9 (2 m, 16F), −118.8 (m, 4 F), −119.4 (m, 4 F), −122.4 (m, 4 F); MS (positive FAB, 3-NBA, peaks > 700): *m/z* = 1043 ([M + H + O]$^+$, 100%), 1027 ([M + H]$^+$, 70%).

[$R_{f6}(CH_2)_2$][$R_{f8}(CH_2)_2$][$R_{f10}(CH_2)_2$]P (9)

A 4-mL vial was charged with **7** (0.450 g, 0.545 mmol), R_{f10}CH=CH$_2$ (0.595 g, 1.09 mmol), and VAZO (0.013 g, 0.054 mmol). The mixture was stirred at 100 °C for 20 h and cooled. Volatiles were removed by oil pump vacuum. Then $CF_3C_6H_5$ (3.0 mL) was added to the brown oily residue. The sample was filtered through SiO_2 (7.4 g, 2.3 Ø cm) with $CF_3C_6H_5$ (80.0 mL). The solvent was removed by oil pump vacuum and the residue distilled (Kugelrohr). This gave **9** as a white solid; yield: 0.498 g (0.363 mmol, 67%); mp 50 °C (capillary), 43.4 °C (DSC, T_e); bp 215 °C/0.0090 Torr; anal. calcd. for $C_{30}H_{12}F_{51}P$: C 26.26, H 0.88; found: C 26.56, H, 0.96; IR (powder film): ν = 1198 (s), 1142 cm^{-1} (s); ^{1}H NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): δ = 2.11 (m, CH_2CF$_2$, 6H), 1.62 (m, PCH_2, 6H); ^{13}C{^{1}H} NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): δ = 27.2 (dt, $^2J_{CP}$ = 20 Hz, $^2J_{CF}$ = 22 Hz, *C*H$_2$CF$_2$), 16.1 (d, $^1J_{CP}$ = 16 Hz, P*C*H$_2$); ^{31}P NMR ($CF_3C_6F_{11}$ + $CDCl_3$ capillary): δ = −25.3 (s); ^{19}F NMR ($CF_3C_6H_5$ + $CDCl_3$ capillary): δ = −80.0 (t, $^4J_{FF}$ = 10 Hz, 9F, C*F*$_3$),[29] −113.6 (m, 6F), −120.4 (m, 18F), −121.4 (m, 6F), −121.9 (m, 6F), −124.9 (m, 6F); MS (positive FAB, 3-NBA): *m/z* = 1389 ([M + H + O]$^+$, 68%), 1373 ([M + H]$^+$, 32%).

[$R_{f8}(CH_2)_2$]$_2$PH·BH_3 (5·BH_3)

A Schlenk flask was charged with **5** (1.228 g, 1.326 mmol) and THF (75 mL). Then BH_3 (1.0 M in THF; 3.40 mL, 3.40 mmol) was slowly added with stirring. After 1 h, the mixture was filtered through a silica gel plug (1 × 2.5 cm) that was rinsed with THF (40 mL). The solvent was removed from the filtrate by oil pump vacuum and the residue dried for an additional hour to give **5**·BH_3 as a white powder; yield: 1.188 g (1.263 mmol, 95%); mp 127 °C (capillary); anal. calcd. for $C_{20}H_{12}BF_{34}P$: C 25.53, H 1.27; found: C 25.47; H 1.25; ^{1}H NMR (THF-d_8): δ = 2.52 (m, 4H, CH_2CF$_2$), 2.26 (m, 2H, PCH*H*′), 2.08 (m, 2H, PC*H*H′), 1.76 (br m, 3H, BH_3), 1.67 (apparent s, 1H, P*H* partially obscured by THF-d_8); ^{13}C{^{1}H} NMR (THF-d_8): δ = 26.8 (t, $^2J_{CF}$ = 21 Hz, $CH_2CH_2CF_2$), 12.4 (d, $^1J_{CP}$ = 37 Hz, $CH_2CH_2CF_2$); ^{31}P{^{1}H} NMR (THF-d_8): δ = −5.4 (br s); MS (positive FAB, 3-NBA): *m/z* = 943 ([M]$^+$, 60%), 927 ([M − BH_3]$^+$, 40%), 525 ([M − R_{f8}]$^+$, 100%), 513 ([M − R_{f8} − BH_3]$^+$, 45%), 497 ([M − $CH_2CH_2R_{f8}$]$^+$, 90%).

$R_{f8}(CH_2)_2PCl_2$ (10)

A 10-mL vial was charged with **2** (0.070 g, 0.14 mmol) and THF (1.00 mL) under argon. Then $(CCl_3O)_2CO$ (0.029 g, 0.098 mmol) was added, and gas evolution began. The solution was stirred for 21 h. The solvent was removed by oil pump vacuum to give **10** as a colorless oil, which was dissolved in $CF_3C_6F_{11}$ and characterized by NMR. In independent experiments, **10** showed no decomposition over the course of 48 h in $CF_3C_6F_{11}$ or THF, as assayed by ^{31}P NMR. ^{1}H NMR ($CF_3C_6F_{11}$ + DMSO-d_6, capillary): δ = 1.94–1.86 and 1.80–1.72 (2 m, PCH_2CH_2); ^{13}C{^{1}H} NMR ($CF_3C_6F_{11}$ + DMSO-d_6, capillary): δ = 30.8 (d, $^1J_{CP}$ = 46 Hz, P*C*H$_2$), 23.5 (dt, $^2J_{CP}$ = 11 Hz, $^2J_{CF}$ = 23 Hz, *C*H$_2$CF$_2$); ^{31}P NMR ($CF_3C_6F_{11}$ + DMSO-d_6, capillary): δ = 185.1 (s); ^{31}P NMR (THF-d_8): δ = 189.1 (s).

[$R_{f8}(CH_2)_2$]$_2$PCl (11)

A 10-mL vial was charged with **5** (0.050 g, 0.054 mmol) and THF-d_8 (2.00 mL) under argon. Then $(CCl_3O)_2CO$ (0.006 g, 0.02 mmol) was added, and gas evolution began. The solution was stirred for 10 min. A ^{31}P NMR spectrum of an aliquot showed the complete conversion of **5** to **11**. The solvent was removed by oil pump vacuum to give **11** as a white solid. The NMR tube with the aliquot was kept for 1 h in a glove box. A white, voluminous precipitate formed that was soluble in $CF_3C_6F_{11}$. No signals for **11** were detected. In contrast, $CF_3C_6F_{11}$ solutions of **11** (generated by extraction of THF solutions) showed no decomposition over 4 d. ^{31}P NMR (THF-d_8 or $CF_3C_6F_{11}$ + DMSO-d_6, capillary): δ = 107.9 (s) or 104.6 (s)

Partition Coefficients

The following is representative of entries 4–8 and 12 of Table 2. A 4-mL vial was charged with **4** (0.0218 g, 0.0300 mmol), $CF_3C_6F_{11}$ (2.000 mL), toluene (2.000 mL), and a stir bar. It was tightly sealed, vigorously shaken (5 min), and vigorously stirred (1 h).[30] After 12–24 h (25 °C) aliquots (0.500 mL) were taken from both phases. Then aliquots of a solution of tridecane (0.0474 g, 0.257 mmol; internal standard) in $CF_3C_6H_5$ (29.2505 g) were added gravimetrically ($CF_3C_6F_{11}$ phase: 0.5869 g solution, 0.005150 mmol tridecane; toluene phase: 0.5832 g solution, 0.005118 mmol tridecane). The samples were diluted with $CF_3C_6H_5$ (0.600 mL) and analyzed by GC (5 or 6 injections each). The procedure was repeated and the result averaged.

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References and Notes

[1] I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72.
[2] *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**.
[3] *Green Reaction Media in Organic Synthesis*, (Ed.: K. Mikami), Blackwell, Oxford, **2005**, Chap. 3.
[4] Review of syntheses: E. G. Hope, A. M. Stuart, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, Chap. 10.7.
[5] R. C. da Costa, J. A. Gladysz, in: *Transition Metals for Organic Synthesis*, 2nd edn., (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**, Chap. 3.2.
[6] a) S. Schneider, C. C. Tzschucke, W. Bannwarth, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, Chap. 10.8; b) E. G. Hope, A. M. Stuart, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, Chap. 10.9; c) E. Monflier, A. Mortreux, Y. Castanet, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, Chap. 10.10; d) S. Takeuchi, Y. Nakamura, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, Chap. 10.14.
[7] a) M. Wende, J. A. Gladysz, *J. Am. Chem. Soc.* **2003**, *125*, 5861; b) F. Seidel, *Diplom Thesis*, Universität Erlangen-Nürnberg, **2004**; c) A. Scherer, *Diplom Thesis*, Universität Erlangen-Nürnberg, **2005**.
[8] a) P. I. Dalko, L. Moisan, *Angew. Chem. Int. Ed.* **2004**, *43,* 5138; *Angew. Chem.* **2004**, *116*, 5248, and references cited therein; b) *Asymmetric Organocatalysis*, (Eds.: A. Berkessel, H. Gröger), Wiley-VCH, Weinheim, **2005**.
[9] J. L. Methot, W. R. Roush, *Adv. Synth. Catal.* **2004**, *346*, 1035.
[10] For literature since the publication of ref.[4] see a) E. de Wolf, E. Riccomagno, J. J. M. de Pater, B.-J. Deelman, G. van Koten, *J. Comb. Chem.* **2004**, *6*, 363; b) E. G. Hope, A. M. Stuart, A. J. West, *Green Chem.* **2004**, *6*, 345; c) G. Vlád, F. Richter, I. T. Horváth, *Org. Lett.* **2004**, *6,* 4559.
[11] a) L. J. Alvey, D. Rutherford, J. J. J. Juliette, J. A. Gladysz, *J. Org. Chem.* **1998**, *63*, 6302; b) L. J. Alvey, R. Meier, T. Soós, P. Bernatis, J. A. Gladysz, *Eur. J. Inorg. Chem.* **2000**, 1975; c) A. Klose, J. A. Gladysz, *Tetrahedron: Asymmetry* **1999**, *10*, 2665.
[12] a) *Encyclopedia of Inorganic Chemistry*, (Ed.: R. B. King), John Wiley & Sons, New York, **1994**, Vol. 6, p. 3160; b) *Dictionary of Inorganic Compounds*, Chapman & Hall, New York, **1992**, Vol. 3, p. 3386; c) A. D. F. Toy, in: *Comprehensive Inorganic Chemistry*, (Eds.: J. C. Bailar Jr., H. J. Emeléus, R. Nyholm, A. F. Trotman-Dickenson), Pergamon, Oxford, **1973**, Vol. 2, p. 414.
[13] C. Emnet, J. A. Gladysz, *Synthesis* **2005**, 1012.
[14] A. K. Bhattacharya, G. Thyagarajan, *Chem. Rev.* **1981**, *81*, 415.
[15] a) D. G. Gusev, M. Madott, F. M. Dolgushin, K. A. Lyssenko, M. Y. Antipin, *Organometallics* **2000**, *19*, 1734; b) E. Hollink, J. C. Stewart, P. Wei, D. W. Stephan, *Dalton Transactions* **2003**, 3968; c) J. C. Grimm, C. Nachtigal, H.-G. Mack, W. C. Kaska, H. A. Mayer, *Inorg. Chem. Commun.* **2000**, *3*, 511; d) H. A. Y. Mohammad, J. C. Grimm, K. Eichele, H.-G. Mack, B. Speiser, F. Novak, M. G. Quintanilla, W. C. Kaska, H. A. Mayer, *Organometallics* **2002**, *21*, 5775; e) D. Hermann, M. Gandelman, H. Rozenberg, L. J. W. Shimon, D. Milstein, *Organometallics* **2002**, *21*, 812.
[16] Abbreviations: AIBN = 2,2′-azobis(isobutyronitrile); VAZO = 2,2′-azobis(cyclohexanecarbonitrile).
[17] a) J. A. Gladysz, R. C. da Costa, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, Chap. 4.5.1; b) K. Ishihara, H. Yamamoto, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, Chap. 10.18.
[18] C. Emnet, *Doctoral Dissertation*, Universität Erlangen-Nürnberg, **2005**.
[19] a) M. Ohff, J. Holz, M. Quirmbach, A. Börner, *Synthesis* **1998**, 1391; b) J. M. Brunel, B. Faure, M. Maffei, *Coord. Chem. Rev.* **1998**, *178–180*, 665. c) B. Carboni, L. Monnier, *Tetrahedron* **1999**, *55*, 1197.
[20] H. Jiao, S. Le Stang, T. Soós, R. Meier, K. Kowski, P. Rademacher, L. Jafarpour, J.-B. Hamard, S. P. Nolan, J. A. Gladysz, *J. Am. Chem. Soc.* **2002**, *124*, 1516.
[21] F. Langer, K. Püntener, R. Stürmer, P. Knochel, *Tetrahedron: Asymmetry* **1997**, *8*, 715.
[22] R. Tuba, V. Tesevic, L. V. Dinh, F. Hampel, J. A. Gladysz, *Dalton Transactions* **2005**, 2275.
[23] L. Cotarca, P. Delogu, A. Nardelli, V. Sunjic, *Synthesis* **1996**, 553.
[24] a) L. Dahlenburg, A. Kaunert, *Eur. J. Inorg. Chem.* **1998**, 885; b) L. Dahlenburg, German Patent 19,732,805 (filed July 30, 1997); *Chem. Abstr.* **1999**, *130*, 168481; c) L. Dahlenburg, V. Kurth, *Eur. J. Inorg. Chem.* **1998**, 597.
[25] J. A. Gladysz, C. Emnet, J. Rábai, in: *Handbook of Fluorous Chemistry*, (Eds.: J. A. Gladysz, D. P. Curran, I. T. Horváth), Wiley-VCH, Weinheim, **2004**, pp. 56–100.
[26] C. Rocaboy, J. A. Gladysz, *Tetrahedron* **2002**, *58*, 4007.
[27] C. Emnet, J. A. Gladysz, manuscript in preparation.
[28] H. K. Cammenga, M. Epple, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1171; *Angew. Chem.* **1995**, *107*, 1284.
[29] A reviewer has noted that the triplets of the CF_3 groups represent $^4J_{FF}$ and not $^3J_{FF}$ values, as reported in some of our earlier papers,[11b,13,26] see: a) H. F. White, *Anal. Chem.* **1966**, *38*, 625; b) A. Foris, *Magn. Reson. Chem.* **2004**, *42*, 534.
[30] In the case of **9**, the sample was vigorously stirred for 12 h at 35 °C.

