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Addition of perfluorooctyl iodide to alkenes. Catalysis by triphenylphosphane

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Abstract—Triphenylphosphane catalyses the addition of perfluorooctyl iodide to linear and cyclic olefines. © 2002 Elsevier Science Ltd. All rights reserved.

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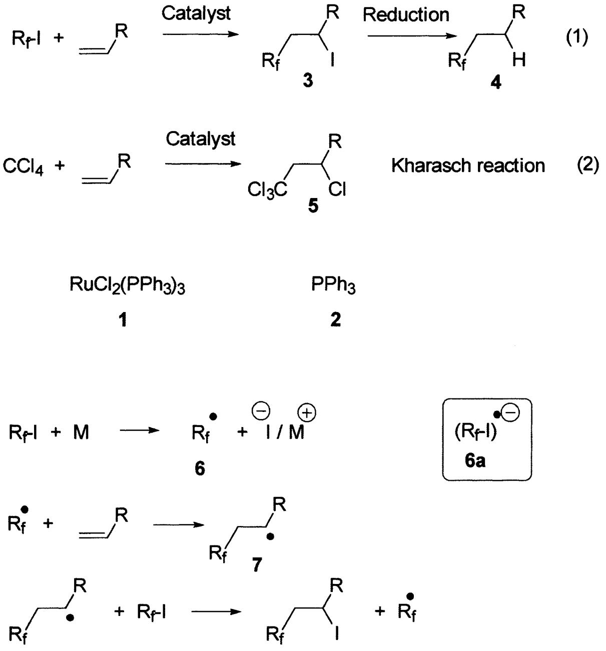
1. Introduction

Per and polyfluorinated organic compounds have exceptional theoretical and practical interest.[1] The addition of perfluoroalkyl iodides to olefins is one of the more useful reactions aimed at the preparation of compounds heavily loaded with fluorine atoms (see (1) in Scheme 1).[2] The reaction is a typical free-radical chain reaction, featuring an initiation step leading to the generation of the R_f radical (**6**) followed by propagation steps.[2,3] Customarily radical-anion **6a** is believed to be an intermediate in the generation of free radical **6**. However, Savéant and co-workers have shown that electron transfer to R_f-I and carbon–iodine bond cleavage are concerted processes leading directly to **6** and iodide anion.[4] Radical **7** can take alternative pathways as, for example, capturing a hydrogen atom from a suitable donor to afford directly the iodine-free compounds **4**.[5] In general compounds **4** are prepared from **3** in an independent reduction step.



Scheme 1. General features of the addition of perfluoroalkyl iodides or tetrachloromethane to olefins.

The addition of perfluoroalkyl iodides to olefins is mechanistically related to the so-called Kharasch reaction, the addition of carbon tetrachloride and other polychlorinated compounds to alkenes (see (2), Scheme 1).[6]

Pioneer work by Brace on the addition of perfluoroalkyl iodides to olefins was performed under a typical free-radical initiator, azobisisobutyronitrile,[2] whereas initial examples of the Kharasch reactions were performed under diacyl peroxides initiation.[6] However, ruthenium(II) chloride tris-(triphenylphosphane) (**1**) has emerged as a very useful catalyst for such a reaction,[7] which occurs by a non-chain sequence involving free-radical intermediates.[7e] Moreover, Grubb's ruthenium carbene and other ruthenium complexes are also active in the Kharasch reaction.[8]

We were surprised by the fact that, in spite of the close mechanistic relationship between both reactions, no examples have been disclosed on the use of **1** as catalyst for the addition of perfluoroalkyl iodides to olefins. However, this addition has been induced or catalyzed by many low-valent metal or transition metal species as well as by other non-metallic sources of radicals, excellent summaries of methods being available.[3]

Keywords: polyfluorinated olefines; catalysis; triphenylphosphane; free radical.

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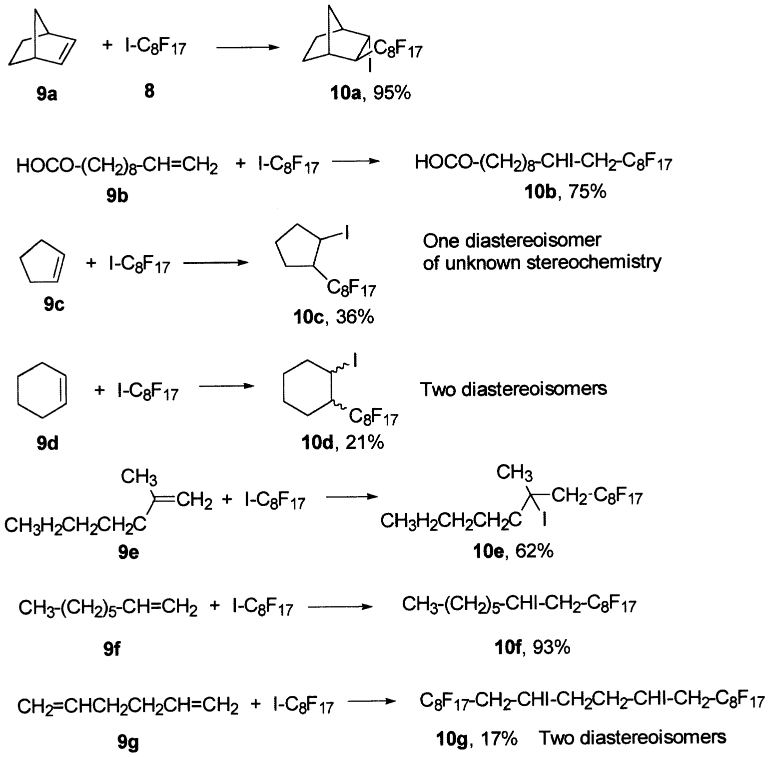
2. Results

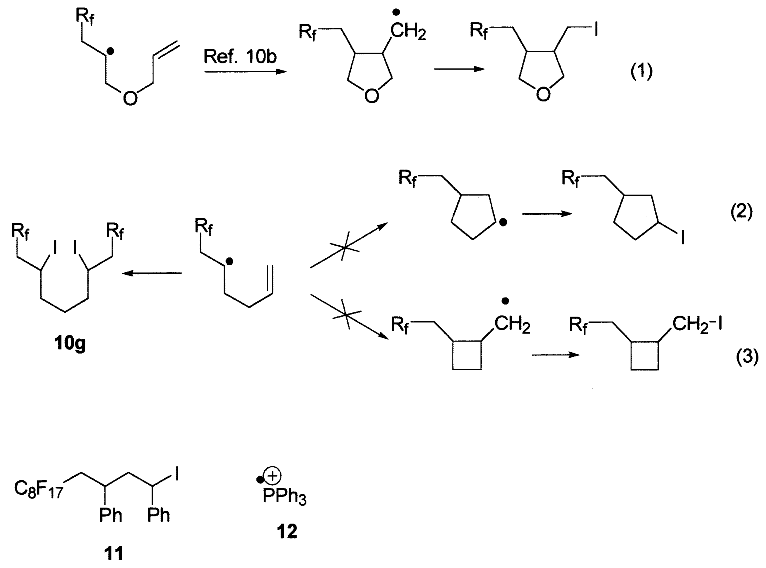
At this point we decided to explore the use of the ruthenium derivative **1**. We have recently found that triphenylphosphane (**2**) is the actual catalyst in the putative catalysis by **1** or by $RuH_2(PPh_3)_4$ for the non-radical conjugate additions of β-dicarbonyl compounds.[9] Our initial studies on the addition of perfluorooctyl iodide (**8**) to olefins catalyzed by **1** were run in parallel with experiments in which only triphenylphosphane **2** was introduced as possible catalyst. To our relative surprise, we immediately realized that **2** catalyzes the addition of **8** to olefins (Scheme 2). A closer scrutiny of the literature revealed also that catalysis by **2** is not without precedent.[10] However, we decided to study further the potential of **2** as catalyst as well as to look at some mechanistic aspects of its behavior.

Our results are in Scheme 2. Monosubstituted olefins react at room temperature with **8** in the presence of only 5% molar **2**. Thus, 10-undecenoic acid (**9b**) and 1-octene (**9f**) afford **10b** and **10f** in good to excellent yields. A 1,1-disubstituted olefin (**9e**) was also active and afforded **10e** in useful yield. An open chain 1,2-disubstituted olefin: *trans*-4-octene, as well as 1*H*,1*H*,2*H*-perfluoro-1-decene, vinyl acetate, and isopropenyl acetate were sluggish and gave no useful reactions. However, cyclic olefins were active enough to afford preparatively useful results. Thus, norbornene (**9a**) gave an excellent yield of (2*RS*,3*SR*)-2-iodo-3-perfluorooctylnorbornane, **10a**. *trans*-Stereochemistry for **10a** was determined by 2D-COSY and 2D-NOESY NMR experiments. This was the only isolated isomer. Monocyclic olefins such as cyclopentene and cyclohexene were less reactive, affording **10c** as one diastereoisomer of unknown stereochemistry, and **10d** as a mixture of diastereoisomers. Using a 18% of catalyst **2** the yield of **10c** increased to 57% working at room temperature for 72 h. Diolefin **9g** posses a problem. It is known that diallyl ether reacts to afford a cyclic tetrahydrofuran derivative by trapping the intermediate secondary radical by the second double bond to afford a primary radical by an 5-*exo*-trig cyclization (see (1), Scheme 3).[10b] In our case trapping the intermediate radical would imply either the formation of a secondary radical in a cyclopentane ring by a disfavored 5-*endo*-trig cyclization step (see (2), Scheme 3) or the formation of a four-membered ring by a favored 4-*exo*-trig cyclization (see (3), Scheme 3). However, no cyclization took place. Instead, formation of **10g** occurred. The low yield of the reaction can be attributed to the use of a defect of **9g** to favor reaction of both olefins. Monitoring of the reaction revealed the saturation of one double bond while the second one was still present. Prolonged reaction time led to the formation of both diastereoisomers **10g** as the only detected reaction products.

Reactions with styrene and with 1,3-cyclohexadiene failed. It seems that intermediate benzylic and allylic radicals **7** are too stable to progress according to the equations of Scheme 1. Only in one case, working under catalysis by ruthenium species **1** we could isolate minor amounts of compound **11** (Scheme 3). This exemplifies another possible pathway for radicals **7**, namely, reaction with a second olefin initiating a polymerization pathway. In any case, the reaction with styrene was erratic and it was given up. The reaction of **9a** with **8** in the presence of one equivalent of distilled styrene did not progress, styrene acting as a radical trap, probably at the level of radical **6**. The same reaction is



Scheme 2. All reactions were performed in acetonitrile at room temperature in the presence of 5% molar **2**. For **10a–f** 2.5-fold molar excess of olefin was used. For **10g**, fourfold molar excess of **8** was used.



Scheme 3.

also stopped in the presence of 1,3-dinitrobenzene, probably by direct electron transfer from **2** to dinitrobenzene.

The simultaneous presence of triphenylphosphane (**2**) and alkyl iodides **10** makes it possible, in principle, the formation of phosphonium salts. However, a mixture of **10f** and **2** in benzene did not give reaction at room temperature or at reflux for 144 h (^{31}P NMR monitoring). More important, the reaction of **8** with **9f** was reproduced in the NMR probe in CD_3CN solvent; ^{31}P NMR monitoring showed that **2** was the only significant phosphorus species detectable (δ ca. 30.6 ppm), only triphenylphosphane oxide (δ ca. 4.1 ppm) appeared slowly as a result of the spurious oxidation of **2**. This is an indication that electron transfer from **2** to **8** is the slow step of the catalytic cycle.

Electron transfer from **2** implies the formation of the radical-cation **12**. This species has been invoked in a number of occasions: in electron transfer to tetracyanoquinodimethane,[11] in the photochemical decomposition of phosphonium salts,[12,13] and in the dediazoniation of arenediazonium salts with triphenylphosphane.[14]

3. Conclusion

Triphenylphosphane is an efficient catalyst for additions of perfluoroalkyl iodides to olefins. Molar percentage of catalysts, temperature, and extraction procedures have been improved with respect to the previously reported.[10] In some cases it has been shown that the putative catalytic action of transition metal complexes is really due to phosphane stabilizing ligands.[9,15–18] This rises a question on the contribution of triphenylphosphane to the proposed catalytic activity of tetrakis(triphenylphosphane)palladium, $Pd(PPh_3)_4$ in the additions of perfluoroalkyl iodides to olefins,[19–21] since it is known that $Pd(PPh_3)_4$ is, in solution, in equilibrium with $Pd(PPh_3)_{4-n}$ and nPPh$_3$.[22]

Moreover, we performed complementary experiments which showed that Kharasch reactions between 1-octene and carbon tetrachloride or carbon tetrabromide did not take place under triphenylphosphane catalysis, in the presence and in the absence of acetonitrile. Therefore, ruthenium species are truly catalysts for the Kharasch reaction. However, phosphorus centered radicals have recently been suggested as intermediates in a Kharasch reaction.[23]

4. Experimental

4.1. (2*RS*,3*SR*)-2-Iodo-3-perfluorooctylnorbornane (10a): typical procedure

A mixture of triphenylphosphane **2** (0.092 g, 0.4 mmol), norbornene **9a** (1.644 g, 17.5 mmol), perfluorooctyl iodide **8** (1.85 mL, 7.0 mmol), and acetonitrile (2.1 mL) was magnetically stirred under argon atmosphere for 48 h. The mixture was evaporated to afford a white solid residue, which was passed through a column of silica gel with acetonitrile as eluent to afford **10a** (4.25 g, 95%), mp 35–36°C (Lit.[24] mp 40–42°C); IR (KBr) 2964, 2873, 1202, 1151, 995 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30–1.35 (m, 2H), 1.60–1.71 (m, 3H), 1.87–1.92 (m, 1H), 2.37–2.44 (dt, $J=11.6$ and 3.9 Hz, 1H), 2.44 (s, 1H), 2.49 (s, 1H), 4.31–4.32 (m, 1H, C*H*I); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 25.9, 27.4, 29.7, 35.0, 37.9, 44.6, 55.7 (t, $J=20$ Hz, *C*HCF$_2$), 109.8–123.0 (*C*$_8$F$_{17}$); MS (*m/z*) 513 (M−I, 100), 115 (28), 77 (20), 67 (25), 41 (35).

4.1.1. 12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluoro-10-iodononadecanoic acid, 10b. Acid **10b** precipitated out after 70 h reaction. It was filtered and recrystallized from acetonitrile to afford 3.81 g (75%) of pure compound: mp 65–68°C (Lit.[25] mp 70–71°C); IR (KBr) 3500–2500, 2928, 2853, 1703, 1202, 1148 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.24–1.40 (m, 10H), 1.63–1.69 (m, 2H), 1.76–1.87 (m, 2H), 2.37 (t, $J=7.0$ Hz, 2H), 2.70–3.03 (m, 2H, C*H*$_2$–CF$_2$), 4.32–4.38 (m, 1H, C*H*I); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 21.2, 25.0, 28.8, 29.3, 29.5, 29.5, 29.9, 34.4, 40.7, 42.1 (t, $J=21$ Hz, *C*H$_2$–CF$_2$), 106.8–119.8 (*C*$_8$F$_{17}$), 180.4.

4.1.2. 1-Iodo-2-perfluorooctylcyclopentane, 10c. This compound was a liquid. Attempted distillation at 0.2 mmHg failed. The liquid was treated with perfluorooctane and the precipitate (phosphorus compounds) was filtered off and washed with more perfluorooctane. The fluorinated solvent phase was evaporated and the residue was pure **10c** (1.57 g, 36%): IR (film) 2971, 1206, 1149 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.82–1.87 (m, 2H), 1.93–2.06 (m, 2H), 2.12–2.24 (m, 2H), 3.21–3.27 (m, 1H, C*H*–CF$_2$), 4.52–4.53 (m, 1H, C*H*–CI); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 18.4, 25.3, 26.3, 41.1, 54.0 (t, *J*=21 Hz, *C*H–CF$_2$), 106.1–124.7 (*C*$_8$F$_{17}$); MS (*m/z*) 487 (M−I, 70), 467 (100), 117 (21), 67 (59), 41 (22). Anal. Calcd for $C_{13}H_8F_{17}I$: C, 25.43; H, 1.31; found: C, 25.37; H, 1.31.

4.1.3. 1-Iodo-2-perfluorooctylcyclohexane, 10d. This compound is a mixture of diastereoisomers (65:35). After evaporation, the liquid residue was treated with cold perfluorooctane (ice bath), the formed solid phase (**2** plus triphenylphosphane oxide) was filtered off, and the solvent was evaporated, then the residue was distilled (75°C/0.26 mmHg) to afford pure **10d** (0.92 g, 21%): IR (film) 2945, 2867, 1452, 1327, 1202, 1149, 964 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.37–1.97 (m, 8H), 2.21–2.26 (m, 1H, C*H*–CF$_2$, major diastereoisomer), 2.64–2.78 (m, 1H, C*H*–CF$_2$, minor diastereoisomer), 4.72 (m, 1H, C*H*I, major diastereoisomer), 4.98–4.99 (m, 1H, C*H*I, minor diastereoisomer); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 21.3, 21.8, 22.0, 22.7, 25.2, 27.3 (t, *J*=4 Hz), 34.7, 37.4, 44.6 (t, *J*=21 Hz, *C*H–CF$_2$, major diastereoisomer), 45.2 (t, *J*=20 Hz, *C*H–CF$_2$, minor diastereoisomer, 103.4–124.6 (*C*$_8$F$_{17}$); MS (*m/z*) 501 (M−I, 9), 131 (40), 81 (100), 41 (95). Anal. Calcd for $C_{14}H_{10}F_{17}I$: C, 26.77; H, 1.60; found: C, 26.60; H, 1.64.

4.1.4. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iodo-10-methyltetradecane, 10e. Isolation of **10e** (1.98 g, 62%) was performed as for **10d**. It was distilled at 64°C/0.19 mmHg: IR (film) 2964, 2938, 2867, 1460, 1207, 1147 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.96 (t, *J*=7.2 Hz, 3H), 1.33–1.59 (m, 4H), 1.74–1.82 (m, 2H), 2.19 (s, 3H), 2.89–3.05 (m, 2H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 13.9, 22.3, 31.1, 36.2, 45.8 (t, *J*=19.7 Hz, *C*H$_2$–CF$_2$), 47.4, 47.8, 110.2–122.8 (*C*$_8$F$_{17}$); MS (*m/z*) 517 (M−I, 7), 69 (22), 57 (37), 55 (32), 43 (100). Anal. Calcd for $C_{15}H_{14}F_{17}I$: C, 27.97; H, 2.19; found: C, 28.08; H, 2.22.

4.1.5. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iodohexadecane, 10f. After evaporation the formed solid (**2** and triphenylphosphane oxide) was filtered off and washed with perfluorohexane. The liquids were evaporated and the residue distilled at 125°C/0.52 mmHg to afford pure **10f** (4.27 g, 93%): IR (film) 2961, 2932, 2861, 1461, 1202, 1153, 1117 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.90 (t, *J*=6.5 Hz, 3H), 1.31–1.50 (m, 8H), 1.75–1.86 (m, 2H), 2.65–3.05 (m, 2H, C*H*$_2$–CF$_2$), 4.29–4.39 (m, 1H, C*H*I); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 13.9, 20.8, 22.6, 28.2, 29.6, 31.6, 40.4, 41.8 (t, *J*=21 Hz, *C*H$_2$–CF$_2$), 106.0–124.6 (*C*$_8$F$_{17}$); MS (*m/z*) 531 (M−I, 7), 489 (23), 57 (100). Anal. Calcd for $C_{16}H_{16}F_{17}I$: C, 29.20; H, 2.45; found: C, 29.10; H, 2.47.

4.1.6. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,15,15,16,16,17,17,18,18,19,19,20,20,21,21,22,22,22-tetratriafluoro-10-13-diododocosane, 10g. For preparation of this compound molar ratio **9g**:**8** was 1:4. After evaporation the formed solid was washed with HFE7100, then with hot acetonitrile, and filtered while hot to afford **10g** (1.425 g, 17%) as a mixture of diastereoisomers: mp 90–91°C (from acetonitrile); IR (KBr) 1202, 1149 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.99–2.27 (m, 4H), 2.75–3.06 (m, 4H, C*H*$_2$-CF$_2$), 4.37–4.41 (m, 2H, C*H*I); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 17.2, 17.5, 40.4, 42.1 (t, *J*=22 Hz, *C*H$_2$–CF$_2$), 42.3 (t, *J*=21 Hz, *C*H$_2$–CF$_2$), 110–130 (*C*$_8$F$_{17}$); Anal. Calcd for $C_{22}H_{10}F_{34}I_2$: C, 22.51; H, 0.86; found: C, 22.55; H, 0.75.

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References

1. For a general monograph on organic compounds heavily loaded with fluorine see: *Organofluorine Chemistry. Principles and Commercial Applications*, Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, 1994.
2. For pioneer work see: (a) Brace, N. O. *J. Org. Chem.* **1971**, *36*, 3187–3191. (b) Brace, N. O. *J. Org. Chem.* **1973**, *38*, 3167–3172.
3. For reviews see: (a) Deev, L. E.; Nazarenko, T. I.; Pashkevich, K. I.; Ponomarev, V. G. *Russ. Chem. Rev.* **1992**, *61*, 40–54. (b) Dolbier Jr., W. R. *Chem. Rev.* **1996**, *96*, 1557–1584. (c) Chen, Q.-Y. *Isr. J. Chem.* **1999**, *39*, 179–192.
4. (a) Andrieux, C. P.; Gélis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3509–3520. (b) Médebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 6872–6879.
5. Delest, B.; Shtarev, A. B.; Dolbier Jr., W. R *Tetrahedron* **1998**, *54*, 9273–9280.
6. (a) Kharasch, M. S.; Urry, W. H.; Jensen, E. V. *J. Am. Chem. Soc.* **1945**, *67*, 1626. (b) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1945**, *67*, 1864–1865. (c) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1946**, *68*, 154–155. (d) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1100–1105. (e) Kharasch, M. S.; Reinmuth, O.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1105–1110.
7. (a) Matsumoto, H.; Nakano, T.; Nagai, Y. *Tetrahedron Lett.* **1973**, 5147–5150. (b) Sasson, Y.; Rempel, G. L. *Synthesis* **1975**, 448–450. (c) Matsumoto, H.; Nakano, T.; Takasu, K.; Nagai, Y. *J. Org. Chem.* **1978**, *43*, 1734–1736. (d) Nagashima, H.; Ara, K.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1985**, 518–519. (e) Bland, W. J.; Davis, R.; Durrant, J. L. A. *J. Organomet. Chem.* **1985**, *280*, 397–406. (f) Ishizuka, T.; Osaki, M.; Ishihara, H.; Kunieda, T. *Heterocycles* **1993**, *35*, 901–908.
8. (a) Tallarico, J. A.; Malnick, L. M.; Snapper, M. L. *J. Org. Chem.* **1999**, *64*, 344–345. (b) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *J. Org. Chem.* **2001**, 2689–2695.

9. Lumbierres, M.; Marchi, C.; Moreno-Mañas, M.; Sebastián, R. M.; Vallribera, A.; Lago, E.; Molins, E. *Eur. J. Org. Chem.* **2001**, 2321–2328.
10. (a) Huang, W. Y.; Zhang, H. Z. *Chin. Chem. Lett.* **1990**, *1*, 153–154. (b) Huang, W.-Y.; Zhang, H.-Z. *J. Fluorine Chem.* **1990**, *50*, 133–140.
11. Powell, R. L.; Hall, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 5403–5404.
12. Alonso, E. O.; Johnston, L. J.; Scaiano, J. C.; Toscano, V. G. *Can. J. Chem.* **1992**, *70*, 1784–1794.
13. Atmaca, L.; Kayihan, I.; Yagci, Y. *Polymer* **2000**, *41*, 6035–6041.
14. Yasui, S.; Fujii, M.; Kawano, C.; Nishimura, Y.; Shioji, K.; Ohno, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 177–183.
15. Trost, B. M.; Schmidt, T. *J. Am. Chem. Soc.* **1988**, *110*, 2301–2303.
16. Trost, B. M.; Kazmaier, U. *J. Am. Chem. Soc.* **1992**, *114*, 7933–7935.
17. Ma, D.; Yu, Y.; Lu, X. *J. Org. Chem.* **1989**, *54*, 1105–1109.
18. Guo, C.; Lu, X. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1921–1923.
19. Ishihara, T.; Kuroboshi, M.; Okada, Y. *Chem. Lett.* **1986**, 1895–1896.
20. Fuchikami, T.; Shibata, Y.; Urata, H. *Chem. Lett.* **1987**, 521–524.
21. Chen, Q.-Y.; Yang, Z.-Y.; Zhao, C.-X.; Qiu, Z.-M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 563–567.
22. Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254–278.
23. Barks, J. M.; Gilbert, B. C.; Parsons, A. F.; Upeandran, B. *Tetrahedron Lett.* **2001**, *42*, 3137–3140.
24. Feiring, A. E. *J. Fluorine Chem.* **1984**, *24*, 191–203.
25. Requirand, N.; Blancou, H.; Commeyras, A. *Bull. Soc. Chim. Fr.* **1993**, *130*, 798–806.