Synthesis of Alkyl and Fluoroalkyl Chains Containing Thioether-Phosphines

Angela M. López-Vinasco,[a] Marlene Bruce,[a] Paola González-Aguirre,[a] Alonso Rosas-Hernández,[a] Carlos Amador-Bedolla,[b] Erika Martin*[a]

[a] Depto. de Química Inorgánica, Facultad de Química, Universidad Nacional Autónoma de México, Av. Universidad 3000, 04510 México D.F., México
Fax +52(55)56223720; E-mail: erikam@unam.mx

[b] Depto. de Física y Química Teórica, Facultad de Química, Universidad Nacional Autónoma de México, Av. Universidad 3000, 04510 México D.F., México

Received 16 June 2010; revised 14 September 2010

Abstract: We prepared new thioether-arylphosphines bearing alkyl and fluoroalkyl chains at the sulfur atom in order to use them in metal-catalyzed reactions in new reaction media, such as a fluorous biphasic system. The characterization of the new compounds is discussed and the partition coefficients in the biphasic system perfluoromethylcyclohexane–cyclohexane were determined. Fluorous thioether-phosphines reacted with [Rh(acac)$(CO)_2$] under fluorous biphasic conditions to produce rhodium species retained in the fluorous phase with ≤2.32 ppm of rhodium loss in the organic phase. The effect of S-ponytails on the coordination properties of the new phosphines and their relation with ^{31}P NMR chemical shifts were supported by DFT calculations.

Key words: P,S-ligands, fluoroalkyl halides, thioether compounds, fluorinated arylphosphines, biphase systems

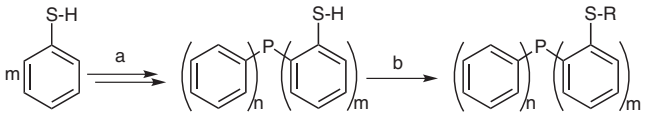
Homogeneous catalysis is one of the most effective synthetic methodologies since it combines high atomic economy with high activity and selectivity under soft reaction conditions in a great variety of chemical tranformations;[1] however, the disadvantage of homogeneous catalysis is the need to separate the products from the catalyst when the reaction ends. In heterogeneous catalysis, separation of products from the catalyst is straightforward, but the activity and selectivity of heterogeneous catalysts is lower compared to homogeneous catalysts. An elegant and effective solution to this problem is multiphasic catalysis:[2] the catalyst resides in one phase and the reagents and products in a second phase, which allows an ideal combination of the advantages of homogeneous catalysis with easy separation and recycling of the catalyst.[3]

One of these approaches, aqueous biphasic catalysis, has been applied at an industrial level in large-scale propene hydroformylation. A drawback to this process is the restriction that water-soluble substrates must be used.[3] Supercritical carbon dioxide is very useful as a reaction medium to dissolve reagents and products allowing both separation and catalyst recycling.[4,5] Fluorinated ligands such as alkyl- or arylphosphines containing fluorous chains have been employed to increase the solubility of metal catalysts in supercritical carbon dioxide.[6–8]

SYNTHESIS 2010, No. 23, pp 4101–4106
Advanced online publication: 22.10.2010
DOI: 10.1055/s-0030-1258309; Art ID: M04310SS

This type of ligand was first applied in fluorous biphasic catalysis (FBC)[9] to obtain catalysts soluble in the fluorous medium. The FBC process is based on temperature-dependent miscibility between a fluorous phase and an organic medium. Therefore, it is possible to have a biphasic system at room temperature and a monophase system at high temperatures (usually 60–80 °C). Developed by Horváth and Rábai, this attractive methodology allows the catalytic reaction to be performed under true homogeneous conditions and the organic phase to be separated from the fluorous phase by simple cooling. Thus, the products of the reaction are separated from the catalyst without distillation and the catalyst in the fluorous phase can be reused.[10–14]

This work is focused on the synthesis of alkyl- and fluoroalkyl-containing thioether-phosphines in order to increase the solubility of the catalyst in fluorous media (Scheme 1).



1a n = 2, m = 1
1b n = 0, m = 3

n = 2, m = 1 or
n = 0, m = 3

3 n = 2, m = 1, RX = $CF_3(CF_2)_3(CH_2)_2I$
4 n = 2, m = 1, RX = $CH_3(CH_2)_5Br$
5 n = 2, m = 1, RX = $CF_3(CF_2)_7(CH_2)_2I$
6 n = 2, m = 1, RX = $CH_3(CH_2)_9Br$
7 n = 0, m = 3, RX = $CF_3(CF_2)_3(CH_2)_2I$
8 n = 0, m = 3, RX = $CF_3(CF_2)_7(CH_2)_2I$

Scheme 1 Synthetic route for thioether-phosphines. *Reagents and conditions*: (a) BuLi, TMEDA, CH_x, 0 °C to 25 °C, 24 h; Ph_nPCl_m, THF, –78 °C to 25 °C, 24 h; H_2SO_4, 0 °C; (b) NaH, THF, 25 °C, 2 h, then RX **2**, 25 °C, 2 h.

The structural features of the new compounds were designed for them to be used as ligands in rhodium-catalyzed hydroformylation reactions in fluorous biphasic media, although their application in supercritical carbon dioxide has not been examined. The strategy showed here differs from previously reported work which used monodentated phosphorus ligands like arylphosphines containing ponytails at the *para* position of the aromatic rings (i.e. alkyl, alkoxy, or silylalkyl ponytails).[15–19] Com-

Table 1 Syntheses of Thioether-Phosphines[a]

Compd	n	m	R	Yield[b] (%)
3	2	1	$(CH_2)_2(CF_2)_3CF_3$	99
4	2	1	$(CH_2)_5Me$	98
5	2	1	$(CH_2)_2(CF_2)_7CF_3$	76
6	2	1	$(CH_2)_9Me$	95
7	0	3	$(CH_2)_2(CF_2)_3CF_3$	63
8	0	3	$(CH_2)_2(CF_2)_7CF_3$	86

[a] The chemical structures of **3**–**8** compounds were determined from their spectra (IR, ^1H, ^{13}C, ^{31}P, and ^{19}F NMR, MS, and HRMS).
[b] Isolated yield of step b.

pounds **4** and **6** were synthesized for comparative purposes.

In thioether-phosphines **3**–**8**, the coordination ability of both donor atoms, P and S, may be used to generate a chelate–metal complex, which under catalytic conditions could act as a hemilabile species. In addition to the usual CH_2CH_2 group, the sulfur atom can function as an insulating entity, to diminish or to avoid the electronic effects of the fluorous chains.

According to the designed synthetic route (Scheme 1), phosphinylbenzenethiols **1** were prepared as previously described in literature[20] through double lithiation of thiophenol followed by the addition of the corresponding phosphorus derivative (Ph_2PCl or PCl_3), the lithium salt obtained was treated with sulfuric acid to give the thiols **1**. In the presence of sodium hydride, the thiophenolate is formed and reacts with fluorous and non-fluorous alkyl halides **2** to form **3**–**8** in good yields as shown in Table 1 (yields for step b). Attempts to prepare **3** by reacting the lithium thiolate (step a) with hexyl bromide were unsuccessful under the conditions employed.

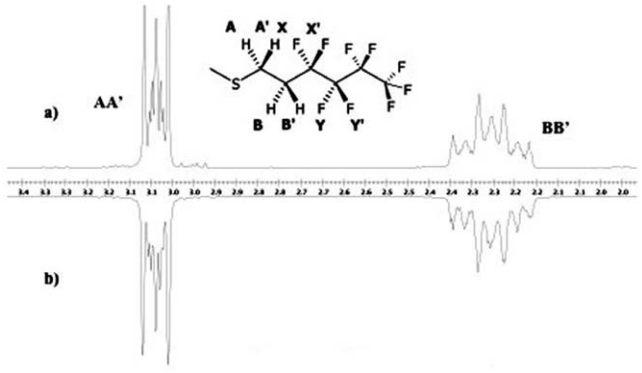


Figure 1 ^1H NMR spectra of the aliphatic region of **3**: (a) experimental spectrum, (b) simulated spectrum as an AA′BB′XX′YY′ magnetic system

^1H NMR spectra show magnetic patterns of the type ABCDX (P = X) for disubstituted aromatic rings in all cases. Since compounds **3**, **5**, **7**, and **8** contain fluorous chains with the fragment CH_2CH_2, two complex signals are observed in the aliphatic region, which are resolved as part of the magnetic system AA′BB′XX′YY′ where the diastereotopic methylenic protons (AA′ or BB′) are coupled with the neighboring fluorine nucleus (XX′YY′). Figure 1 displays (a) experimental and (b) simulated spectra for protons AA′BB′ of compound **3**.

In contrast, non-fluorous compounds **4** and **6** show the magnetic system AA′BB′C_2D_2 for the aliphatic region. The main differences between **3** vs. **5** and **4** vs. **6** are observed in the number of signals in the ^{13}C and ^{19}F NMR spectra. In the cases of **7** and **8**, the three aromatic rings are equivalent and the magnetic pattern ABCDX is observed in the aromatic region of the ^1H NMR spectra. The aliphatic part is similar to the one discussed for **3** and **5**.

All compounds show a singlet in the ^{31}P NMR spectra and the chemical shifts are near to the corresponding precursor thiolphosphine **1a** $\delta = -12.3$ and **1b** $\delta = -25.3$. These results indicate that there is no 'chain effect' on the phosphorus atom when either the alkyl or the fluoroalkyl group is present; it suggests that the fragment SCH_2CH_2 acts as an electronic insulator of chain effects. The signals in the ^{13}C NMR spectra were assigned by using HSQC and HMBC experiments and coupling constants.

Analyzing the data obtained by ^{13}C and ^{31}P NMR, the following comparisons of the synthesized compounds can be carried out: (a) Thioether-phosphine vs. thiol-phosphine. In ^{13}C NMR, the chain effect resides mainly in C_{ipso}–P or C_{ipso}–S. In the case of compounds **3**, **5**, **7**, and **8**, C_{ipso}–P mainly experiences the effect of the fluorous chain, the unshielded signal being higher for **7** and **8** than **3** and **5**, respectively. In contrast, **4** and **6** show the major effects at C_{ipso}–S. Meanwhile, the ^{31}P chemical shift signals do not suffer significant modification, hence phosphorus shielding is similar for monosubstituted compounds independent of the nature or size of the chain; (b) Fluorous vs. non-fluorous compounds. Interesting behavior for C_{ipso}–P and C_{ipso}–S is identified in the ^{13}C NMR spectra. The chemical shifts of these carbon atoms are inverted as one would expect and this may be caused by the change of the electronic density when electron-withdrawing fluorous chains are present. However, as in the previous case, phosphorus chemical shifts are similar, so again the phosphorous shielding is not modified by the nature of the chain; (c) Chain fluorous size and number. No significant shift for carbon signals is observed in the ^{13}C NMR spectra, but the ^{31}P NMR spectrum of **7** shows a remarkable shift towards smaller frequencies than the signal for **3** ($\Delta\delta = 9.9$) and the same occurs in the case of **8** vs. **5**. This behavior is a consequence of the number of aromatic rings that are S_{ortho}-substituted since we previously observed that the nature and size of the chain do not affect the ^{31}P chemical shift.

In order to relate the effects of fluorous ponytails on phosphorus donor–acceptor σ/π properties, density functional theory (DFT) studies of the thioether-phosphine and thiol-phosphine compounds were carried out. We obtain the en-

ergy difference between the highest occupied molecular orbital located mainly on phosphorus (which we will call HOPMO) and the lowest unoccupied molecular orbital located on phosphorus (LUPMO), since this gap is mostly responsible for variations in chemical shielding and, thus, on ^{31}P chemical shift.[21] As expected,[22] the HOMO for our calculated set of phosphines is the same as the highest occupied PMO, but the lowest unoccupied PMO differs from the LUMO in most cases (see supporting information). The resulting gap is displayed in Table 2 and correlates with experimentally measured ^{31}P chemical shifts.

Table 2 HOMO Energies and GAP Sizes[a]

Compd	ε_{HOMO} (eV)	GAP (eV)	^{31}P δ
PPh_3	–7.048	7.456	– 5.9
1a	–7.048	7.238	–12.3
1b	–7.048	7.102	–25.3
3	–6.993	7.292	–13.7
4	–6.857	7.238	–13.6
5	–6.966	7.292	–12.9
7	–7.102	6.912	–23.6

[a] GAP size was calculated from molecular orbitals located mainly on phosphorus.

Alkyl-substitution on the sulfur atom does not change the HOMO level or the unoccupied PMO level thus preserving the gap size, and this is in agreement with the observed phosphorus chemical shift. When the nature of the chain is changed (**3** vs. **4**), the gap size is also the same. The fluorous chain size of the ponytails (**3** vs. **5**) does not modify the gap or the chemical shift, whereas the number of aromatic rings S_{ortho}-substituted (PPh_3 vs. **1a**, **4**, **5** vs. **1b**, **7**) significantly changes the chemical shift by lowering the unoccupied PMO. We conclude that there is no effect of the number, size, or nature of the chains on the phosphorus σ-donor properties; the S_{ortho}-substitution on phenyl groups diminishes the energy of lowest unoccupied PMO, thus increasing the phosphorus π-acceptor properties.

We also examined the solubility of the ligands in different solvents with the purpose of selecting solvents to form a two-phase system. Compounds **3**–**6** are soluble in common organic solvents, such as tetrahydrofuran, toluene, dichloromethane, and diethyl ether, but they are insoluble in cyclohexane. Compounds **7** and **8** are soluble in tetrahydrofuran, but due to their high fluorine content they show low solubilities in other common organic solvents (they are insoluble in hexane and cyclohexane at 25 °C). Compounds **3**, **5**, **7**, and **8** dissolve in perfluoromethylcyclohexane when the temperature is increased to 70–75 °C, however, only **7** and **8** remain in solution when the temperature is lowered. On the other hand, the fluorinated compounds were soluble in perfluorobenzene as they display similar polarities, but this solvent is miscible in most common organic solvents including cyclohexane. Consequently, the solvents perfluoromethylcyclohexane–cyclohexane (5 mL:2.5 mL) was selected as the fluorous biphasic system (FBS) and the partition coefficients of fluorous thioether-phosphines in this FBS were determined by NMR. The value of the partition coefficient in the fluorous phase increases with chain length and number of attached ponytails. For **3**, **5**, **7**, and **8**, values of 9%, 25%, 49%, and 88% were obtained respectively, from perfluoromethylcyclohexane solutions.

Since the preferential solubility of a perfluorinated ligand does not directly imply preferential solubility of the corresponding catalyst,[18] we prepared rhodium catalyst precursors in situ under FBS conditions by reacting [Rh(acac)$(CO)_2$] and the fluorous ligands, and identified three different behaviors. The color of the rhodium complexes provides a tool for their identification in the fluorous or organic phase. In the case of **3** (32 wt% of fluorine), we observed the rhodium species present in cyclohexane prior to heating. A homogeneous phase was formed by heating the reaction to 60 °C and once the system was cooled to 25 °C; the rhodium species were clearly soluble in cyclohexane. A suspension was observed using **5** (44 wt% of fluorine) or **7** (47 wt% of fluorine) at 25 °C, a monophasic system was formed in both cases at 60 °C and lowering temperature allowed the phases to separate; the rhodium complexes were soluble in cyclohexane. The rhodium species with thioether-phosphine **8** (57 wt% of fluorine) were soluble in the perfluoromethylcyclohexane phase at 25 °C, a homogeneous system was observed when the temperature was increased and on cooling, the rhodium precursor was retained in the fluorous phase (Figure 2). Rhodium losses in the organic phase employing **8** were 2.59 and 2.32 ppm for molar ratios [L]/[Rh] = 1.25:1 and 2:1, respectively.

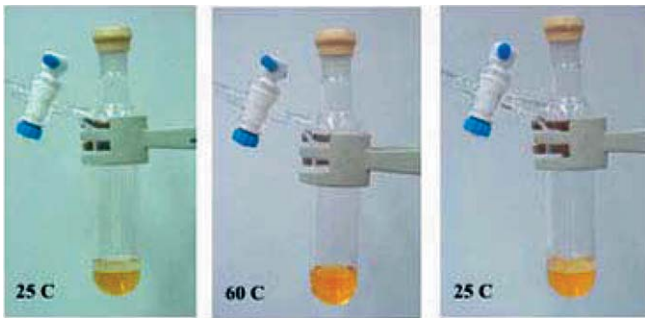


Figure 2 Fluorous biphasic system with [Rh(acac)$(CO)_2$]/**8**

The compounds in the fluorous solutions were investigated by ^{31}P NMR and IR spectroscopy. The NMR spectra showed a doublet shifted to δ = 77.8 (J_{Rh-P} = 138.3 Hz) characteristic of rhodium chelate complexes in a square arrangement,[23] and free ligand at δ = –24.1. No signal corresponding to CO vibration of the metal-carbonyl was detected in the infrared spectra. These results suggest that ligand **8** coordinates to the rhodium center as a bidentate ligand, by phosphorus and sulfur atoms, producing a

square planar complex containing also the acetylacetonate (acac) ligand.

All air- and water-sensitive reactions were performed under N_2 in oven-dried flasks using Schlenk-type techniques. All the reagents are available commercially and they were used without further purification. PCl_3 was distilled under N_2 and PhSH was purified with silica gel. The solvents were dried and distilled under N_2 before their use. The thiophenols **1a** and **1b** were synthesized following published procedures.[20] IR spectra were recorded in a Perkin Elmer FT-IR 1605 spectrophotometer with KBr discs or as pellets. NMR spectra were recorded in Varian (Unity Inova) spectrometers operating at 300 MHz (^{1}H), 77.5 MHz (^{13}C), 282 MHz (^{19}F), and 121 MHz (^{31}P) using $CDCl_3$ (**3**–**6**) or THF-d_8 (**7** and **8**). TMS was used as internal reference for ^{1}H and ^{13}C NMR experiments, TFA (δ = –77.00) and 85% H_3PO_4 were used as external references for ^{19}F and ^{31}P NMR, respectively. LR-MS and HRMS (IE, FAB$^+$) were obtained on a Jeol JMS-5X102A mass spectrometer. Nitrobenzylic alcohol was used as matrix in FAB$^+$ experiments. Rhodium loss was determined by ICP techniques using Termo Jarrel Ash IRIS advantage equipment.

All calculations were performed at the DFT level, by means of the hybrid meta exchange correlation functional M06-2X[24] as implemented in GAMESS.[25] The 6-31*G*(*d*,*p*) basis set was used for all atoms.[26] The structures of the ligands were fully optimized in gas phase without any symmetry restriction.

Experimental and theoretical details are given in the Supporting Information. See Figure 3 for label code used for NMR assignments.

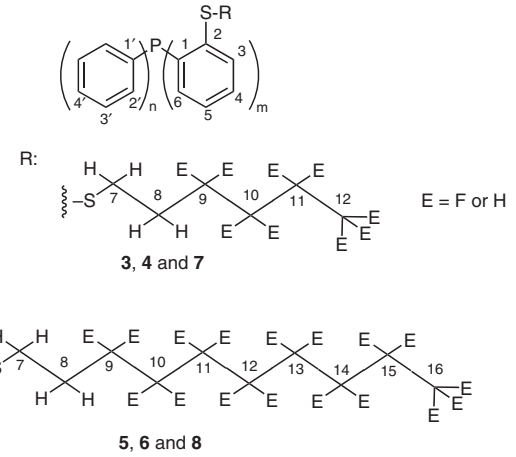


Figure 3 NMR label code for compounds **3**–**8**

{2-[(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)sulfanyl]phenyl}diphenylphoshine (3); Typical Procedure for 3–6

A 50-mL Schlenk tube was charged with NaH [60% in mineral oil, 32.64 mg, 0.82 mmol; previously washed with hexane (3 × 10 mL)] under an inert atmosphere and THF (5 mL) was added. At 0 °C, a soln of **1a** (200 mg, 0.68 mmol) in THF (10 mL) was slowly added. The reaction was stirred at r.t. for 2 h. The a soln of 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide (0.16 mL, 0.68 mmol) was added and the mixture was stirred for 2 h. The solvent was evaporated and the crude product was dissolved in CH_2Cl_2 and filtered, and the solvent was evaporated. The solid obtained was purified by column chromatography (hexane–EtOAc, 10:1) and dried under vacuum for 18 h to give a yellowish solid; yield: 366.15 mg (99%); mp 41–42 °C.

IR (KBr): 3064, 1584, 1434, 1222, 1355, 747, 694, 529 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (ddd, $^3J_{H3\text{-}H4}$ = 7.8 Hz, $^4J_{H3\text{-}H5}$ = 1.2 Hz, $^4J_{H3\text{-}P}$ = 4.2 Hz, 1 H, H3), 7.3 (m, 10 H, H2′–H4′), 7.33 (td, $^3J_{H4\text{-}H5}$ = 7.5 Hz, $^4J_{H3\text{-}P}$ = 1.3 Hz, 1 H, H4), 7.16 (td, $^3J_{H5\text{-}H6}$ = 7.6 Hz, 1 H, H5), 6.82 (ddd, $^3J_{H6\text{-}P}$ = 3.5 Hz, 1 H, H6), 3.04 (AA′BB′XX′YY′, $^2J_{A\text{-}A'}$ = 20.5 Hz, $^3J_{A\text{-}B}$ = 2.8 Hz, $^3J_{A\text{-}B'}$ = 15.2 Hz, $^4J_{A\text{-}X}$ = 0.6 Hz, $^4J_{A\text{-}X'}$ = 4.5 Hz, $^5J_{A\text{-}Y}$ = –0.7 Hz, $^5J_{A\text{-}Y'}$ = –3.3 Hz, $^3J_{A'\text{-}B}$ = 11.6 Hz, $^3J_{A'\text{-}B'}$ = 6.2 Hz, $^4J_{A'\text{-}X}$ = –0.9 Hz, $^4J_{A'\text{-}X'}$ = –2.8 Hz, $^5J_{A'\text{-}Y}$ = 1.3 Hz, $^5J_{A'\text{-}Y'}$ = 3.4 Hz, 2 H, H7), 2.26 (AA′BB′XX′YY′, $^2J_{B\text{-}B'}$ = –17.9 Hz, $^3J_{B\text{-}X}$ = 16.7 Hz, $^3J_{B\text{-}X'}$ = 18.2 Hz, $^4J_{B\text{-}Y}$ = –1.3 Hz, $^4J_{B\text{-}Y'}$ = 5.8 Hz, $^3J_{B'\text{-}X}$ = 21.5 Hz, $^3J_{B'\text{-}X'}$ = 16.8 Hz, $^4J_{B'\text{-}Y}$ = –2.2 Hz, $^4J_{B'\text{-}Y'}$ = –4.5 Hz, 2 H, H8).

^{13}C NMR (77.5 MHz, $CDCl_3$): δ = 140.6 (d, $^1J_{C\text{-}P}$ = 7.8 Hz, C1), 139.4 (d, $^2J_{C\text{-}P}$ = 21.4 Hz, C2), 136.4 (d, $^1J_{C\text{-}P}$ = 8.0 Hz, C1′), 134.0 (d, $^2J_{C\text{-}P}$ = 20.2 Hz, C2′), 133.9 (s, C3), 130.7 (d, $^2J_{C\text{-}P}$ = 2.4 Hz, C6), 129.7 (s, C4), 128.9 (s, C4′), 128.6 (d, $^3J_{C\text{-}P}$ = 7.3 Hz, C3′), 127.4 (s, C5), 104–124 (m, C9–C12, CF_2, CF_3), 31.2 (t, $^2J_{C\text{-}F}$ = 22.2 Hz, C8), 25.9 (m, C7).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –126.5 (m, 2 F, F9), –124.7 (m, 2 F, F10), –114.9 (m, 2 F, F11), –81.5 (tt, $^3J_{F\text{-}F}$ = 9.7 Hz, $^4J_{F\text{-}F}$ = 3.3 Hz, 3 F, F12).

^{31}P NMR (121 MHz, $CDCl_3$): δ = –13.7 (s).

HRMS (IE): *m*/*z* [M] calcd for $C_{24}H_{18}F_9PS$: 540.0700; found: 540.0718.

[2-(Hexylsulfanyl)phenyl]diphenylphosphine (4)

Creamy oil; yield: 630 mg (98%).

IR(film): 3052, 2926, 2850, 1572, 1477, 1433, 744, 696, 506 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (ddd, $^3J_{H3\text{-}H4}$ = 7.9 Hz, $^4J_{H3\text{-}H5}$ = 1.0 Hz, $^4J_{H3\text{-}P}$ = 4.1 Hz, 1 H, H3), 7.26 (td, $^3J_{H4\text{-}H5}$ = 7.3 Hz, $^4J_{H4\text{-}H6}$ = 1.5 Hz, 1 H, H4), 7.23 (m, 10 H, H2′–H4′), 7.06 (td, $^3J_{H5\text{-}H6}$ = 7.5 Hz, 1 H, H5), 6.76 (ddd, $^3J_{H6\text{-}P}$ = 3.6 Hz, 1 H, H6), 2.85 (AA′BB′C_2D_2, $^2J_{A\text{-}A'}$ = 12.2 Hz, $^3J_{A\text{-}B}$ = 3.7 Hz, $^3J_{A\text{-}B'}$ = 8.4 Hz, $^4J_{A\text{-}C}$ = 0.3 Hz, $^5J_{A\text{-}D}$ = 1.1 Hz, $^3J_{A'\text{-}B}$ = 11.3 Hz, $^3J_{A'\text{-}B'}$ = 2.4 Hz, $^4J_{A'\text{-}C}$ = –0.6 Hz, $^5J_{A'\text{-}D}$ = –0.8 Hz, 2 H, H7), 1.57 (AA′BB′C_2D_2, $^2J_{B\text{-}B'}$ = –17.2 Hz, $^3J_{B\text{-}C}$ = 6.6 Hz, $^4J_{B\text{-}D}$ = –0.1 Hz, $^3J_{B'\text{-}C}$ = 7.3 Hz, $^4J_{B'\text{-}D}$ = 1.0 Hz, 2 H, H8), 1.24 (m, 6 H, H9–H11), 0.86 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 3 H, H12).

^{13}C NMR (77.5 MHz, $CDCl_3$): δ = 142.5 (d, $^2J_{C\text{-}P}$ = 27.9 Hz, C2), 138.7 (d, $^1J_{C\text{-}P}$ = 9.3 Hz, C1), 136.9 (d, $^1J_{C\text{-}P}$ = 10.1 Hz, C1′), 134.1 (d, $^2J_{C\text{-}P}$ = 20.2 Hz, C2′), 133.5 (s, C6), 129.3 (d, $^2J_{C\text{-}P}$ = 3.6 Hz, C3), 129.2 (s, C4), 128.6 (d, $^3J_{C\text{-}P}$ = 6.8 Hz, C3′), 128.8 (s, C4′), 126.1 (s, C5), 35.0 (d, $^4J_{C\text{-}P}$ = 6.4 Hz, C7), 31.5 (s, C8), 29.0 (s, C9), 28.8 (s, C10), 22.6 (s, C11), 14.2 (s, C12).

^{31}P NMR (121 MHz, $CDCl_3$): δ = –13.6 (s).

HRMS (IE): *m*/*z* [M] calcd for $C_{24}H_{27}PS$: 378.1600; found: 378.1557.

{2-(1*H*,1*H*,2*H*,2*H*-Perfluorodecyl)sulfanyl]phenyl}diphenylphosphine (5)

White solid: yield: 950 mg (76%); mp 72–73 °C.

IR(KBr): 3057, 1584, 1435, 1369, 1204, 1149, 748, 695, 530 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (ddd, $^3J_{H3\text{-}H4}$ = 7.8 Hz, $^4J_{H3\text{-}H5}$ = 1.5 Hz, $^4J_{H3\text{-}P}$ = 4.1 Hz, 1 H, H3), 7.33 (td, $^3J_{H4\text{-}H5}$ = 7.4 Hz, $^4J_{H4\text{-}H6}$ = 1.5 Hz, 1 H, H4), 7.30 (m, 10 H, H2′–H4′), 7.16 (td, $^3J_{H5\text{-}H6}$ = 7.7 Hz, 1 H, H5), 6.81 (ddd, $^3J_{H6\text{-}P}$ = 3.4 Hz, 1 H, H6), 3.04 (AA′BB′XX′YY′, $^2J_{A\text{-}A'}$ = 20.2 Hz, $^3J_{A\text{-}B}$ = 2.5 Hz, $^3J_{A\text{-}B'}$ = 13.6 Hz, $^4J_{A\text{-}X}$ = 1.0 Hz, $^4J_{A\text{-}X'}$ = 4.0 Hz, $^5J_{A\text{-}Y}$ = 0.7 Hz, $^5J_{A\text{-}Y'}$ = –2.7 Hz, $^3J_{A'\text{-}B}$ = 2.2 Hz, $^3J_{A'\text{-}B'}$ = 6.0 Hz, $^4J_{A'\text{-}X}$ = –0.9 Hz, $^4J_{A'\text{-}X'}$ = –1.8 Hz, $^5J_{A'\text{-}Y}$ = –0.3 Hz, $J_{A'\text{-}Y'}$ = 2.9 Hz, 2 H, H7), 2.26 (AA′BB′XX′YY′, $^2J_{B\text{-}B'}$ = –16.0 Hz, $^3J_{B\text{-}X}$ = 19.3 Hz, $^3J_{B\text{-}X'}$ = 17.8 Hz, $^4J_{B\text{-}Y}$ = –1.2 Hz, $^4J_{B\text{-}Y'}$ = 5.6 Hz, $^3J_{B'\text{-}X}$ = 21.3 Hz, $^3J_{B'\text{-}X'}$ = 17.4 Hz, $^4J_{B'\text{-}Y}$ = –2.4 Hz, $^4J_{B'\text{-}Y'}$ = –5.7 Hz, 2 H, H8).

^{13}C NMR (77.5 MHz, $CDCl_3$): δ = 140.7 (d, $^1J_{C\text{-}P}$ = 10.0 Hz, C1), 139.5 (d, $^2J_{C\text{-}P}$ = 27.4 Hz, C2), 136.4 (d, $^1J_{C\text{-}P}$ = 10.5 Hz, C1′), 134.2 (d, $^2J_{C\text{-}P}$ = 19.8 Hz, C2′), 133.9 (s, C6), 130.8 (d, $^2J_{C\text{-}P}$ = 3.6 Hz, C3),

129.7 (s, C4), 129.1 (s, C4′), 128. 9 (d, $^3J_{C\text{-}P}$ = 6.9 Hz, C3′), 127.6 (s, C5), 104–124 (m, C9–C16), 31.4 (t, $^2J_{C\text{-}F}$ = 22.2 Hz, C7), 26.0 (m, C8).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –126.6 (m, 2 F, F9), –123.8 (m, 2 F, F10), –123.20 (m, 2 F, F11), –122.4 (m, 6 F, F12–F14), –114.2 (q, $^3J_{F\text{-}F}$ = 14.2 Hz, 2 F, F15), –81.2 (t, $^3J_{F\text{-}F}$ = 10.7 Hz, 3 F, F16).

^{31}P NMR (121 MHz, $CDCl_3$): δ = –12.9 (s).

HRMS (IE): *m*/*z* [M] calcd for $C_{28}H_{18}F_{17}PS$: 740.0600; found: 740.0614.

[2-(Decylsulfanyl)phenyl]diphenylphosphine (6)

Creamy oil; yield: 1.39 g (95%).

IR (film): 3051, 2923, 2852, 1571, 1477, 1433, 743, 695, 501 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (ddd, $^3J_{H3\text{-}H4}$ = 7.7 Hz, $^4J_{H3\text{-}H5}$ = 1.2 Hz, $^4J_{H3\text{-}P}$ = 4.2 Hz, 1 H, H3), 7.31 (td, $^3J_{H4\text{-}H5}$ = 7.5 Hz, $^4J_{H4\text{-}H6}$ = 1.5 Hz, 1 H, H4), 7.30 (m, 10 H, H2′–H4′), 7.06 (td, $^3J_{H5\text{-}H6}$ = 7.7 Hz, 1 H, H5), 6.76 (ddd, $^3J_{H6\text{-}P}$ = 3.7 Hz, 1 H, H6), 2.86 (AA′BB′CC′DD′, $^2J_{A\text{-}A'}$ = 13.9 Hz, $^3J_{A\text{-}B}$ = 3.5 Hz, $^3J_{A\text{-}B'}$ = 7.5 Hz, $^4J_{A\text{-}C}$ = –0.5 Hz, $^4J_{A\text{-}C'}$ = –0.4 Hz, $^5J_{A\text{-}D}$ = –0.8 Hz, $^5J_{A\text{-}D'}$ = –0.8 Hz, $^3J_{A'\text{-}B}$ = 7.2 Hz, $^3J_{A'\text{-}B'}$ = 6.4 Hz, $^4J_{A'\text{-}C}$ = 0.7 Hz, $^4J_{A'\text{-}C'}$ = 0.7 Hz, $^5J_{A'\text{-}D}$ = –1.2 Hz, $^5J_{A'\text{-}D'}$ = –1.3 Hz, 2 H, H7), 1.56 (AA′BB′CC′DD′, $^2J_{B\text{-}B'}$ = –13.3 Hz, $^3J_{B\text{-}C}$ = 8.4 Hz, $^4J_{B\text{-}C'}$ = 8.1 Hz, $^4J_{B\text{-}D}$ = –5.3 Hz, $^4J_{B\text{-}D'}$ = –1.6 Hz, $^3J_{B'\text{-}C}$ = 6.4 Hz, $^4J_{B'\text{-}C'}$ = 6.4 Hz, $^4J_{B'\text{-}D}$ = 2.6 Hz, $^4J_{B'\text{-}D'}$ = 0.4 Hz, 2 H, H8), 1.23 (m, 14 H, H9–H15), 0.88 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 3 H, H16).

^{13}C NMR (77.5 MHz, $CDCl_3$): δ = 142.5 (d, $^1J_{C\text{-}P}$ = 9.9 Hz, C1), 138.8 (d, $J_{C\text{-}P}$ = 27.4 Hz, C2), 136.9 (d, $^1J_{C\text{-}P}$ = 10.7 Hz, C1′), 134.1 (d, $^2J_{C\text{-}P}$ = 20.2 Hz, C2′), 133.5 (s, C6), 129.4 (d, $^2J_{C\text{-}P}$ = 3.5 Hz, C3), 129.2 (s, C4), 128.9 (s, C4′), 128.6 (d, $^3J_{C\text{-}P}$ = 7.3 Hz, C3′), 126.1 (s, C5), 35.1 (d, $^4J_{C\text{-}P}$ = 6.5 Hz, C7), 29.3 (s, C9), 29.1 (s, C8), 29.1, 29.4, 29.6, 29.7, and 32.0 (s, C10–C14), 22.8 (s, C15), 14.2 (s, C16).

^{31}P NMR (121 MHz, $CDCl_3$): δ = –13.6 (s).

HRMS (IE): *m*/*z* [M] calcd for $C_{28}H_{35}PS$: 434.2200; found: 434.2212.

Tris{2-[(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)sulfanyl]phenyl}phosphine (8); Typical Procedure for 7 and 8

A 50-mL Schlenk tube was charged with NaH [60% in mineral oil, 65.80 mg, 1.64 mmol; previously washed with hexane (3 × 10 mL)] under an inert atmosphere and THF (5 mL) was added. At 0 °C, a soln of **1b** (150 mg, 0.42 mmol) in THF (10 mL) was slowly added. The mixture was stirred at r.t. for 2 h. Then a soln of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide (828.70 mg, 1.38 mmol) in THF (5 mL) was added and the mixture was stirred for 48 h. Then, the solvent was evaporated and the crude was dissolved in CH_2Cl_2 and filtered, and the solvent was evaporated. The solid obtained was recrystallized (EtOH–hexane) and dried under vacuum for 18 h to give a white solid; yield: 537 mg (85%); mp 125–127 °C.

IR(KBr): 3039, 1355, 1202, 1146, 748, 529 cm^{-1}.

^{1}H NMR (300 MHz, THF-d_8): δ = 7.65 (ddd, $^3J_{H3\text{-}H4}$ = 7.8 Hz, $^4J_{H3\text{-}H5}$ = 1.2 Hz, $^4J_{H3\text{-}P}$ = 4.3 Hz, 3 H, H3), 7.39 (td, $^3J_{H4\text{-}H5}$ = 7.3 Hz, $^4J_{H4\text{-}H6}$ = 1.5 Hz, $^4J_{H4\text{-}P}$ = 0.2 Hz, 3 H, H4), 7.21 (td, $^3J_{H5\text{-}H6}$ = 7.8 Hz, 3 H, H5), 6.69 (ddd, $^3J_{H6\text{-}P}$ = 2.5 Hz, 3 H, H6), 3.20 (AA′BB′XX′YY′, $^2J_{A\text{-}A'}$ = 20.1 Hz, $^3J_{A\text{-}B}$ = 5.1 Hz, $^3J_{A\text{-}B'}$ = 10.6 Hz, $^4J_{A\text{-}X}$ = –1.3 Hz, $^4J_{A\text{-}X'}$ = –0.4 Hz, $^5J_{A\text{-}Y}$ = 0.5 Hz, $^5J_{A\text{-}Y'}$ = –5.0 Hz, $^3J_{A'\text{-}B}$ = 13.1 Hz, $^3J_{A'\text{-}B'}$ = 1.7 Hz, $^4J_{A'\text{-}X}$ = 1.7 Hz, $^4J_{A'\text{-}X'}$ = –1.3 Hz, $^5J_{A'\text{-}Y}$ = –1.7 Hz, $J_{A'\text{-}Y'}$ = 7.6 Hz, 6 H, H7), 2.47 (AA′BB′XX′YY′, $^2J_{B\text{-}B'}$ = –14.8 Hz, $^3J_{B\text{-}X}$ = 14.9 Hz, $^3J_{B\text{-}X'}$ = 15.9 Hz, $^4J_{B\text{-}Y}$ = –1.1 Hz, $^4J_{B\text{-}Y'}$ = 1.4 Hz, $^3J_{B'\text{-}X}$ = 21.8 Hz $^3J_{B'\text{-}X'}$ = 20.1 Hz, $^4J_{B'\text{-}Y}$ = 4.1 Hz, $^4J_{B'\text{-}Y'}$ = –4.9 Hz, 6 H, H8).

^{13}C NMR (77.5 MHz, THF-d_8): δ = 141.5 (d, $^1J_{C\text{-}P}$ = 9.9 Hz, C1), 139.1 (d, $^2J_{C\text{-}P}$ = 31.9 Hz, C2), 133.9 (s, C6), 133.4 (d, $^2J_{C\text{-}P}$ = 2.7 Hz, C3), 129.6 (s, C4), 128.3 (s, C5), 104–124 (m, C9–C16), 31.2 (t, $^2J_{C\text{-}F}$ = 22.0 Hz, C8), 26.6 (m, C7).

^{19}F NMR (282 MHz, THF-d_8): δ = –127.2 (m, 6 F, F9), –123.9 (m, 6 F, F10), –123.7 (m, 6 F, F11), –122.8 (m, 18 F, F12–F14), –114.9 (m, 6 F, F15), –82.1 (m, 9 F, F16).

^{31}P NMR (121 MHz, THF-d_8): δ = –24.1 (s).

HRMS (FAB): *m*/*z* [M – H]$^+$ calcd for $C_{48}H_{24}F_{51}PS_3$: 1697.7900; found: 1697.9900.

Tris{2-[(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)sulfanyl]phenyl}phosphine (7)

Compound **7**, the solid was purified by five consecutive recrystallizations (EtOH–hexane) causing low yield for the isolated compound; white solid: yield: 470 mg (63%); mp 41–42 °C.

IR(KBr): 3048, 2963, 1445, 1355, 1222, 1133, 748, 692, 528 cm^{-1}.

^{1}H NMR (300 MHz, THF-d_8): δ = 7.63 (ddd, $^3J_{H3\text{-}H4}$ = 7.8 Hz, $^4J_{H3\text{-}P}$ = 4.2 Hz, $^4J_{H3\text{-}H5}$ = 1.2 Hz, 3 H, H3), 7.39 (td, $^3J_{H4\text{-}H5}$ = 7.8 Hz, $^4J_{H4\text{-}H6}$ = 1.5 Hz, 3 H, H4), 7.20 (td, $^3J_{H5\text{-}H6}$ = 7.8 Hz, 3 H, H5), 6.69 (ddd, $^3J_{H6\text{-}P}$ = 2.5 Hz, 3 H, H6), 3.20 (AA′BB′XX′YY′, $^2J_{A\text{-}A'}$ = 19.9 Hz, $^3J_{A\text{-}B}$ = 5.8 Hz, $^3J_{A\text{-}B'}$ = 10.7 Hz, $^4J_{A\text{-}X}$ = –0.2 Hz, $^4J_{A\text{-}X'}$ = –0.6 Hz, $^5J_{A\text{-}Y}$ = –0.9 Hz, $^5J_{A\text{-}Y'}$ = –5.0 Hz, $^3J_{A'\text{-}B}$ = 12.9 Hz, $^3J_{A'\text{-}B'}$ = 1.7 Hz, $^4J_{A'\text{-}X}$ = 1.7 Hz, $^4J_{A'\text{-}X'}$ = –1.9 Hz, $^5J_{A'\text{-}Y}$ = –0.2 Hz, $^5J_{A'\text{-}Y'}$ = 7.6 Hz, 2 H, H7), 2.46 (AA′BB′XX′YY′, $^2J_{B\text{-}B'}$ = –14.9 Hz, $^3J_{B\text{-}X}$ = 13.8 Hz, $^4J_{B\text{-}X'}$ = 14.6 Hz, $^4J_{B\text{-}Y}$ = 0.0 Hz, $^4J_{B\text{-}Y'}$ = 2.1 Hz, $^3J_{B'\text{-}X}$ = 20.8 Hz, $^4J_{B'\text{-}X'}$ = 20.4 Hz, $^4J_{B'\text{-}Y}$ = 3.7 Hz, $^4J_{B'\text{-}Y'}$ = –4.9 Hz, 2 H, H8).

^{13}C NMR (77.5 MHz, THF-d_8): δ = 142.4 (d, $^1J_{C\text{-}P}$ = 9.7 Hz, C1), 140.4 (d, $^2J_{C\text{-}P}$ = 29.7 Hz, C2), 135.2 (s, C6), 134.0 (d, $^4J_{C\text{-}P}$ = 2.9 Hz, C3), 130.8 (s, C4), 129.4 (s, C5), 125–106 (m, C9–C12), 32.3 (t, $^2J_{C\text{-}F}$ = 22.6 Hz, C8), 27.4 (m, C7).

^{19}F NMR (282 MHz, THF-d_8): δ = –127.1 (m, 6 F, F9), –125.1 (m, 6 F, F10), –115.3 (m, 6 F, F11), –82.4 (m, 9 F, F12).

^{31}P NMR (121 MHz, THF-d_8): δ = –23.6 (s).

HRMS (FAB): *m*/*z* [M – H]$^+$ calcd for $C_{36}H_{23}F_{27}PS_3$: 1097.0300; found: 1097.0419.

Partition Coefficient Determination

A round-bottom flask was charged with the desired compound (0.024 mmol) and perfluoromethylcyclohexane (5 mL) was added. Subsequently, cyclohexane (2.5 mL) was added to form a biphasic system at r.t. The system was stirred at 60 °C in order to form a monophasic system. The system was allowed to cool to r.t. forming a biphasic system again. The two phases were separated and the solvents were removed under reduced pressure each. The solids recovered from each phase were dissolved in a deuterated solvent (THF-d_8, $CDCl_3$) and dodecane (16.6 mL, 0.073 mmol) was added as internal standard. The samples obtained in each phase were analyzed separately by ^{1}H NMR techniques. The amount of compound retained in each phase was determined by comparison to the internal standard.

Reaction of [Rh(acac)(CO)$_2$] with 3, 5, 7, or 8 under Biphasic Conditions

Experiments with precursor [Rh(acac)(CO)$_2$] and compounds **3**, **5**, **7**, and **8** were performed using molar ratios [L]/[Rh] = 2 and 1.25. We describe the procedure for molar ratio = 2. A Schlenk flask was charged with **3**, **5**, **7**, or **8** (0.025 mmol). Perfluoromethylcyclohexane (5 mL) was added and the soln was stirred at 60 °C until the solid was completely dissolved. Afterwards, [Rh(acac)(CO)$_2$] (0.0125 mmol) was added under inert gas flow. After a few seconds the soln or suspension turned yellow and cyclohexane (2.5 mL) was added and a biphasic system was formed. The mixture was stirred at 60 °C obtaining a homogeneous phase. The system was allowed to cool to r.t. forming a biphasic system again. For compound **8** the fluorous

phase was dried under reduced pressure and the solid obtained was characterized by ^{31}P NMR techniques and IR spectroscopy.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

Acknowledgment

We gratefully acknowledge the financial support from DGAPA-UNAM (PAPIIT IN-210607) and CONACYT (CB060430). We also thank for computational resources provided by DGSCA-UNAM Supercomputing Department. A.M.L.V. and P.G.A. thank to CONACYT for the scholarship grant.

References

(1) (a) *Rhodium Catalyzed Hydroformylation*; van Leeuwen, P. W. N. M.; Claver, C., Eds.; Kluwer Academic Publishers: Dordrecht, **2002**. (b) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B.; Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, **1996**.

(2) (a) *Multiphase Homogeneous Catalysis*; Cornils, B.; Herrmann, W. A.; Horváth, I. T.; Leitner, W.; Mecking, S.; Olivier-Bourgbigou, H.; Vogt, D., Eds.; Wiley-VCH: Weinheim, **2005**. (b) Special issue on *Multiphase Catalysis, Green solvents and immobilization*; Baker, T.; Kobayashi, S.; Leitner, W., Eds.: *Adv. Synth. Catal.* **2006**, *348*, 1317-1771. (c) Sheldon, R. A. *Green Chem.* **2005**, *7*, 267. (d) Cole-Hamilton, D. J. *Science* **2003**, *299*, 1702. (e) Keim, W. *Green Chem.* **2003**, *5*, 105. (f) Tzschucke, C.; Markert, C.; Bannwarth, W.; Roller, S.; Hebel, A.; Haag, R. *Angew. Chem. Int. Ed.* **2002**, *41*, 3964.

(3) (a) *Aqueous-Phase Organometallic Chemistry*; Cornils, B.; Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, **2004**. (b) Cornils, B.; Kunz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177.

(4) Morgenstern, D. A.; LeLacheur, R. M.; Morita, D. K.; Borkowsky, S. L.; Feng, S.; Brown, G. H.; Luan, L.; Gross, M. F.; Burk, M. J.; Tumas, W. *Supercritical Carbon Dioxide as a Substitute Solvent for Chemical Synthesis and Catalysis,* In *Green Chemistry: Designing Chemistry for the Environment, ACS Symposium Series 626*; Anastas, P. T.; Williamson, T. C., Eds.; American Chemical Society: Washington DC, **1996**, 132.

(5) (a) Jessop, P. G.; Ikaraya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475. (b) Leitner, W. *Acc. Chem. Res.* **2002**, *35*, 746.

(6) *Chemical Synthesis Using Supercritical Fluids*; Jessop, P. G.; Leitner, W., Eds.; Wiley-VCH: Weinheim, **1999**.

(7) Koch, D.; Leitner, W. *J. Am. Chem. Soc.* **1998**, *120*, 13398.

(8) Sellin, M. F.; Bach, I.; Webster, J. M.; Montilla, F.; Rosa, V.; Aviles, T.; Poliakoff, M.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4569.

(9) (a) *Handbook of Fluorous Chemistry*; Gladysz, J. A.; Curran, D. P.; Horváth, I. T., Eds.; Wiley-VCH: Weinheim, **2004**. (b) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72. (c) Gladysz, J. A.; Curran, D. P. *Tetrahedron* **2002**, *58*, 3823.

(10) Horváth, I. T. *J. Am. Chem. Soc.* **1998**, *120*, 3133.

(11) Barthel-Rosa, L. P.; Gladysz, J. A. *Coord. Chem. Rev.* **1999**, *190-192*, 605.

(12) Foster, D. F.; Gudmunsen, D.; Adams, D. J.; Stuart, A. M.; Hope, R. G.; Cole-Hamilton, D. J.; Schwarz, G. P.; Pogorzelec, P. *Tetrahedron* **2002**, *58*, 3901.

(13) Hope, E. G.; Stuart, A. M. *J. Fluorine Chem.* **1999**, *100*, 75.

(14) Chen, W. P.; Xu, L. J.; Hu, Y. L.; Osuna, A. M. B.; Xiao, J. L. *Tetrahedron* **2002**, *58*, 3889.

(15) Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641.

(16) Richter, B.; de Wolf, E.; van Koten, G.; Deelman, B. J. *J. Org. Chem.* **2000**, *65*, 3885.

(17) Zhang, Q.; Luo, Z.; Curran, D. P. *J. Org. Chem.* **2000**, *65*, 8866.

(18) Adams, D. J.; Cole-Hamilton, D. J.; Hope, E. G.; Pogorzelec, P. J.; Stuart, A. M. *J. Organomet. Chem.* **2004**, *689*, 1413.

(19) Sinou, D.; Maillard, D.; Aghmiz, A.; Masdeu-Bultó, A. M. *Adv. Synth. Catal.* **2003**, *345*, 603.

(20) Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 2327.

(21) Eichele, K.; Wasylishen, R. E.; Corrigan, J. F.; Taylor, N. J.; Carty, A. J.; Feindel, K. W.; Bernard, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1541.

(22) Fey, N.; Orpen, A. G.; Harvey, J. N. *Coord. Chem. Rev.* **2009**, *253*, 704.

(23) (a) Lee, H.-S.; Bae, J.-Y.; Kim, D.-H.; Kim, H. S.; Kim, S.-J.; Cho, S.; Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 210. (b) Sanger, R. A. *Can. J. Chem.* **1983**, *61*, 2214.

(24) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(25) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(26) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.