Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 1859–1870
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Monophosphine and diphosphine ligands for diplatinum polyynediyl complexes: Efficient syntheses of new functionality-containing systems and model compounds

Laura de Quadras, Jürgen Stahl, Fedor Zhuravlev, John A. Gladysz *

Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany

Received 8 November 2006; received in revised form 18 December 2006; accepted 18 December 2006
Available online 23 December 2006

Dedicated with affection to Prof. Dr. Gyula Palyi on the occasion of his 70th birthday.

Abstract

$Br(CH_2)_4Br$ and $NaO(CH_2)_2CH{=}CH_2$ react under suitable conditions to give $Br(CH_2)_4O(CH_2)_2CH{=}CH_2$ (55%), which is treated with $KPPh_2$ to yield the ether-containing phosphine $Ph_2P(CH_2)_4O(CH_2)_2CH{=}CH_2$ (83%). The reaction of $CH_3CH_2OC(O)CH{=}C(CH_3)_2$ and $BrMg(CH_2)_3CH{=}CH_2$ in the presence of CuCl (cat.) and $ClSiMe_3$ yields $CH_3CH_2OC(O)CH_2C(CH_3)_2(CH_2)_3CH{=}CH_2$ (67%), which is reduced to an alcohol that is brominated, reacted with Grubbs' catalyst, hydrogenated, and treated with $KPPh_2$ to give the bis(geminally dimethylated) diphosphine $Ph_2P(CH_2)_2C(CH_3)_2(CH_2)_8C(CH_3)_2(CH_2)_2PPh_2$ (47% overall). The photochemical reaction of $I(CF_2)_8I$ and $H_2C{=}CHCH_2SnBu_3$ yields $H_2C{=}CHCH_2(CF_2)_8CH_2CH{=}CH_2$ (52%), which is converted with 9-BBN to a diol (92%) that is brominated and treated with $LiPR_2$ to give the fluorinated diphosphines $R_2P(CH_2)_3(CF_2)_8(CH_2)_3PR_2$ (R = **a**, *p*-tol, 67%; **b**, *t*-Bu, 69%; **c**, *o*-tol, 86%). Reactions of $Br(CH_2)_mBr$ and $LiPR_2$ similarly yield $R_2P(CH_2)_mPR_2$ (*m*/R = 8/**a**, 95%; 14/**a**, 96%; 14/*p*-C_6H_4-*t*-Bu, 98%). Reactions of $KPPh_2$ with $Br(CH_2)_{m'}CH{=}CH_2$and $Br(CH_2)_7CH_3$ give the corresponding monophosphines $Ph_2P(CH_2)_{m'}CH{=}CH_2$ ($m' = 7$, 82%; 10, 84%) and $Ph_2P(CH_2)_7CH_3$ (85%). When the former is combined with $[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (tht = tetrahydrothiophene), *trans*-$(C_6F_5)(Ph_2P(CH_2)_{m'}CH{=}CH_2)_2PtCl$ (77–70%) is isolated. When the latter (excess) is combined with *trans*,*trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_4Pt(Pp\text{-}tol_3)_2(C_6F_5)$ (RT, 65 °C), *trans*,*trans*-$(C_6F_5)(Ph_2P(CH_2)_7CH_3)_2Pt(C{\equiv}C)_4Pt(Ph_2P(CH_2)_7CH_3)_2(C_6F_5)$ (53%) is isolated.

Keywords: Functionalized phosphine; Fluorous; Platinum; Polyyne; Olefin metathesis

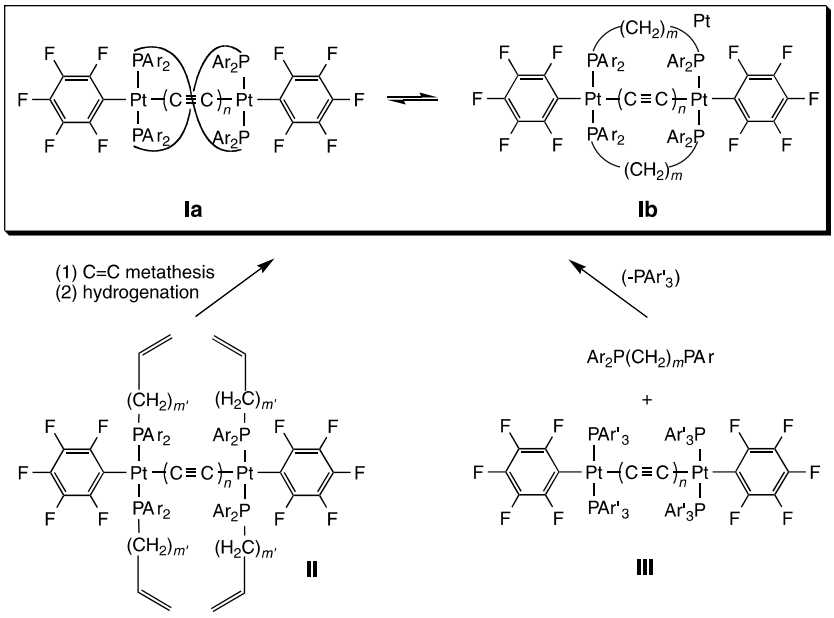
1. Introduction

Over the last five years, we have developed syntheses of diplatinum polyynediyl complexes, $L_yPt(C{\equiv}C)_nPtL_y$, in which the sp carbon chains are sterically shielded by two flexible sp^3 carbon chains that span the platinum termini [1]. As shown in Scheme 1, such assemblies can adopt two limiting conformations, **Ia** and **Ib**. In nearly all cases where the sp^3 chains are long enough, double helical conformations (**Ia**) are found in the solid state. Since the platinum endgroups of **I** are redox active, there are tantalizing possibilities for "insulated molecular wires". Others have also sought to sterically shield unsaturated ligands that bridge two electroactive endgroups [2].

The synthesis and study of such complexes has required a variety of monophosphines and α,ω-diphosphines. Polyynediyl precursors with four monophosphine ligands that contain $P(CH_2)_{m'}CH{=}CH_2$ moieties (**II**, Scheme 1) can be subjected to alkene metathesis/hydrogenation sequences [1a,1c,3]. Although the yields of **I** are sometimes modest, this approach has broad generality. Alternatively, in favorable cases precursors of the type **III** and diphosphines react to give **I**. These can be viewed

* Corresponding author. Tel.: +49 9131 8522540 fax: +49 9131 8526865.
E-mail address: gladysz@chemie.uni-erlangen.de (J.A. Gladysz).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.12.023



Scheme 1. Limiting structures for diplatinum polyynediyl complexes with termini-spanning diphosphines $Ar_2P(CH_2)_mPAr_2$ (**Ia**, **Ib**), and synthetic pathways ($m = 2m' + 2$).

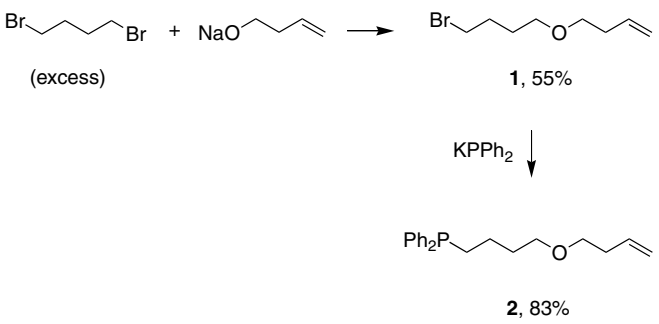
as coordination-driven self assembly processes [1a,1b,3]. In our most recent efforts, we have sought to extend this work to functionalized phosphines, for example with heteroatom or alkyl substituents [1c,3c].

In a previous full paper, an extensive series of diphosphines of the formula $Ph_2P(CH_2)_mPPh_2$ was described [4]. In this manuscript, syntheses of some related PAr_2 species are reported, as well as new oxygen-, fluorine-, methyl-, and alkene-substituted monophosphines and diphosphines that play key roles in upcoming full papers [3]. This avoids the fragmentation of similar sequences, which in some cases might be relegated to supporting information. Platinum complexes of selected ligands are also described, some of which represent "missing links" with respect to series in existing full papers [5] but have assumed importance in subsequent efforts [3b]. Additional details can be found in two dissertations [6].

2. Results

2.1. Oxygen-containing monophosphines

One current goal involves the introduction of Lewis basic functionality into the sp^3 chains of **I**. Thus, expedient syntheses of polyether analogs were sought. One obvious route would require alkene-containing monophosphines of the formula $Ph_2P(CH_2)_{m''}O(CH_2)_{m'''}CH{=}CH_2$. As shown in Scheme 2, a Williamson ether synthesis involving the alkoxide of 3-buten-1-ol and the α,ω-dibromide $Br(CH_2)_4Br$ (twofold excess) was attempted. After distillation to remove the diether byproduct $H_2C{=}CH(CH_2)_2O(CH_2)_4O(CH_2)_2CH{=}CH_2$, the new α,ω-bromoalkene $Br(CH_2)_4O(CH_2)_2CH{=}CH_2$ (**1**) could be isolated in 55% yield based upon the alkoxide.

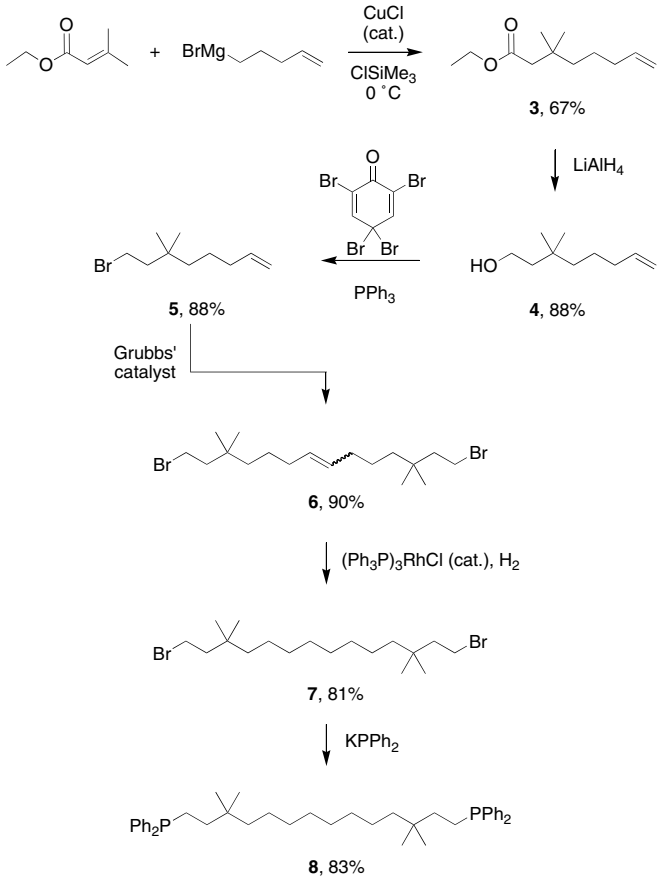


Scheme 2. Synthesis of the oxygen-containing monophosphine **2**.

Next, **1** and commercial $KPPh_2$ were reacted. Workup afforded the target polyfunctional monophosphine $Ph_2P(CH_2)_4O(CH_2)_2CH{=}CH_2$ (**2**) as an air-sensitive oil in 83% yield. All new compounds were characterized by NMR spectroscopy (^1H, ^{13}C, and (for phosphines) ^{31}P), and often by IR and mass spectrometry. Data are summarized in the experimental section. In all cases, features were routine. Although **2** was ⩾97% pure by ^1H and ^{31}P NMR, a satisfactory microanalysis was not obtained.

2.2. Diphosphines with geminal dimethyl groups

Geminal dialkyl substituents can have a profound influence on conformational equilibria and product distributions (e.g. intramolecular vs. intermolecular condensations) [7]. Accordingly, we sought to probe for effects on the equilibrium **Ia**/**Ib**, or the corresponding energy barrier. In view of our many results with $Ar_2P(CH_2)_{14}PAr_2$-bridged systems [1a,1b], symmetrically-substituted diphosphines with bridges of fourteen sp^3 carbon atoms were sought.



Scheme 3. Synthesis of the bis(geminally dimethylated) diphosphine **8**.

As shown in Scheme 3, ethyl 3-methylcrotonoate and the Grignard reagent derived from $Br(CH_2)_3CH{=}CH_2$ were combined in the presence of copper(I). In accord with a report of Brunel and Rousseau [8], conjugate addition occurred, giving the α,ω-carboethoxyalkene CH_3CH_2O-$C(O)CH_2C(CH_3)_2(CH_2)_3CH{=}CH_2$ (**3**) in 67% yield after workup. This compound, which features a geminal dimethyl group β to the carbonyl group, has only been partially characterized [8,9]. Routine reduction and bromination [10] steps gave the α,ω-hydroxyalkene $HOCH_2$-$CH_2C(CH_3)_2(CH_2)_3CH{=}CH_2$ (**4**) [9] and α,ω-bromoalkene $BrCH_2CH_2C(CH_3)_2(CH_2)_3CH{=}CH_2$ (**5**) [9] in 88% and 88% yields. We have previously synthesized the latter compound, but by a less efficient pathway [5a].

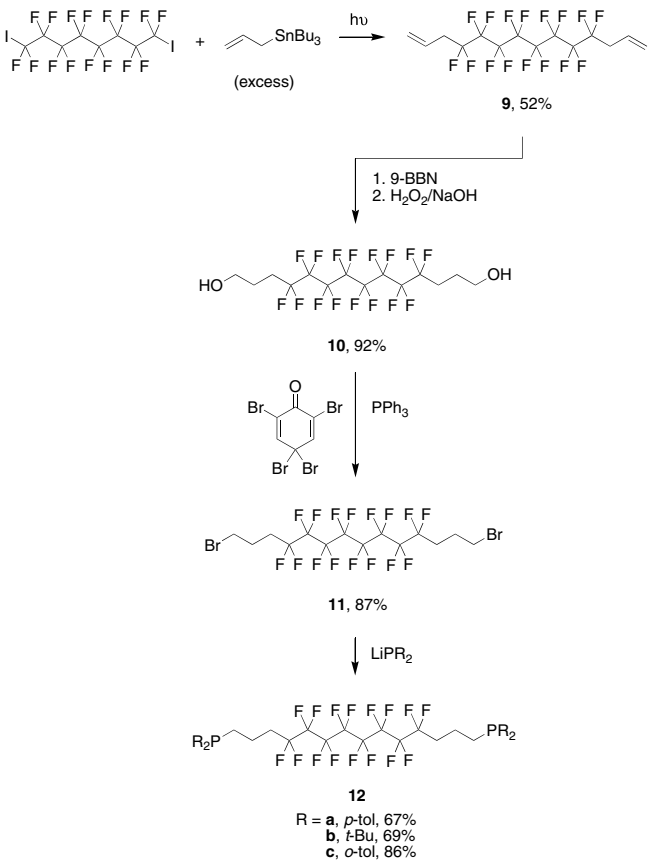
Reaction of **5** with Grubbs' catalyst gave the crude metathesis product **6** (Scheme 3) as a mixture of *Z*/*E* isomers in 90% yield. Subsequent hydrogenation afforded the saturated α,ω-dibromide $Br(CH_2)_2C(CH_3)_2(CH_2)_8$-$C(CH_3)_2(CH_2)_2Br$ (**7**) in 81% yield. Treatment with 2.0 equiv. of $KPPh_2$ afforded the target diphosphine $Ph_2P(CH_2)_2C(CH_3)_2(CH_2)_8C(CH_3)_2(CH_2)_2PPh_2$ (**8**), with a 14-carbon bridge and a geminal dimethyl group γ to each phosphorus, as a spectroscopically pure white solid in 83% yield. Solutions of **8** were quite air sensitive, but solid samples survived brief exposures. The ^1H and ^{13}C NMR spectra of this entire series of compounds showed the expected singlets for the dimethyl groups.

2.3. Diphosphines with difluoromethylene segments

Perfluoroalkanes and other compounds with difluoromethylene segments are known to adopt helical conformations [11]. It was thought that this might have an effect on equilibria of the type **Ia**/**Ib**, and therefore appropriately fluorinated diphosphines were sought. Although many phosphines with perfluoroalkyl groups are known [12], diphosphines of the formula $Ar_2P(CF_2)_mPAr_2$ would be too weakly nucleophilic and basic to give substitution reactions as in Scheme 1 [13]. Hence, analogs with insulating methylene groups were targeted. For reasons outlined above, a system with fourteen sp^3 carbon atoms was preferred.

Perfluoroalkyl iodides and allyl tin compounds readily undergo free radical chain reactions to give allyl perfluoroalkyl species and tin iodides [14]. Thus, as shown in Scheme 4, the commercial "fluorous" [15] α,ω-diiodide $I(CF_2)_8I$ and $H_2C{=}CHCH_2SnBu_3$ were irradiated. Twofold allylation occurred to give the 14-carbon-atom α,ω-bis-(alkene) $H_2C{=}CHCH_2(CF_2)_8CH_2CH{=}CH_2$ (**9**), which was isolated in 52% yield after distillation. A hydroboration/oxidation sequence afforded the α,ω-diol HO-$(CH_2)_3(CF_2)_8(CH_2)_3OH$ (**10**, 92%), which was subsequently brominated to give the α,ω-dibromide $Br(CH_2)_3(CF_2)_8$-$(CH_2)_3Br$ (**11**, 87%).

As shown in Scheme 4, **11** was treated with aromatic and aliphatic $LiPR_2$ reagents that had been generated by



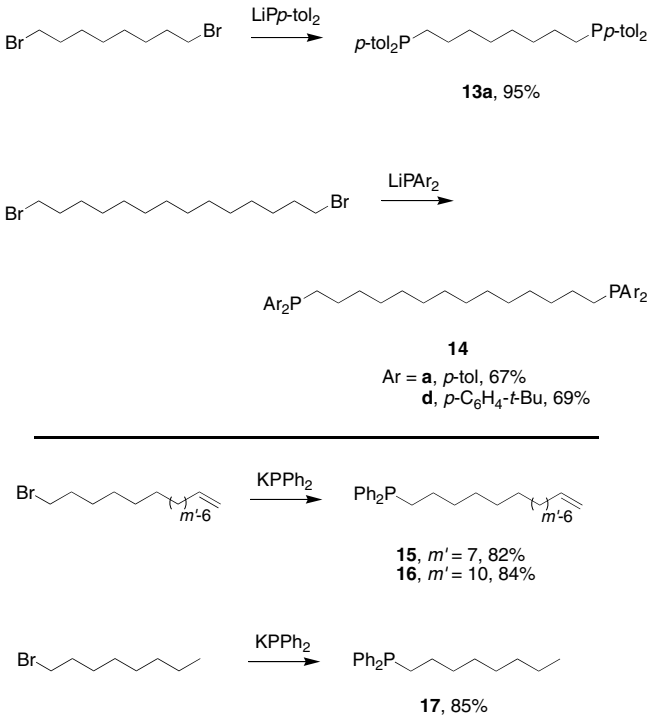
Scheme 4. Syntheses of the fluorinated diphosphines **12**.

deprotonations of secondary phosphines. Workups gave the target diphosphines $R_2P(CH_2)_3(CF_2)_8(CH_2)_3PR_2$ (**12**; R = **a**, *p*-tol; **b**, *t*-Bu; **c**, *o*-tol) in 67–86% yields. In contrast to the other diphosphines in this paper, **12a–c** were stable for extended periods in air, presumably due to the residual electron-withdrawing effects of the perfluoroalkyl segments at phosphorus [13]. The ^1H and ^{13}C NMR signals associated with the $PCH_2CH_2CH_2$ moieties were similar to those of closely related fluorous trialkylphosphines [14].

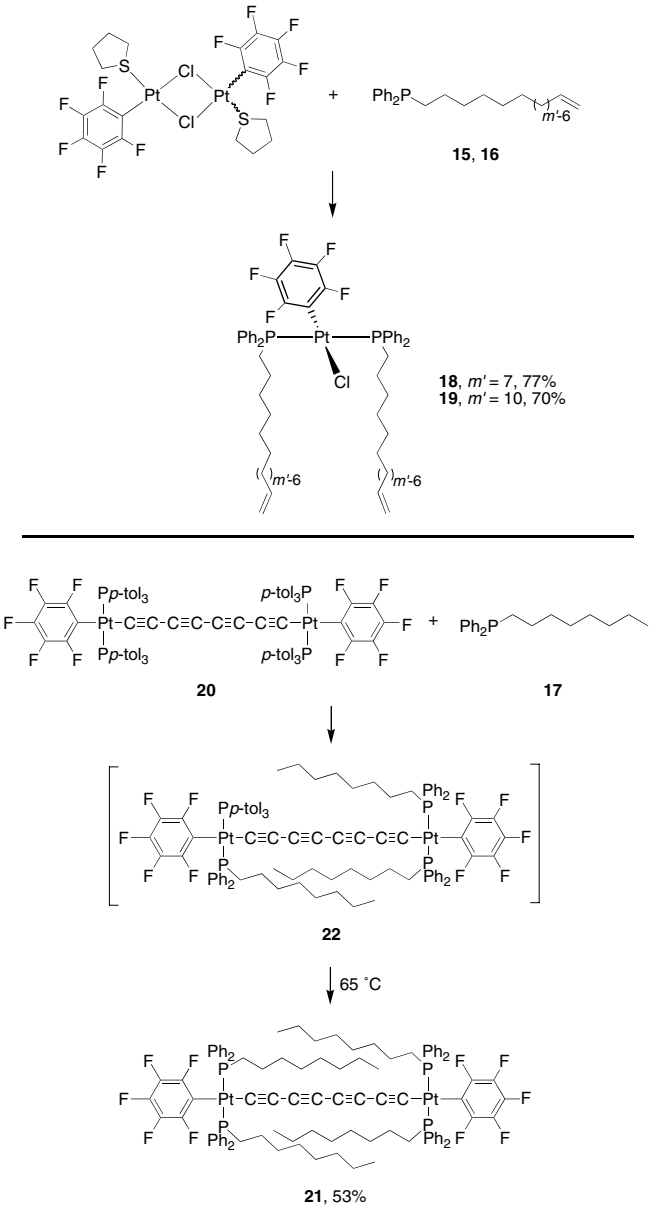
Interestingly, all of the fluorinated compounds except **9** were white solids, and correct microanalyses were obtained in each case. Free radical additions of secondary phosphines to terminal alkenes – including $R_fCH{=}CH_2$ and $R_fCH_2CH{=}CH_2$ systems – are often efficient preparative reactions [14,16]. However, extensive efforts to access **12** via additions of $HPAr_2$ species to **9** were unsuccessful.

2.4. Additional diphosphines and monophosphines

Non-fluorinated diphosphines with substituted aryl groups that would give easily monitored NMR signals were sought. Thus, as shown in Scheme 5 (top), the commercial α,ω-dibromide $Br(CH_2)_8Br$ was treated with Li*p*-tol_2. Workup gave the diphosphine *p*-$tol_2P(CH_2)_8P$*p*-tol_2 (**13a**) as a white solid in 95% yield. Similarly, the longer-chain dibromide $Br(CH_2)_{14}Br$ was treated with Li*p*-tol_2 and $LiP(p\text{-}C_6H_4\text{-}t\text{-}Bu)_2$. Workups gave *p*-$tol_2P(CH_2)_{14}P$*p*-$tol_2$ (**14a**) and $(p\text{-}t\text{-}BuC_6H_4)_2P(CH_2)_{14}P(p\text{-}C_6H_4\text{-}t\text{-}Bu)_2$ (**14d**) as analytically pure white solids in 96% and 98% yields. As expected, the ^1H and ^{13}C NMR spectra of all three compounds exhibited sharp singlets for the *p*-methyl and *p*-*t*-butyl groups. Their air sensitivities were similar to that of **8**.



Scheme 5. Other new syntheses of monophosphines and diphosphines.



Scheme 6. Syntheses of new platinum complexes.

In order to better define the generality of the synthesis of **I** from **II** as a function of sp and sp^3 carbon chain lengths, a wider variety of alkene-containing monophosphines $Ph_2P(CH_2)_{m'}CH{=}CH_2$ were required. As shown in Scheme 5 (bottom), two examples were synthesized by reactions of $KPPh_2$ and the corresponding α,ω-bromoalkenes. Workups gave $Ph_2P(CH_2)_7CH{=}CH_2$ (**15**) and $Ph_2P(CH_2)_{10}CH{=}CH_2$ (**16**) as moderately air sensitive oils in 82% and 84% yields. The spectroscopic properties were similar to those of previously reported analogs ($m' = 4, 5, 6, 8, 9$) [5]. In order to provide a non-cyclized reference compound for **I**, the phosphine $Ph_2P(CH_2)_7CH_3$ (**17**) was similarly prepared from $KPPh_2$ and $Br(CH_2)_7CH_3$ (Scheme 5, bottom). Although this compound has been reported twice

previously [17], one synthesis is longer; for the other (from the corresponding alkyl chloride), only a ^{31}P NMR spectrum was given.

2.5. Selected platinum complexes

The three preceding monophosphines were applied in syntheses. Complexes of the formula *trans*-$(C_6F_5)(L)_2PtCl$ are easily prepared from the substitution-labile platinum tetrahydrothiophene complex $[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ [18]. As shown in Scheme 6 (top), reactions with **15** and **16** gave the new adducts *trans*-$(C_6F_5)(Ph_2P(CH_2)_{m'}CH{=}CH_2)_2PtCl$ ($m' = 7$, **18**; 10, **19**) in 77–70% yields. The spectroscopic properties were similar to those of previously reported analogs [5].

A reference compound that would electronically resemble the alkyl(diaryl)phosphine complexes **I** but lack the termini-spanning sp^3 chains was sought. As shown in Scheme 6 (bottom), the diplatinum octatetraynediyl complex *trans*,*trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_4Pt(P\textit{p}\text{-}tol_3)_2(C_6F_5)$ (**20**) [19] was treated with an excess of the *n*-octyl phosphine **17** at room temperature. Substitution occurred to give the target molecule *trans*,*trans*-$(C_6F_5)(Ph_2P(CH_2)_7CH_3)_2Pt(C{\equiv}C)_4Pt(Ph_2P(CH_2)_7CH_3)_2(C_6F_5)$ (**21**). However, an appreciable amount of the corresponding trisubstitution product **22** (Scheme 6) was also present, as evidenced by three ^{31}P NMR signals. Two were of lesser intensity, and strongly coupled to each other ($^2J_{PP} = 409$ Hz; P*p*-tol_3 and **17** with *trans* relationship). Reaction of the mixture with a second charge of **17** at 65 °C gave analytically pure **21** in 53% yield after chromatography. The ^{13}C NMR spectrum of **21** exhibited $PtC{\equiv}CC{\equiv}C$ signals that were very similar to those of the precursor **20** (100.0, 94.2, 63.7, 57.9 ppm vs. 100.6, 96.7, 64.1, 58.1 ppm) [19], and the UV–vis spectra were essentially identical.

3. Discussion

This study has provided efficient syntheses of a variety of functionalized monophosphines and diphosphines. To our knowledge, the oxygenated and fluorinated systems **2** and **12a**–**c** (Schemes 2 and 4) have no previous counterpart. However, there is a substantial literature involving oxygenated *di*phosphines that can give crown-ether-like metal complexes [20]. Also, Gray has reported the synthesis of the tetraether $Ph_2PCH_2(CH_2OCH_2)_4CH_2PPh_2$, in which the phosphorus atoms are linked by 14 sp^3 hybridized atoms [21]. The diphosphines **12a**–**c** and their precursors (Scheme 4) may have independent applications in fluorous chemistry [15].

No close analogs of the bis(geminally dimethylated) diphosphine **18** (Scheme 3) are known. However, the dimethylated monophosphine **23**, depicted in Fig. 1, has been prepared from the α,ω-bromoalkene **5** (Scheme 3) and $KPPh_2$ [5a]. As noted above, a number of alkene containing phosphines that complement **15** and **16** have been reported [5]; these are also summarized in Fig. 1. In all cases, platinum complexes analogous to **18** and **19** have been prepared. In connection with other objectives, related dialkyl and trialkyl phosphines of the formulae $PhP((CH_2)_{m'}CH{=}CH_2)_2$ and $P((CH_2)_{m'}CH{=}CH_2)_3$ have also been synthesized [22–24]. The diphosphines **13a** and **14a**,**d** (Scheme 5) complement the extensive series of phenyl-substituted analogs $Ph_2P(CH_2)_mPPh_2$ reported in our previous full paper (Fig. 1) [4].

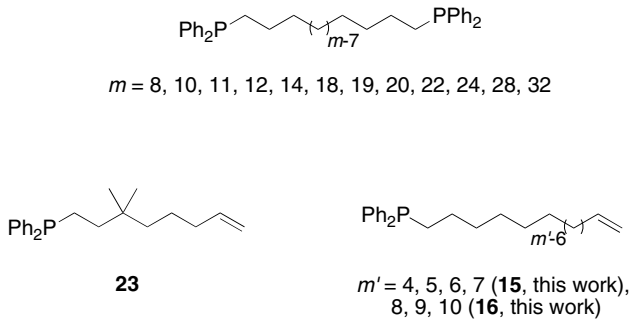


Fig. 1. Related phosphine ligands reported previously.

As will be detailed in future full papers [3], nearly all of the above types of functionalized monophosphines and diphosphines can be elaborated into analogs of **I**. For these, complex **21** in Scheme 6 – derived from an unfunctionalized monophosphine – provides an important reference compound. Other types of functional phosphines that may serve as precursors to derivatives of **I** are under active investigation and will be reported in due course [25].

4. Experimental

4.1. General

Instrumentation and general methods were identical to those in previous papers [5a]. Chemicals were used as follows: THF and Et_2O, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2; hexanes, simple distillation; $HO(CH_2)_2CH{=}CH_2$ (Aldrich), distilled from Na; toluene and $Br(CH_2)_4Br$ (Acros), distilled; *n*-BuLi (Acros, 1.6 M in hexane) and *t*-BuLi (Aldrich, 1.52 M in pentane), standardized [26]; CuCl (Aldrich, 99.99%), $ClSiMe_3$ (Acros, 98%), $Br(CH_2)_3CH{=}CH_2$, $Br(CH_2)_8Br$ (2 × Acros), $CH_3CH_2OC(O)CH{=}C(CH_3)_2$, 9-BBN, 2,4,4,6-tetrabromo-2,5-cyclohexadienone, $Br(CH_2)_7CH_3$ (4 × Aldrich), $LiAlH_4$ (Fluka), Grubbs' catalyst (Strem), $KPPh_2$ (Fluka, 0.5 M in THF), Ph_3P, $I(CF_2)_8I$, $CF_3C_6F_{11}$ (3 × ABCR), $H_2C{=}CHCH_2SnBu_3$ (Lancaster), $(Ph_3P)_3RhCl$, HP*p*-tol_2, HP-$(t\text{-}Bu)_2$ (3 × Strem), and other materials, used as received.

4.2. $Br(CH_2)_4O(CH_2)_2CH{=}CH_2$ (1)

A Schlenk flask was fitted with a condenser and charged with sodium (0.831 g, 36.1 mmol), and $HO(CH_2)_2CH{=}CH_2$ (12.0 mL, 139 mmol) was slowly added with stirring. The mixture was heated at 80 °C until the sodium dissolved (ca. 2 h). Then $Br(CH_2)_4Br$ was added (8.3 mL, 73 mmol),

and the mixture was refluxed. After 3 h, excess alcohol was recovered by distillation (110 °C). The residue was cooled and poured into water (30 mL). The organic layer was separated. The aqueous layer was washed with ether (2 × 10 mL). The combined organic phases were washed with water (2 × 5 mL) and dried ($CaCl_2$). The solvent was removed by rotary evaporation. The residue was chromatographed on a silica gel column (20 × 2.5 cm, 70:30 v/v hexanes/CH_2Cl_2). The first fraction contained the excess $Br(CH_2)_4Br$. The solvent was removed from the second fraction by rotary evaporation and oil pump vacuum to give **1** as a colorless oil (4.284 g, 19.92 mmol, 55%).

NMR (δ, $CDCl_3$), ^1H 5.79 (ddt, 1H, $^3J_{HHtrans} = 17.1$ Hz, $^3J_{HHcis} = 10.3$ Hz, $^3J_{HH} = 6.8$ Hz, CH=), 5.05 (br d, 1H, $^3J_{HHtrans} = 17.2$ Hz, $=CH_EH_Z$), 5.00 (br d, 1H, $^3J_{HHcis} = 10.2$ Hz, $=CH_EH_Z$), 3.45–3.39 (m, 6H, $BrCH_2CH_2CH_2CH_2OCH_2$), 2.32–2.27 (m, 2H, $CH_2CH=$), 1.93–1.88 and 1.70–1.67 (2 m, 4H, $BrCH_2CH_2CH_2$); $^{13}C\{^1H\}$ 135.2 (s, CH=), 116.3 (s, $=CH_2$), 70.1, 69.7 (2 s, CH_2OCH_2), 34.2, 33.8 (2 s, $CH_2CH=$ and $BrCH_2$), 29.7, 28.2 (2 s, $BrCH_2CH_2CH_2$).

4.3. $Ph_2P(CH_2)_4O(CH_2)_2CH=CH_2$ (2)

A Schlenk flask was charged with $Br(CH_2)_4O(CH_2)_2CH=CH_2$ (0.929 g, 4.49 mmol) and THF (20 mL), and cooled to 0 °C. Then $KPPh_2$ (9.0 mL, 0.5 M in THF, 4.5 mmol) was added dropwise with stirring until a red color persisted. A white precipitate formed. The mixture was stirred at 0 °C for 0.5 h, and the cold bath was removed. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2. The extract was filtered through a short silica gel column (5 × 2.5 cm, CH_2Cl_2 rinses). The solvent was removed from the filtrate by oil pump vacuum to give **2** as an air sensitive, spectroscopically pure white oil (1.16 g, 3.73 mmol, 83%).

NMR (δ, $CDCl_3$), ^1H 7.45–7.37 (m, 4H of 2 Ph), 7.33–7.29 (m, 6H of 2 Ph), 5.81–5.74 (m, 1H, CH=), 5.07–4.98 (m, 2H, $=CH_2$), 3.43–3.38 (m, 4H, CH_2OCH_2), 2.34–2.26 (m, 2H, $CH_2CH=$), 2.07–2.00 (m, 2H, PCH_2), 1.70–1.67 (m, 2H, PCH_2CH_2), 1.54–1.47 (m, 2H, OCH_2CH_2); $^{13}C\{^1H\}$ [27] 138.8 (d, $^1J_{CP} = 13.0$ Hz, *i* to P), 135.3 (s, CH=), 132.6 (d, $^2J_{CP} = 18.4$ Hz, *o* to P), 128.4 (s, *p* to P), 128.3 (d, $^3J_{CP} = 6.5$ Hz, *m* to P), 116.2 (s, $=CH_2$), 70.3 and 70.0 (2 s, CH_2OCH_2), 34.2 (s, $CH_2CH=$), 31.1 (d, $^1J_{CP}$ = 13.0 Hz, $PCH_2CH_2CH_2$), 27.9 (d, $^1J_{CP}$ = 11.2 Hz, PCH_2), 22.7 (d, $^1J_{CP}$ = 16.7 Hz, PCH_2CH_2); $^{31}P\{^1H\}$ −15.8 (s).

4.4. $CH_3CH_2OC(O)CH_2C(CH_3)_2(CH_2)_3CH=CH_2$ (3)

A Schlenk flask was charged with Mg (0.920 g, 37.8 mmol), THF (40 mL), and $Br(CH_2)_3CH=CH_2$ (5.14 g, 34.6 mmol). The mixture was stirred for 1.5 h at 50 °C. A second Schlenk flask was charged with $CH_3CH_2OC(O)CH=C(CH_3)_2$ (4.18 g, 32.6 mmol), THF (50 mL), CuCl (0.098 g, 1.00 mmol), and $ClSiMe_3$ (5.00 mL, 39.2 mmol), and cooled to 0 °C. The Grignard solution was transferred via cannula to the second flask with stirring [8]. The cold bath was removed. After 1.5 h, saturated aqueous NH_4Cl (60 mL) was added. The aqueous phase was washed with Et_2O (2 × 60 mL). The combined organic phases were dried ($MgSO_4$). The solvent was removed by rotary evaporation. The residue was distilled (Kugelrohr) to give **3** as a colorless liquid (4.32 g, 21.8 mmol, 67%) [8,9].

NMR (δ, $CDCl_3$), ^1H 5.79 (ddt, 1H, $^3J_{HHtrans} = 17.0$ Hz, $^3J_{HHcis} = 10.5$, $^3J_{HH} = 6.5$ Hz, CH=), 4.97 (dm, 1H, $^3J_{HHtrans} = 17.0$ Hz, $=CH_EH_Z$), 4.90 (dm, 1H, $^3J_{HHcis} = 10.5$ Hz, $=CH_EH_Z$), 4.07 (q, 2H, $^3J_{HH} = 7.1$ Hz, CH_2O), 2.15 (s, 2H, $C(O)CH_2$), 1.99 (apparent quartet, 2H, $^3J_{HH} = 6.9$ Hz, $CH_2CH=$), 1.40–1.24 (m, 4H, CH_2), 1.21 (t, 3H, $^3J_{HH}$ 7.1 = Hz, CH_3CH_2), 0.95 (s, 6H, $C(CH_3)_2$); $^{13}C\{^1H\}$ 172.3 (s, C=O), 138.9 (s, CH=), 114.3 (s, $=CH_2$), 59.8 (s, CH_2O), 46.0 (s, $C(O)CH_2$), 41.7 (s, $C(CH_3)_2CH_2$), 34.4 (s, $CH_2CH=$), 33.2 (s, $C(CH_3)_2$), 27.3 (s, $C(CH_3)_2$), 23.4 (s, $CH_2CH_2CH=$), 14.3 (s, CH_3CH_2). IR (cm^{-1}, liquid film), 3080 (w), 2961 (m), 2937 (m), 1733 (vs), 1644 (w), 1467 (w), 1455 (w), 1370 (m), 1227 (s), 1146 (s), 1127 (m), 1034 (m), 996 (w), 911 (m), 849 (w).

4.5. $HOCH_2CH_2C(CH_3)_2(CH_2)_3CH=CH_2$ (4)

A Schlenk flask was charged with $LiAlH_4$ (0.436 g, 11.5 mmol) and Et_2O (30 mL), and fitted with a condenser. A solution of **3** (4.100 g, 20.67 mmol) in Et_2O (20 mL) was added with stirring. The mixture was refluxed (2 h) and cooled to room temperature. Then ice water (3 mL) and H_2SO_4 (10 mL, 10% in H_2O) were added with stirring. The aqueous phase was separated and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with saturated brine and dried ($MgSO_4$). The solvent was removed by rotary evaporation to give **4** as a colorless liquid (2.857 g, 18.28 mmol, 88%) [9].

NMR (δ, $CDCl_3$), ^1H 5.77 (ddt, 1H, $^3J_{HHtrans} = 17.0$ Hz, $^3J_{HHcis} = 10.5$, $^3J_{HH} = 6.5$ Hz, CH=), 4.98 (dm, 1H, $^3J_{HHtrans} = 17.0$ Hz, $=CH_EH_Z$), 4.90 (dm, 1H, $^3J_{HHcis} = 10.5$ Hz, $=CH_EH_Z$), 3.63 (m, 2H, $HOCH_2$), 1.98 (apparent quartet, 2H, $^3J_{HH} = 7.1$ Hz, $CH_2CH=$), 1.57 (br s, 1H, HO), 1.48 (m, 2H, $HOCH_2CH_2$), 1.35–1.28 (m, 2H, CH_2), 1.19–1.13 (m, 2H, CH_2), 0.85 (s, 6H, CH_3). IR (cm^{-1}, liquid film), ν_{OH} 3339 (m); 3080 (w), 2957 (m), 2937 (s), 2868 (w), 1640 (w), 1471 (m), 1444 (w), 1417 (w), 1386 (m), 1366 (m), 1104 (m), 1046 (s), 1031 (s), 996 (m), 911 (vs).

4.6. $BrCH_2CH_2C(CH_3)_2(CH_2)_3CH=CH_2$ (5)

A Schlenk flask was charged with Ph_3P (5.54 g, 21.1 mmol) and CH_2Cl_2 (50 mL), and cooled to 0 °C. Then 2,4,4,6-tetrabromocyclohexa-2,5-dienone (8.65 g, 21.1 mmol) was added with stirring. After 1.5 h, **4** (1.500 g, 9.600 mmol) was added [10]. The cold bath was removed. The mixture was stirred for 16 h. The solvent was removed

by rotary evaporation. The yellow residue was extracted with hexanes (5 × 20 mL). The extract was filtered through silica gel (10 cm, hexanes rinses). The solvent was removed from the filtrate by rotary evaporation to give **5** as a colorless liquid (1.854 g, 8.460 mmol, 88%) [5a,9].

NMR (δ, $CDCl_3$), ^1H 5.78 (ddt, 1H, $^3J_{HHtrans} = 17.1$ Hz, $^3J_{HHcis} = 10.4$, $^3J_{HH} = 6.7$ Hz, CH=), 4.97 (dm, 1H, $^3J_{HHtrans} = 17.1$ Hz, $=CH_EH_Z$), 4.93 (dm, 1H, $^3J_{HHcis} = 10.4$ Hz, $=CH_EH_Z$), 3.35 (m, 2H, $BrCH_2$), 2.00 (apparent quartet, 2H, $^3J_{HH} = 7.2$ Hz, $=CHCH_2$), 1.85–1.78 (m, 2H, $BrCH_2CH_2$), 1.36–1.27 (m, 2H, CH_2), 1.20–1.14 (m, 2H, CH_2), 0.86 (s, 6H, CH_3); $^{13}C\{^1H\}$ 138.8 (s, $CH_2CH=$), 114.5 (s, $=CH_2$), 45.5 (s, CH_2), 41.3 (s, CH_2), 34.4 (s, $C(CH_3)_2$), 34.3 (s, CH_2), 29.6 (s, CH_2), 26.9 (s, CH_3), 23.3 (s, CH_2). The IR spectrum [6a] agreed with those reported earlier [5a,9]. MS [28], 218 (**11**$^+$, 1%), 190 ([**11**–$2CH_2$]$^+$, 6%), 176 ([**11**–$3CH_2$]$^+$, 42%), 149 ($BrC_5H_{10}^+$, 50%), 111 ($C_8H_{15}^+$, 61%), 69 ($C_5H_9^+$, 100%).

4.7. $BrCH_2CH_2C(CH_3)_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2C(CH_3)_2CH_2CH_2Br$ (*6*)

A Schlenk flask was charged with Grubbs' catalyst (0.124 g, 0.150 mmol), CH_2Cl_2 (50 mL), and **5** (0.548 g, 2.50 mmol). The mixture was stirred for 4 h. A second charge of Grubbs' catalyst (0.041 g, 0.050 mmol) was added. After 16 h, the solvent was removed by rotary evaporation. The brown residue was extracted with hexanes (2 × 5 mL). The extracts were filtered through a silica gel pad (15 cm, hexanes rinses). The solvent was removed from the filtrate by oil pump vacuum to give **6** as a colorless liquid (0.464 g, 1.13 mmol, 90%, mixture of *Z*/*E* isomers with minor impurities).

NMR (δ, $CDCl_3$, major isomer only), ^1H 5.39–5.35 (m, 2H, =CH), 3.37–3.32 (m, 4H, CH_2Br), 2.01–1.90 (m, 4H, $=CHCH_2$), 1.84–1.78 (m, 4H, CH_2CH_2Br), 1.33–1.22 (m, 4H, CH_2), 1.20–1.12 (m, 4H, CH_2), 0.86 (s, 12H, CH_3); $^{13}C\{^1H\}$ 130.4 (s, =CH), 45.5 (s, CH_2), 41.3 (s, CH_2), 34.3 (s, $C(CH_3)_2$), 33.2 (s, CH_2), 29.6 (s, CH_2), 26.9 (s, $C(CH_3)_2$), 24.0 (s, CH_2). IR (cm^{-1}, liquid film), 2957 (vs), 2934 (vs), 2868 (m), 1471 (s), 1390 (w), 1366 (m), 1336 (w), 1235 (s), 969 (s), 745 (w), 695 (w). MS [28], 410 (**6**$^+$, 1%), 301 ([**6**–CH_2CH_2Br]$^+$, 2%), 259 ($C_{13}H_{24}Br^+$, 3%), 219 ($C_{10}H_{20}Br^+$, 50%), 191 ($C_8H_{16}Br^+$, 62%), 149 ($BrC_5H_{10}^+$, 76%), 111 ($C_8H_{15}^+$, 87%).

4.8. $Br(CH_2)_2C(CH_3)_2(CH_2)_8C(CH_3)_2(CH_2)_2Br$ (*7*)

A Fisher-Porter bottle was charged with **6** (0.142 g, 0.346 mmol), toluene (35 mL), and $(Ph_3P)_3RhCl$ (0.032 g, 0.035 mmol). Then H_2 (4 bar) was introduced, and the mixture was stirred. After 16 h, the solvent was removed by oil pump vacuum. The residue was extracted with hexanes (2 × 5 mL). The extracts were filtered through a silica gel pad (4 cm, hexanes rinses). The solvent was removed from the filtrate by oil pump vacuum to give **7** as a colorless liquid (0.115 g, 0.279 mmol, 81%).

NMR (δ, $CDCl_3$), ^1H 3.38–3.31 (m, 4H, CH_2Br), 1.85–1.77 (m, 4H, CH_2CH_2Br), 1.31–1.11 (m, 16H, remaining CH_2), 0.85 (s, 12H, CH_3); $^{13}C\{^1H\}$ 45.6 (s, CH_2), 41.9 (s, CH_2), 34.3 (s, $C(CH_3)_2$), 30.5 (s, CH_2), 29.7 (s, CH_2), 29.6 (s, CH_2), 26.9 (s, CH_3), 23.9 (s, CH_2). IR (cm^{-1}, liquid film), 2957 (s), 2930 (vs), 2856 (s), 1471 (s), 1390 (w), 1366 (m), 1336 (w), 1239 (m), 749 (w), 722 (w); MS [28], 303 ([7–CH_2CH_2Br]$^+$, 23%), and additional ions from the loss of CH_2.

4.9. $Ph_2P(CH_2)_2C(CH_3)_2(CH_2)_8C(CH_3)_2(CH_2)_2PPh_2$ (*8*)

A Schlenk flask was charged with **7** (0.600 g, 1.46 mmol) and THF (15 mL). Then $KPPh_2$ (5.84 mL, 0.5 M in THF, 2.92 mmol) was added dropwise with stirring until a light yellow color persisted. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2 (3 × 10 mL). The extracts were filtered through a silica gel pad (4 cm, CH_2Cl_2 rinses). The solvent was removed from the filtrate by oil pump vacuum to give a colorless oil. The oil was distilled (Kugelrohr, 200 °C, oil pump vacuum) to give **8** as a spectroscopically pure white solid (0.753 g, 1.21 mmol, 83%).

NMR (δ, $CDCl_3$), ^1H 7.44–7.38 (m, 8H of 4Ph), 7.34–7.26 (m, 12H of 4Ph), 1.98–1.91 (m, 4H, PCH_2), 1.33–1.23 (m, 4H, PCH_2CH_2), 1.23–1.03 (m, 16H, remaining CH_2), 0.82 (s, 12H, CH_3); $^{13}C\{^1H\}$ [27] 138.7 (d, $^1J_{CP} = 12.6$ Hz, *i* to P), 132.7 (d, $^2J_{CP} = 18.1$ Hz, *o* to P), 128.5 (s, *p* to P), 128.4 (d, $^3J_{CP} = 6.6$ Hz, *m* to P), 41.1 (s, CH_2), 37.6 (d, $^2J_{CP} = 16.5$ Hz, PCH_2CH_2C) [34], 33.4 (d, $^3J_{CP} = 13.2$ Hz, PCH_2CH_2C) [29], 30.6 (s, CH_2), 29.8 (s, CH_2), 27.0 (s, CH_3), 23.9 (s, CH_2), 22.4 (d, $^1J_{CP} = 9.9$ Hz, PCH_2) [29]; $^{31}P\{^1H\}$ −13.6 (s). IR (cm^{-1}, powder film), 2922 (s), 2856 (m), 1471 (m), 1432 (m), 1386 (w), 1363 (w), 1096 (w), 1069 (w), 1031 (w), 1000 (w), 737 (s), 718 (m), 691 (vs). MS [28], 622 (**8**$^+$, 20%), 325 ($C_{22}H_{30}P^+$, 60%), and additional ions from the loss of CH_2.

4.10. $H_2C{=}CHCH_2(CF_2)_8CH_2CH{=}CH_2$ (*9*)

A Schlenk flask was charged with $I(CF_2)_8I$ (3.190 g, 4.880 mmol), $H_2C{=}CHCH_2SnBu_3$ (6.460 g, 19.50 mmol), and carefully degassed CH_2Cl_2 (three freeze/pump/thaw cycles; total volume 50 mL). The solution was cooled to 0 °C and photolyzed (high pressure mercury lamp; through Pyrex) with stirring. After 5 h, the solvent was removed by rotary evaporation. The residue was distilled (Kugelrohr). The distillate (which contained traces of $ISnBu_3$) was filtered through a short alumina column with $CF_3C_6F_{11}$. The solvent was removed from the filtrate by rotary evaporation to give **9** as a clear liquid (1.220 g, 2.53 mmol, 52%). Calcd. for $C_{14}H_{10}F_{16}$: C, 34.87; H 2.09. Found: C, 34.30; H, 2.28%.

NMR (δ, $CDCl_3$), ^1H 5.87–5.70 (m, 2H, CH=), 5.36–5.26 (m, 4H, $=CH_2$), 2.86 (pseudo td, 4H, $^3J_{HH} = 7$ Hz, $^3J_{HF} = 18$ Hz, CF_2CH_2); $^{13}C\{^1H\}$ 126.1, 123.3 (2 s,

*C*H=*C*H$_2$), 36.7 (t, $^2J_{CF} = 45$ Hz, CF_2CH_2) [19]; F{^{1}H} −113.7 to −114.0 (m, 4F), −122.1 to −122.7 (m, 8F), −123.6 to −123.9 (m, 4F). IR (cm^{-1}, powder film), 1208, 1150.

4.11. $HO(CH_2)_3(CF_2)_8(CH_2)_3OH$ (**10**)

A flask was charged with **9** (1.481 g, 3.071 mmol), 9-BBN (0.900 g 7.37 mmol), and toluene (5 mL) in a glove box. The mixture was stirred overnight, and the solvent was removed by rotary evaporation. Then NaOH (25 mL, 5 M) and 30% H_2O_2 (25 mL; exotherm!) were slowly added with stirring. After 2 h, the white solid was filtered, washed with water, and dried by oil pump vacuum to give **10** as a white solid (1.457 g, 2.811 mmol, 92%), m.p. 109–112 °C. Calcd. for $C_{14}H_{14}F_{16}O_2$: C, 32.45; H 2.72. Found: C, 32.62; H, 2.99%.

NMR (δ, CD_3OD), ^{1}H 3.53 (t, 4H, $^3J_{HH} = 6$ Hz, C*H*$_2$OH), 2.24–2.06 (m, 4H, CF_2CH_2), 1.75–1.66 (m, 4H, CH_2CH_2OH); ^{13}C{^{1}H} 60.9 (s, CH_2OH), 28.2 (t, $^2J_{CF} = 22$ Hz, CF_2CH_2), 23.9 (s, *C*H$_2$CH$_2$OH); ^{19}F{^{1}H} −115.8 to −115.9 (m, 4F), −123.2 to −123.4 (m, 8F), −124.9 to −125.1 (m, 4F). IR (cm^{-1}, powder film), ν_{OH} 3250; 1206, 1142.

4.12. $Br(CH_2)_3(CF_2)_8(CH_2)_3Br$ (**11**)

A flask was charged with PPh_3 (4.050 g, 15.44 mmol), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (6.330 g, 15.44 mmol) and CH_2Cl_2 (15 mL). The mixture was cooled to 0 °C and stirred. After 15 min, **10** (2.00 g, 3.86 mmol) was added. After 12 h, the solvent was removed by rotary evaporation. Chromatography of the residue (silica gel column, hexane) gave **11** as a white solid, which was dried by oil pump vacuum (2.157 g, 3.349 mmol, 87%), m.p. 109–112 °C. Calcd. for $C_{14}H_{12}Br_2F_{16}$: C, 26.11; H, 1.88. Found: C, 26.83; H, 2.18%.

NMR (δ, $CDCl_3$), ^{1}H 3.46 (t, 4H, $^3J_{HH} = 6$ Hz, CH_2Br), 2.38–2.10 (m, 8H, $CF_2CH_2CH_2$); ^{13}C{^{1}H} 32.0 (s, CH_2Br), 30.0 (t, $^2J_{CF} = 22$ Hz, CF_2CH_2), 23.9 (s, *C*H$_2$CH$_2$Br); ^{19}F{^{1}H} −114.2 to −114.6 (m, 4F), −121.9 to −122.6 (m, 8F), −123.7 to −124.2 (m, 4F). IR (cm^{-1}, powder film), 1208, 1191, 1144, 735.

4.13. *p*-$tol_2P(CH_2)_3(CF_2)_8(CH_2)_3P$*p*-$tol_2$ (**12a**)

A Schlenk flask was charged with HP*p*-tol_2 (0.514 g, 2.40 mmol) and THF (35 mL, via vacuum transfer), and *n*-BuLi (1.62 mL, 1.49 M in hexane, 2.41 mmol) was slowly added with stirring. After 15 min, **11** (0.773 g, 1.20 mmol) in THF (15 mL) was added to the red solution. After 1 h, the solvent was removed by rotary evaporation. Chromatography of the residue (silica gel column, 2:1 v/v hexane/toluene) gave **12a** as an oil, which was dried by oil pump vacuum and gave a white solid upon standing (0.732 g, 0.800 mmol, 67%), m.p. 60–63 °C. Calcd. for $C_{42}H_{40}F_{16}P_2$: C, 55.39; H, 4.43. Found: C, 55.38; H, 4.50%.

NMR (δ, C_6D_6), ^{1}H 7.37 and 6.96 (2 d, 8H and 8H, $^3J_{HH} = 7$ Hz, C_6H_4), 2.06 (s, 12H, CH_3), 1.92–1.58 (m, 12H, $CH_2CH_2CH_2$); ^{13}C{^{1}H} [27b] 138.7 (s, *p* to P), 135.7 (d, $^1J_{CP} = 13$ Hz, *i* to P), 133.1 (d, $^2J_{CP} = 19$ Hz, *o* to P), 129.6 (d, $^3J_{CP} = 7$ Hz, *m* to P), 30.6 (m, CF_2CH_2), 27.9 (d, $^2J_{CP} = 13$ Hz, $CH_2CH_2CH_2$), 21.1 (s, CH_3), 17.3 (br d, $^1J_{CP} = 20$ Hz, CH_2P); ^{31}P{^{1}H} −18.9 (s); ^{19}F{^{1}H} −114.1 to −114.6 (m, 4F), −121.6 to −122.0 (m, 8F), −123.5 to −123.9 (m, 4F). IR (cm^{-1}, powder film), 2952, 1208, 1102, 1065, 800, 733.

4.14. *t*-$Bu_2P(CH_2)_3(CF_2)_8(CH_2)_3P$*t*-$Bu_2$ (**12b**)

A Schlenk flask was charged with HP*t*-Bu_2 (0.455 g, 3.19 mmol) and THF (30 mL), and cooled to 0 °C. Then *t*-BuLi (2.44 mL, 1.52 M in pentane, 3.71 mmol) was added with stirring. After 5 min, **11** (0.742 g, 1.01 mmol) in THF (15 mL) was added to the yellow solution. After 1 h, the flask was connected via a frit to another Schlenk flask. The solvent was removed by oil pump vacuum and the residue extracted with hexane. In a glove box, the extract was filtered through a short plug of silica gel (toluene rinses). The solvent was removed from the filtrate by oil pump vacuum to give **12b** as a waxy white solid (0.543 g, 0.70 mmol, 69%), m.p. 52–54 °C. Calcd. for $C_{30}H_{48}F_{16}P_2$: C, 46.52; H, 6.25. Found: C, 46.39; H, 6.08%.

NMR (δ, C_6D_6), ^{1}H 2.10–1.93, 1.82–1.68, and 1.44–1.39 (3 m, 4H, 4H, and 4H, $CH_2CH_2CH_2$), 1.01 (d, 36H, $^3J_{CP} = 11$ Hz, CH_3); ^{13}C{^{1}H} 32.0 (m, CF_2CH_2), 31.1 (d, $^1J_{CP} = 22$ Hz, $C(CH_3)_3$), 29.6 (d, $^2J_{CP} = 14$ Hz, CH_3), 21.1 (d, $^2J_{CP} = 25$ Hz, $CH_2CH_2CH_2$), 20.8 (d, $^1J_{CP} = 23$ Hz, *C*H$_2$P); ^{31}P{^{1}H} 25.5 (s); ^{19}F{^{1}H} −113.7 to −114.6 (m, 4F), −121.6 to −122.3 (m, 8F), −123.4 to −123.9 (m, 4F).

4.15. *o*-$tol_2P(CH_2)_3(CF_2)_8(CH_2)_3P$*o*-$tol_2$ (**12c**)

A procedure analogous to that for **12a** but using HP*o*-tol_2 (0.429 g, 2.00 mmol) [30] and **11** (0.645 g, 1.01 mmol) gave **12c** as a white solid (0.786 g, 0.863 mmol, 86%), m.p. 94–96 °C. Calcd. for $C_{42}H_{40}F_{16}P_2$: C, 55.39; H, 4.43. Found: C, 55.34; H, 4.87%.

NMR (δ, C_6D_6): ^{1}H 7.21–6.24 (m, 16H, C_6H_4), 2.39 (s, 12H, CH_3), 1.91–1.76 and 1.72–1.55 (2 m, 4H and 8H, $CH_2CH_2CH_2$); ^{13}C{^{1}H} 142.6 (d, $J_{CP} = 26$ Hz, C_{sp2}), 137.0 (d, $J_{CP} = 14$ Hz, C_{sp2}), 131.3 (s, C_{sp2}), 130.5 (d, $J_{CP} = 4$ Hz, C_{sp2}), 128.9 (s, C_{sp2}), 126.5 (s, C_{sp2}) 31.9 (m, CF_2CH_2), 26.8 (d, $^2J_{CP} = 13$ Hz, $CH_2CH_2CH_2$), 21.2 (d, $^3J_{CP} = 22$ Hz, CH_3), 17.2 (d, $^1J_{CP} = 20$ Hz, CH_2P); ^{31}P{^{1}H} −39.3 (s); ^{19}F −114.1 to −114.7 (m, 4F), −121.6 to −122.3 (m, 8F), −123.3 to −124.0 (m, 4F). IR (cm^{-1}, powder film), 2952, 1208, 1102, 1065, 800, 733.

4.16. *p*-$tol_2P(CH_2)_8P$*p*-tol_2 (**13a**)

A Schlenk flask was charged with $Br(CH_2)_8Br$ (0.544 g, 2.00 mmol) and THF (8 mL). Then LiP*p*-tol_2 (10.0 mL,

0.40 M in THF/hexane, 4.00 mmol), freshly prepared from *n*-BuLi and HP*p*-tol$_2$ (1:1) [31], was added via syringe with stirring until a light yellow color persisted. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2 (2 × 10 mL). The extracts were filtered through a silica gel pad (3 cm, CH_2Cl_2 rinses). The solvent was removed from the filtrate at −40 °C by oil pump vacuum to give **13a** as a white solid (1.025 g, 1.90 mmol, 95%), m.p. 66–69 °C (capillary).

NMR (δ, $CDCl_3$), ^{1}H 7.36–7.31 (m, 8H, *o* to P), 7.17–7.13 (m, 8H, *m* to P), 2.35 (s, 12H, CH_3), 2.01 (t, $^3J_{HH} = 7.6$ Hz, 4H, PCH_2), 1.41 (m, 8H, $PCH_2CH_2CH_2CH_2$), 1.26 (m, 4H, $PCH_2CH_2CH_2CH_2$); ^{13}C{^{1}H} [27] 138.2 (s, *p* to P), 135.6 (d, $^1J_{CP} = 11.5$ Hz, *i* to P), 132.6 (d, $^2J_{CP} = 18.7$ Hz, *o* to P), 129.1 (d, $^3J_{CP} = 7.1$ Hz, *m* to P), 31.8 (d, $^3J_{CP} = 13.2$ Hz, $PCH_2CH_2CH_2$), 29.0 (s, CH_2), 28.1 (d, $^1J_{CP} = 10.4$ Hz, PCH_2), 25.9 (d, $^2J_{CP} = 15.9$ Hz, PCH_2CH_2), 21.2 (s, CH_3); ^{31}P{^{1}H} −17.7 (s). IR (cm^{-1}, powder film), 3069 (w), 3034 (w), 3015 (w), 2926 (m), 2853 (m), 1598 (w), 1498 (m), 1463 (m), 1413 (w), 1309 (w), 1189 (w), 1092 (m), 1023 (m), 965 (w), 803 (vs), 722 (s). MS [28], 539 (**13a**$^+$, 94%), 447 ([**13a**–tol]$^+$, 20%), 325 ([**13a**–Ptol$_2$]$^+$, 100%), and additional ions from loss of CH_2, 213 ([Ptol$_2$]$^+$, 59%).

4.17. *p*-tol$_2$P(CH$_2$)$_{14}$P*p*-tol$_2$ (**14a**)

THF (10 mL), Br(CH$_2$)$_{14}$Br (0.712 g, 2.00 mmol) [32], and LiP*p*-tol$_2$ (10.0 mL, 0.40 M in THF/hexanes, 4.00 mmol) were combined in a procedure analogous to that for **13a**. An identical workup gave **14a** as a white solid (1.196 g, 1.92 mmol, 96%), m.p. 69–73 °C. Calcd. for $C_{42}H_{56}P_2$: C, 80.99; H, 9.06. Found: C, 81.05; H, 8.91%.

NMR (δ, $CDCl_3$), ^{1}H, 7.32–7.28 (m, 8H, *o* to P), 7.14–7.11 (m, 8H, *m* to P), 2.32 (s, 12H, CH_3), 1.99 (t, $^3J_{HH} = 7.6$ Hz, 4H, PCH_2), 1.42–1.37 (m, 8H, $PCH_2CH_2CH_2$), 1.24–1.17 (br m, 16H, remaining CH_2); ^{13}C{^{1}H} [27] 138.2 (s, *p* to P), 135.6 (d, $^1J_{CP} = 11.4$ Hz, *i* to P), 132.6 (d, $^2J_{CP} = 18.7$ Hz, *o* to P), 129.1 (d, $^3J_{CP} = 6.9$ Hz, *m* to P), 31.2 (d, $^3J_{CP} = 12.6$ Hz, $PCH_2CH_2CH_2$), 29.6 (br s, CH_2), 29.6 (s, CH_2), 29.5 (s, CH_2), 28.2 (d, $^1J_{CP} = 10.7$ Hz, PCH_2), 25.9 (d, $^2J_{CP} = 16.0$ Hz, PCH_2CH_2), 21.2 (s, CH_3); ^{31}P{^{1}H} −17.7 (s). IR (cm^{-1}, powder film), 3073 (w), 3038 (w), 3019 (w), 2918 (s), 2849 (m), 1602 (w), 1498 (m), 1467 (m), 1397 (w), 1309 (w), 1189 (w), 1092 (w), 1023 (w), 807 (vs), 776 (w), 737 (m), 722 (s). MS [28], 622 (**14a**$^+$, 54%), 531 ([**14a**–tol]$^+$, 10%), 409 ([**14a**–Ptol$_2$]$^+$, 100%), and additional ions from the loss of CH_2, 213 ([Ptol$_2$]$^+$, 53%), 122 ([Ptol]$^+$, 42%).

4.18. (*p*-*t*-BuC$_6$H$_4$)$_2$P(CH$_2$)$_{14}$P(*p*-C$_6$H$_4$-*t*-Bu)$_2$ (**14d**)

THF (10 mL), Br(CH$_2$)$_{14}$Br (0.712 g, 2.00 mmol) and LiP(*p*-C$_6$H$_4$-*t*-Bu)$_2$ (11.4 mL, 0.35 M in THF/hexanes, 4.00 mmol) that had been freshly prepared from HP(*p*-C$_6$H$_4$-*t*-Bu)$_2$ and *n*-BuLi (1.0 equiv.) [31] were combined in a procedure analogous to that for **13a**. An identical workup gave **14d** as a white solid (1.550 g, 1.96 mmol, 98%), m.p. 82–85 °C. Calcd for $C_{54}H_{80}P_2$: C, 81.98; H, 10.19. Found: C, 81.60; H, 10.19%.

NMR (δ, $CDCl_3$), ^{1}H 7.39–7.32 (m, 16H, C_6H_4), 2.03 (t, $^3J_{HH} = 7.5$ Hz, 4H, PCH_2), 1.46–1.36 (m, 8H, $PCH_2CH_2CH_2$), 1.29 (s, 36H, CH_3), 1.27–1.18 (m, 16H, remaining CH_2); ^{13}C{^{1}H} [27] 151.8 (s, *p* to P), 135.2 (d, $^1J_{CP} = 9.8$ Hz, *i* to P), 132.5 (d, $^2J_{CP} = 18.0$ Hz, *o* to P), 125.4 (d, $^3J_{CP} = 6.9$ Hz, *m* to P), 34.6 (s, $C(CH_3)_3$), 31.2 (s, CH_3), 31.1 (d, $^3J_{CP} = 12.6$ Hz, $PCH_2CH_2CH_2$), 29.7 (br s, CH_2), 29.6 (s, CH_2), 29.5 (s, CH_2), 29.2 (s, CH_2), 28.2 (d, $^1J_{CP} = 9.9$ Hz, PCH_2), 25.9 (d, $^2J_{CP} = 16.0$ Hz, PCH_2CH_2); ^{31}P{^{1}H} −17.7 (s). IR (cm^{-1}, powder film), 3073 (w), 3022 (w), 2964 (m), 2926 (s), 2853 (m), 1598 (w), 1494 (w), 1467 (m), 1390 (m), 1363 (w), 1266 (m), 1085 (s), 1019 (m), 822 (vs), 753 (m), 741 (m), 730 (m). MS [28], 791 (**14d**$^+$, 15%), 493 ([**14d**–P(C$_6$H$_4$Bu)$_2$]$^+$, 26%), and additional ions from the loss of CH_2, 297 ([P(C$_6$H$_4$Bu)$_2$]$^+$, 100%), 164 ([PC$_6$H$_4$Bu]$^+$, 61%).

4.19. Ph$_2$P(CH$_2$)$_7$CH=CH$_2$ (**15**)

A Schlenk flask was charged with Br(CH$_2$)$_7$CH=CH$_2$ (2.216 g, 10.82 mmol) [6b,33] and THF (50 mL), and cooled to 0 °C. Then KPPh$_2$ (21.6 mL, 0.5 M in THF, 10.8 mmol) was added dropwise with stirring until a red color persisted. A white precipitate formed. The mixture was stirred for 0.5 h at 0 °C, and the cold bath was removed. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2. The extract was filtered through a short silica gel column (5 × 2.5 cm), which was rinsed with CH_2Cl_2 until UV monitoring showed no absorbing material (ca. 200 mL). The solvent was removed from the filtrate by oil pump vacuum to give **15** as a viscous cloudy oil (2.728 g, 8.872 mmol, 82%).

NMR (δ, $CDCl_3$), ^{1}H 7.41–7.38 (m, 4H of 2 Ph), 7.31–7.29 (m, 6H of 2 Ph), 5.78 (ddt, 1H, $^3J_{HHtrans} = 17.0$ Hz, $^3J_{HHcis} = 10.3$ Hz, $^3J_{HH} = 6.6$ Hz, CH=), 4.95 (br d, 1H, $^3J_{HHtrans} = 17.1$ Hz, =CH$_E$H$_Z$), 4.91 (br d, 1H, $^3J_{HHcis} = 10.2$ Hz, =CH$_E$H$_Z$), 2.04–1.98 (m, 4H, PCH_2, CH_2CH=), 1.41–1.25 (m, 2H, CH_2), 1.42–1.28 (m, 8H, remaining CH_2); ^{13}C{^{1}H} [27] 139.5 (s, CH=), 139.4 (d, $^1J_{CP} = 13.0$ Hz, *i* to P), 133.1 (d, $^2J_{CP} = 18.3$ Hz, *o* to P), 128.8 (d, $^3J_{CP} = 3.0$ Hz, *m* to P), 128.7 (s, *p* to P), 114.1 (s, =CH_2), 34.2 (s, CH_2CH=), 31.5 (d, $^3J_{CP} = 12.9$ Hz, $PCH_2CH_2CH_2$), 29.6 (s, CH_2), 29.38 (s, CH_2), 29.35 (s, CH_2), 29.2 (s, CH_2), 28.5 (d, $^1J_{CP} = 11.1$ Hz, PCH_2), 26.3 (d, $^2J_{CP} = 15.9$ Hz, PCH_2CH_2); ^{31}P{^{1}H} −15.6 (s).

4.20. Ph$_2$P(CH$_2$)$_{10}$CH=CH$_2$ (**16**)

Br(CH$_2$)$_{10}$CH=CH$_2$ (3.600 g, 14.58 mmol) [6b,33], THF (50 mL), and KPPh$_2$ (29.5 mL, 0.5 M in THF, 14.6 mmol) were combined in a procedure analogous to that for **15**. An identical workup gave **16** as a viscous cloudy oil (4.290 g, 12.25 mmol, 84%).

NMR (δ, $CDCl_3$), ^1H 7.45–7.43 (m, 4H of 2 Ph), 7.34–7.32 (m, 6H of 4 Ph), 5.79 (ddt, 1H, $^3J_{HH\,trans} = 17.0$ Hz, $^3J_{HH\,cis} = 10.2$ Hz, $^3J_{HH} = 6.7$ Hz, CH=), 5.00 (br d, 1H, $^3J_{HH\,trans} = 17.1$ Hz, $=CH_EH_Z$), 4.94 (br d, 1H, $^3J_{HH\,cis} = 10.2$ Hz, $=CH_EH_Z$), 2.07–2.02 (m, 4H, PCH_2, and $CH_2CH=$), 1.44–1.20 (m, 16H, $8CH_2$); $^{13}C\{^1H\}$ [27] 139.1 (s, CH=), 139.0 (d, $^1J_{CP} = 13.1$ Hz, *i* to P), 132.6 (d, $^2J_{CP} = 18.3$ Hz, *o* to P), 128.3 (d, $^3J_{CP} = 2.7$ Hz, *m* to P), 128.2 (s, *p* to P), 114.1 (s, $=CH_2$), 33.8 (s, $CH_2CH=$), 31.1 (d, $^3J_{CP} = 12.9$ Hz, $PCH_2CH_2CH_2$), 29.5 (s, CH_2), 29.4 (s, double intensity, $2CH_2$), 29.2 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 28.0 (d, $^1J_{CP} = 11.2$ Hz, PCH_2), 25.9 (d, $^2J_{CP} = 15.9$ Hz, PCH_2CH_2); $^{31}P\{^1H\}$ −15.6 (s).

4.21. $Ph_2P(CH_2)_7CH_3$ (17)

A Schlenk flask was charged with $Br(CH_2)_7CH_3$ (1.39 mL, 8.00 mmol) and THF (20 mL). Then $KPPh_2$ (16.0 mL, 0.5 M in THF, 8.0 mmol) was added with stirring until a light yellow color persisted. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2 (2 × 10 mL). The extracts were filtered through a silica gel pad (3 cm, CH_2Cl_2 rinses). The solvent was removed from the filtrate by oil pump vacuum to give **17** as a colorless oil (2.036 g, 6.823 mmol, 85%) [17].

NMR (δ, $CDCl_3$), ^1H 7.43–7.37 (m, 4H of 2 Ph), 7.32–7.28 (m, 6H of 2 Ph), 2.02 (t, $^3J_{HH} = 7.7$ Hz, 2H, PCH_2), 1.40 (m, 4H, $PCH_2CH_2CH_2$), 1.28–1.20 (m, 8H, remaining CH_2), 0.85 (t, $^3J_{HH} = 6.9$ Hz, 3H, CH_3); $^{13}C\{^1H\}$ [27] 138.9 (d, $^1J_{CP} = 12.2$ Hz, *i* to P), 132.7 (d, $^2J_{CP} = 18.3$ Hz, *o* to P), 128.4 (s, *p* to P), 128.3 (d, $^3J_{CP} = 6.6$ Hz, *m* to P), 31.8 (s, CH_2), 31.2 (d, $^3J_{CP} = 12.4$ Hz, $PCH_2CH_2CH_2$), 29.2 (s, CH_2), 29.1 (s, CH_2), 28.0 (d, $^1J_{CP} = 11.0$ Hz, PCH_2), 25.9 (d, $^2J_{CP} = 15.4$ Hz, PCH_2CH_2), 22.6 (s, CH_2CH_3), 14.1 (s, CH_3); $^{31}P\{^1H\}$ −15.5 (s). IR (cm^{-1}, liquid film), 3073 (w), 2957 (w), 2926 (m), 2856 (w), 1586 (w), 1482 (w), 1463 (w), 1436 (m), 1200 (w), 1123 (w), 1096 (w), 1027 (w), 737 (s), 695 (vs).

4.22. trans-$(C_6F_5)(Ph_2P(CH_2)_7CH{=}CH_2)_2PtCl$ (18)

A Schlenk flask was charged with $[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (1.010 g, 1.039 mmol; tht = tetrahydrothiophene) [18], **15** (1.668 g, 5.373 mmol), and CH_2Cl_2 (60 mL) with stirring. After 20 h, the solvent was removed by rotary evaporation. The residue was chromatographed (15 × 1.5 cm silica gel column, 70:30 v/v hexanes/CH_2Cl_2). The solvent was removed from the product-containing fractions by oil pump vacuum to give **18** as a colorless oil (1.571 g, 1.542 mmol, 77%), which gave a white wax upon storage. Calcd. for $C_{48}H_{54}ClF_5P_2Pt$: C, 56.61; H, 5.34. Found: C, 57.44; H, 5.78%.

NMR (δ, $CDCl_3$), ^1H 7.51–7.45 (m, 8H of 4 Ph), 7.34–7.21 (m, 12H of 4 Ph), 5.84–5.75 (m, 2H, CH=) 4.99–4.90 (m, 4H, $=CH_2$), 2.58–2.54 (m, 4H, PCH_2), 2.03–2.01 (m, 4H, $CH_2CH=$), 1.88–1.86 (m, 4H, PCH_2CH_2), 1.40–1.25 (m, 16H, remaining CH_2); $^{13}C\{^1H\}$ [34] 145.1 (dm, $^1J_{CF} = 219$ Hz, *o* to Pt), 139.0 (s, CH=), 136.2 (dm, $^1J_{CF} = 247$ Hz, *m*/*p* to Pt), 133.0 (virtual t, $^2J_{CP} = 5.7$ Hz, *o* to P), 130.8 (virtual t, $^1J_{CP} = 27.2$ Hz, *i* to P), 130.2 (s, *p* to P), 127.9 (virtual t, $^3J_{CP} = 5.0$ Hz, *m* to P), 114.2 (s, $=CH_2$), 33.7 (s, $CH_2CH=$), 31.3 (virtual t, $^3J_{CP} = 7.6$ Hz, $PCH_2CH_2CH_2$), 29.0 (s, CH_2), 28.9 (s, CH_2), 28.8 (s, CH_2), 25.9 (virtual t, $^1J_{CP} = 17.3$ Hz, PCH_2), 25.5 (s, PCH_2CH_2); $^{31}P\{^1H\}$ 16.4 (s, $^1J_{PPt} = 2658$ Hz) [35]. IR (cm^{-1}, oil film), 3076 (vw), 2930 (m), 2856 (m), 1640 (s), 1502 (s), 1459 (s), 1436 (m), 1104 (m), 1058 (m), 996 (w), 953 (vs), 911 (w), 803 (m), 741 (s), 695 (vs). MS [28], 1017 (**18**$^+$, 10%), 982 ([**18**–Cl]$^+$, 100%), 813 ([**18**–Cl–C_6F_5]$^+$, 30%).

4.23. trans-$(C_6F_5)(Ph_2P(CH_2)_{10}CH{=}CH_2)_2PtCl$ (19)

$[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (2.103 g, 2.165 mmol), **16** (3.298 g, 9.356 mmol), and CH_2Cl_2 (150 mL) were combined in a procedure analogous to that for **18**. A similar workup (20 × 2.5 cm silica gel column, 80:20 v/v hexanes/CH_2Cl_2) gave **19** as a colorless oil (3.341 g, 3.032 mmol, 70%). Calcd. for $C_{54}H_{66}ClF_5P_2Pt$: C, 58.83; H, 6.03. Found: C, 59.63; H, 6.67%.

NMR (δ, $CDCl_3$), ^1H 7.51–7.46 (m, 8H of 4 Ph), 7.34–7.32 (m, 4H of 4 Ph), 7.29–7.23 (m, 8H of 4 Ph), 5.81 (ddt, 2H, $^3J_{HH\,trans} = 17.0$ Hz, $^3J_{HH\,cis} = 10.2$ Hz, $^3J_{HH} = 6.7$ Hz, CH=), 4.99 (br d, 2H, $^3J_{HH\,trans} = 17.1$ Hz, $=CH_EH_Z$), 4.92 (br d, 2H, $^3J_{HH\,cis} = 10.2$ Hz, $=CH_EH_Z$), 2.62–2.58 (m, 4H, PCH_2), 2.06–2.01 (m, 4H, $CH_2CH=$), 1.80–1.77 (m, 4H, PCH_2CH_2), 1.40–1.37 (m, 28H, remaining CH_2); $^{13}C\{^1H\}$ [34] 139.2 (s, CH=), 133.0 (virtual t, $^2J_{CP} = 5.8$ Hz, *o* to P), 131.4 (virtual t, $^1J_{CP} = 27.9$ Hz, *i* to P), 130.2 (s, *p* to P), 127.9 (virtual t, $^3J_{CP} = 5.1$ Hz, *m* to P), 114.1 (s, $=CH_2$), 33.8 (s, $CH_2CH=$), 31.3 (virtual t, $^3J_{CP} = 7.5$ Hz, $PCH_2CH_2CH_2$), 29.6 (s, CH_2), 29.47 (s, CH_2), 29.46 (s, CH_2), 29.2 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 28.2 (virtual t, $^1J_{CP} = 17.8$ Hz, PCH_2), 25.5 (s, PCH_2CH_2); $^{31}P\{^1H\}$ 16.1 (s, $^1J_{PPt} = 2665$ Hz) [35]. IR (cm^{-1}, oil film), 3078 (vw), 2925 (m), 2854 (m), 1640 (m), 1501 (s), 1461 (s), 1436 (m), 1104 (m), 1061 (m), 957 (vs), 908 (w), 804 (m), 741 (s), 695 (vs). MS [28], 1102 (**19**$^+$, 10%), 1067 ([**19**–Cl]$^+$, 100%), 898 ([**19**–Cl–C_6F_5]$^+$, 60%).

4.24. trans,trans-$(C_6F_5)(Ph_2P(CH_2)_7CH_3)_2Pt(C{\equiv}C)_4Pt(Ph_2P(CH_2)_7CH_3)_2(C_6F_5)$ (21)

A Schlenk flask was charged with **17** (1.730 g, 5.800 mmol) and *trans*,*trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_4Pt(P\textit{p}\text{-}tol_3)_2(C_6F_5)$ (**20** [19]; 0.408 g, 0.200 mmol) with stirring. After 0.5 h, CH_2Cl_2 (2 mL) was added. After 16 h, the solvent was removed by oil pump vacuum. The residue was chromatographed (25 cm silica gel column, 80:20 v/v hexanes/CH_2Cl_2) to give a yellow oil (0.235 g), that contained **21** and an intermediate (**22**, Scheme 6; $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$) 17.9 (d, $^2J_{PP} = 409$ Hz, $^1J_{PPt} = 2624$ Hz [35], P_A), 14.2 (s, $^1J_{PPt} = 2566$ Hz [35], $P_{CC'}$), 14.1 (d, $^2J_{PP} = 409$ Hz, $^1J_{PPt} = 2588$ Hz [35], P_B)). A Schlenk flask

was charged with this mixture, a fresh charge of $Ph_2P(CH_2)_7CH_3$ (0.750 g, 2.51 mmol), and CH_2Cl_2 (2 mL) with stirring. After 16 h, the solution was concentrated. The flask was immersed in a 65 °C oil bath, and the sample stirred for 0.5 h. Chromatography as above gave a yellow fraction. The solvent was removed by oil pump vacuum to give **21** as a yellow oil that solidified after several days (0.215 g, 0.107 mmol, 53%), m.p. 97–100 °C, dec. pt. 230 °C (onset). Calcd. for $C_{100}H_{108}F_{10}P_4Pt_2$: C, 59.64; H, 5.41. Found: C, 59.40; H, 5.33%. DSC [36]: melting endotherm with T_i, 90.3 °C; T_e, 97.4 °C; T_p, 102.4 °C; T_c, 107.3 °C; T_f, 112.2 °C; exotherm with T_i, 243 °C. TGA [36]: onset of mass loss (T_i), 260 °C.

NMR (δ, $CDCl_3$), ^1H 7.48–7.42 (m, 16H of 8Ph), 7.34–7.30 (m, 8H of 8Ph), 7.27–7.22 (m, 16H of 8Ph), 2.54 (m, 8H, PCH_2), 1.75 (m, 8H, PCH_2CH_2), 1.37 (m, 8H, $PCH_2CH_2CH_2$), 1.30–1.20 (m, 32H, remaining CH_2), 0.87 (t, $^1J_{HH} = 6.8$ Hz, 12H, CH_3); $^{13}C\{^1H\}$ [34] 145.9 (dd, $^1J_{CF} = 222$ Hz, $^2J_{CF}$ 22 Hz, *o* to Pt), 136.5 (dm, $^1J_{CF} = 240$ Hz, *m*/*p* to Pt), 133.0 (virtual t, $^2J_{CP} = 6.0$ Hz, *o* to P), 131.3 (virtual t, $^1J_{CP} = 27.7$ Hz, *i* to P), 130.2 (s, *p* to P), 127.9 (virtual t, $^3J_{CP} = 5.2$ Hz, *m* to P), 124.0 (t, $^2J_{CF} = 50.5$ Hz, *i* to Pt), 100.0 (s, $^1J_{CPt} = 998$ Hz, PtC≡), 94.2 (s, $^2J_{CPt} = 271$ Hz [35], PtC≡*C*), 63.7 (s, $^3J_{CPt} = 32$ Hz [35], PtC≡C*C*), 57.9 (s, PtC≡CC≡*C*), 31.8 (s, *C*$H_2CH_2CH_3$), 31.3 (virtual t, $^3J_{CP} = 7.4$ Hz, $PCH_2CH_2CH_2$), 29.1 (s, $2CH_2$), 28.2 (virtual t, $^1J_{CP} = 17.8$ Hz, PCH_2), 25.5 (s, PCH_2CH_2), 22.6 (s, *C*H_2CH_3), 14.1 (s, CH_3); $^{31}P\{^1H\}$ 14.2 (s, $^1J_{PPt} = 2566$ Hz) [35]; $^{19}F\{^1H\}$ −116.6 (m, $^3J_{FPt} = 289$ Hz [35], 4F, *o* to Pt), −163.3 (t, $^3J_{FF} = 19.6$ Hz, 2F, *p* to Pt), −164.0 (m, $^4J_{FPt} = 106$ Hz [35], 4F, *m* to Pt). IR (cm^{-1}, powder film), $\nu_{C\equiv C}$ 2146 (s), 2007 (m). UV–vis (nm (ε, $M^{-1}\,cm^{-1}$), 1.25×10^{-5} M in CH_2Cl_2), 263 (89 800), 292 (107 000), 320 (132 000), 353 (6400), 380 (5400), 412 (2900). MS [28], 2013 ([**21**–H]$^+$, 30%), 1353 ([$(C_6F_5)Pt(Ph_2P(CH_2)_7CH_3)_3C_8$]$^+$, 30%), 958 ([$(C_6F_5)Pt(Ph_2P(CH_2)_7CH_3)_2$]$^+$, 100%), 789 ([$Pt(Ph_2P(CH_2)_7CH_3)_2$–2H]$^+$, 76%), 565 ([$Pt(Ph_2P)_2$]$^+$, 80%).

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (SFB 583) and Johnson Matthey PMC (platinum loan) for support.

References

[1] (a) J. Stahl, J.C. Bohling, E.B. Bauer, T.B. Peters, W. Mohr, J.M. Martín-Alvarez, F. Hampel, J.A. Gladysz, Angew. Chem., Int. Ed. 41 (2002) 1871;
Angew. Chem. 114 (2002) 1951;
(b) G.R. Owen, J. Stahl, F. Hampel, J.A. Gladysz, Organometallics 23 (2004) 5889;
(c) L. de Quadras, F. Hampel, J.A. Gladysz, Dalton Trans. (2006) 2929.

[2] (a) Lead references to active groups: A.P.H.J. Schenning, J.-D. Arndt, M. Ito, A. Stoddart, M. Schreiber, P. Siemsen, R.E. Martin, C. Boudon, J.-P. Gisselbrecht, M. Gross, V. Gramlich, F. Diederich, Helv. Chim. Acta 84 (2001) 296;
(b) J. Terao, A. Tang, J.J. Michels, A. Krivokapic, H.L. Anderson, Chem. Commun. (2004) 56;
(c) P.H. Kwan, T.M. Swager, Chem. Commun. (2005) 5211;
(d) C. Li, M. Numata, A.-H. Bae, K. Sakurai, S. Shinkai, J. Am. Chem. Soc. 127 (2005) 4548.

[3] (a) J. Stahl, W. Mohr, L. de Quadras, T.B. Peters, J.C. Bohling, J.M. Martín-Alvarez, G.R. Owen, F. Hampel, J.A Gladysz (in preparation);
(b) L. de Quadras, E.B. Bauer, W. Mohr, J.C. Bohling, T.B. Peters, J.M. Martín-Alvarez, F. Hampel, J.A. Gladysz (in preparation);
(c) L. de Quadras, E.B. Bauer, J. Stahl, F. Zhuravlev, F. Hampel, J.A. Gladysz (in preparation).

[4] W. Mohr, C.R. Horn, J. Stahl, J.A. Gladysz, Synthesis (2003) 1279.

[5] (a) E.B. Bauer, F. Hampel, J.A. Gladysz, Organometallics 22 (2003) 5567;
(b) N. Lewanzik, T. Oeser, J. Blümel, J.A. Gladysz, J. Mol. Catal. A 254 (2006) 20.

[6] (a) J. Stahl, Doctoral Dissertation, Universität Erlangen-Nürnberg, 2004;
(b) L. de Quadras, Doctoral Dissertation, Universität Erlangen-Nürnberg, 2006.

[7] M.E. Jung, G. Piizzi, Chem. Rev. 105 (2005) 1735.

[8] (a) Y. Brunel, G. Rousseau, J. Org. Chem. 61 (1996) 5793, Only ^1H NMR data for **3** are reported;
(b) See also G. Cahiez, M. Alami, Tetrahedron Lett. 31 (1990) 7425.

[9] For alternative syntheses of 3–5, see J.R. Dias, Y. Sheikh, C. Djerassi, J. Am. Chem. Soc. 94 (1972) 473, This paper reports IR and mass spectrometric data for **3** and **5** and ^1H NMR data for **3**, but no data for **4** and no reaction conditions.

[10] A. Tanaka, T. Oritani, Tetrahedron Lett. 38 (1997) 1955.

[11] (a) B. Albinsson, J. Michl, J. Phys. Chem. 100 (1996) 3418;
(b) J.D. Dunitz, A. Gavezzotti, W.B. Schweizer, Helv. Chim. Acta 86 (2003) 4073;
(c) S.S. Jang, M. Blanco, W.A. Goddard III, G. Caldwell, R.B. Ross, Macromolecules 36 (2003) 5331;
(d) A. Casnati, R. Liantonio, P. Metrangolo, G. Resnati, R. Ungaro, F. Ugozzoli, Angew. Chem., Int. Ed. 45 (2006) 1915;
Angew. Chem. 118 (2006) 1949.

[12] M.B. Murphy-Jolly, L.C. Lewis, A.J.M. Caffyn, Chem. Commun. (2005) 4479, and references therein.

[13] 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. 124 (2002) 1516.

[14] (a) L.J. Alvey, D. Rutherford, J.J.J. Juliette, J.A. Gladysz, J. Org. Chem. 63 (1998) 6302;
(b) M. Wende, F. Seidel, J.A. Gladysz, J. Fluorine Chem. (2003) 45.

[15] J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley/VCH, Weinheim, 2004, pp. 1–4.

[16] D.G. Gilheany, C.M. Mitchell, in: F.R. Hartley (Ed.), The Chemistry of Organophosphorus Compounds, vol. 1, Wiley & Sons, New York, 1990, p. 173.

[17] (a) A. Langer, K. Püntener, R. Strümer, P. Knochel, Tetrahedron: Asymmetry 8 (1997) 715;
(b) E. Valls, J. Suades, R. Mathieu, Organometallics 18 (1999) 5475.

[18] R. Usón, J. Forniés, P. Espinet, G. Alfranca, Synth. React. Inorg. Met.-Org. Chem. 10 (1980) 579.

[19] W. Mohr, J. Stahl, F. Hampel, J.A. Gladysz, Chem. Eur. J. 9 (2003) 3324.

[20] (a) G.M. Gray, Comments Inorg. Chem. 17 (1995) 95;
(b) D.C. Smith Jr., C.H. Lake, G.M. Gray, Dalton Trans. (2003) 2950, and earlier papers cited therein.

[21] A. Varshney, G.M. Gray, Inorg. Chem. 30 (1991) 1748.

[22] T. Shima, E.B. Bauer, F. Hampel, J.A. Gladysz, Dalton Trans. (2004) 1012.

[23] T. Shima, F. Hampel, J.A. Gladysz, Angew. Chem., Int. Ed. 43 (2004) 5537.

[24] A.J. Nawara, T. Shima, F. Hampel, J.A. Gladysz, J. Am. Chem. Soc. 128 (2006) 4962.

[25] H. Kuhn, Work in progress, Universität Erlangen-Nürnberg.
[26] S.C. Watson, J.F. Eastham, J. Organomet. Chem. 9 (1967) 165.
[27] (a) Phosphines with $Ph_2PCH_2CH_2CH_2$ linkages exhibit a characteristic pattern of ^{13}C NMR signals that have been assigned by 2D NMR experiments; see footnote 33 of Ref. [4];
(b) For Ar_2P assignments, see footnote 36 of Ref. [5a].
[28] EI (phosphines and organic compounds) or FAB (platinum complexes; 3-nitrobenzyl alcohol matrix); *m/z* for the most intense peak of the isotope envelope.
[29] Tentative assignment based upon coupling constants; the normal chemical shift pattern[27] was not observed.
[30] S. Grim, A.W. Yankowsky, J. Org. Chem. 42 (1977) 1236.
[31] (a) G. Reinhard, R. Soltek, G. Huttner, A. Barth, O. Walter, L. Zsolnai, Chem. Ber. 129 (1996) 97;
(b) For these syntheses, the known secondary phosphines HP*p*-tol_2 and HP(*p*-C_6H_4-*t*-Bu)$_2$ were in turn prepared by reactions of P*p*-tol_3 and P(*p*-C_6H_4-*t*-Bu)$_3$ with lithium, followed by the addition of deoxygenated aqueous NH_4^+ Cl^- [30].
[32] Prepared from the commercial α,ω-diol as described by G.C.H. Stone, J. Am. Chem. Soc. 62 (1940) 571, This compound is also sometimes commercially available.
[33] M.-C. Roux, R. Paugam, G. Rousseau, J. Org. Chem. 66 (2001) 4304, see page 4307, column 2, line 18.
[34] (a) In most ^{13}C NMR spectra, the C_6F_5 signals were not observed;
(b) For virtual triplets W.H. Hersh, J. Chem. Educ. 74 (1997) 1485, the *J* values represent the *apparent* couplings between adjacent peaks.
[35] This coupling represents a satellite (d; $^{195}Pt = 33.8\%$), and is not reflected in the peak multiplicity given.
[36] These data were treated as recommended by H.K. Cammenga, M. Epple, Angew. Chem., Int. Ed. Engl. 34 (1995) 1171;
Angew Chem. 107 (1995) 1284.