Syntheses and Palladium, Platinum, and Borane Adducts of Symmetrical Trialkylphosphines with Three Terminal Vinyl Groups, $P((CH_2)_mCH{=}CH_2)_3$

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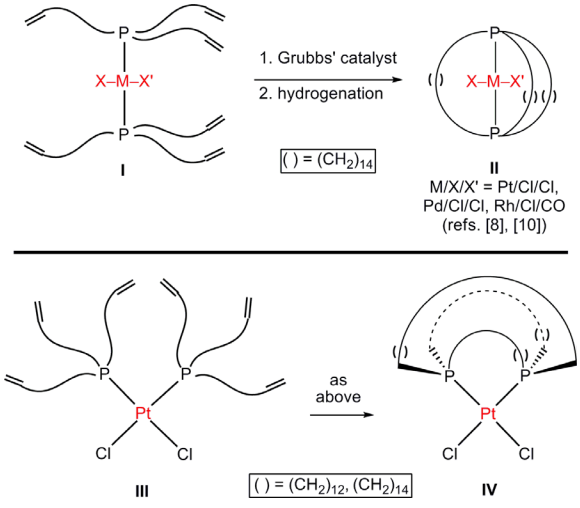
Reactions of $Br(CH_2)_mCH{=}CH_2$ with Mg powder and then PCl_3 (0.33 equiv.) afford $P((CH_2)_m$-$CH{=}CH_2)_3$ (**1**; m = **a**, 4; **b**, 5; **c**, 6; **d**, 7; **e**, 8; **f**, 9; 52 – 87 %). Reactions of **1a** – **c**, **e** with $PdX_2(COD)$ (X = Cl, Br) give *trans*-$PdX_2(P((CH_2)_mCH{=}CH_2)_3)_2$ (35 – 92 %). Reactions of **1b** – **e** with $PtCl_2$ in benzene give mainly *trans*-$PtCl_2(P((CH_2)_mCH{=}CH_2)_3)_2$ (*trans*-**5b**–**e**; 52 – 75 %), whereas those with K_2PtCl_4 in water give mainly *cis*-**5b**–**e** (33 – 70 %). The reaction of equimolar quantities of **1c** and $H_3B{\cdot}S(CH_3)_2$ gives the 1 : 1 adduct $H_3B{\cdot}P((CH_2)_6CH{=}CH_2)_3$ (85 %). In none of these transformations are by-products derived from the C=C linkages observed.

Key words: Phosphine, Phosphine Borane, Palladium, Platinum, α,ω-Diene

Introduction

In 1997, our group initiated an in-depth study of alkene metatheses in metal coordination spheres [1], a subject that was pioneered by Sauvage [2] and has since seen attention in many other groups [3]. Among various themes [4 – 13], we have systematically studied ring-closing macrocyclizations involving *trans* phosphine ligands of the formulae (a) $Ar_2P(CH_2)_m$-$CH{=}CH_2$ [5], (b) $ArP((CH_2)_mCH{=}CH_2)_2$ [6], and (c) $P((CH_2)_mCH{=}CH_2)_3$ [7 – 11], each of which features one or more alkyl substituents with a terminal vinyl group. In all cases, metatheses are followed by hydrogenations.

For square-planar adducts with $4 \leq m \leq 9$, such sequences afford, respectively, (a) thirteen- to twenty three-membered monomacrocycles in good yields [5], (b) analogous dimacrocycles in fair to poor yields [6], (c) analogous trimacrocycles in 37 – 43 % yields in the case of seventeen membered rings [8, 10], but lower yields as well as products derived from intraligand metathesis with larger rings [14]. Syntheses of the trimacrocyclic systems, which resemble toy gyroscopes in their connectivities and symmetries [15], are illustrated in Scheme 1 (**II**). Similar transformations can be conducted with trigonal-bipyramidal and octahedral complexes, often in high yields [7, 11].



Scheme 1. Gyroscope-like and parachute-like complexes derived from the title molecules.

Although detailed full papers describing metatheses of square-planar complexes with phosphines of the

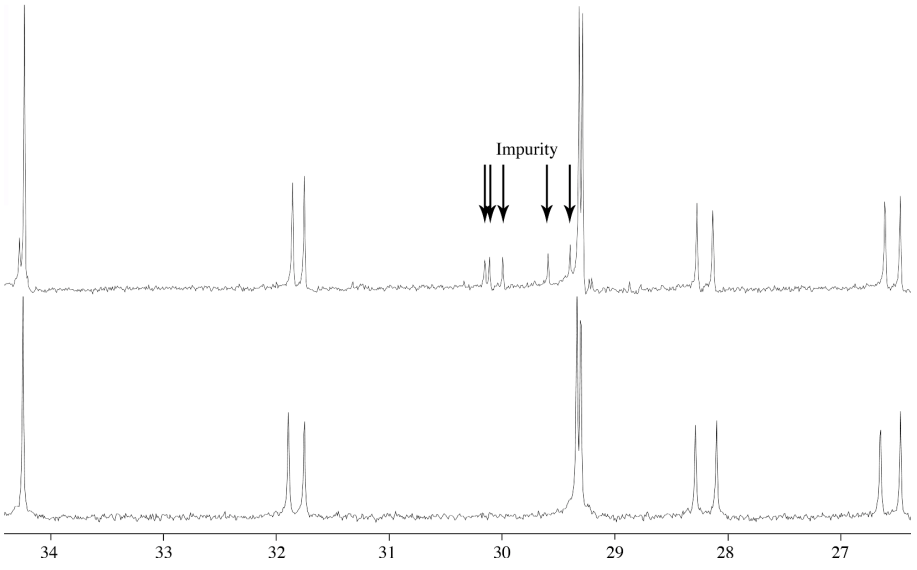


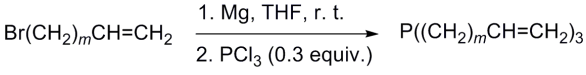
Fig 1. Partial $^{13}C\{^1H\}$ NMR spectra of **1c** with (top) and without (bottom) the α,ω-diene impurity $H_2C{=}CH(CH_2)_{12}$-$CH{=}CH_2$.

types (a) [5] and (b) [6] have appeared, to date all results with phosphines of the type (c) have been communicated [7 – 11, 13]. As a prelude to the next generation of full papers, we report herein syntheses of the trialkylphosphines $P((CH_2)_mCH{=}CH_2)_3$ (**1**), including several details necessary for optimum results, and the preparation and characterization of palladium and platinum dihalide complexes thereof. The platinum chemistry is furthermore optimized for the isolation of either *trans* or *cis* isomers, the latter being precursors to the parachute-like complexes **IV** in Scheme 1 [13]. Additional details are archived in [14].

Results

Many α,ω-bromoalkenes $Br(CH_2)_mCH{=}CH_2$ (**2**; m = **a**, 4; **b**, 5; **c**, 6; **d**, 7; **e**, 8; **f**, 9) are commercially available. However, during the course of this project some supplies were erratic. Hence, samples were occasionally prepared by monoelimination reactions of the corresponding α,ω-dibromides using *t*-BuOK, per a slightly modified [14] literature procedure [16].

As shown in Scheme 2, the α,ω-bromoalkenes were then converted to the Grignard reagents $BrMg(CH_2)_m$-$CH{=}CH_2$. Subsequent reactions with PCl_3 (0.33 equiv.) gave the title phosphines $P((CH_2)_mCH{=}CH_2)_3$ (**1a** – **f**) as air-sensitive tan oils in 52 – 87 % yields after workup. In initial efforts, magnesium turnings that had been activated mechanically or chemically were employed. However, magnesium powder that had been stored in a glove box gave superior results, and reac-



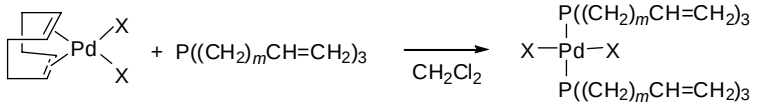
m = 4, **2a**	m = 4, **1a**, 61 %
5, **2b**	5, **1b**, 52 %
6, **2c**	6, **1c**, 87 %
7, **2d**	7, **1d**, 72 %
8, **2e**	8, **1e**, 58 %
9, **2f**	9, **1f**, 66 %

Scheme 2. Syntheses of alkene-containing phosphines.

tions were easily conducted on gram scales. As summarized in the Experimental Section, **1a** – **f** were characterized by ^1H-, ^{13}C-, and ^{31}P-NMR spectroscopy.

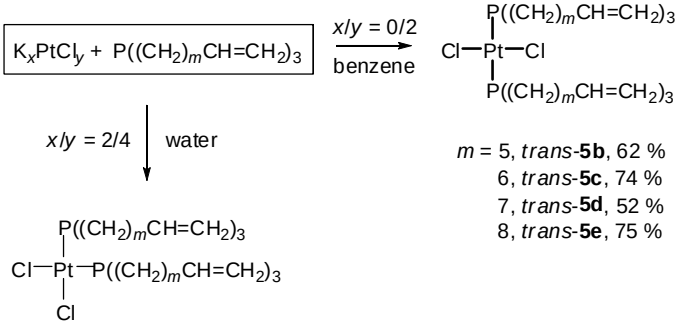
Samples were generally pure by NMR. However, in the course of repeating these syntheses hundreds of times using various sources of reagents in Europe and North America, some coworkers have occasionally encountered complications. The most important among these is a byproduct that is silent by ^{31}P-NMR, and in the case of **1c** has the characteristic ^{13}C-NMR signature shown in Fig. 1. This has been shown to be the α,ω-diene $H_2C{=}CH(CH_2)_{12}CH{=}CH_2$, a known compound for which a ^1H-NMR spectrum has been previously reported [17]. A sample of this material, which is derived from the reductive homocoupling of **2c**, was isolated from a large scale preparative sequence, and completely characterized as summarized in the Experimental Section.

With some synthetic applications, the α,ω-diene byproduct can be carried along as an impurity, as it is removed in the course of subsequent product purifica-



X = Cl, *m* = 4, *trans*-**3a**, 92 %
5, *trans*-**3b**, 35 %
6, *trans*-**3c**, 88 %
8, *trans*-**3e**, 75 %
Br, *m* = 4, *trans*-**4a**, 61 %
5, *trans*-**4b**, 60 %
6, *trans*-**4c**, 55 %

Scheme 3. Syntheses of palladium complexes.



m = 5, *trans*-**5b**, 62 %
6, *trans*-**5c**, 74 %
7, *trans*-**5d**, 52 %
8, *trans*-**5e**, 75 %

m = 5, *cis*-**5b**, 70 %
6, *cis*-**5c**, 33 %
7, *cis*-**5d**, 47 %
8, *cis*-**5e**, 45 %

Scheme 4. Syntheses of platinum complexes.

tions. With a few applications, it complicates downstream workups. In these cases, crude **1a**–**f** can be placed on top of a silica gel or neutral alumina column. Rinsing with hexane elutes the byproduct, and rinsing with CH_2Cl_2 elutes **1a**–**f**. Various "tricks" for minimizing reductive homocoupling are favored by some coworkers [18], but these should be regarded as anecdotal. Nonetheless, if one wants to optimize the chances of success of a new synthetic sequence, it is important to verify by an appropriate spectroscopic or analytical method that the α,ω-diene is absent. In some cases **2a** contained a minor phosphorus-containing byproduct (^{31}P-NMR (C_6D_6) $\delta = -32.8$), but this did not interfere with subsequent chemistry.

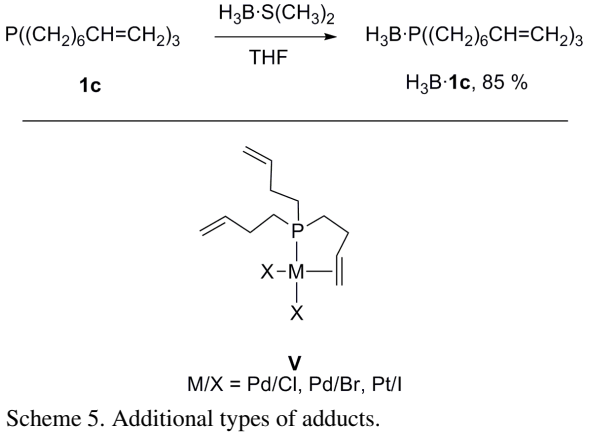
As shown in Scheme 3, CH_2Cl_2 solutions of the palladium cyclooctadiene complexes PdX_2(COD) [19] were generally treated with 2.0–2.3 equivalents of **1a**–**c**, **e** (X = Cl) or **1a**–**c** (X = Br). Workups gave the bis(phosphine) complexes *trans*-$PdX_2(P((CH_2)_m$-$CH{=}CH_2)_3)$ (X = Cl, *trans*-**3a**–**c**, **e**; X = Br, *trans*-**4a**–**c**) as pale-yellow or orange oils in 35–92 % yields. All new complexes were characterized by IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, and mass spectrometry (Experimental Section). In most cases, satisfactory elemental analyses were also obtained. Although none of the spectroscopic properties decisively established the stereochemistry, all complexes were assumed to be *trans* isomers, consistent with crystallographic data for species derived from *trans*-**3c** and *trans*-**4c** [8, 14], as well as other palladium bis(phosphine) dichloride complexes that have been similarly synthesized [20]. When the crude reaction mixtures were analyzed by ^{31}P-NMR spectroscopy, small amounts of byproducts were observed that may correspond to *cis* isomers (5 % for **3a**–**c**, **e**; 20 % for **4a**–**c**).

Analogous *trans* platinum complexes were sought next. Conveniently, there is a well established relationship between stereochemistry and $^1J_{PPt}$ values for such adducts (*trans*, *ca.* 2500 Hz; *cis*, *ca.* 3500 Hz) [21]. After several exploratory experiments, it was found that reactions of $PtCl_2$ and **1b**–**e** (2.0 equiv.) in benzene gave the target complexes *trans*-

$PtCl_2(P((CH_2)_mCH{=}CH_2)_3)_2$ (*trans*-**5b**–**e**) as pale-yellow oils in 52–75 % yields after chromatographic workups (Scheme 4; $^1J_{PPt}$ = 2380–2382 Hz). When the reaction with **1c** was monitored by ^{31}P-NMR spectroscopy, no *cis*-**5c** was detected. When the reaction with **1c** was conducted on an NMR scale in the more polar solvent CH_2Cl_2, both *trans*-**5c** and *cis*-**5c** ($^1J_{PPt}$ = 2398 and 3509 Hz) were detected (59 : 41). An analogous experiment with *trans*-$(PhCN)_2PtCl_2$ [22] and **1c** gave a 40 : 60 *trans*-**5c**/*cis*-**5c** mixture ($^1J_{PPt}$ = 2390 and 3503 Hz), as described in greater detail in [14].

The preceding data suggested that the formation of the more polar *cis* isomer is favored in more polar media. Thus, as shown in Scheme 4, K_2PtCl_4 and **1b**–**e** (2.0 equiv.) were combined in the polar solvent water. Simple chromatographic workups produced two bands, the first of which gave *trans*-**5b**–**e** and the second of which gave *cis*-**5b**–**e** in 33–70 % yields ($^1J_{PPt}$ = 3510–3513 Hz). Similar recipes have been used to access related *trans* platinum bis(phosphine) complexes, but more elaborate extraction/recrystallization purification sequences have normally been required [23].

Finally, it was sought to probe whether the vinyl groups in **1a**–**f** might complicate the formation of phosphine borane adducts. Thus, as shown in Scheme 5, a representative reaction was conducted with **1c** and $H_3B{\cdot}S(CH_3)_2$ (1.0 equiv.). A chromatographic workup gave the target molecule $H_3B{\cdot}$**1c** as a colorless oil in 85 % yield. When a THF solution of $BH_3{\cdot}$**1c** was treated with additional $H_3B{\cdot}S(CH_3)_2$, the sample solidified, consistent with oligomers or polymers derived by borane additions to the C=C linkages. However, THF solutions of $H_3B{\cdot}$**1c** showed no significant decomposition over the course of two days at r. t.



Scheme 5. Additional types of adducts.

Discussion

Scheme 2 establishes the ready availability of the title phosphines **1** for m = 4–9, all of which were unknown compounds prior to this work. The two lowest homologs, trivinylphosphine and triallylphosphine (**1** with m = 0, 1) are commercially available, and have an extensively developed coordination chemistry. The remaining lower homologs (m = 2, 3) have been prepared some time ago by routes identical to that in Scheme 2 [24, 25]. Some descriptive coordination chemistry has been reported [26–28]. This includes a lower homolog of **3a**–**c**, **e** of unassigned stereochemistry, $PdCl_2(P((CH_2)_2CH{=}CH_2)_3)_2$ [26].

As would be expected, **1a**–**e** readily coordinate to palladium and platinum, with no complications from the vinyl groups at the stoichiometries employed (Schemes 3, 4). The same chemoselectivity is found with $H_3B{\cdot}S(CH_3)_2$ (Scheme 5). However, previous studies with the lower homologs with m = 2, 3 have shown that the phosphines can serve as bidentate, tridentate, and tetradentate ligands in square-planar and trigonal-bipyramidal d^8 systems [25–27]. In the case of palladium and platinum dihalide monophosphine adducts of the type **V** (Scheme 5), there is rapid exchange of coordinated and non-coordinated vinyl groups [26].

The spectroscopic properties of the new complexes provide useful reference data for the definition of "cage effects" in the gyroscope-like molecules **II** (Scheme 1), or "parachute effects" in the isomers **IV**. For example, the P***C***H_2, PCH_2***C***H_2, and PCH_2CH_2***C***H_2 ^{13}C-NMR signals of *trans*-**5b**–**e** have been rigorously assigned, and fall into narrow chemical shift (21.5–20.4, 24.2–23.5, and 31.5–30.6 ppm) and coupling constant (J_{CP} = 16.2–16.0, < 2.0, and 6.6–6.2 Hz) ranges. Platinum complexes of the related phosphines $Ar_2P(CH_2)_mCH{=}CH_2$ and $ArP((CH_2)_mCH{=}CH_2)_2$ exhibit similar values [5, 6]. The chemical shifts of the P***C***H_2 signals of *trans*-**5b**–**e** are, as commonly seen, 3–6 ppm upfield of those of the free phosphines **1b**–**e**.

The ^{13}C-NMR spectra of the palladium dichloride and dibromide complexes *trans*-**3a**–**c**, **e** and *trans*-**4a**–**c** are remarkably similar, except that in all cases save one the $^1J_{CP}$ values are somewhat lower (13.0–13.5 Hz). In the cases of *cis*-**5b**–**e** the $^1J_{CP}$ values are not resolved, but the $^3J_{CP}$ values (7.1–6.9 Hz) are close to those of the other complexes. The ^{31}P-NMR chemical shifts of *cis*-**5b**–**e** are slightly upfield of those of *trans*-**5b**–**e** (1.6–2.3 *vs.* 5.1–5.2 ppm).

However, other than the large difference in $^1J_{PPt}$ values noted above, the isomers do not exhibit distinctive spectroscopic features. The mass spectra of most of the complexes exhibit a strong peak for the free phosphine, in contrast to the gyroscope-like complexes **II**, for which the cage effect disfavors this fragmentation mode.

All of the new complexes are oils that have so far resisted crystallization. Hence, we lack structural comparisons for **II** and the many crystalline species that can be derived therefrom. In a platinum complex with *trans* $Ar_2P(CH_2)_5CH{=}CH_2$ ligands, the vinyl groups are "preorganized" in the crystal for macrocyclization [5b]. However, all of the preceding complexes would exhibit many conformations of comparable energies in solution.

In summary, convenient syntheses of symmetrical trialkylphosphines with three terminal vinyl groups have been described. These serve as springboards, *via* coordination/metathesis/hydrogenation sequences, to a variety of gyroscope- or parachute-like complexes [7 – 11, 13]. Palladium and platinum adducts have been characterized, and the further elaboration of these species will be fully detailed in future reports [29].

Experimental Section

General

Reactions were conducted under nitrogen atmospheres. Chemicals were treated as follows: THF and C_6H_6, distilled from Na/benzophenone; CH_2Cl_2 (for reactions), distilled from CaH_2; hexanes, CH_2Cl_2 (for workups), and CH_3OH, simple distillation; magnesium powder (Riedel-de Haen, 99 %), kept in a glove box; $Br(CH_2)_mCH{=}CH_2$ (**2**, m = **a**/4, **b**/5, **c**/6, **d**/7, **e**/8, **f**/9; Fluka or Aldrich), 1,2-dibromoethane (Aldrich, 99 %), PCl_3 (Merck), NH_4Cl (Grüssing, 99 %), $PtCl_2$, K_2PtCl_4 (2 × ABCR, 99.9 %), $H_3B{\cdot}S(CH_3)_2$ (Aldrich, 2.0 M in THF), C_6D_6, and CD_2Cl_2 (2 × Deutero GmbH, ≥ 99.5 %), used as received. NMR data were obtained on a Bruker 400 Hz spectrometer and referenced as follows: ^{1}H-NMR, residual $CHCl_3$ (7.24 ppm) or C_6D_5H (7.15 ppm); ^{13}C-NMR, internal $CDCl_3$ (77.0 ppm) or C_6D_6 (128.0 ppm); ^{31}P-NMR, external H_3PO_4 (0.00 ppm). IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. Elemental analyses were conducted with a Carlo Erba EA 1110 instrument.

*$P((CH_2)_4CH{=}CH_2)_3$ (**1a**)*

A Schlenk flask was charged with magnesium powder (1.500 g, 61.7 mmol), THF (40 mL), and 1,2-dibromoethane (0.30 mL, 3.5 mmol), and was cooled to 0 °C. Then **2a** (5.0 mL, 37 mmol) was added dropwise with stirring. The cooling bath was removed. After 16 h, the mixture was cooled to 0 °C, and a solution of PCl_3 (1.05 mL, 12.1 mmol) in THF (8 mL) was added dropwise over 1 h. The cooling bath was removed. After 17 h, saturated aqueous NH_4Cl (20 mL) was added. The aqueous phase was removed *via* syringe. The solvent was removed from the organic phase by oil pump vacuum. The residue was filtered through a pad of neutral alumina (1.5 × 7 cm, rinsed with CH_2Cl_2). The solvent was removed from the filtrate by oil pump vacuum to give **1a** as a tan oil (1.870 g, 7.41 mmol, 61 %). – NMR (C_6D_6) [30]: ^{1}H: δ = 5.75 (ddt, 3H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.00 (br d, 3H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$H$_Z$), 4.97 (br d, 3H, $^3J_{HHcis}$ = 10.5 Hz, =CH$_E$H$_Z$), 1.98 – 1.96 (m, 6H, CH_2CH=), 1.45 – 1.39 (m, 6H, PCH_2), 1.31 – 1.26 (m, 12H, remaining CH_2); ^{13}C{^{1}H}: δ = 138.8 (s, *C*H=), 114.5 (s, = *C*H$_2$), 34.0 (s, *C*H$_2$CH=), 31.0 (d, J_{CP} = 10.5 Hz, *C*H$_2$), 27.9 (d, J_{CP} = 14.1 Hz, *C*H$_2$), 25.8 (d, J_{CP} = 13.4 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = −30.9 (s).

*$P((CH_2)_5CH{=}CH_2)_3$ (**1b**)*

Magnesium powder (1.400 g, 57.6 mmol), THF (10 mL), 1,2-dibromoethane (0.30 mL, 3.5 mmol), **2b** (6.0 mL, 29 mmol), PCl_3 (0.87 mL, 9.7 mmol) in THF (3 mL), and saturated aqueous NH_4Cl (8 mL) were combined in a procedure analogous to that for **1a**. An identical workup gave **1b** as a tan oil (1.625 g, 5.04 mmol, 52 %). – NMR (C_6D_6) [30]: ^{1}H: δ = 5.75 (ddt, 3H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H* =), 5.10 (br d, 3H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$H$_Z$), 5.01 (br d, 3H, $^3J_{HHcis}$ = 10.1 Hz, =CH$_E$H$_Z$), 2.05 – 2.00 (m, 6H, CH_2CH=), 1.52 – 1.47 (m, 6H, PCH_2), 1.30 (m, 18H, remaining CH_2); ^{13}C{^{1}H}: δ = 139.2 (s, *C*H=), 114.3 (s, = *C*H$_2$), 34.1 (s, *C*H$_2$CH=), 31.3 (d, J_{CP} = 10.5 Hz, *C*H$_2$), 29.0 (s, *C*H$_2$), 28.0 (d, $^1J_{CP}$ = 14.1 Hz, *C*H$_2$), 26.4 (d, J_{CP} = 13.4 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = −30.8 (s).

*$P((CH_2)_6CH{=}CH_2)_3$ (**1c**)*

Magnesium powder (1.883 g, 78.8 mmol), THF (40 mL), 1,2-dibromoethane (0.40 mL, 4.6 mmol), **2c** (5.000 g, 26.2 mmol), PCl_3 (0.77 mL, 8.7 mmol) in THF (5 mL), and saturated aqueous NH_4Cl (10 mL) were combined in a procedure analogous to that for **1a**. An identical workup gave **1c** as a tan oil (2.753 g, 7.56 mmol, 87 %). – NMR (C_6D_6) [31]: ^{1}H: δ = 5.90 (ddt, 3H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.11 (br d, 3H, $^3J_{HHtrans}$ = 17.0 Hz, =CH$_E$H$_Z$), 5.02 (br d, 3H, $^3J_{HHcis}$ = 10.1 Hz, =CH$_E$H$_Z$), 2.12 – 2.08 (m, 6H, CH_2CH=), 1.63 – 1.58 (m, 6H, PCH_2), 1.50 – 1.39 (m, 24H, remaining CH_2); ^{13}C{^{1}H}: δ = 139.4 (s, *C*H=), 114.7 (s, =*C*H$_2$), 34.4 (s, *C*H$_2$CH=), 31.9 (d, J_{CP} = 10.4 Hz, *C*H$_2$), 29.28 (s, *C*H$_2$), 29.26 (s, *C*H$_2$), 28.3 (d, J_{CP} = 14.0 Hz, *C*H$_2$), 26.7 (d, $^1J_{CP}$ = 13.5 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = −30.9 (s).

*$P((CH_2)_7CH{=}CH_2)_3$ (**1d**)*

Magnesium powder (1.510 g, 62.1 mmol), THF (40 mL), 1,2-dibromoethane (0.30 mL, 3.5 mmol), **2d** (4.300 g, 21.0 mmol), PCl_3 (0.61 mL, 6.9 mmol) in THF (7 mL), and saturated aqueous NH_4Cl (17 mL) were combined in a procedure analogous to that for **1a**. An identical workup gave **1d** as a tan oil (2.007 g, 4.96 mmol, 72 %). – NMR (C_6D_6) [30]: ^{1}H: δ = 5.89 (ddt, 3H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.12 (br d, 3H, $^3J_{HHtrans}$ = 17.0 Hz, =CH$_E$H$_Z$), 5.09 (br d, 3H, $^3J_{HHcis}$ = 9.1 Hz, =CH$_E$H$_Z$), 2.11 – 2.08 (m, 6H, CH_2CH=), 1.63 – 1.51 (m, 6H, PCH_2), 1.50 – 1.38 (m, 30H, remaining CH_2); ^{13}C{^{1}H}: δ = 139.1 (s, *C*H=), 114.4 (s, = *C*H$_2$), 34.2 (s, CH_2CH=), 31.8 (d, J_{CP} = 17.0 Hz, *C*H$_2$), 29.8 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 28.2 (d, J_{CP} = 14.3 Hz, *C*H$_2$), 26.6 (d, $^1J_{CP}$ = 13.4 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = −30.9 (s).

*$P((CH_2)_8CH{=}CH_2)_3$ (**1e**)*

Magnesium powder (1.700 g, 69.9 mmol), THF (45 mL), 1,2-dibromoethane (0.35 mL, 4.1 mmol), **2e** (5.000 g, 22.8 mmol), PCl_3 (0.66 mL, 7.6 mmol) in THF (10 mL), and saturated aqueous NH_4Cl (20 mL) were combined in a procedure analogous to that for **1a**. An identical workup gave **1e** as a tan oil (1.970 g, 4.39 mmol, 58 %). – NMR (C_6D_6) [30]: ^{1}H: δ = 5.90 (ddt, 3H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.12 (br d, 3H, $^3J_{HHtrans}$ = 17.0 Hz, =CH$_E$H$_Z$), 5.09 (br d, 3H, $^3J_{HHcis}$ = 10.1 Hz, =CH$_E$H$_Z$), 2.12 – 2.08 (m, 6H, CH_2CH=), 1.63 – 1.58 (m, 6H, PCH_2), 1.50 – 1.39 (m, 36H, remaining CH_2); ^{13}C{^{1}H}: δ = 139.4 (s, *C*H=), 114.7 (s, = *C*H$_2$), 34.4 (s, *C*H$_2$CH=), 31.9 (d, J_{CP} = 10.4 Hz, *C*H$_2$), 29.8 (s, *C*H$_2$), 29.7 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 28.3 (d, J_{CP} = 14.0 Hz, *C*H$_2$), 26.7 (d, $^1J_{CP}$ = 13.5 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = −30.9 (s).

*$P((CH_2)_9CH{=}CH_2)_3$ (**1f**)*

Magnesium powder (0.620 g, 25.8 mmol), THF (12 mL), 1,2-dibromoethane (0.20 mL, 2.3 mmol), **2f** (2.683 g, 11.5 mmol), PCl_3 (0.42 mL, 4.8 mmol) in THF (4 mL), and saturated aqueous NH_4Cl (8 mL) were combined in a procedure analogous to that for **1a**. An identical workup gave **1f** as a tan oil (1.231 g, 2.51 mmol, 66 %). – NMR (C_6D_6) [30]: ^{1}H: δ = 5.87 (ddt, 3H, $^3J_{HHtrans}$ = 16.2 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.0 Hz, C*H*=), 5.12 (br d, 3H, $^3J_{HHtrans}$ = 17.4 Hz, =CH$_E$H$_Z$), 5.08 (br d, 3H, $^3J_{HHcis}$ = 10.3 Hz, =CH$_E$H$_Z$), 2.09 – 2.08 (m, 6H, CH_2CH=), 1.63 – 1.60 (m, 6H, PCH_2), 1.51 – 1.34 (m, 42H, remaining CH_2); ^{13}C{^{1}H}: δ = 139.2 (s, *C*H=), 114.5 (s, = *C*H$_2$), 34.2 (s, *C*H$_2$CH=), 32.0 (d, J_{CP} = 10.5 Hz, *C*H$_2$), 30.01 (s, *C*H$_2$), 29.96 (s, *C*H$_2$), 29.90 (s, *C*H$_2$), 29.7 (s, *C*H$_2$), 29.4 (s, *C*H$_2$), 28.2 (d, J_{CP} = 14.4 Hz, *C*H$_2$), 26.6 (d, $^1J_{CP}$ = 13.4 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = −30.9 (s).

*$PdCl_2(P((CH_2)_4CH{=}CH_2)_3)_2$ (**3a**)*

A Schlenk flask was charged with **1a** (0.686 g, 2.45 mmol), $PdCl_2$(COD) (0.349 g, 1.22 mmol) [19], and CH_2Cl_2 (15 mL). The mixture was stirred for 16 h. The solvent was removed by rotary evaporation [32]. The residue was chromatographed on a silica column (2 × 17 cm, 3 : 1 v/v CH_2Cl_2/hexanes). The pale-yellow fraction was collected, and CH_3OH (10 mL) [33] was added. The solvent was removed by rotary evaporation to give *trans*-**3a** as a yellow oil (0.830 g, 1.12 mmol, 92 %). – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.79 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.02 (br d, 6H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$H$_Z$), 4.85 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =CH$_E$H$_Z$), 2.11 – 1.93 (m, 12H, CH_2CH=), 1.87 – 1.81 (m, 12H, PCH_2), 1.61 – 1.42 (m, 24H, remaining CH_2); ^{13}C{^{1}H}: δ = 138.3 (s, *C*H=), 114.6 (s, = *C*H$_2$), 33.1 (s, *C*H$_2$CH=), 30.2 (virtual t [36], $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$*C*H$_2$), 23.3 (s, PCH$_2$*C*H$_2$), 21.2 (virtual t [36], $^1J_{CP}$ = 13.3 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 10.4 (s). – IR (cm^{-1}, oil film): ν = 3076 (w), 2926 (s), 2856 (m), 1695 (w), 1640 (m), 1417 (m), 1169 (w), 992 (m), 907 (s), 791 (m), 718 (m). – MS [34]: *m/z* (%) = 701 (100) [M–Cl]$^+$, 666 (80) [M–2Cl]$^+$, 560 (50) [P((CH$_2$)$_4$CH=CH$_2$)$_3$]$^+$.

*$PdCl_2(P((CH_2)_5CH{=}CH_2)_3)_2$ (**3b**)*

Phosphine **1b** (0.585 g, 1.81 mmol), $PdCl_2$(COD) (0.249 g, 0.872 mmol) [19], and CH_2Cl_2 (10 mL) were combined in a procedure analogous to that for **3a** [32]. A similar workup (2 × 9 cm column) gave *trans*-**3b** as a yellow oil (0.249 g, 0.302 mmol, 35 %). – Anal. for $C_{42}H_{78}Cl_2P_2Pd$: calcd. C 57.92, H 9.11; found C 57.75, H 9.08. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.77 (ddt, 6H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.99 (br d, 6H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$H$_Z$), 4.92 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =CH$_E$H$_Z$), 2.03 – 1.98 (m, 12H, CH_2CH=), 1.79 – 1.75 (m, 12H, PCH_2), 1.55 – 1.53 (m, 12H, PCH$_2$CH_2), 1.41 – 1.31 (m, 24H, remaining CH_2); ^{13}C{^{1}H}: δ = 139.2 (s, *C*H=), 114.4 (s, = *C*H$_2$), 33.5 (s, *C*H$_2$CH=), 30.7 (virtual t [36], $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$*C*H$_2$), 28.4 (s, PCH$_2$CH$_2$CH$_2$*C*H$_2$), 23.8 (s, PCH$_2$*C*H$_2$), 21.5 (virtual t [36], $^1J_{CP}$ = 13.3 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 11.2 (s). – IR (cm^{-1}, oil film): ν = 3076 (w), 2926 (s), 2856 (m), 1640 (m), 1459 (m), 1417 (m), 1139 (w), 992 (m), 907 (s), 719 (w), 722 (m). – MS [30]: *m/z* (%) = 822 (20) [M]$^+$, 785 (100) [M–Cl]$^+$, 750 (85) [M–2Cl]$^+$.

*$PdCl_2(P((CH_2)_6CH{=}CH_2)_3)_2$ (**3c**)*

Phosphine **1c** (0.327 g, 0.897 mmol), $PdCl_2$(COD) (0.116 g, 0.401 mmol) [19], and CH_2Cl_2 (5 mL) were combined in a procedure analogous to that for **3a** (3.5 h reaction) [32]. A similar workup (2 × 11 cm column) gave

trans-**3c** as a yellow oil (0.322 g, 0.355 mmol, 88 %). – Anal. for $C_{48}H_{90}Cl_2P_2Pd$: calcd. C 63.62, H 9.94; found C 63.44, H 9.93. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.82 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.95 (br d, 6H, $^3J_{HHtrans}$ = 17.2 Hz, =CH$_E$*H*$_Z$), 4.88 (br d, 6H, $^3J_{HHcis}$ = 9.1 Hz, =C*H*$_E$H$_Z$), 2.09 – 2.03 (m, 12H, C*H*$_2$CH=), 1.79 – 1.75 (m, 12H, PC*H*$_2$), 1.61 – 1.50 (m, 12H, PCH$_2$C*H*$_2$), 1.45 – 1.29 (m, 36H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 139.2 (s, *C*H=), 114.5 (s, =*C*H$_2$), 34.0 (s, *C*H$_2$CH=), 31.3 (virtual t [36], $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.0 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 24.2 (s, PCH$_2$*C*H$_2$), 21.7 (virtual t [36], $^1J_{CP}$ = 13.0 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 11.5 (s). – IR (cm^{-1}, oil film): ν = 3076 (w), 2926 (s), 2856 (m), 1640 (m), 1459 (m), 1440 (m), 1417 (m), 992 (m), 907 (s), 799 (w), 733 (s), 566 (s). – MS [34]: *m/z* (%) = 365 (100) [P((CH$_2$)$_6$CH=CH$_2$)$_3$]$^+$.

*$PdCl_2(P((CH_2)_8CH{=}CH_2)_3)_2$ (**3e**)*

Phosphine **1e** (1.701 g, 3.79 mmol), $PdCl_2$(COD) (0.541 g, 1.89 mmol) [19], and CH_2Cl_2 (20 mL) were combined in a procedure analogous to that for **3a** [32]. A similar workup (2.5 × 16 cm column) gave *trans*-**3e** as a yellow oil (1.530 g, 1.42 mmol, 75 %). – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.82 (ddt, 6H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.98 (br d, 6H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$*H*$_Z$), 4.94 (br d, 6H, $^3J_{HHcis}$ = 10.1 Hz, =C*H*$_E$H$_Z$), 2.15 – 1.98 (m, 12H, C*H*$_2$CH=), 1.98 – 1.88 (br m, 12H, PC*H*$_2$), 1.70 – 1.68 (br m, 12H, PCH$_2$C*H*$_2$), 1.50 – 1.18 (br m, 60H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 139.1 (s, *C*H=), 114.0 (s, =*C*H$_2$), 33.8 (s, *C*H$_2$CH=), 31.2 (virtual t [36], $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.6 (s, *C*H$_2$), 29.4 (s, *C*H$_2$), 29.1 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 24.0 (s, PCH$_2$*C*H$_2$), 21.4 (virtual t [36], $^1J_{CP}$ = 16.1 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 11.4 (s). – IR (cm^{-1}, oil film): ν = 3078 (m), 2923 (s), 2854 (s), 1642 (m), 1465 (m), 1441 (s), 992 (m), 907 (s), 722 (m). – MS [34]: *m/z* (%) = 449 (100) [P((CH$_2$)$_8$CH=CH$_2$)$_3$]$^+$.

*$PdBr_2(P((CH_2)_4CH{=}CH_2)_3)_2$ (**4a**)*

Phosphine **1a** (0.400 g, 1.43 mmol), $PdBr_2$(COD) (0.233 g, 0.622 mmol) [19], and CH_2Cl_2 (10 mL) were combined in a procedure analogous to that for **3a** [37]. A similar workup (1.5 × 7 cm column) gave *trans*-**4a** as an orange oil (0.316 g, 0.382 mmol, 61 %). – Anal. for $C_{36}H_{66}Br_2P_2Pd$: calcd. C 52.28, H 8.04; found C 53.04, H 8.23 [38]. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.76 (ddt, 6H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.98 (br d, 6H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$*H*$_Z$), 4.93 (br d, 6H, $^3J_{HHcis}$ = 10.1 Hz, =C*H*$_E$H$_Z$), 2.09 – 2.03 (br m, 12H, C*H*$_2$CH=), 2.03 – 1.95 (br m, 12H, PC*H*$_2$), 1.80 – 1.41 (br m, 24H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 138.7 (s, *C*H=), 115.1 (s, = *C*H$_2$), 33.6 (s, *C*H$_2$CH=), 30.6 (virtual t [36], $^3J_{CP}$ = 6.5 Hz, PCH$_2$CH$_2$*C*H$_2$), 24.1 (s, PCH$_2$*C*H$_2$), 23.3 (virtual t [36], $^1J_{CP}$ = 13.5 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 8.3 (s). – IR (cm^{-1}, oil film): ν = 3076 (w), 2926 (s), 2856 (m), 1640 (m), 1459 (m), 1417 (m), 992 (m), 907 (s), 791 (m), 718 (m). – MS [34]: *m/z* (%) = 747 (100) [M–Br]$^+$, 665 (50) [M–2Br]$^+$, 560 (50) [P((CH$_2$)$_4$CH=CH$_2$)$_3$]$^+$.

*$PdBr_2(P((CH_2)_5CH{=}CH_2)_3)_2$ (**4b**)*

Phosphine **1b** (0.479 g, 1.49 mmol), $PdBr_2$(COD) (0.278 g, 0.743 mmol) [19], and CH_2Cl_2 (15 mL) were combined in a procedure analogous to that for **4a** [37]. An identical workup gave *trans*-**4b** as an orange oil (0.413 g, 0.453 mmol, 61 %). – Anal. for $C_{42}H_{78}Br_2P_2Pd$: calcd. C 55.36, H 8.63; found C 56.13, H 8.94 [38]. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.76 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.94 (br d, 6H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$*H*$_Z$), 4.84 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$H$_Z$), 2.09 – 2.03 (br m, 12H, C*H*$_2$CH=), 2.03 – 1.95 (br m, 12H, PC*H*$_2$), 1.79 – 1.43 (br m, 36H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 138.7 (s, *C*H=), 115.1 (s, = *C*H$_2$), 33.6 (s, *C*H$_2$CH=), 30.6 (virtual t [36], $^3J_{CP}$ = 6.5 Hz, PCH$_2$CH$_2$*C*H$_2$), 24.1 (s, PCH$_2$CH$_2$CH$_2$*C*H$_2$), 23.5 (s, PCH$_2$*C*H$_2$), 23.3 (virtual t [36], $^1J_{CP}$ = 13.5 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 8.3 (s). – IR (cm^{-1}, oil film): ν = 2926 (s), 2856 (m), 1640 (m), 1459 (m), 1417 (m), 992 (m), 907 (s), 791 (m), 718 (m). – MS [34]: *m/z* (%) = 831 (100) [M–Br]$^+$, 750 (80) [M–2Br]$^+$, 664 (50) [P((CH$_2$)$_5$CH=CH$_2$)$_3$]$^+$.

*$PdBr_2(P((CH_2)_6CH{=}CH_2)_3)_2$ (**4c**)*

Phosphine **1c** (1.163 g, 3.19 mmol), $PdBr_2$(COD) (0.675 g, 1.80 mmol) [19], and CH_2Cl_2 (20 mL) were combined in a procedure analogous to that for **4a** [37]. A similar workup (1.5 × 12 cm column) gave *trans*-**4c** as an orange oil (0.879 g, 0.883 mmol, 55 % based upon limiting **1c**). – Anal. for $C_{48}H_{90}Br_2P_2Pd$: calcd. C 57.92, H 9.11; found C 58.15, H 9.31. – NMR ($CDCl_3$ [35]): ^{1}H: δ = 5.77 (ddt, 6H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.95 (br d, 6H, $^3J_{HHtrans}$ = 17.0 Hz, =CH$_E$*H*$_Z$), 4.89 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$*H*$_Z$), 2.03 – 1.99 (m, 12H, C*H*$_2$CH=), 1.92 – 1.90 (m, 12H, PC*H*$_2$), 1.50 – 1.48 (m, 12H, PCH$_2$C*H*$_2$), 1.42 – 1.29 (m, 36H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 139.2 (s, *C*H=), 114.3 (s, = *C*H$_2$), 33.8 (s, *C*H$_2$CH=), 31.0 (virtual t [36], $^3J_{CP}$ = 6.5 Hz, PCH$_2$CH$_2$*C*H$_2$), 28.8 (s, *C*H$_2$), 28.7 (s, *C*H$_2$), 24.2 (s, PCH$_2$*C*H$_2$), 23.3 (virtual t [30], $^1J_{CP}$ = 13.5 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 8.2 (s). – IR (cm^{-1}, oil film): ν = 3076 (w), 2926 (s), 2856 (m), 1640 (m), 1459 (m), 1440 (m), 1413 (m), 992 (m), 907 (s), 795 (m), 718 (m). – MS [34]: *m/z* (%) = 916 (5) [M–Br]$^+$, 365 (100) [P((CH$_2$)$_6$CH=CH$_2$)$_3$]$^+$.

*$PtCl_2(P((CH_2)_5CH{=}CH_2)_3)_2$ (**5b**)*

A. A Schlenk flask was charged with **1b** (0.299 g, 0.936 mmol), $PtCl_2$ (0.123 g, 0.469 mmol), and C_6H_6

(10 mL). The suspension was stirred for 18 h. The solvent was removed by rotary evaporation. The residue was chromatographed on a silica column (1.5 × 20 cm, 1 : 3 v/v CH_2Cl_2/hexanes). The pale-yellow fraction was collected. The solvent was removed by rotary evaporation to give *trans*-**5b** as a pale-yellow oil (0.266 g, 0.292 mmol, 62 %). – Anal. for $C_{42}H_{78}Cl_2P_2Pt$: calcd. C 55.37, H 8.63; found C 55.56, H 8.50. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.77 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 4.97 (br d, 6H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$*H*$_Z$), 4.91 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$H$_Z$), 2.28 – 2.27 (m, 12H, C*H*$_2$CH=), 2.03 – 2.02 (m, 12H, PC*H*$_2$), 1.82 – 1.79 (br m, 12H, PCH$_2$C*H*$_2$), 1.41 – 1.39 (m, 24H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 138.8 (s, *C*H=), 114.4 (s, =*C*H$_2$), 33.6 (s, *C*H$_2$CH=), 30.6 (virtual t [36], $^3J_{CP}$ = 6.6 Hz, PCH$_2$CH$_2$*C*H$_2$), 28.4 (s, *C*H$_2$), 23.5 (2 s, PCH$_2$*C*H$_2$CH$_2$*C*H$_2$), 20.4 (virtual t [36], $^1J_{CP}$ = 16.0 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 6.1 (s [39], $^1J_{PPt(195)}$ = 2382 Hz). – MS [34]: *m/z* (%) = 875 (5) [M–Cl]$^+$, 838 (10) [M–2Cl]$^+$, 323 (100) [P((CH$_2$)$_5$CH=CH$_2$)$_3$]$^+$.

B. A Schlenk flask was charged with K_2PtCl_4 (0.300 g, 0.723 mmol), degassed distilled water (10 mL), and **1b** (0.4660 g, 1.45 mmol). The red mixture was stirred vigorously until the color of the aqueous supernatant did not lighten further (*ca.* 12 h). The supernatant was decanted, and the residue was washed with water and dried by oil pump vacuum (30 °C, 1 h). The mixture was chromatographed on a silica column (3 × 20 cm, CH_2Cl_2). Two fractions were collected. The solvent was removed from both by oil pump vacuum to give yellow oils. The first consisted of *trans*-**5b**, and the second of *cis*-**5b** (0.459 g, 0.504 mmol, 70 %). – Anal. for $C_{42}H_{78}Cl_2P_2Pt$: calcd. C 55.37, H 8.63; found C 56.02, H 8.87 [38]. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.74 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, CH=), 4.98 (dd, 6H, $^3J_{HHtrans}$ = 16.9 Hz, $^2J_{HH}$ = 1.5 Hz, =CH$_E$*H*$_Z$), 4.94 (br d, 6H, $^3J_{HHcis}$ = 9.0 Hz, =C*H*$_E$CH$_Z$), 2.04 – 2.03 (m, 12H, C*H*$_2$CH=), 1.96 – 1.94 (m, 12H, PC*H*$_2$), 1.53 – 1.40 (m, 36H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 138.8 (s, *C*H=), 115.1 (s, =*C*H$_2$), 33.9 (s, *C*H$_2$CH=), 30.9 (virtual t [36], J_{CP} = 7.1 Hz, PCH$_2$CH$_2$*C*H$_2$), 28.8 (s, *C*H$_2$), 25.2 (br s, P*C*H$_2$), 24.8 (s, *C*H$_2$); ^{31}P{^{1}H}: δ = 2.3 (s [39], $^1J_{PPt}$ = 3511 Hz). – MS [34]: *m/z* (%) = 910 (1) [M]$^+$, 875 ([M–Cl]$^+$, 10), 838 (25) [M–2Cl]$^+$, 323 (100) [P((CH$_2$)$_5$CH=CH$_2$)$_3$]$^+$.

*PtCl$_2$(P((CH$_2$)$_6$CH=CH$_2$)$_3$)$_2$ (**5c**)*

A. Phosphine **1c** (2.643 g, 7.25 mmol), $PtCl_2$ (0.945 g, 3.63 mmol), and C_6H_6 (45 mL) were combined in a procedure analogous to ***A*** for **5b**. A similar workup (3.0 × 29 cm column) gave *trans*-**5c** as a pale-yellow oil (2.660 g, 2.67 mmol, 74 %). – Anal. for $C_{48}H_{90}Cl_2P_2Pt$: calcd. C 57.93, H 9.12; found C 58.14, H 9.41. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.78 (ddt, 6H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.96 (br d, 6H, $^3J_{HHtrans}$ = 17.0 Hz, =CH$_E$*H*$_Z$), 4.93 (br d, 6H, $^3J_{HHcis}$ = 10.1 Hz, =C*H*$_E$H$_Z$), 2.20 – 2.00 (m, 12H, C*H*$_2$CH=), 2.00 – 1.80 (br m, 12H, PC*H*$_2$), 1.71 – 1.50 (br m, 12H, PCH$_2$C*H*$_2$), 1.50 – 1.22 (m, 36H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 139.1 (s, *C*H=), 114.6 (s, =*C*H$_2$), 34.2 (s, *C*H$_2$CH=), 31.5 (virtual t [36], $^3J_{CP}$ = 6.2 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.3 (s, *C*H$_2$), 29.2 (s, *C*H$_2$), 24.2 (s, PCH$_2$*C*H$_2$), 21.5 (virtual t [36], $^1J_{CP}$ = 16.2 Hz, P*C*H$_2$); ^{31}P{^{1}H}: δ = 5.2 (s [39], $^1J_{PPt(195)}$ = 2381 Hz). – IR (cm^{-1}, oil film): ν = 3076 (m), 2925 (s), 2854 (s), 1642 (m), 1463 (m), 1439 (m), 1414 (m), 994 (m), 907 (s), 799 (m), 719 (m). – MS [34]: *m/z* (%) = 365 (100) [P((CH$_2$)$_6$CH=CH$_2$)$_3$]$^+$.

B. Phosphine **1c** (0.527 g, 1.45 mmol), K_2PtCl_4 (0.300 g, 0.723 mmol), and degassed distilled water (10 mL) were combined in a procedure analogous to ***B*** for **5b**. After the vacuum drying step, the mixture was chromatographed on a silica column (3 × 20 cm, 3 : 2 v/v hexanes/CH_2Cl_2). A yellow fraction was collected. The column was eluted with CH_2Cl_2. A second yellow fraction was collected. The solvent was removed from both by oil pump vacuum to give yellow oils. The first consisted of *trans*-**5c**, and the second of *cis*-**5c** (0.236 g, 0.237 mmol, 33 %). – Anal. for $C_{48}H_{90}Cl_2P_2Pt$: calcd. C 57.93, H 9.11; found C 57.32, H 9.22 [38]. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.87 (ddt, 6H, $^3J_{HHtrans}$ = 17.2 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 4.98 (dd, 6H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.9 Hz, =CH$_E$C*H*$_Z$), 4.93 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$CH$_Z$), 2.04 – 2.02 (m, 12H, C*H*$_2$CH=), 1.94 – 1.80 (m, 12H, PC*H*$_2$), 1.52 – 1.32 (m, 48H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 139.1 (s, *C*H=), 114.9 (s, =*C*H$_2$), 34.1 (s, *C*H$_2$CH=), 31.3 (virtual t [36], $^3J_{CP}$ = 6.9 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.13 (s, *C*H$_2$), 29.11 (s, *C*H$_2$), 25.2 (br s, P*C*H$_2$), 24.9 (s, *C*H$_2$); ^{31}P{^{1}H}: δ = 2.2 (s [39], $^1J_{PPt}$ = 3510 Hz). – MS [34]: *m/z* (%) = 960 (7) [M–Cl]$^+$, 844 (10) [M–2Cl]$^+$, 365 (100) [P((CH$_2$)$_6$CH=CH$_2$)$_3$]$^+$.

*PtCl$_2$(P((CH$_2$)$_7$CH=CH$_2$)$_3$)$_2$ (**5d**)*

A. Phosphine **1d** (3.180 g, 7.83 mmol), $PtCl_2$ (1.401 g, 3.91 mmol), and C_6H_6 (150 mL) were combined in a procedure analogous to ***A*** for **5b**. A similar workup (3.5 × 22 cm column) gave *trans*-**5d** as a pale-yellow oil (2.195 g, 2.03 mmol, 52 %). – Anal. for $C_{54}H_{102}Cl_2P_2Pd$: calcd. C 60.09, H 9.53; found C 59.48, H 9.24 [38]. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.77 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.98 (br d, 6H, $^3J_{HHtrans}$ = 17.1 Hz, =CH$_E$*H*$_Z$), 4.93 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$H$_Z$), 2.10 – 2.03 (m, 12H, C*H*$_2$CH=), 1.91 – 1.78 (m, 12H, PC*H*$_2$), 1.68 – 1.51 (m, 12H, PCH$_2$C*H*$_2$), 1.43 – 1.27 (m, 48H, remaining C*H*$_2$); ^{13}C{^{1}H}: δ = 139.2 (s, *C*H=), 114.2 (s, =*C*H$_2$), 33.8 (s, *C*H$_2$CH=), 31.1 (virtual t [36], $^3J_{CP}$ = 6.3 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.1 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.0 (s, *C*H$_2$), 23.6 (s, PCH$_2$*C*H$_2$), 20.4 (virtual

t [36], $^1J_{CP}$ = 16.0 Hz, PCH$_2$); $^{31}P\{^1H\}$: δ = 5.2 (s [39], $^1J_{PPt(195)}$ = 2380 Hz). – IR (cm^{-1}, oil film): ν = 2925 (s), 2854 (s), 1642 (m), 1463 (m), 1441 (m), 994 (m), 907 (s), 797 (m), 720 (m). – MS [34]: *m/z* (%) = 407 (100) $[P((CH_2)_7CH{=}CH_2)_3]^+$.

B. Phosphine **1d** (0.392 g, 0.964 mmol), K_2PtCl_4 (0.200 g, 0.482 mmol), and degassed distilled water (7 mL) were combined in a procedure analogous to ***B*** for **5c**. A similar workup (1.0 × 20 cm column) gave *cis*-**5d** as a pale-yellow oil (0.247 g, 0.229 mmol, 47 %). – Anal. for $C_{54}H_{102}Cl_2P_2Pt$: calcd. C 60.09, H 9.53; found C 60.20, H 10.10. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.81 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 4.97 (dd, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.6 Hz, =CH$_E$C*H*$_Z$), 4.92 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$CH$_Z$), 2.04 – 1.99 (m, 12H, C*H*$_2$CH=), 1.97 – 1.91 (br m, 12H, PC*H*$_2$), 1.52 (br s, 12H, PCH$_2$C*H*$_2$), 1.37 – 1.27 (m, 48H, remaining C*H*$_2$); $^{13}C\{^1H\}$: δ = 138.9 (s, *C*H=), 114.3 (s, =*C*H$_2$), 33.7 (s, *C*H$_2$CH=), 31.0 (virtual t [36], J_{CP} = 7.1 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.1 (s, *C*H$_2$), 29.0 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 24.9 (br s, P*C*H$_2$), 24.5 (s, *C*H$_2$); $^{31}P\{^1H\}$: δ = 1.6 (s [39], $^1J_{PPt}$ = 3508 Hz). – MS [34]: *m/z* (%) = 1045 (20) $[M–Cl]^+$, 1090 (8) $[M–2Cl]^+$, 408 (100) $[P((CH_2)_7CH{=}CH_2)_3]^+$.

*$PtCl_2(P((CH_2)_8CH{=}CH_2)_3)_2$ (**5e**)*

A. Phosphine **1e** (1.750 g, 3.90 mmol), $PtCl_2$ (0.518 g, 1.95 mmol), and C_6H_6 (80 mL) were combined in a procedure analogous to ***A*** for **5b**. A similar workup (3.5 × 20 cm column) gave *trans*-**5e** as a pale-yellow oil (1.557 g, 1.44 mmol, 75 %). – Anal. for $C_{60}H_{114}Cl_2P_2Pt$: calcd. C 61.94, H 9.88; found C 61.97, H 9.86. – NMR ($CDCl_3$) [31]: ^{1}H: δ = 5.78 (ddt, 6H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.92 (dd, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.9 Hz, =CH$_E$*H*$_Z$), 4.89 (br d, 6H, $^3J_{HHcis}$ = 10.1 Hz, =C*H*$_E$H$_Z$), 2.10 – 1.98 (m, 12H, C*H*$_2$CH=), 1.88 – 1.71 (br m, 12H, PC*H*$_2$), 1.65 – 1.50 (br m, 12H, PCH$_2$C*H*$_2$), 1.49 – 1.20 (br m, 60H, remaining C*H*$_2$); $^{13}C\{^1H\}$: δ = 139.1 (s, *C*H=), 114.1 (s, =*C*H$_2$), 33.8 (s, *C*H$_2$CH=), 31.1 (virtual t [36], $^3J_{CP}$ = 6.5 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.3 (s, *C*H$_2$), 29.2 (s, *C*H$_2$), 29.1 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 23.6 (s, PCH$_2$*C*H$_2$), 20.4 (virtual t [36], $^1J_{CP}$ = 16.1 Hz, P*C*H$_2$); $^{31}P\{^1H\}$: δ = 5.1 (s [39], $^1J_{PPt(195)}$ = 2381 Hz). – IR (cm^{-1}, oil film): ν = 2926 (s), 2856 (s), 1640 (m), 1463 (m), 1417 (m), 1075 (w), 992 (m), 907 (s), 799 (m), 721 (m). – MS [34]: *m/z* (%) = 449 (100) $[P((CH_2)_8CH{=}CH_2)_3]^+$.

B. Phosphine **1e** (0.4324 g, 0.964 mmol), K_2PtCl_4 (0.200 g, 0.482 mmol), and degassed distilled water (10 mL) were combined in a procedure analogous to ***B*** for **5c**. A similar workup (1.5 × 25 cm column) gave *cis*-**5e** as a pale-yellow oil (0.251 g, 0.215 mmol, 45 %). – Anal. for $C_{60}H_{114}Cl_2P_2Pt$: calcd. C 61.94, H 9.88; found C 61.35, H 9.47 [38]. – NMR ($CDCl_3$) [35]: ^{1}H: δ = 5.78 (ddt, 6H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 4.97 (dd, 6H, $^3J_{HHtrans}$ = 17.1 Hz, ^2JHH = 1.9 Hz, =CH$_E$C*H*$_Z$), 4.92 (br d, 6H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$CH$_Z$), 2.16 – 1.99 (m, 12H, C*H*$_2$CH=), 1.95 – 1.93 (br m, 12H, PC*H*$_2$), 1.54 (br s, 12H, PCH$_2$C*H*$_2$), 1.37 – 1.27 (m, 60H, remaining C*H*$_2$); $^{13}C\{^1H\}$: δ = 139.0 (s, *C*H=), 114.2 (s, = *C*H$_2$), 33.8 (s, *C*H$_2$CH=), 31.1 (virtual t [36], J_{CP} = 7.2 Hz, PCH$_2$CH$_2$*C*H$_2$), 30.9 (s, *C*H$_2$), 29.4 (s, *C*H$_2$), 29.2 (s, *C*H$_2$), 29.1 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 24.5 (br s, P*C*H$_2$); $^{31}P\{^1H\}$: δ = 2.2 (s [39], $^1J_{PPt}$ = 3513 Hz). – MS [34]: *m/z* (%) = 1127 (10) $[M–Cl]^+$, 1090 (20) $[M–2Cl]^+$, 449 (100) $[P((CH_2)_8CH{=}CH_2)_3]^+$.

*$H_3B{\cdot}P((CH_2)_6CH{=}CH_2)_3$ ($H_3B{\cdot}$**1c**) and $H_2C{=}CH(CH_2)_{12}CH{=}CH_2$* [17]

A Schlenk flask was charged with **2c** (2.277 g, 6.245 mmol), for which the ^{13}C-NMR signals highlighted in Fig. 1 (top) were apparent, and THF (7 mL) and cooled to 0 °C. Then $H_3B{\cdot}S(CH_3)_2$ (3.1 mL, 6.2 mmol, 2.0 M in THF; 1.0 equiv. after correction for the purity of **2c**) [40] was added dropwise over 10 min with stirring. The mixture was placed at the top of a 25 cm silica gel column that had been packed in hexanes. Elution with hexanes gave fractions containing the α,ω-diene, which were combined and taken to dryness *via* oil pump vacuum to give a colorless oil (0.134 g, 0.607 mmol). – Anal. for $C_{16}H_{30}$: calcd. C 86.40, H 13.60; found C 85.71, H 13.38. – Elution with hexanes/CH_2Cl_2 (2 : 1 to 1 : 1 v/v) similarly afforded $H_3B{\cdot}$**1c** as a colorless oil (2.003 g, 5.299 mmol, 85 %). – Anal. for $C_{24}H_{48}BP$: calcd. C 76.17, H 12.79; found C 75.78, H 12.74.

Data for $H_2C{=}CH(CH_2)_{12}CH{=}CH_2$ [17]

NMR ($CDCl_3$): ^{1}H: δ = 5.80 (ddt, 2H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, CH=), 4.97 (br d, 2H, $^3J_{HHtrans}$ = 16.9 Hz, =CH$_E$*H*$_Z$), 4.91 (br d, 2H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$H$_Z$), 2.02 (m, 4H, C*H*$_2$CH=), 1.50 – 1.07 (m, 20H, remaining C*H*$_2$); $^{13}C\{^1H\}$: δ = 139.3 (s, *C*H=), 114.1 (s, *C*H$_2$=), 33.8 (s, *C*H$_2$CH=), 29.7 (s, CH$_2$), 29.6 (s, CH$_2$), 29.5 (s, CH$_2$), 29.2 (s, CH$_2$), 29.0 (s, CH$_2$); $^{31}P\{^1H\}$ silent. – IR (cm^{-1}, oil film): ν = 2926 (s), 2856 (m), 1640 (w), 1463 (br w), 992 (w), 907 (s), 722 (w). – MS (EI): *m/z* (%) = 222 (4) $[M]^+$.

*Data for $H_3B{\cdot}$**1c***

NMR ($CDCl_3$): ^{1}H: δ = 5.77 (ddt, 3H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 4.97 (br d, 3H, $^3J_{HHtrans}$ = 16.9 Hz, =CH$_E$*H*$_Z$), 4.91 (br d, 3H, $^3J_{HHcis}$ = 10.2 Hz, =C*H*$_E$H$_Z$), 2.06 – 1.97 (m, 6H, C*H*$_2$CH=), 1.63 – 1.22 (m, 30H, remaining C*H*$_2$), 0.3 (br d, 3H, $^1J_{BH}$ = 115 Hz, $w_{1/2}$ = *ca.* 280 Hz, B*H*$_3$); $^{13}C\{^1H\}$: δ = 138.8 (s, *C*H=), 114.3 (s, *C*H$_2$=), 33.6 (s, *C*H$_2$CH=), 31.0 (d, J_{CP} = 12.1 Hz,

CH_2), 28.6 (s, CH_2), 28.5 (s, CH_2), 23.0 (d, J_{CP} = 34.1 Hz, CH_2), 22.5 (d, J_{CP} = 2.1 Hz, CH_2); $^{31}P\{^1H\}$: δ = 15.7 (br d, J_{PB} = 71 Hz, $w_{1/2}$ = 169 Hz). – IR (cm^{-1}, oil film): ν = 2926 (s), 2856 (m), 2366 (br m), 1640 (w), 1463 (br w), 1058 (m), 996 (m), 907 (s), 803 (br w), 726 (w). – MS (EI): *m/z* (%) = 378 (2) $[M]^+$, 364 (30) $[M–BH_3]^+$, 323 (100) $[M–BH_3–CH_2CH=CH_2]^+$.

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[30] The ^{1}H- and ^{13}C-NMR assignments were made by analogy to those of **1c**.
[31] The ^{1}H- and ^{13}C-NMR assignments were made by ^{1}H,^{1}H COSY and ^{1}H, ^{13}C{^{1}H} COSY spectra.
[32] The ^{31}P{^{1}H}-NMR spectrum of the crude mixture shows two signals with a 95 : 5 area ratio.
[33] The addition of CH_3OH appears to aid the volatilization of traces of COD.
[34] FAB, 3-NBA; the most intense peak of isotope envelope is given.
[35] These ^{1}H- and ^{13}C-NMR assignments were made by analogy to those of *trans*-**5e**.
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[37] The ^{31}P{^{1}H}-NMR spectrum of the crude mixture shows two signals with an 80 : 20 area ratio.
[38] This microanalysis only marginally agrees with the empirical formula, but is nonetheless reported as the best obtained to date. The NMR spectra indicate high purities ($\geq$ 98 %).
[39] The coupling represents a satellite (d, ^{195}Pt = 33.8 %) and is not reflected in the peak multiplicity given.
[40] This represents 1.0 equiv. after correction for the purity of **2c**. Excess H_3B affords oligomers (see text).