Generation of trans-spanning diphosphine ligands via alkene metathesis: Synthesis, structure, and dynamic behavior of a missing link in a series of square-planar platinum complexes

Natascha Lewanzik a, Thomas Oeser a, Janet Blümel a,*, John A. Gladysz b,∗

a Department of Organic Chemistry, University of Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
b Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany

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Abstract

Reaction of KPPh2 and Br(CH2)5CH=CH2 gives the phosphine PPh2(CH2)5CH=CH2 (89%), which is treated with the platinum tetrahydrothiophene complex [Pt(μ-Cl)(C6F5)(S(CH2CH2–)2)]2 to yield trans-(Cl)(C6F5)Pt(PPh2(CH2)5CH=CH2)2 (4b, 80%). Ring-closing alkene metathesis (Grubbs' catalyst) gives trans-(Cl)(C6F5)Pt(PPh2(CH2)5CH=CH2)PPh2 (5b, 84%), which features a trans-spanning diphosphine ligand. The Z/E C=O mixture is hydrogenated (1 atm, 10% Pd/C) to give trans-(Cl)(C6F5)Pt(PPh2(CH2)5CH=CH2)2 (6b, 99%). The crystal structures of 4b and (Z)-5b are determined. In the former, both (CH2)5CH=CH2 moieties are directed on the same side of the platinum square plane. Low temperature 13C NMR spectra of 6b show two sets of signals for the diastereotopic PPh2 groups. These coalesce upon warming, which requires the passage of the chloride ligand through the macrocycle. Analysis by the complete bandwidth method gives ΔH‡ and ΔS‡ values of 6.0 ± 0.4 kcal mol⁻¹ and −13.9 ± 2.6 eu. The 31P, 13C, and 2H CP/MAS NMR spectra of polycrystalline 6b and 6b–d2 are studied, and indicate appreciable conformational mobility of the methylene chain in the solid state.

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1. Introduction

This paper is part of a collection of articles describing developments reported at the 16th International Symposium on Olefin Metathesis and Related Chemistry, which was held August 7–12 in Poznań, Poland. One prominent theme was the emergence of alkene metathesis, particularly with the Grubbs' catalyst family, for the synthesis of architecturally sophisticated organometallic compounds [1,2]. In this context, we have shown that a variety of complexes that contain trans-phosphine ligands with one or more substituents of the formula (CH2)nCH=CH2 (n ≥ 4) undergo efficient ring-closing metathesis [3–5]. The macrocyclic products feature trans-spanning diphosphine ligands [6]. In nearly all cases, the C=C linkages can be cleanly hydrogenated. Schemes 1 and 2 illustrate sequences leading to the triply bridged iron tricarbonyl complexes 2a–c [5] and the singly bridged platinum complexes 6a,c,e,f [3].

When the bridges connecting the phosphorus atoms are long enough, and the central LₙM fragments are small enough, such compounds can be viewed as molecular rotors [7]. The symmetries of the iron complexes 2 are too high for Fe(CO)₃ rotation to be probed by conventional solution NMR techniques. However, the corresponding Fe(CO)₂(NO)⁺ complexes 3 [5] are ideal. The 13C NMR spectrum of 3b, which features 12 methylene groups in each bridge, showed two sets of methylene signals (2:1) at room temperature. These coalesced at elevated temperature. The 13C NMR spectrum of 3c, which features 14 methylene groups in each bridge, showed only one set of methylene signals at room temperature. This decoalesced to two sets at low temperature. Complete bandwidth analysis gave ΔH‡ and ΔS‡ values of 9.5 kcal mol⁻¹ and −6.5 eu for Fe(CO)₂(NO)⁺ rotation. Pathways involving ligand dissociation could be excluded.

Unfortunately, in the case of the singly bridged platinum complexes 6a,c,e,f, no rotational barriers could be determined [3]. As illustrated in Scheme 3, the PPh₂ groups and PCH₂ protons of 6 are diastereotropic. When the bridge is sufficiently long, the smaller chloride ligand can pass underneath, and the groups

* Corresponding authors.
E-mail addresses: gladysz@organik.uni-erlangen.de (J.A. Gladysz), j.bluemel@urz.uni-heidelberg.de (J. Blümel).

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Scheme 1. Iron carbonyl complexes with trans-spanning diphosphine ligands.

Scheme 2. Previously synthesized platinum complexes with trans-spanning diphosphine ligands.


Scheme 4. Syntheses of new platinum complexes with trans-spanning diphosphine ligands.

are rendered equivalent [8]. When this process is rapid enough, the corresponding signals will coalesce. For 6a, which features 10 methylene groups in the bridge, two sets of PPh₂¹³C NMR signals were observed at room temperature. These did not coalesce at 95 °C in toluene-d₈. Application of the coalescence formula allowed a lower limit of 17.4 kcal/mol ($\Delta G^\ddagger$, 95 °C) to be placed upon the barrier. With 6c, which features 14 methylene groups in the bridge, only one set of signals was observed at room temperature. No decoalescence occurred at −90 °C in THF-d₈. From these data, an upper limit of 8.4 kcal/mol could be estimated for the barrier.

In order to better design related platinum-based molecular rotors, it was desirable to obtain an exact barrier for a member of this series of molecules. Hence, we set out to synthesize and study the variable temperature NMR spectra of the missing link 6b, with 12 methylene groups in each bridge. In this paper, we report the successful realization of these objectives, as well as (a) crystal structures of two precursor complexes that exhibit several surprising features, and (b) multinuclear solid-state CP/MAS NMR data for polycrystalline 6b and a deuterio derivative 6b-d₂ that provide further information on dynamic properties.

2. Results

2.1. Syntheses

As expected from similar procedures described earlier [3], reaction of KPPh₂ and the α,ω-bromoalkene Br(CH₂)₅CH=CH₂ gave PPh₂(CH₂)₅CH=CH₂ in 89% yield. As shown in Scheme 4, this phosphine was combined with the platinum tetrahydrothiophene complex [Pt(Cl)(C₆F₅)(S(CH₂CH₂–)₂)]₂ [9] under...
conditions analogous to those previously used for the synthesis of 4a,c,e–f. Workup gave the bis(phosphine) complex trans-Cl(C6F5)Pt(PPh2(CH2)5CH=CH2)2 (4b) as a white solid in 80% yield, which was characterized by NMR (1H, 13C, 31P, 19F) and IR spectroscopy and mass spectrometry as summarized in Section 4. All properties were similar to those of 4a,c,e–f. As expected, the enantiotopic PPh2 groups gave a single set of 13C NMR signals, most of which were triplets due to virtual coupling to both phosphorus nuclei [10]. The original NMR spectra for all new compounds in this paper have been depicted elsewhere [11].

Alkene metathesis was conducted under conditions analogous to those used in Scheme 2. As shown in Scheme 4, CH2Cl2 solutions of 4b (ca. 0.0021 M) and Grubbs’ catalyst (8 mol%, added in three portions) were refluxed for 5 h. Workup gave the crude macrocycle trans(Cl)(C6F5)Pt(PPh2(CH2)5CH=CH(CH2)5PPh2) (5b) in 84% yield. The 31P NMR spectrum indicated a 74:26 mixture of C=C isomers. Based upon the calculated values of the chemical shifts of the =CH–H NMR signals, and the crystal structure below, the major isomer is tentatively proposed to be Z (cis). Subsequent hydrogenation (1 atm, 10% Pd/C catalyst) gave the title complex trans(Cl)(C6F5)Pt(PPh2(CH2)5PPh2) (6b) in 99% yield. This material was characterized analogously to 4b. The diastereotopic PPh2 groups gave a single set of 13C NMR signals.

In order to prepare a substrate for a solid-state NMR experiment below, the preceding reaction was repeated with D2. The 13C 1H NMR spectrum of the resulting 6b-d2 showed that deuterium had also been incorporated into what would correspond to the allylic position of 5b. This suggested a competing C=C isomerization. Accordingly, an analogous reaction was conducted with Wilkinson’s catalyst. The resulting 6b-d2 showed only a single 13C NMR signal with a directly bound deuterium atom, and a single 2H NMR signal.

### 2.2. Crystal structures

The crystal structures of 6a,c,e–f have been reported previously. However, no data on the precursors 4a,c–e or 5a,c,e–f have heretofore been available. Interestingly, single crystals of 4b could be obtained from CH2Cl2/ethanol. X-ray data were collected as summarized in Table 1 and Section 4. Refinement revealed considerable disorder, involving both (CH2)4CH=CH2 moieties, one PPh2 moiety, and certain C6F5 fluorine atoms. Nonetheless, the structure could be solved, and a representative conformation is depicted in Fig. 1. The other conformations were similar, and the structure is further analyzed below.

A crystal of 5b was also obtained from CH2Cl2/ethanol. X-ray data were collected, and refinement gave the cis or Z structure shown in Fig. 2. However, NMR spectra showed the presence of both C=C isomers in the sample (74:26). Key metrical parameters for 4b and (Z)-5b are summarized in Table 2. In each case, stacking interactions involving the pentafluorophenyl ligand and a phenyl group on each phosphorus are evident. The averages of the two centroid–centroid distances are 3.76 Å (4b) and 4.05 Å (Z)-5b. In (Z)-5b, the distances from the platinum atom to the most remote carbon atoms of the macrocycle, C(54), C(55),...
2.3. Solution NMR studies

As noted in the introduction, the \(^{13}\)C NMR spectra of the 17–23-membered macrocycles 6c–e (Scheme 2) gave only a single set of PPh\(_2\) signals, whereas that of the 13-membered macrocycle 6a gave two sets. This indicates that the chloride ligands rapidly pass underneath the methane chains of the trans-spanning diphosphine ligands in 6c–e on the NMR time scale (Scheme 3). Complex 6b similarly gave a single set of \(^{13}\)C NMR signals for the PPh\(_2\) groups at room temperature. At \(-95^\circ\)C in THF-\(d_8\), the signals broadened, but did not decoalesce. No decoalescence phenomena were observed when \(^1\)H NMR spectra were recorded at \(-95^\circ\)C.

\(^{13}\)C NMR spectra were therefore recorded in CDFCl\(_2\) [12], which has a lower melting point than THF-\(d_8\) (\(-135^\circ\)C versus \(-108^\circ\)C), between room temperature and \(-110^\circ\)C (163 K). Two limiting spectra are shown in Fig. 3. The signals for the ortho, para, and meta carbon atoms in the higher temperature spectrum (bottom; ca. 132.8, 130.4, and 128.1 ppm) decoalesced into two sets (top). This process is traced by the spectra in Fig. 4, which furthermore illustrate a moderate temperature dependence of the chemical shifts. The evolution of the weaker and more strongly coupled signal for the ipso carbon atoms is obscured by the noise and other signals. At the low temperature limit, the splittings of the para and meta signals (1.9 and 1.2 ppm or 191 and 121 Hz) are less than that of the ortho signals (4.3 ppm or 433 Hz).

The spectra in Fig. 4 (left) were simulated using the Complete Bandshape Simulation (CBS) routine of the program gNMR 4.1 (right) [13]. The simulation of the spectrum in Fig. 3 is shown elsewhere [11]. The overall agreement was reasonably satisfying, and rate constants could be calculated at each temperature. An Eyring plot gave \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) values of 6.0 ± 0.4 kcal mol\(^{-1}\) and −13.9 ± 2.6 eu for the process that renders the PPh\(_2\) groups equivalent. The virtual coupling of the ipso, ortho, and meta signals to both phosphorus nuclei at the high-temperature limit excludes mechanisms involving phosphine dissociation. The \(^{31}\)P NMR signal also remains coupled to platinum at the high-temperature limit \(1J_{PPt} = 2683\) Hz.

2.4. Solid-state NMR studies

The wideline \(^{31}\)P CP NMR spectrum of 6b was measured first (depicted elsewhere [11]). The chemical shift anisotropy (CSA) [14] was typical for polycrystalline metal complexes with two phosphine ligands. The span (\(\Delta\delta_{11–33}\)) of the signal amounted
Fig. 3. $^{13}$C NMR spectra of 6b in CDCF$_2$ (100.6 MHz, aromatic region only). Top, 163 K; bottom, 273 K.

to 125 ppm, with $\delta_{11} = 85.1$, $\delta_{22} = 13.2$, and $\delta_{33} = -31.0$ ppm. From these data, an isotropic chemical shift of 13.6 ppm could be calculated ($\delta_{iso} = 1/3(\delta_{11} + \delta_{22} + \delta_{33})$), which in turn allowed the asymmetry parameter $\eta$ of 0.25 to be calculated ($\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{iso})$) [14]. Fig. 5 shows the $^{31}$P CP/MAS spectrum of polycrystalline 6b, rotated at 11 kHz. Interestingly, $^{195}$Pt satellites are visible close to the isotropic line, and the $J_{PPt}$ value (2685 Hz) is in good agreement with the solution data.

Two $^{13}$C CP/MAS spectra of polycrystalline 6b are illustrated in Fig. 6. The signals of the aliphatic carbons overlap (26 ppm), but they have rather small CSA values, such that even at the low spinning speed of 4 kHz there are no rotational sidebands. This indicates that the aliphatic chain is rather flexible and mobile even in the solid state. The $^{13}$C signals of the phenyl carbon atoms at about 132 ppm (ortho, meta, and para) and 146 ppm (ipso) show however characteristically large CSA values with multiple sets of rotational sidebands.
CH2 groups are C linkages CH(CH2)4 bridges [4], and (c) the C isomers. We suggest rotational sidebands. The CSA values in the 31P and 13C CP/MAS spectra were not with those obtained for hexane-

3. Discussion

The syntheses of the new complexes 4b–6b in Scheme 4 proceed analogously to those of the lower and higher homologs described earlier (Scheme 2). However, several types of complementary data could be acquired. For example, the first crystal structure of a complex of the type 4 has been determined. As shown in Fig. 1, the substituents on the two phosphorus atoms in 4b are eclipsed along the P–Pt–P axis (torsion angles ±3°).

When 6b was brought as a monolayer on a silica surface, the CSA values in the 31P and 13C CP/MAS spectra were not reduced, and identical signal patterns resulted. This is a clear indication that no adsorption on (or reaction with) the silica surface occurs, important information for the later use of such compounds as immobilized catalysts [15].

The 2H CP/MAS spectrum of polycrystalline 6b–d2 is depicted in Fig. 7, together with a simulated lineshape [16]. In contrast to spectra of crystalline compounds with non-mobile 2H nuclei, no “classical” Pake pattern is observed. The quadrupolar coupling constant can only be roughly estimated as between 6 and 15 kHz. Nonetheless, this indicates that the methylene chain in 6b–d2 is conformationally mobile, although the compound is crystalline with a high melting point near 200°C. In view of the large size of the pentafluorophenyl ligand in Fig. 2, it is clear that the methylene chain cannot completely rotate about the metal center. Otherwise, the phenyl carbon signals (Fig. 7) would have displayed reduced CSA values. However, ca. 60° and 180° torsional motions about CH2–CH2–CH2–CH2 segments are feasible [17]. Comparing the lineshape in Fig. 7 with those obtained for hexane-d14 and decane-d22 [17], it can be concluded that the frequency of such conformational changes involving the CHD carbons of 6b–d2 is between 100 and 1000 kHz.

Attempts have been made to qualitatively correlate the crystal structures of 6a and c to the rates of the exchange process in Scheme 3 [3]. The distances from the platinum atoms to the most remote macrocyclic carbon atoms are 5.62 and 7.83 Å, respectively. When the van der Waals radius of an sp3 carbon atom is subtracted (1.78 Å), a “vehicle height” of 4.14 Å is obtained. With 6a, the clearance is obviously not sufficient for the chloride ligand to pass under the macrocycle, whereas with 6c it is ample.

Although a crystal structure of 6b is not available, the distance from the platinum atom to the most remote macrocyclic carbon atom in (Z)-5b (6.21 Å) can be taken as an approximation. This translates to a “bridge height” of 4.51 Å for a “vehicle height”...
of 4.14 Å. Empirically, the transit of the chlorine ligand through the macrocycle remains fast on the NMR time scale at room temperature. However, the clearance becomes low enough such that decoalescence can be observed at very low temperatures (Figs. 3 and 4) and activation parameters determined. Although this model is intuitive, it is vastly oversimplified, and it is important to emphasize that correlated conformational changes of the macrocycle are to be expected along the reaction coordinate.

In this regard, the solid-state NMR data verify the conformational mobility of the CH$_2$–CH$_2$–CH$_2$–CH$_2$ segments of the macrocycle. These facile solid-state torsional equilibria have major implications for the use of such complexes as molecular “compasses” [19] and related devices. Although the goal of this initial effort was to establish the feasibility of certain types of solid-state NMR measurements, it can be expected that the frequencies of torsional conformational changes will increase upon going from the smallest and presumably somewhat strained macrocycle 6a–6b and then to 6c and higher homologs. This will be tested with related complexes in future work.

In conclusion, this study has filled in important gaps regarding (1) syntheses of square-planar platinum complexes 6 with trans-spanning diphosphine ligands, (2) their dynamic properties, and (3) solid-state structures of cyclic and acyclic alkene-containing precursors to 6. Future reports will describe new families of square-planar platinum and palladium complexes with trans-spanning ligands analogous to those in 2 [20].

4. Experimental

4.1. General data

All reactions were conducted in the absence of oxygen. Chemicals were treated as follows: THF, distilled from Na/benzophenone; CH$_2$Cl$_2$, distilled from CaH$_2$ (reactions) or simple distillation (chromatography); ClCH$_2$CH$_2$Cl (99%, Fluka) and ethanol, used as received; CDCl$_3$, prepared by a literature procedure [12]; CDC$_3$, CD$_2$D$_6$, THF-d$_8$ (3 × Deutero GmbH or Eurisotop), Br(CH$_2$)$_5$CH$_2$ and 2C$_6$H$_4$D$_3$. Other spectra were recorded on standard modern instruments as described in previous papers [3,4]. Additional details are supplied elsewhere [11].

4.2. PPh$_2$(CH$_2$)$_3$CH=CH$_2$

A Schlenk flask was charged with Br(CH$_2$)$_3$CH=CH$_2$ (0.92 mL, 1.80 g, 10.2 mmol) and THF (14 mL), and cooled to −18 °C. Then KPPH$_2$ (0.5 M in THF, 20.3 mL, 10.2 mmol) was added dropwise with stirring. The mixture was stirred for 1 h, and then allowed to warm to room temperature. The solvent was removed by oil pump vacuum, and CH$_2$Cl$_2$ (3–6 mL) was added. The sample was chromatographed on silica gel (15 cm × 2.5 cm column; eluted with i:2, v:v, CH$_2$Cl$_2$/hexanes). The solvent was removed from the product fraction by rotary evaporation and oil pump vacuum to give PPh$_2$(CH$_2$)$_3$CH=CH$_2$ as a clear oil (2.559 g, 9.06 mmol, 89%). Calc. for C$_{19}$H$_{23}$P:C, 80.82; H, 8.21. Found: C, 80.40; H, 8.35%.

NMR (δ, C$_6$D$_6$): $^1$H (500.1 MHz) [22] 7.43 (t, $^3$J$_{HH}$ = 7 Hz, 4H of 2C$_6$H$_3$), 7.08 (m, 6H of 2C$_6$H$_3$), 5.70 (m, CH=CH$_2$), 4.96 (m, =CH$_2$), 1.93 (m, PCH$_2$), 1.88 (m, CH$_2$CH$_2$), 1.41 (m, PCH$_2$CH$_2$), 1.28 (quintet, $^3$J$_{HH}$ = 8 Hz, PCH$_2$CH$_2$CH$_2$), 1.20 (quintet, $^3$J$_{HH}$ = 8 Hz, CH$_2$CH$_2$CH$_2$); $^{13}$C$_{6}$D$_6$): 1H (202.5 MHz) [22] 132.4 (d, $^3$J$_{CP}$ = 15.0 Hz, o-Ph), 133.1 (d, $^3$J$_{CP}$ = 18.8 Hz, o-Ph), 128.6 (d, $^3$J$_{CP}$ = 6.5 Hz, m-Ph), 128.5 (s, p-Ph), 114.6 (s, =CH$_2$), 31.0 (s, CH$_2$CH=), 28.5 (d, $^3$J$_{CP}$ = 12.8 Hz, PCH$_2$CH$_2$), 26.2 (d, $^3$J$_{CP}$ = 16.2 Hz, PCH$_2$CH$_2$; $^{31}$P( $^1$H) (202.5 MHz) −16.8 (s).

IR (cm$^{-1}$, oil film) 3071 (m), 3054 (s), 2945 (w), 1884 (w), 1812 (w), 1640 (m), 1481 (m), 1462 (s), 1431 (m), 1328 (w), 1279 (m), 1103 (s), 1059 (m), 999 (m), 909 (s), 739 (s), 696 (s). MS$^1$ 283 (M$^+$ + H, 100%), 282 (M$^+$, 57%).

4.3. trans-(Cl)(C$_6$F$_5$)Pt(PPh$_2$(CH$_2$)$_3$CH=CH$_2$) (4b)

A Schlenk flask was charged with [Pt(μ-Cl)(C$_6$F$_5$)-]($^2$)(0.491 g, 0.505 mmol) [9], PPh$_2$(CH$_2$)$_3$CH=CH$_2$ (0.570 g, 2.02 mmol), and CH$_2$Cl$_2$ (30 mL). The mixture was stirred (16 h) and the solvent was removed by oil pump vacuum. Then CH$_2$Cl$_2$ (1 mL) was added, followed by ethanol (6 mL). The sample was shaken, and a white solid precipitated. The sample was stored for several days at −30 °C. The supernatant was removed by pipette and the residue dried by oil pump vacuum to give 4b as a white solid (0.780 g, 0.811 mmol, 80%), mp 110–116 °C.

NMR (δ, C$_6$D$_6$) [22]: $^1$H (500.1 MHz) 7.55 (br s, 8H of 4C$_6$H$_3$), 7.37–7.27 (br s, 12H of 4C$_6$H$_3$), 5.73 (m, 2CH=), 5.01 (m, 2 =CH$_2$), 2.60 (m, 2PCH$_2$), 1.95 (m, 2PCH$_2$CH$_2$ and 2CH=CH$_2$), 1.25 (m, 2CH$_2$CH$_2$CH=CH$_2$); $^{13}$C$_{6}$D$_6$ (125.8 MHz) [22,24,25] 132.9 (s, CH$_2$), 133.5 (virtual t [10], $^3$J$_{CP}$ = 5.7 Hz, o-Ph), 131.5 (virtual t [10], $^1$J$_{CP}$ = 28.4 Hz, i-Ph), 130.4 (s, p-Ph), 128.4 (partially obscured by solvent signal, m-Ph), 114.7 (s, =CH$_2$), 33.9 (s, CH$_2$CH=), 31.0 (virtual t [10], $^3$J$_{CP}$ = 7.6 Hz, PCH$_2$CH$_2$CH$_2$), 28.7 (s, CH$_2$CH$_2$CH=), 26.4 (virtual t [10], $^1$J$_{CP}$ = 17.2 Hz, PCH$_2$), 25.7 (s, PCH$_2$CH$_2$); $^{31}$P( $^1$H) (202.5 MHz) 16.1 (s, $^3$J$_{PP}$ = 2656 Hz) [26], $^{19}$F (282.4 MHz) −118.8 (d, $^3$J$_{FP}$ = 23 Hz, $^3$J$_{FP}$ = 402 Hz [26], o-C$_6$F$_5$), −165.5 (m, m- and p-C$_6$F$_5$).

IR (cm$^{-1}$, oil film) 3077 (m), 2950 (s), 2855 (m), 2639 (m), 1855 (w), 1812 (w), 1643 (s), 1407 (s), 1403 (s), 1333 (s), 1273 (m), 1231 (m), 1109 (s), 999 (m), 909 (s), 739 (s), 696 (s).
A two-necked flask was charged with 4b (0.165 g, 0.171 mmol), Grubbs’ catalyst (0.004 g, 0.005 mmol), and CH2Cl2 (80 mL; the resulting solution is 0.0021 M in 4b), and fitted with a condenser. The solution was refluxed. After 2 h, a second charge of Grubbs’ catalyst was added (0.004 g, 0.005 mmol). After another 2 h, a third charge of Grubbs’ catalyst was added (0.003 g, 0.004 mmol; 8 mol% total). After 1 h, the mixture was cooled to room temperature. The solvent was removed by rotary evaporation and oil pump vacuum. Then CH2Cl2 (1 mL) was added, followed by ethanol (4 mL). The mixture was swirled, and a white solid precipitated. The sample was stored overnight at −30 ºC. The supernatant was removed by pipette. The residue was washed with ethanol (4 mL) and dried by oil pump vacuum (1 day) to give 6b as a white powder (0.135 g, 0.144 mmol, 84%) that was recrystallized from ethanol/CH2Cl2. Data were collected as outlined in see text), mp 190–206 ºC.

NMR (δ, C6D6): 1H (500.1 MHz, major/minor) 7.46 (br d, 3JHH = 5.2 Hz, 8H of 4C6H5), 7.31 (t, 3JHH = 7.3 Hz, 4H of 4C6H5), 7.24 (t, 3JHH = 7.3 Hz, 8H of 4C6H5), 5.45/5.62 (t, 3JHH = 4.9/3.8 Hz, CH−CH2), 2.63 (br s, 2PCH2), 2.41 (br s, 2PCH2CH2), 1.72/1.75 (m, 2CH2CH3), 1.60/1.61, 1.54/1.56 (2 m, 2CH2CH2CH2CH2); 13C[1H] (125.8 MHz, major isomer unless noted) [24,25] 132.6 (virtual t [10], 2PCH = 5.6 Hz, o-Ph), 132.2 (virtual t [10], 1JCP = 27.3 Hz, i-Ph), 130.4 (s, p-Ph), 130.18/130.14 (2 s, minor/major CH−CH), 128.0 (virtual t [10], 3JCP = 5.2 Hz, m-Ph), 30.9 (s, CH2CH3), 29.5 (virtual t [10], 3JCP = 8.3 Hz, PCH2CH2CH2), 28.3 (s, CH2CH2CH2), 26.9 (virtual t [10], 1JCP = 19.1 Hz, PCH2), 25.4 (s, PCH2CH2); 31P[1H] (202.5 MHz) 1.46 (s, 16% (m, m- and p-C6F5). IR (cm−1, KBr pellet) 2928 (m), 2853 (w), 1634 (br), 1502 (s), 1461 (s), 1447 (m), 1104 (s), 957 (s), 805 (m), 740 (m), 694 (m). MS [23] 933 ([6b]+, 23%), 900 ([6b-Cl]+, 100%), 733 ([6b-Cl-C6D5]+, 85%).

A Schlenk flask was charged with 5b (0.080 g, 0.086 mmol), 10% Pd/C (0.0089 g, 0.0089 mmol Pd), CICH2CH2Cl (4.5 mL), and ethanol (4.5 mL), flushed with H2, and fitted with a balloon of H2. The mixture was stirred for 96 h, during which time the balloon was periodically recharged with H2. The mixture was filtered through Celite, and the solvent was removed by oil pump vacuum. Then CH2Cl2 (0.5 mL) was added, followed by ethanol (3 mL). The mixture was concentrated under vacuum until a precipitate began to form. The sample was stored overnight at −30 ºC. The supernatant was removed by pipette. The residue was washed with ethanol and dried by oil pump vacuum (1 day)

Colorless irregular crystals of 4b and (Z)-5b were obtained from ethanol/CH2Cl2. Data were collected as outlined in Table 1. Lorentz, polarization, and absorption (empirical, using SABABS (2.03) [29] and based upon the Laue symmetry of reciprocal space) corrections were applied. The structures were solved by direct methods (4b, Sir-97 [30]; (Z)-5b, XS [29]). The parameters were refined with all data by full-matrix-least-squares on F2 using XL of the SHELXL (6.12) software package [29]. Non-hydrogen atoms were refined with anisotropic thermal parameters unless disordered. The
hydrogen atoms were fixed in idealized positions using a riding model. In 4b, one set of PPh$_2$ rings and the meta and para C$_6$F$_5$ fluorine atoms were disordered between two sites that refined to 50:50 occupancy. The five terminal carbon atoms of the (CH$_2$)$_3$CH=CH$_2$ segments were disordered between two or more sites, the occupancies for which could not be refined.

CCDC-283900 (4b) and CCDC-283901 ((Z)-5b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving/html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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References

[2] Lead references to contributions from other research groups:
[8] The exchange of H$_a$ and H$_h$ in Scheme 3 can be analyzed as follows. In both I and II, H$_a$ and H$_h$ are enantiotopic as are H$_h$ and H$_h$. H$_a$ is diastereotopic with H$_h$ and H$_h$ in I exchanges with H$_h$ in II, which is in turn chemical shift equivalent with enantiotopic H$_h$. Similarly, H$_a$ in I exchanges with H$_h$ in II, which is in turn chemical shift equivalent with enantiotopic H$_h$. The diastereotopic PPh$_2$ groups (Ph$_a$, Ph$_h$) exchange analogously.
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   (f) Y. Yang, J. Blümel, in preparation;
   (g) A. Seifert, R. Fetouaki, J. Blümel, in preparation.
[22] Definitive $^1$H and $^{13}$C NMR assignments for this compound were made using $^1$H,$^1$H-COSY and $^1$H,$^{13}$C-COSY spectra, as detailed elsewhere.
[23] m/e (FAB) for most intense peak of isotope envelope (relative intensity, %).
[24] The C$_6$F$_5$ carbon resonances were not observed. These require larger numbers of transients due to the fluorine and platinum couplings.
[26] This coupling represents a satellite (d, $^{195}$Pt = 33.8%), and is not reflected in the peak multiplicity given.
[27] Definitive $^1$H and $^{13}$C NMR assignments for this compound were made using $^1$H,$^1$H-COSY, $^1$H,$^{13}$C-COSY, and HMBC spectra, as detailed elsewhere.
[28] The aliphatic $^1$H NMR and $^{13}$C NMR signals were assigned from a $^1$H,$^1$H-COSY spectrum.