Alkene Metatheses in Transition Metal Coordination Spheres: Effect of Ring Size and Substitution on the Efficiencies of Macrocyclizations That Join *trans* Positions of Square-Planar Platinum Complexes

Eike B. Bauer, Frank Hampel, and J. A. Gladysz*

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

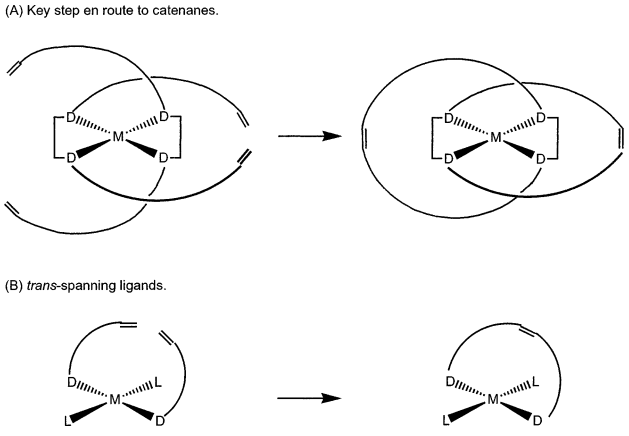
Received August 22, 2003

Reactions of $KPPh_2$ and $Br(CH_2)_nCH{=}CH_2$ give the phosphines $PPh_2(CH_2)_nCH{=}CH_2$ (n = **a**, 4; **b**, 6; **c**, 8; **d**, 9; 95−41%), which are combined with the platinum tetrahydrothiophene complex $[Pt(\mu\text{-}Cl)(C_6F_5)(S(CH_2CH_2{-})_2)]_2$ to give *trans*-$(Cl)(C_6F_5)Pt(PPh_2(CH_2)_nCH{=}CH_2)_2$ (**3a**−**d**, 71−54%). When treated with Grubbs' catalyst, ring-closing alkene metatheses occur to give 13- to 23-membered macrocycles with *trans*-spanning diphosphine ligands (96−85%, including some dimeric or oligomeric byproducts). The mixtures of C=C isomers are hydrogenated (1 atm, 10% Pd/C) to give *trans*-$(Cl)(C_6F_5)Pt(PPh_2(CH_2)_{2n+2}PPh_2)$ (**6a**−**d**), which are isolated in 72−50% yields. Comparable results are obtained with (1) the second-generation dihydroimidazolylidene Grubbs' catalyst and (2) a series of compounds derived from the dimethylated phosphine $Ph_2P(CH_2)_2C(CH_3)_2(CH_2)_3CH{=}CH_2$, in turn prepared by sequential reactions of $BrCH_2CH_2C(CH_3)_2CH_2CH_2Br$ with $BrMgCH_2CH{=}CH_2/Li_2CuCl_4$ and $KPPh_2$. The crystal structures of **6a**−**d** are analyzed, but no special features that would promote intramolecular macrocyclizations are noted. A reaction of $[Pt(\mu\text{-}Cl)(C_6F_5)(S(CH_2\text{-}CH_2{-})_2)]_2$ and the diphosphine $Ph_2P(CH_2)_{14}PPh_2$ leads to a multitude of products and little **6b** (<15%).

Introduction

Alkene metathesis is being increasingly utilized in the synthesis of metal-containing molecules.[1] At the same time, there is growing interest in various types of metal-containing macrocycles and improved strategies for their synthesis.[2−4] Targets include both metallo- and metallamacrocycles, which are furthermore in many cases topologically novel. These themes were first combined by Sauvage, who developed elegant syntheses of catenanes via metathesis reactions of the type depicted schematically in Scheme 1A (top).[5] Macrocyclization methods that had been traditionally employed in organic synthesis gave inferior results. However, alternative cyclization modes as well as intermolecular reactions are possible, and the ring size and substituents play critical roles in the success of a given reaction.

Scheme 1. Syntheses of Metallamacrocycles via Alkene Metathesis



We and others have also generated a variety of unusual metallo- and metallamacrocycles via alkene metathesis,[6−8] and a representative reaction type is

(1) Bauer, E. B.; Gladysz, J. A. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 2, pp 403−431.

(2) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795.

(3) Bessel, C. A.; Aggarwal, P.; Marschilok, A. C.; Takeuchi, K. J. *Chem. Rev.* **2001**, *101*, 1031.

(4) Pecoraro, V. L.; Stemmler, A. J.; Gibney, B. R.; Bodwin, J. J.; Wang, H.; Kampf, J. W.; Barwinski, A. *Prog. Inorg. Chem.* **1997**, *45*, 83.

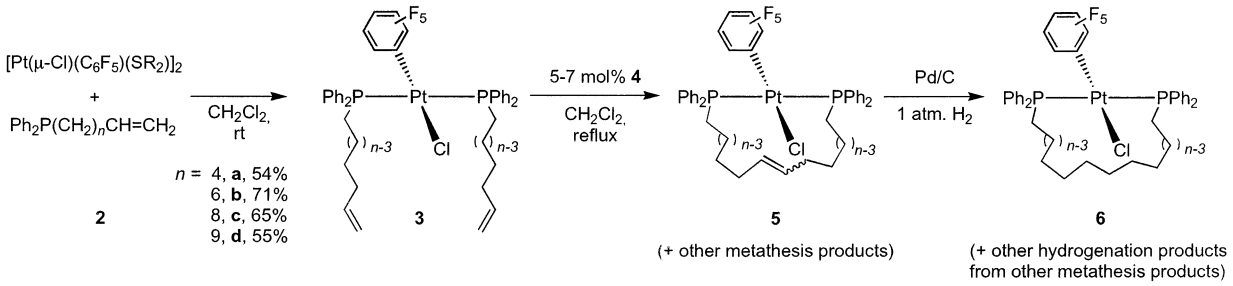
(5) (a) Weck, M.; Mohr, B.; Sauvage, J.-P.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 5463. (b) Dietrich-Buchecker, C.; Rapenne, G.; Sauvage, J.-P. *Chem. Commun.* **1997**, 2053. (c) Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Commun.* **1999**, 615. (d) Rapenne, G.; Dietrich-Buchecker, C.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 994. (e) Belfrekh, N.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Inorg. Chem.* **2000**, *39*, 5169. (f) Mobian, P.; Kern, J.-M.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2003**, *125*, 2016.

(6) (a) Martín-Alvarez, J. M.; Hampel, F. A.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, *18*, 955. (b) Bauer, E. B.; Ruwwe, J.; Martín-Alvarez, J. M.; Peters, T. B.; Bohling, J. C.; Hampel, F. A.; Szafert, S.; Lis, T.; Gladysz, J. A. *Chem. Commun.* **2000**, 2261. (c) Ruwwe, J.; Martín-Alvarez, J. M.; Horn, C. R.; Bauer, E. B.; Szafert, S.; Lis, T.; Hampel, F.; Cagle, P. C.; Gladysz, J. A. *Chem. Eur. J.* **2001**, *7*, 3931.

(7) Chuchuryukin, A. V.; Dijkstra, H. P.; Suijkerbuijk, B. M. J. M.; Klein Gebbink, R. J. M.; van Klink, G. P. M.; Mills, A. M.; Spek, A. L.; van Koten, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 228; *Angew. Chem.* **2003**, *115*, 238.

10.1021/om034121u CCC: $25.00
Publication on Web 11/26/2003

Scheme 2. Syntheses of Platinamacrocycles



n	Number of ^{31}P NMR signals, crude **5**	Yield, major ^{31}P NMR signal, crude **5** (%)	Yield, isolated **5** and other metathesis products (%)[a]	Yield, major ^{31}P NMR signal, isolated **5** (%)	Yield, isolated **6** and other hydrogenation products (%)[b]	Yield, pure **6** after chromatography (%)[b]
4	5 (5)[c]	84 (88)[c]	95[d] (91)[c,e]	80	87	70
6	2 (2)[c]	87 (91)[c]	96[f] (96)[c,g]	88	94	72
8	5 (5)[c]	67 (57)[c]	90[h] (90)[c,i]	67	86	59
9	5	48	85[i]	54	76	50

[a] Yields based upon **3**. [b] Yields based upon isolated **5** including other metathesis products. [c] Value for catalyst **7**. [d] E/Z = 90 : 10. [e] E/Z = 93 : 7. [f] E/Z = 83 : 17. [g] E/Z = 74 : 26. [h] E/Z = 80 : 20. [i] Determination of E/Z ratio not possible.

depicted schematically in Scheme 1B (bottom). Here two alkene-containing monophosphine ligands, *trans*-disposed about a 16-valence-electron, square-planar platinum or rhodium, are joined to generate a novel *trans*-spanning diphosphine complex.[3] However, in this as well as several related reactions, the length of the bridge was not varied. The monophosphines always featured $(CH_2)_6CH{=}CH_2$ moieties, resulting in 17-membered macrocycles. Thus, the obvious question whether the six methylene groups between the donor atom and terminal alkene constitute a lucky starting point or "magic" number has remained unanswered.

Accordingly, we sought to systematically vary the number of methylene groups in such *trans*-macrocyclizations and better define the limits of ring sizes that can be accessed. Of the square-planar systems studied previously,[6] platinum complexes were selected for their robustness and ease of crystallization. In this paper, we report the synthesis of a series of compounds of the formula *trans*-(Cl)(C_6F_5)Pt$(PPh_2(CH_2)_nCH{=}CH_2)_2$ and subsequent alkene metatheses that yield platinamacrocycles with rings ranging from 13 to 23 atoms. Each of these are, after C=C hydrogenation, structurally characterized. We also describe the effect of replacing one methylene group of the $(CH_2)_n$ segment by a geminal dimethyl group. In many circumstances, geminal dialkyl groups increase the efficiency of cyclization.[9,10]

Results

1. Starting Complexes. As shown in eq 1, reactions of the bromoalkenes $Br(CH_2)_nCH{=}CH_2$ (**1**; *n* = **a**, 4; **b**, 6; **c**, 8; **d**, 9) and commercial $KPPh_2$ afforded the requisite monophosphines $PPh_2(CH_2)_nCH{=}CH_2$ (**2a**−**d**) as viscous colorless liquids in 95−41% yields after workup. The bromoalkenes **1a**,**b**,**d** were commercially available, and **1c** was prepared from the corresponding alcohol by a slight modification of literature procedures.[11] The phosphines **2a**−**d** were stable in air on the time scale of hours, and the preparation of **2b** (and all other compounds in the **b** series) has been described previously.[6c,12] The synthesis of **2d** was developed by W. Mohr.[13]

$$\underset{\textbf{1}}{Br(CH_2)_nCH{=}CH_2} + KPPh_2 \xrightarrow{THF} \underset{\textbf{2}}{Ph_2P(CH_2)_nCH{=}CH_2} \quad (1)$$

n = 4, **a**, 41%; 6, **b**, 74%; 8, **c**, 95%; 9, **d**, 91%

The phosphines **2a**,**c**,**d** were combined with the platinum tetrahydrothiophene complex $[Pt(\mu\text{-}Cl)(C_6F_5)(S(CH_2CH_2{-})_2)]_2$[14] under conditions used for **2b** earlier.[15] As shown in Scheme 2, workups gave the bis(phosphine) complexes *trans*-(Cl)(C_6F_5)Pt$(PPh_2(CH_2)_nCH{=}CH_2)_2$ (**3a**,**c**,**d**) as colorless oils in 71−54% yields. They solidified over the course of several days. The new phosphines and platinum complexes were characterized by NMR (^{1}H, ^{13}C, ^{31}P), IR, mass spectroscopy, and microanalyses, as summarized in the Experimental Section. Upon phosphine ligand coordination, the PCH_2 ^{1}H NMR signals shift to lower field (ca. δ 2.1 to ca. δ 2.6). Other properties were very similar to those re-

(8) (a) Stahl, J.; Bohling, J. C.; Bauer, E. B.; Peters, T. B.; Mohr, W.; Martín-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1872; *Angew. Chem.* **2002**, *114*, 1951. (b) Horn, C. R.; Martín-Alvarez, J. M.; Gladysz, J. A. *Organometallics* **2002**, *21*, 5386.

(9) Sammes, P. G.; Weller, D. J. *Synthesis* **1995**, 1205.

(10) Forbes, M. D. E.; Patton, J. T.; Myers, T. L.; Maynard, H. D.; Smith, D. W., Jr.; Schulz, G. R.; Wagener, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 10978.

(11) (a) Kobayashi, Y.; Okui, H. *J. Org. Chem.* **2000**, *65*, 612. (b) Kamat, V. P.; Hagiwara, H.; Katsumi, T.; Hoshi, T.; Suzuki, T.; Ando, M. *Tetrahedron* **2000**, *56*, 4397. (c) Singh, A.; Markowitz, M. A. *New J. Chem.* **1994**, *18*, 377.

(12) Complete experimental procedures for previously reproted compounds (**b** series)[6c] are provided in the Supporting Information. Spectroscopic and related data are repeated in the Experimental Section to facilitate comparisons with the new homologues (**a**, **c**, **d**, **e** series).

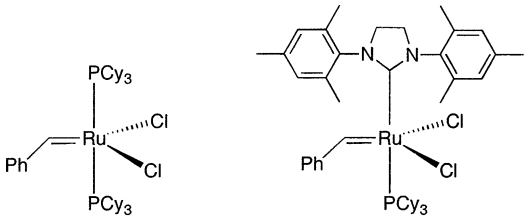
(13) Mohr, W. Doctoral Thesis, University of Erlangen-Nuremberg, 2002.

(14) Usón, R.; Forniés, J.; Espinet, P.; Alfranca, G. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 579.

(15) Usón, R.; Forniés, J.; Espinet, P.; Navarro, R.; Fortuño, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2077.

Table 1. General Crystallographic Data

	6a	**6b**	**6c**	**6d**·(toluene)$_{0.5}$
formula	$C_{40}H_{40}ClF_5P_2Pt$	$C_{44}H_{48}ClF_5P_2Pt$	$C_{48}H_{56}ClF_5P_2Pt$	$C_{50}H_{60}ClF_5P_2Pt\cdot(C_7H_8)_{0.5}$
fw	908.02	964.33	1020.41	1094.02
diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
temperature [K]	173(2)	173(2)	173(2)	173(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$C2/c$	$Pbca$	$C2/c$
a [Å]	15.5388(1)	31.7963(7)	18.8320(2)	31.6164(3)
b [Å]	17.8699(1)	10.7342(3)	15.71700(10)	10.90640(10)
c [Å]	27.5950(2)	24.9213(6)	31.3740(4)	32.1159(3)
α [deg]	90	90	90	90
β [deg]	99.4800(2)	102.2800(10)	90	111.2526(3)(3)
γ [deg]	90	90	90	90
V [Å^3]	7557.84(8)	8311.2(4)	9286.16(17)	10321.09(17)
Z	8	8	8	8
ρ_{calc} [Mg/m^3]	1.596	1.541	1.460	1.408
abs coeff [mm^{-1}]	3.921	3.570	3.200	2.884
F(000)	3600	3856	4112	4436
cryst size [mm^3]	0.25 × 0.20 × 0.20	0.2 × 0.2 × 0.1	0.30 × 0.30 × 0.20	0.25 × 0.20 × 0.20
θ limit [deg]	1.33 to 27.48	1.31 to 27.50	1.30 to 27.51	1.36 to 27.48
index ranges (h, k, l)	−19 to 19; −22 to 23; −35 to 35	−41 to 41; −12 to −13; −32 to −32	−24 to 24; −20 to 20; −40 to 40	−40 to 40; −12 to 14; −41 to 41
no. of reflns collected	32 517	15 944	19 819	21 617
no. of indep reflns	17 232	9273	10 580	11 719
no. of reflns [$I > 2\sigma(I)$]	13 002	4884		9999
no. of data/restraints/params	17 232/0/883	9273/44/486	15 080/0/514	11 719/122/523
goodness-of-fit on F^2	1.049	0.998	1.099	1.129
final R indices [$I>2\sigma(I)$]	R1 = 0.0329, wR2 = 0.0754	R1 = 0.0435, wR2 = 0.0913	R1 = 0.0354, wR2 = 0.0930	R1 = 0.0515, wR2 = 0.1423
R indices (all data)	R1 = 0.0559, wR2 = 0.0917	R1 = 0.1207, wR2 = 0.1278	R1 = 0.0590, wR2 = 0.1072	R1 = 0.0628, wR2 = 0.1540
Δp (max) [e/Å^3]	1.082	1.885	1.084	1.705



4 **7**

Figure 1. Alkene metathesis catalysts employed.

ported for the bis(triarylphosphine) complexes *trans*-(Cl)(C_6F_5)Pt(PAr_3)$_2$.[16]

2. Title Reactions. Alkene metatheses were conducted under conditions analogous to those previously used for **3b**.[6c] The initial experiments utilized Grubbs' catalyst **4**, which is depicted in Figure 1. As shown in Scheme 2, CH_2Cl_2 solutions of **3a**−**d** (ca. 0.0025 M) and **4** (5−7 mol %, added in two portions) were refluxed for 4−5 h. The solvent was removed, and the crude mixtures were assayed by NMR. The ^{1}H NMR spectra showed no terminal alkene residues, indicating metathesis to be ≥98% complete. The ^{31}P NMR spectra showed two to five signals, with the dominant one representing 87−48% of the total peak area, as summarized in Scheme 2. The reaction mixtures were filtered through alumina to separate the catalyst residue. This gave the target macrocycles *trans*-(Cl)(C_6F_5)Pt(PPh$_2$(CH$_2$)$_n$CH=CH(CH$_2$)$_n$PPh$_2$) (**5a**−**d**), together with byproducts believed to be dimers and/or oligomers arising from intermolecular metathesis, in 96−85% yields.

The dominant ^{31}P NMR signal in each isolated sample represented 88−54% of the total peak area. The mass spectra (FAB) showed weak molecular ions and stronger ions derived from loss of chloride and/or pentafluorophenyl groups. No ions derived from dimers or oligomers were detected. With **5a**−**c**, for which NMR spectra suggested fewer byproducts, two groups of =CH ^{1}H NMR signals could be discerned ($\Delta\delta$ ca. 0.15 ppm, $CDCl_3$). The major signal was tentatively assigned to the *E* C=C isomer, in accord with our past experience in such macrocyclizations (**5a**, downfield; **5b**,**c**, upfield).[6a] In all cases, the chemical shift of the *C*H$_2$CH= ^{13}C NMR signal, another sensitive probe of *E*/*Z* stereochemistry,[17] was constant and in the expected range (31.7−32.1 ppm). Integration of the =CH resonances indicated 90:10 to 80:20 *E*/*Z* mixtures. The C=C ^{13}C NMR signals of the smallest macrocycle **5a** were in the range of those of **5b**−**d** (130.9 vs 131.1−130.7 ppm), suggesting no special interactions with the platinum. In all cases, the major components could be further purified by careful column chromatography. However, this came at the expense of considerable material loss.

To simplify analysis, the samples of **5a**−**d** were hydrogenated (1 atm) using 10% Pd/C as catalyst. The mixtures were filtered through alumina to give the crude saturated macrocycles *trans*-(Cl)(C_6F_5)Pt(PPh$_2$-(CH$_2$)$_{2n+2}$PPh$_2$) (**6a**−**d**), together with any dimeric and oligomeric species (94−76% total yields). The ^{1}H NMR spectra showed that all double bonds had been hydrogenated. The ^{31}P NMR spectra showed one major product and various minor products, as summarized in Scheme 2. Careful column chromatography afforded spectroscopically and analytically pure **6a**−**d** in 72−50%

(16) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2003**, *9*, 3324.

(17) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792.

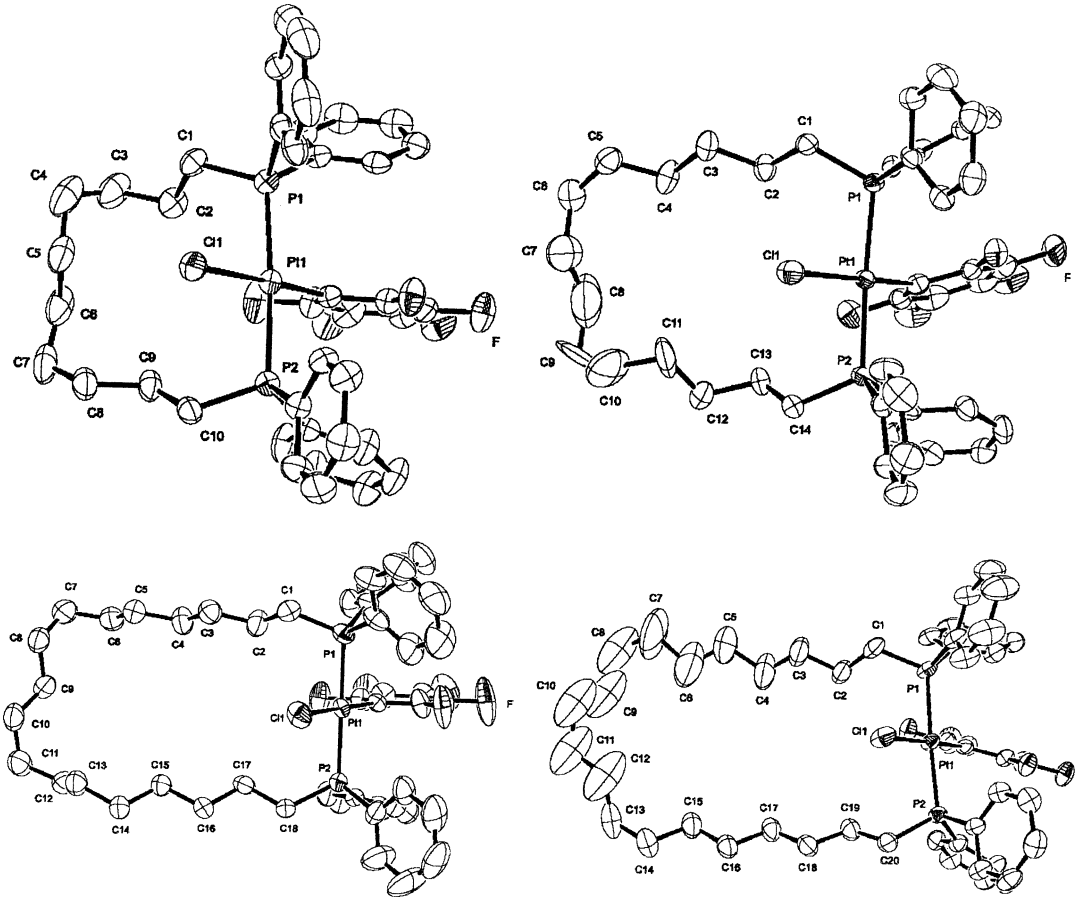


Figure 2. Molecular structures of platinamacrocycles **6a**,**b** (top) and **6c**,**d** (bottom).

yields. These were characterized analogously to the other new compounds above.

3. Structural and Dynamic Properties. The crystal structure of **6b** has been reported previously,[6c] and those of **6a**,**c** and the solvate **6d**·(toluene)$_{0.5}$ were similarly determined as summarized in Table 1 and the Experimental Section. The molecular structures of all are depicted in Figure 2, which highlights the basket-handle-like *trans*-spanning ligands. Key bond lengths, bond angles, and torsion angles are listed in Table 2. In the case of **6a**, two independent molecules were present in the unit cell. However, since the macrocycle conformations were analogous, as indicated by the close correspondence of the torsion angles in Table 2, only one is shown in Figure 2.

An alternative view of **6c** is given in Figure 3. This illustrates a stacking interaction involving the pentafluorophenyl ligand and a phenyl group on each phosphorus, which is common to all structures and analyzed further below. The averages of the two centroid−centroid distances in **6a**−**d** were 3.91, 3.60, 3.73, and 3.72 Å, respectively.

The NMR properties of the 13-membered macrocycle **6a** differed from those of **6b**−**d**. The latter group gave only a single set of PPh_2 ^{13}C NMR resonances and PCH_2CH_2 ^1H NMR resonances. However, **6a** exhibited two sets of signals (50:50). In principle, all geminal phenyl groups and methylene protons are diastereotopic in these compounds. However, they can be exchanged by a 180° rotation of the Cl−Pt−C_6F_5 moiety, as illustrated in Scheme 3.[18] Said differently, the methylene chain of the *trans*-spanning phosphine must be able to pass over the smaller chloride ligand. At room temperature, this is fast on the NMR time scale for **6b**−**d**, but slow for **6a**.

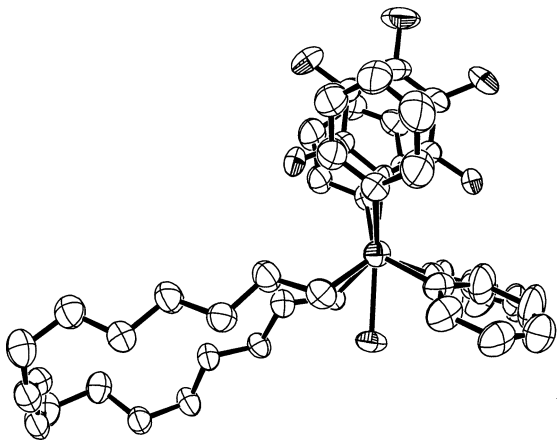


Figure 3. View of **6c** down the P−Pt−P axis highlighting the $C_6H_5/C_6F_5/C_6H_5$ stacking interaction.

A toluene-d_8 solution of **6a** was gradually warmed to 95 °C, and ^{13}C and ^1H NMR spectra were periodically recorded. No coalescence or significant broadening of the

(18) The exchange of H_a and H_b in Scheme 3 can be analyzed as follows. In both **I** and **II**, H_a and H_d are enantiotopic, as are H_b and H_c. H_a is diastereotopic with H_b and H_c. H_a in **I** exchanges with H_c in **II**, which is in turn chemical shift equivalent with enantiotopic H_b. Similarly, H_b in **I** exchanges with H_d in **II**, which is in turn chemical shift equivalent with enantiotopic H_a. The diastereotopic phenyl groups exchange analogously.

Table 2. Key Bond Lengths, Bond Angles, and Torsion Angles

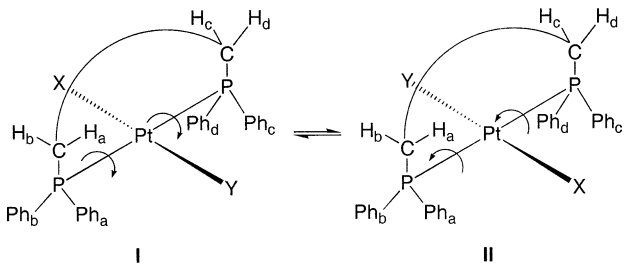
	6a[a]	6b	6c	6d
		Bond Lengths (Å)		
Pt−P(1)	2.3054(11)/2.3066(11)	2.306(2)	2.2984(11)	2.3017(16)
Pt−P(2)	2.3100(11)/2.3235(11)	2.299(2)	2.2995(12)	2.3101(16)
Pt−Cl	2.3742(10)/2.3595(10)	2.359(2)	2.3524(12)	2.3719(16)
Pt−C(41)	2.025(4)/2.005(4)	1.996(7)	2.008(4)	2.016(6)
C(1)−C(2)	1.537(7)/1.526(7)	1.531(9)	1.532(6)	1.513(11)
C(2)−C(3)	1.516(6)/1.514(7)	1.505(9)	1.506(6)	1.517(9)
C(3)−C(4)	1.552(8)/1.418(8)	1.510(9)	1.520(6)	1.485(11)
C(4)−C(5)	1.511(9)/1.547(8)	1.488(9)	1.530(6)	1.526(12)
C(5)−C(6)	1.514(7)/1.473(7)	1.506(9)	1.525(7)	1.446(14)
C(6)−C(7)	1.509(8)/1.522(8)	1.529(11)	1.505(7)	1.516(14)
C(7)−C(8)	1.446(8)/1.571(7)	1.385(12)	1.549(7)	1.458(14)
C(8)−C(9)	1.508(7)/1.527(8)	1.458(13)	1.510(8)	1.472(14)
C(9)−C(10)	1.532(6)/1.520(7)	1.408(15)	1.489(7)	1.497(13)
C(10)−C(11)		1.425(15)	1.531(7)	1.514(14)
C(11)−C(12)		1.376(15)	1.499(8)	1.505(13)
C(12)−C(13)		1.475(10)	1.507(7)	1.483(13)
C(13)−C(14)		1.508(9)	1.513(7)	1.503(10)
C(14)−C(15)			1.527(7)	1.514(9)
C(15)−C(16)			1.484(7)	1.495(9)
C(16)−C(17)			1.520(7)	1.519(9)
C(17)−C(18)			1.514(7)	1.536(11)
C(18)−C(19)				1.513(8)
C(19)−C(20)				1.522(10)
		Bond Angles (deg)		
C(41)−Pt−P(1)	90.43(11)/91.27(12)	91.7(2)	90.52(12)	91.54(17)
C(41)−Pt−P(2)	92.80(11)/93.35(12)	91.4(2)	92.22(12)	90.62(17)
P(1)−Pt−P(2)	176.25(4)/175.16(4)	172.00(7)	176.94(4)	174.26(6)
C(41)−Pt−Cl	177.55(12)/179.52(13)	174.3(2)	177.04(12)	176.35(19)
P(1)−Pt−Cl	88.52(4)/88.56(4)	88.67(7)	89.85(4)	88.91(6)
P(2)−Pt−Cl	88.17(4)/86.84(7)	89.07(7)	87.34(4)	89.28(6)
		Torsion Angles (deg)		
P(2)−Pt(1)−P(1)−C(1)	18.4(6)/−26.84(6)	−114.6(6)	65.6(8)	−119.4(6)
P(1)−Pt(1)−P(2)−C(n)[b]	−33.1(6)/38.7(6)	126.8(6)	−75.8(8)	112.0(6)
Pt(1)−P(1)−C(1)−C(2)	44.2(3)/50.9(4)	−46.3(6)	40.5(4)	−44.3(7)
P(1)−C(1)−C(2)−C(3)	−151.6(3)/155.4(3)	166.5(6)	−169.6(3)	175.6(7)
C(1)−C(2)−C(3)−C(4)	−176.1(4)/−178.9(4)	−169.6(7)	176.8(4)	179.7(11)
C(2)−C(3)−C(4)−C(5)	−58.0(6)/56.7(8)	177.6(7)	−174.6(4)	−174.3(14)
C(3)−C(4)−C(5)−C(6)	−54.2(6)/54.7(8)	−174.7(7)	172.0(4)	−169(2)
C(4)−C(5)−C(6)−C(7)	−171.1(4)/170.1(4)	69.0(12)	68.8(6)	176(2)
C(5)−C(6)−C(7)−C(8)	−54.0(7)/52.3(7)	−106.4(16)	173.6(4)	174(2)
C(6)−C(7)−C(8)−C(9)	−55.4(7)/56.4(6)	178.6(12)	58.2(7)	44(3)
C(7)−C(8)−C(9)−C(10)	−61.4(7)/64.4(7)	−163.1(17)	61.0(7)	89(3)
C(8)−C(9)−C(10)−C(11)		59(3)	−179.7(5)	−174.1(16)
C(9)−C(10)−C(11)−C(12)		84(3)	−170.7(5)	85(2)
C(10)−C(11)−C(12)−C(13)		177.2(18)	−60.0(7)	−160.8(17)
C(11)−C(12)−C(13)−C(14)		−175.3(13)	−61.7(7)	178.3(17)
C(12)−C(13)−C(14)−C(15)			178.6(5)	−66.7(16)
C(13)−C(14)−C(15)−C(16)			176.6(5)	176.3(9)
C(14)−C(15)−C(16)−C(17)			178.5(5)	178.9(8)
C(15)−C(16)−C(17)−C(18)			175.0(5)	168.4(7)
C(16)−C(17)−C(18)−C(19)				177.8(6)
C(17)−C(18)−C(19)−C(20)				175.0(6)
C(n-2)−C(n-1)−C(n)−P(2)[b]	176.1(4)/−176.2(4)	−163.7(7)	168.3(4)	−167.9(5)
Pt(1)−P(2)−C(*n*)−C(*n*−1)[b]	−50.2(4)/−47.3(4)	43.2(7)	−53.9(4)	47.6(6)

[a] Two independent molecules are present in the unit cell. [b] n = number of methylene groups in the macrocycle.

para-C_6H_5 ^{13}C or $PCHH'CHH'$ ^1H signals were noted. Application of the coalescence formula,[19] using the $\Delta\nu$ value for the para carbons (155.2 Hz, 25 °C), allowed a lower limit of 17.4 kcal/mol (95 °C) to be placed upon the barrier for the dynamic process in Scheme 3. A complementary series of low-temperature spectra were recorded with a THF-d_8 solution of the 17-membered macrocycle **6b**. Between −5 and −90 °C, no decoalescence or significant broadening of the PPh_2 ^{13}C or PCH_2CH_2 ^1H signals was observed. Application of the coalescence formula, using the $\Delta\nu$ value for the para carbons of **6a**, allowed an upper limit of 8.4 kcal/mol (−90 °C) to be placed on the barrier for the dynamic process in Scheme 3.

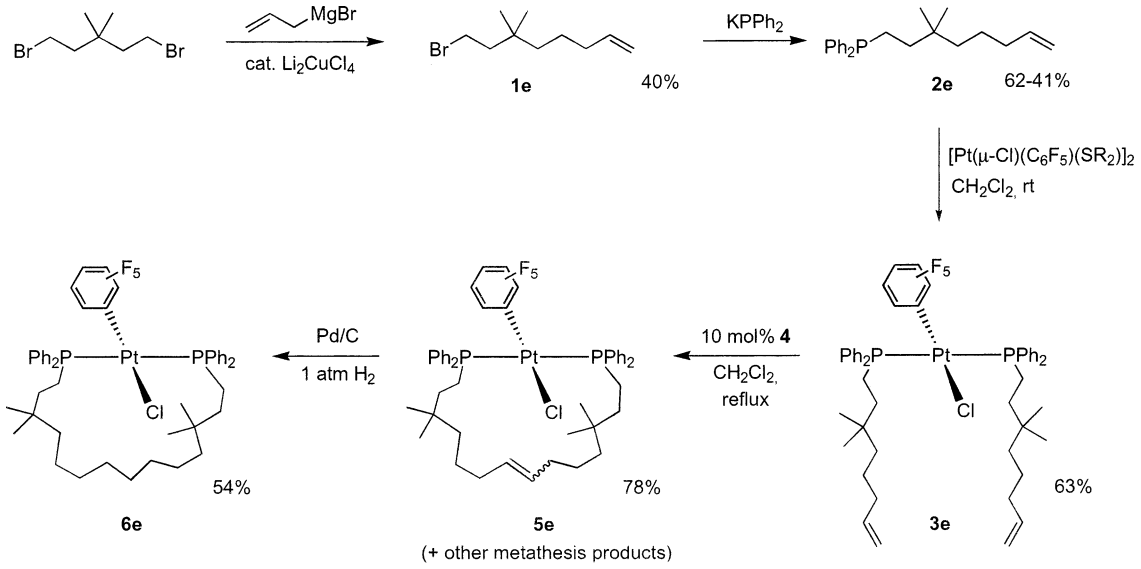
(19) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982. Calculations utilized eq 7.4 b.

Scheme 3. Exchange of Diasterotopic Groups in Macrocyclic Complexes



4. Effect of Geminal Dimethyl Substituents. As noted in the Introduction, geminal dimethyl groups can have a beneficial effect upon cyclization efficiency.[9,10] Accordingly, when this project was still in the planning stage and before any preliminary success, the synthesis

Scheme 4. Synthesis of a Monophosphine and Platinamacrocycles Containing Geminal Dimethyl Groups



of a dimethyl derivative of phosphine ligand **2b** was undertaken.[20] For obvious reasons, it was sought to avoid neopentyl functionality or $PCH_2C(CH_3)_2$ or $(CH_3)_2CCH_2CH{=}CH_2$ linkages. Thus, the synthesis of the phosphine $Ph_2P(CH_2)_2C(CH_3)_2(CH_2)_3CH{=}CH_2$ (**2e**) shown in Scheme 4 was developed.

The symmetrical dibromide $BrCH_2CH_2C(CH_3)_2CH_2CH_2Br$ (Scheme 4) is easily obtained in two steps from commercial 3,3-dimethylglutaric acid.[21] It could be desymmetrized by a cross-coupling with $BrMgCH_2CH{=}CH_2$ in the presence of catalytic quantities of Li_2CuCl_4.[22] Distillation gave the monosubstitution product, bromoalkene $Br(CH_2)_2C(CH_3)_2(CH_2)_3CH{=}CH_2$ (**1e**), in 40% yield. Subsequent reaction with $KPPh_2$ gave the target phosphine **2e** in 62−41% yields. These new compounds were characterized analogously to the other bromides and phosphines above. The ^1H and ^{13}C NMR spectra showed intense singlets for the geminal dimethyl groups.

The reaction of **2e** and platinum complex $[Pt(\mu\text{-}Cl)(C_6F_5)(S(CH_2CH_2-)_2)]_2$ as described for the other phosphines above gave the bis(phosphine) complex *trans*-$(Cl)(C_6F_5)Pt(PPh_2(CH_2)_2C(CH_3)_2(CH_2)_3CH{=}CH_2)_2$ (**3e**) in 63% yield. As shown in Scheme 4, reaction with Grubbs' catalyst **4** afforded, after workup, the expected macrocyclic metathesis product *trans*-$(Cl)(C_6F_5)Pt(PPh_2(CH_2)_2C(CH_3)_2(CH_2)_3CH{=}CH(CH_2)_3C(CH_3)_2(CH_2)_2PPh_2)$ (**5e**) in 78% yield. The ^1H NMR spectrum suggested a 88:12 ratio of *E*/*Z* C=C isomers. The ^{31}P NMR spectrum of the crude reaction mixture showed only two signals in a 9:91 area ratio.

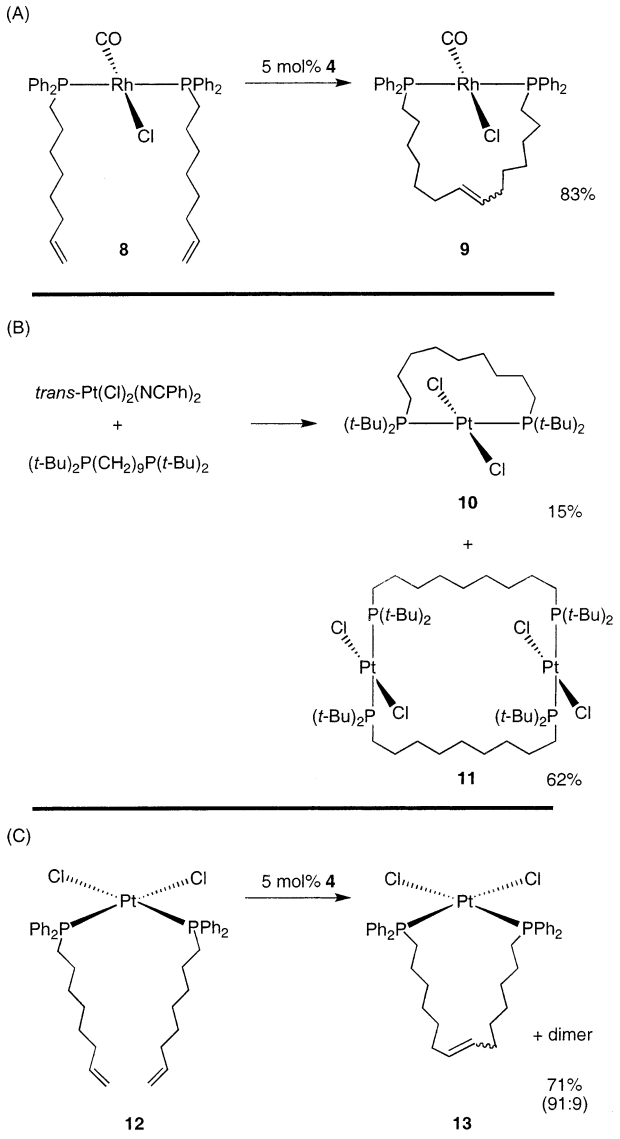
Hydrogenation as above gave the saturated macrocycle *trans*-$(Cl)(C_6F_5)Pt(PPh_2(CH_2)_2C(CH_3)_2(CH_2)_8C(CH_3)_2(CH_2)_2PPh_2)$ (**6e**). However, in both the crude and analytically pure product (66% and 54% yields, respectively), a second minor ^{31}P NMR signal was present (ca. 11%). Hence, we suspect that the minor ^{31}P NMR signal of **5e** represents some type of dimeric or oligomeric byproduct, as opposed to a C=C geometric isomer. In any event, the geminal dimethyl groups in **3e** clearly present no impediment to macrocyclization. However, the analogous complex lacking dimethyl groups (**3b**) is such a good substrate that no beneficial effect is apparent.

5. Other Reactions. Additional experiments were conducted to help interpret the preceding data. First, many macrocyclizations of organic α,ω-dienes have been conducted with both catalyst **4** and Grubbs' "second-generation" catalyst $Ru(=CHPh)(H_2IMes)(PCy_3)(Cl)_2$ (**7**, Figure 1).[23] The latter sometimes gives markedly different distributions of intra- and intermolecular products[24] and is more reactive toward endocyclic macrocyclic alkenes.[25] Thus, CH_2Cl_2 solutions of **3a**,**b**,**c** (0.0025 M) and **7** (10 mol %; added in two portions) were refluxed for ca. 4 h. The product distributions before and after workup were very close to those obtained under similar conditions with **4**, as indicated by the bracketed values in Scheme 2. Hence, the catalyst **7** has no significant effect on the yield or fraction of major product.

We next wondered whether macrocycles of the type **6** might be efficiently accessed without recourse to alkene metathesis. Thus, the platinum starting material in Scheme 2, $[Pt(\mu\text{-}Cl)(C_6F_5)(S(CH_2CH_2-)_2)]_2$, and the diphosphine $Ph_2P(CH_2)_{14}PPh_2$[8a,26] were combined in a NMR tube in CD_2Cl_2 (1:1 Pt/diphosphine ratio, ca. 0.018 M). A multitude of products formed, as assayed by NMR and TLC. The ^{31}P NMR spectrum allowed an upper limit

(20) Bauer, E. B. Diploma Thesis, University of Erlangen-Nuremberg, 1999.
(21) Eilbracht, P.; Acker, P.; Totzauer, W. *Chem Ber.* **1983**, *116*, 238.
(22) (a) Tamura, M.; Kochi, J. *Synthesis* **1971**, 303. (b) Johnson, D. K.; Donohoe, J.; Kang, J. *Synth. Commun.* **1994**, *24*, 1557.
(23) (a) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247. (b) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (c) H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene.
(24) Fürstner, A.; Thiel, O. R.; Ackermann, L. *Org. Lett.* **2001**, *3*, 449.
(25) One good recent example involves an alkene-containing crown ether: Kilbinger, A. F. M.; Cantrill, S. J.; Waltman, A. W.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 3281; *Angew. Chem.* **2003**, *115*, 3403.
(26) Mohr, W.; Horn, C. R.; Stahl, J.; Gladysz, J. A. *Synthesis* **2003**, 1279.

Scheme 5. Other Relevant Macrocyclizations



of 15% to be placed upon the yield of **6b**. Hence, metathesis provides a singularly successful route to such macrocycles.

Discussion

1. Scope of Macrocyclizations. Schemes 2 and 4 clearly establish that 13- to 23-membered macrocycles can be accessed in high yields by ring-closing metatheses of square-planar platinum complexes with *trans*-disposed alkene-containing phosphines. As depicted in Scheme 5A (top), the related square-planar rhodium complex **8** reacts similarly to give the 17-membered macrocycle **9**.[6a] There is every reason to believe that alkene-containing sulfur, nitrogen, and other donor ligands, as well as other metals, can be analogously employed.[1]

To our knowledge, the shortest conformationally unconstrained *trans*-spanning diphosphorus donor ligand is found in the platinum complex **10** (Scheme 5B, middle).[3,27,28] This 12-membered platinacycle was obtained in low yield together with the dimer **11** by a simple substitution reaction. Still smaller rings are likely to have significant strain energy, and such targets are unlikely to be accessible by our methodology. However, we are optimistic regarding larger metallamacrocycles. Although the data in Scheme 2 suggest that intramolecular metathesis becomes less efficient for the 21- and 23-membered macrocycles **5c**,**d**, reactions at higher dilution, which might have ameliorated this trend, were not conducted.

2. Macrocyclization Efficiency. The most important question regarding this work is "why are these macrocyclizations so successful"? Only modest amounts of dimeric or oligomeric byproducts form, despite conditions that are not particularly dilute (ca. 0.0025 M, corresponding to ca. 160 mg of **3a**−**e** in 70 mL of CH_2Cl_2). In certain macrocyclizations, some type of favorable conformational factor can be identified. For example, there is a well-established "geminal dialkyl effect" in carbocycle synthesis.[9,10] When two alkyl groups are present on the same carbon atom, C−CR_2−C−C segments with gauche conformations become energetically more competitive with anti conformations. Chains of atoms with exclusively anti conformations are incapable of cyclization, and all carbocycles require a certain number of C−C−C−C torsion angles in the range of 0−90°.

In related metallamacrocyclizations involving *cis* ligands, it is possible to identify features reminiscent of the geminal dialkyl effect. Consider the *cis* bis(phosphine) platinum complex **12** in Scheme 5C (bottom).[6c] The phenyl groups in the M−PPh_2−CH_2−CH_2 segments should, relative to compounds with M−PH_2−CH_2−CH_2 or M−CH_2−CH_2−CH_2 segments, increase the fraction of gauche conformations. As illustrated by the sequence of Newman-type projections **III** (anti/anti), **IV** (gauche/anti), and **V** (gauche/gauche) in Scheme 6A (top), this should enhance the rate of macrocyclization. The alternative gauche/gauche conformation **VI** should also be favorable for macrocyclization. Accordingly, **13**, which features a 17-membered ring, is obtained in good yield.

However, in substrates such as **3a**−**e**, the pendant alkenes must furthermore be directed on the same side of the metal square plane. Some relevant conformations, as viewed down the $PtPPh_2$−CH_2CH_2 bond in the direction of the Cl−Pt−C_6F_5 axis, are given in Scheme 6B (middle). At present, we see no special feature that would favor reaction of the macrocyclization-prone gauche/gauche conformation **IX** over the oligomerization-prone gauche/gauche conformation **X**. Other conformations are possible (e.g., a 180° rotation about *one* Pt−P bond will generate another series), but the conclusion remains the same. Since no bonding interactions are evident between the coordinatively unsaturated platinum moieties and C=C linkages in **5a**−**e**, we believe it unlikely that the platinum somehow serves as a template for macrocyclization.

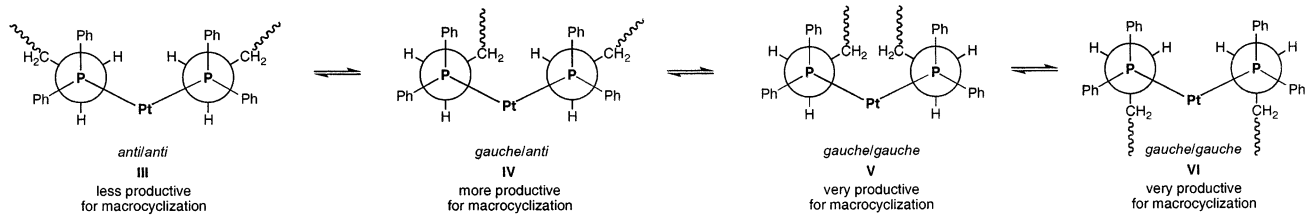
It is now well established that C_6H_5/C_6F_5 π interactions are attractive and a driving force in many crystallizations.[29] These are evident in each of the crystal

(27) (a) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856. (b) Pryde, A.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton. Trans.* **1976**, 322.

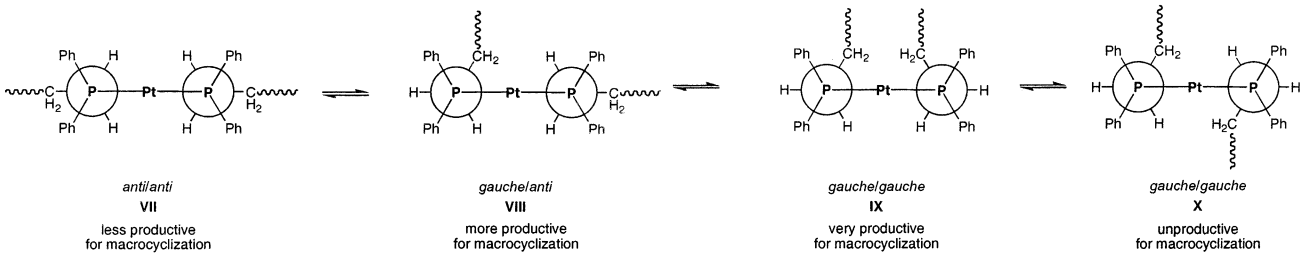
(28) Other *trans*-spanning diphosphines that give 12-membered or smaller metallacycles contain arene rings as part of the backbone.[3] An early report of a nickel complex with a *trans*-spanning $Cy_2P(CH_2)_5PCy_2$ ligand has been questioned.[3,27]

Scheme 6. Selected Conformational Equilibria

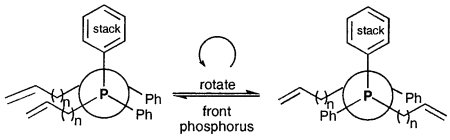
(A) Representative equilibria in *cis*-bis(phosphine) complex **12**



(B) Representative equilibria in *trans*-bis(phosphine) complexes **3a-e**.



(C) Equilibria for *trans*-bis(phosphine) complexes **3a-e** with $C_6H_5/C_6F_5/C_6H_5$ stacks.



XI XII

structures of **6a**−**d** (Figures 2, 3). Could they somehow template the macrocyclizations? Since the rhodium complex **8**, which lacks a pentafluorophenyl ligand, reacts similarly (Scheme 5A), such interactions are definitely not required. Furthermore, consider the conformations **XI** and **XII** of **3a**−**e** in Scheme 6C (bottom), in which $C_6H_5/C_6F_5/C_6H_5$ π stacks are assumed. There would seem to be a roughly equal energetic probability for the pendant alkenes to be on opposite versus identical sides of the platinum square plane. Thus, no net bias for ring closure would result.

Regardless of the exact basis for the good yields of our *trans*-spanning diphosphine complexes, Shaw has provided strong support for the general importance of phosphorus-based geminal-dialkyl effects.[27] He studied substitution reactions analogous to that in Scheme 5B (middle), but with diphosphines with 10- and 12-methylene chains. With bulky P(*t*-Bu)$_2$ endgroups, *trans*-spanning diphosphine complexes and dimers thereof were the major products. Note that in Pt−P(*t*-Bu)$_2$−CH_2−CH_2 segments with anti conformations, the methylene chain must occupy the interstice between the two large *tert*-butyl groups. In contrast, anti conformations involving smaller PPh_2 endgroups should be energetically more accessible. Accordingly, analogous reactions with the diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 9, 10, 12) led only to open-chain oligomeric species.

3. Other Structural and Dynamic Properties. Additional structural features of **6a**−**d** are relevant to phenomena analyzed above. First, Table 2 shows that all complexes generally have similar bond lengths and angles about platinum. The angles involving the *trans* ligands show the greatest variance. However, the P−Pt−P bond angle in the smallest macrocycle **6a**, which might have contracted if ring strain were significant, was larger than those of **6b**,**d** (176.25(4)°/175.16(4)° vs 172.00(7)° and 174.26(6)°).

Consider the torsion angle patterns of the macrocycles next. All Pt−PPh_2−CH_2−CH_2 segments (Pt(1)−P(1)−C(1)−C(2) and Pt(1)−P(2)−C(n)−C(n−1)) exhibit gauche conformations with torsion angles in the narrow range of ±40.5(4)° to ±53.9(4)°. All PPh_2−CH_2−CH_2−CH_2 segments in turn exhibit anti conformations, with torsion angles in the range of ±151.6(3)° to ±176.2(4)°. The neighboring sequences of four carbon atoms also show anti conformations, with the exception of C(7)−C(8)−C(9)−C(10) in the smallest macrocycle **6a** (torsion angle −61.4(7)°/64.4(7)°). Complex **6a** features a total of five all-carbon gauche segments, as does **6c**. However, **6b** and **6c** exhibit three and four, respectively. Naturally, all of these macrocycles will have a distribution of conformations in solution, and crystallization in identical motifs is not to be expected.

Shaw and Mason have reported the crystal structures of an Ir(CO)(Cl) adduct of the *trans*-spanning diphosphine (*t*-Bu)$_2$P(CH$_2$)$_{10}$P(*t*-Bu)$_2$ and a Pt(Cl)$_2$ adduct of

(29) (a) Collings, J. C.; Roscoe, K. P.; Robins, E. G.; Batsanov, A. S.; Stimson, L. M.; Howard, J. A. K.; Clark, S. J.; Marder, T. B. *New J. Chem.* **2002**, *26*, 1740, and references therein. (b) Ponzini, F.; Zagha, R.; Hardcastle, K.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2323; *Angew. Chem.* **2000**, *112*, 2413. (c) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641. (d) Renak, M. L.; Bartholomew, G. P.; Wang, S.; Ricatto, P. J.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 7787.

the longer diphosphine $(t\text{-Bu})_2P(CH_2)_{12}P(t\text{-Bu})_2$.[30] These 13- and 15-membered macrocycles exhibit torsion angle patterns for the six-atom $M-PR_2-CH_2-CH_2-CH_2-CH_2$ segments analogous to those of **6b**−**d**. They feature three and four all-carbon gauche segments, respectively.

When **6a**−**d** are viewed with atoms at van der Waals radii, the macrocycles contain little "void space". Nonetheless, passage of the chloride ligand through the macrocycle, as shown for a Pt-X moiety in Scheme 3, is rapid on the NMR time scale for **6b**−**d**. Steric interactions in these dynamic processes can be analyzed as follows. First, the distances from platinum to the *furthest* of the two most remote carbons (e.g., C(5) and C(6) in **6a**) in each macrocycle are calculated (**6a**, 5.62 Å; **6b**, 7.83 Å; **6c**, 10.22 Å; **6d**, 11.44 Å). The van der Waals radius of an sp^3 carbon (1.70 Å)[31] is then subtracted (**6a**, 3.92 Å; **6b**, 6.13 Å; **6c**, 8.52 Å; **6d**, 9.74 Å). These values are compared to the sum of the platinum−chlorine bond distance (ca. 2.36 Å) *plus* the van der Waals radius of chlorine (1.78 Å),[31] or 4.14 Å.

Hence, even without taking into account the methylene hydrogen atoms (van der Waals radius 1.20 Å), it is readily apparent that there will be substantial steric interactions for such a process with **6a** (4.14 Å "vehicle height" vs 3.92 Å "bridge height"). Accordingly, the barrier could not be measured by NMR and is at least 17.4 kcal/mol at 95 °C. Given the more generous spacing in **6b** (4.14 vs 6.13 Å), the much lower barrier, less than 8.4 kcal/mol at −90 °C, is easy to rationalize. However, since the coalescence or decalescence of diastereotopic groups could not be observed, it has not been possible to measure an exact barrier. For this purpose, an analogous 15-membered macrocycle should be ideal.

4. Prospective. This work has significantly advanced the application of alkene metathesis to the synthesis of topologically novel inorganic and organometallic systems. As noted above, the extension of Schemes 2 and 4 to the preparation of a variety of other adducts of *trans*-spanning ligands can be anticipated. Furthermore, alkyne metathesis has recently been employed to convert an analogue of **3b** with carbon−carbon triple bonds to a platinamacrocycle.[32] This avoids the complication of *E*/*Z* C=C isomers. Finally, novel macrocyclizations involving more complex educts—such as when the *trans* phosphorus or other donor atoms contain two $(CH_2)_nCH=CH_2$ moieties—will be described in upcoming full papers.[6b,33]

Experimental Section

General Data. All reactions were conducted under N_2 (or H_2) atmospheres. Chemicals were treated as follows: THF, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2 for reactions or simple distillation for chromatography; hexanes and ethanol, simple distillation; acetic acid, $ClCH_2CH_2$-Cl (99%, Fluka), $CDCl_3$, C_6D_6, toluene-d_8, THF-d_8, $Br(CH_2)_4$-$CH=CH_2$ (**1a**; 97%, Fluka), $Br(CH_2)_6CH=CH_2$ (**1b**; 97%, Aldrich or Fluka), $HO(CH_2)_8CH=CH_2$ (97%, Fluka), CBr_4 (98%, Lancaster), PPh_3 (99%, Acros), $Br(CH_2)_9CH=CH_2$ (**1d**, 97% Aldrich), $KPPh_2$ (Fluka, 0.5 M in THF), $Ru(=CHPh)(PCy_3)_2(Cl)_2$ (**4**, Strem), $Ru(=CHPh)(H_2IMes)(PCy_3)(Cl)_2$ (**7**, Strem),[23c] Pd/C (10%, Lancaster or Acros), and $BrMgCH_2CH=CH_2$ (1 M in ether, Fluka), used as received. All Li_2CuCl_4 solutions were freshly generated from LiCl (0.424 g, 10.00 mmol), $CuCl_2$ (0.673 g, 5.00 mmol), and THF (50 mL).[22] NMR spectra were obtained on Bruker or JEOL 400 MHz spectrometers. IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. DSC and TGA data were obtained with a Mettler-Toledo DSC-821 instrument.[34] Microanalyses were conducted on a Carlo Erba EA1110 instrument.

$Br(CH_2)_8CH=CH_2$ (1c).[11] A Schlenk flask was charged with $HO(CH_2)_8CH=CH_2$ (2.000 g, 12.8 mmol), CBr_4 (4.788 g, 14.4 mmol), and CH_2Cl_2 (20 mL) and cooled to 0 °C. Over the course of 20 min, PPh_3 (4.510 g, 17.2 mmol) was added in portions. The mixture was stirred for 2 h at 0 °C. After ca. 30 min, a white precipitate formed. The mixture was stirred for 22 h at room temperature. The solvent was removed by rotary evaporation and oil pump vacuum. The residue was suspended in hexane (5 mL) and the mixture filtered through silica gel (5 × 2.5 cm column; rinsed with 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed from the filtrate by rotary evaporation, and distillation (9×10^{-3} mbar, 58 °C) gave **1c** as a colorless oil (2.084 g, 9.597 mmol, 75%). NMR (δ, $CDCl_3$): ^{1}H 5.86−5.79 (m, 1 H, C*H*=), 5.04−4.94 (m, 2 H, =CH_2), 3.44−3.40 (t, $^3J_{HH} = 8.7$, 2 H, BrCH_2), 2.07−2.04 (m, 2 H, CH_2CH=), 1.91−1.83 (m, 2 H, $BrCH_2CH_2$), 1.46−1.32 (m, 10 H, 5CH_2); ^{13}C-{^{1}H} 139.5 (s, *C*H=), 114.6 (s, =*C*H_2), 34.4 (s, *C*H_2), 34.2 (s, *C*H_2), 33.2 (s, *C*H_2), 29.7 (s, *C*H_2), 29.4 (s, *C*H_2), 29.3 (s, *C*H_2), 29.1 (s, *C*H_2), 28.5 (s, *C*H_2).

$PPh_2(CH_2)_4CH=CH_2$ (2a). A Schlenk flask was charged with **1a** (0.500 g, 3.066 mmol) and THF (7 mL) and cooled to 0 °C. Then $KPPh_2$ (0.5 M in THF, 6.1 mL, 3.1 mmol) was added dropwise with stirring to the colorless solution over 20 min.[35] A white precipitate formed. The mixture was stirred for 1 h at 0 °C and 1 h at room temperature. The solvent was removed by oil pump vacuum and the residue suspended in CH_2Cl_2 (5 mL). The suspension was chromatographed on silica gel (5 × 2.5 cm column; eluted with 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed from the product fraction by rotary evaporation and oil pump vacuum to give **2a** as a viscous cloudy liquid (0.345 g, 1.282 mmol, 41%). Anal. Calcd for $C_{18}H_{21}P$: C, 80.57; H 7.89. Found: C, 80.35; H, 7.89. NMR (δ, $CDCl_3$): ^{1}H 7.49−7.45 (m, 4 H of 2Ph), 7.37−7.36 (m, 6 H of 2Ph), 5.86−5.79 (m, 1 H, C*H*=), 5.05−4.96 (m, 2 H, =CH_2), 2.12−2.07 (m, 4 H, CH_2CH= + PCH_2), 1.61−1.48 (m, 4 H, 2CH_2); ^{13}C{^{1}H} 138.9 (d, $^1J_{CP} = 13.1$, *i*-Ph),[36] 138.6 (s, *C*H=), 132.6 (d, $^2J_{CP} = 18.3$, *o*-Ph),[36] 128.4 (s, *p*-Ph),[36] 128.3 (d, $^3J_{CP} = 6.6$, *m*-Ph),[36] 114.5 (s, =*C*H_2), 33.3 (s, *C*H_2CH=), 30.4 (d, $^3J_{CP} = 13.0$, $PCH_2CH_2CH_2$),[37] 27.9 (d, $^1J_{CP} = 11.4$, P*C*H_2),[37] 25.4 (d, $^2J_{CP} = 16.2$, PCH_2CH_2);[37] ^{31}P{^{1}H} −15.5 (s). IR (cm^{-1}, oil film): 3057, 2926, 2864, 1436, 1177, 1119, 1069, 718, 695. MS:[38] 269 (**2a**$^+$, 100%).

$PPh_2(CH_2)_6CH=CH_2$ (2b).[6c,12] Anal. Calcd for $C_{20}H_{25}P$ (viscous liquid, 74%): C, 81.05; H, 8.50. Found: C, 79.91; H, 8.44. NMR (δ, $CDCl_3$): ^{1}H 7.45−7.32 (m, 10 H of 2Ph), 5.79 (m, 1 H, C*H*=), 5.02−4.91 (m, 2 H, =CH_2), 2.07−1.99 (m, 4 H,

(30) March, F. C.; Mason, R.; Thomas, K. M.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, 584.
(31) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(32) Bauer, E. B.; Szafert, S.; Hampel, F.; Gladysz, J. A. *Organometallics* **2003**, *22*, 2184.
(33) Shima, T.; Bauer, E. B.; Hampel, F.; Gladysz, J. A. Manuscript in preparation.
(34) Cammenga, H. K.; Epple, M. *Angew. Chem.* **1995**, *107*, 1284; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1171.
(35) The addition of the red $KPPh_2$ solution was continued until some color began to persist.
(36) The PC_6H_5 ^{13}C NMR signals were assigned as described by: Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30. The resonance with the chemical shift closest to benzene was attributed to the meta carbon, and the least intense phosphorus-coupled resonance was attributed to the ipso carbon.
(37) The $PCH_2CH_2CH_2$ ^{13}C NMR signals were assigned by analogy to chemical shift and coupling constant trends established (by COSY and INADEQUATE pulse sequences) for other compounds with Ar_2P-$(CH_2)_6X$ linkages.[8a,26]
(38) *m*/*z* (FAB, 3-NBA) for most intense peak of isotope envelope (relative intensity, %).

$CH_2CH{=}$ + PCH_2), 1.45−1.27 (m, 8 H, $4CH_2$); $^{13}C\{^1H\}$ 139.0 (d, $^1J_{CP}$ = 14.7, *i*-Ph),[36] 138.98 (s, $CH{=}$), 132.7 (d, $^2J_{CP}$ = 18.3, *o*-Ph),[36] 128.3 (d, $^3J_{CP}$ = 4.5, *m*-Ph),[36] 128.2 (s, *p*-Ph),[36] 114.2 (s, $={CH_2}$), 33.6 (s, $CH_2CH{=}$), 31.0 (d, $^3J_{CP}$ = 13.7, $PCH_2CH_2CH_2$),[37] 28.0 (br s, double intensity, $CH_2CH_2CH_2CH{=}$), 28.0 (d, $^1J_{CP}$ = 10.7, PCH_2),[37] 25.7 (d, $^2J_{CP}$ = 15.3, PCH_2CH_2);[37] $^{31}P\{^1H\}$ −15.8 (s). IR (cm^{-1}, oil film): 3073, 2927, 2855, 1481, 1462, 1434, 1096, 1026, 912, 740, 696. MS:[38] 297 (**2b**$^+$, 100%).

$PPh_2(CH_2)_8CH{=}CH_2$ (2c). A Schlenk flask was charged with **1c** (1.000 g, 4.605 mmol) and THF (22 mL) and cooled to 0 °C. Then $KPPh_2$ (0.5 M in THF, 9.2 mL, 4.6 mmol) was added dropwise with stirring to the colorless solution over 20 min.[35] A white precipitate formed. The mixture was stirred for 0.5 h at 0 °C and 1 h at room temperature. The solvent was removed by oil pump vacuum and the residue suspended in CH_2Cl_2 (5 mL). The suspension was filtered through neutral alumina (5 × 2.5 cm column, rinsed with 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **2c** as a viscous cloudy liquid (1.422 g, 4.383 mmol, 95%). Anal. Calcd for $C_{22}H_{29}P$: C, 81.45; H, 9.01. Found: C, 81.11; H, 8.93. NMR (δ, $CDCl_3$): ^1H 7.44−7.42 (m, 10 H of 2Ph), 5.85−5.82 (m, 1 H, $CH{=}$), 5.05−4.95 (m, 2 H, $={CH_2}$), 2.10−2.03 (m, 4 H, $CH_2CH{=}$ + PCH_2), 1.46−1.29 (m, 12 H, $6CH_2$); $^{13}C\{^1H\}$ 139.6 (s, $CH{=}$), 139.0 (d, $^1J_{CP}$ = 13.0, *i*-Ph),[36] 132.7 (d, $^2J_{CP}$ = 18.3, *o*-Ph),[36] 128.6 (s, *p*-Ph),[36] 128.3 (d, $^3J_{CP}$ = 6.6, *m*-Ph),[36] 114.5 (s, $={CH_2}$), 34.2 (s, $CH_2CH{=}$), 31.6 (d, $^3J_{CP}$ = 13.0, $PCH_2CH_2CH_2$),[37] 29.8 (s, CH_2), 29.6 (s, CH_2), 29.5 (s, CH_2), 29.3 (s, CH_2), 28.5 (d, $^1J_{CP}$ = 11.7, PCH_2),[37] 26.4 (d, $^2J_{CP}$ = 15.8, PCH_2CH_2);[37] $^{31}P\{^1H\}$ −14.8 (s). IR (cm^{-1}, oil film): 2922, 2853, 1440, 1181, 1119, 1073, 996, 783, 748, 718, 695. MS:[38] 341 ([**2c**=**O**]$^+$, 60%), 325 (**2c**$^+$, 100%).

$PPh_2(CH_2)_9CH{=}CH_2$ (2d).[13] A Schlenk flask was charged with **1d** (2.500 g, 10.72 mmol) and THF (50 mL). Then $KPPh_2$ (0.5 M in THF, 21.4 mL, 10.7 mmol) was added dropwise with stirring.[35] After 1 h, the solvent was removed by oil pump vacuum. Then CH_2Cl_2 was added, and the mixture was filtered through silica gel (5 × 2.5 cm column, rinsed with CH_2Cl_2). The solvent was removed from the filtrate by rotary evaporation, and the residue distilled under reduced pressure to give **2d** as a colorless liquid (3.287 g, 9.71 mmol, 91%). NMR (δ, $CDCl_3$): ^1H 7.42 (m, 4 H of 2Ph), 7.32 (m, 6 H of 2Ph), 5.81 (m, 1 H, $CH{=}$), 4.92 (m, 2 H, $={CH_2}$), 2.03 (m, 4 H, $CH_2CH{=}$ + PCH_2), 1.44 (m, 2 H, PCH_2CH_2), 1.37 (m, 2H, $PCH_2CH_2CH_2$), 1.27 (m, 10 H, $5CH_2$); $^{13}C\{^1H\}$ 139.2 (s, $CH{=}$), 139.0 (d, $^1J_{CP}$ = 14.7, *i*-Ph),[36] 132.6 (d, $^2J_{CP}$ = 18.3, *o*-Ph),[36] 128.4 (d, $^3J_{CP}$ = 4.5, *m*-Ph),[36] 128.3 (s, *p*-Ph),[36] 114.1 (s, $={CH_2}$), 33.7 (s, $CH_2CH{=}$), 31.2 (d, $^3J_{CP}$ = 13.7, $PCH_2CH_2CH_2$),[37] 29.4 (s, double intensity, CH_2), 29.2 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 28.0 (d, $^1J_{CP}$ = 10.7, PCH_2),[37] 25.9 (d, $^2J_{CP}$ = 15.3, PCH_2CH_2);[37] $^{31}P\{^1H\}$ −15.3 (s). IR (cm^{-1}, oil film): 3073, 2926, 2853, 1640, 1482, 1459, 1436, 911, 737, 695. MS:[38] 339 (**2d**, 100%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_4CH{=}CH_2$)$_2$ (3a).** A Schlenk flask was charged with [Pt(μ-Cl)(C_6F_5)($S(CH_2CH_2-)_2$)]$_2$ (0.200 g, 0.206 mmol),[14] **2a** (0.222 g, 0.823 mmol), and CH_2Cl_2 (12 mL). The mixture was stirred (16 h), and the solvent was removed by oil pump vacuum. The residue was chromatographed on neutral alumina (10 × 2.5 cm column) using CH_2Cl_2/hexanes (1:1 v/v). The solvent was removed from the product fraction by oil pump vacuum to yield **3a** as a colorless oil (0.205 g, 0.219 mmol, 54%). Anal. Calcd for $C_{42}H_{42}ClF_5P_2Pt$: C, 54.00; H, 4.53. Found: C, 53.66; H, 4.47. NMR (δ, $CDCl_3$): ^1H 7.55−7.52 (m, 8 H of 4Ph), 7.37−7.27 (m, 12 H of 4Ph), 5.86−5.80 (m, 2 H, $2CH{=}$), 5.08−4.98 (m, 4 H, 2 $={CH_2}$), 2.67−2.61 (m, 4 H, $2PCH_2$), 2.16−2.11 (m, 4 H, $2CH_2CH{=}$), 2.01−1.94 (m, 4 H, $2PCH_2CH_2$), 1.61−1.55 (m, 4 H, $2CH_2$); $^{13}C\{^1H\}$[39] 138.3 (s, $CH{=}$), 133.0 (virtual t,[40] J_{CP} = 5.8, *o*-Ph),[41] 130.7 (virtual t,[40] J_{CP} = 27.4, *i*-Ph),[41] 130.3 (s, *p*-Ph),[41] 128.0 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 114.1 (s, $={CH_2}$), 33.3 (s, $CH_2CH{=}$), 30.5 (virtual t,[40] J_{CP} = 7.7, $PCH_2CH_2CH_2$),[42] 25.8 (virtual t,[40] J_{CP} = 17.2, PCH_2),[42] 25.0 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$ 16.5 (s, $^1J_{PPt}$ = 2661).[43] IR (cm^{-1}, oil film): 3080, 3061, 2930, 2860, 1502, 1463, 1436, 1104, 1061, 957, 907, 807, 737, 691. MS:[38] 933 (**3a**$^+$, 5%), 898 ([**3a** − Cl]$^+$, 95%), 730 ([**3a** − Cl − C_6F_5]$^+$, 30%), 461 ([**3a** − Cl − C_6F_5 − Ph_2PR]$^+$, 40%), 268 (Ph_2PR^+, 100%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_6CH{=}CH_2$)$_2$ (3b).**[6c,12] Anal. Calcd for $C_{46}H_{50}ClF_5P_2Pt$ (colorless oil, 71−79%): C, 55.79; H, 5.09. Found: C, 55.87; H, 5.17. NMR (δ, $CDCl_3$): ^1H 7.50−7.46 (m, 8 H of 4Ph), 7.32−7.22 (m, 12 H of 4Ph), 5.84−5.74 (m, 2 H, $2CH{=}$), 5.01−4.90 (m, 4 H, 2 $={CH_2}$), 2.60−2.54 (m, 4 H, $2PCH_2$), 2.05−2.00 (m, 4 H, $2CH_2CH{=}$), 1.97−1.85 (m, 4 H, $2PCH_2CH_2$), 1.44−1.30 (m, 12 H, $6CH_2$); $^{13}C\{^1H\}$[39] 138.9 (s, $CH{=}$), 133.0 (virtual t,[40] J_{CP} = 5.5, *o*-Ph),[41] 130.8 (virtual t,[40] J_{CP} = 27.6, *i*-Ph),[41] 130.2 (s, *p*-Ph),[41] 128.0 (virtual t,[40] J_{CP} = 5.5, *m*-Ph),[41] 114.3 (s, $={CH_2}$), 33.8 (s, $CH_2CH{=}$), 31.3 (virtual t,[40] J_{CP} = 7.4, $PCH_2CH_2CH_2$),[42] 28.8, (s, double intensity, CH_2), 26.0 (virtual t,[40] J_{CP} = 16.5, PCH_2),[42] 25.6 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$ 16.6 (s, $^1J_{PPt}$ = 2659).[43] IR (cm^{-1}, oil film): 3080, 2930, 2856, 1502, 1463, 1436, 1104, 1061, 1000, 953, 911, 803, 741, 690. MS:[38] 989 (**3b**$^+$, 3%), 954 ([**3b** − Cl]$^+$, 30%), 785 ([**3b** − Cl − C_6F_5]$^+$, 20%), 489 ([Pt($Ph_2P(CH_2)_6CH{=}CH_2$)]$^+$, 80%), 297 ([$Ph_2P(CH_2)_6CH{=}CH_2$]$^+$, 100%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_8CH{=}CH_2$)$_2$ (3c).** A Schlenk flask was charged with [Pt(μ-Cl)(C_6F_5)($S(CH_2CH_2-)_2$)]$_2$ (0.304 g, 0.313 mmol),[14] **2c** (0.406 g, 1.252 mmol), and CH_2Cl_2 (16 mL). The mixture was stirred (11 h), and the solvent was removed by oil pump vacuum. The residue was chromatographed on neutral alumina (14 × 2.5 cm column) using CH_2Cl_2/hexanes (1:1 v/v). The solvent was removed from the product fraction by rotary evaporation and oil pump vacuum to yield **3c** as a colorless oil (0.425 g, 0.406 mmol, 65%), which solidified upon storage to a white powder. Anal. Calcd for $C_{50}H_{58}ClF_5P_2Pt$: C, 57.39; H, 5.59. Found: C, 57.42; H, 5.39. NMR (δ, $CDCl_3$): ^1H 7.54−7.51 (m, 8 H of 4Ph), 7.36−7.26 (m, 12 H of 4Ph), 5.87−5.80 (m, 2 H, $2CH{=}$), 5.05−4.97 (m, 4 H, 2 $={CH_2}$), 2.63−2.59 (m, 4 H, $2PCH_2$), 2.07−2.04 (m, 4 H, $2CH_2CH{=}$), 1.94−1.90 (m, 4 H, $2PCH_2CH_2$), 1.46−1.32 (m, 20 H, $10CH_2$); $^{13}C\{^1H\}$[39] 139.2 (s, $CH{=}$), 133.0 (virtual t,[40] J_{CP} = 5.8, *o*-Ph),[41] 130.9 (virtual t,[40] J_{CP} = 27.4, *i*-Ph),[41] 130.2 (s, *p*-Ph),[41] 127.9 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 114.1 (s, $={CH_2}$), 33.8 (s, $CH_2CH{=}$), 31.4 (virtual t,[40] J_{CP} = 7.5, $PCH_2CH_2CH_2$),[42] 29.3 (s, CH_2), 29.2 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 26.0 (virtual t,[40] J_{CP} = 17.4, PCH_2),[42] 25.6 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$ 17.3 (s, $^1J_{PPt}$ = 2659).[43] IR (cm^{-1}, powder film): 3076, 2934, 2856, 1498, 1459, 1436, 1104, 1058, 996, 953, 907, 803, 741, 695. MS:[38] 1046 (**3c**$^+$, 1%), 1010 ([**3c** − Cl]$^+$, 100%), 842 ([**3c** − Cl − C_6F_5]$^+$, 40%), 515 ([Pt($Ph_2P(CH_2)_6CH{=}CH_2$)]$^+$, 95%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_9CH{=}CH_2$)$_2$ (3d).** Complex [Pt(μ-Cl)(C_6F_5)($S(CH_2CH_2-)_2$)]$_2$ (0.147 g, 0.151 mmol),[14] **2d** (0.406 g, 1.252 mmol), and CH_2Cl_2 (8 mL) were combined in a procedure analogous to that for **3c**. An identical workup gave **3d** as a colorless oil (0.180 g, 0.168 mmol, 55%), which became a wax upon storage. Anal. Calcd for $C_{52}H_{62}ClF_5P_2Pt$: C, 58.13; H, 5.82. Found: C, 57.84; H, 5.40. NMR (δ, $CDCl_3$): ^1H 7.56−7.53 (m, 8 H of 4Ph), 7.36−7.27 (m, 12 H of 4Ph), 5.88−5.81 (m, 2 H, $2CH{=}$), 5.06−4.95 (m, 4 H, 2 $={CH_2}$), 2.66−2.60 (m, 4 H, $2PCH_2$), 2.10−2.05 (m, 4 H, $2CH_2CH{=}$), 1.95−1.92 (m, 4

(39) The C_6F_5 carbon resonances were not observed. These require larger numbers of transients due to the fluorine and platinum couplings.

(40) Pregosin, P. S.; Venanzi, L. M. *Chem. Brit.* **1978**, 276. The *apparent* coupling between adjacent peaks of the triplet is given.

(41) The $PtPC_6H_5$ ^{13}C NMR assignments have abundant precedent. See for example: Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 1981.

(42) Complexes with $PtPCH_2CH_2CH_2$ linkages exhibit characteristic ^{13}C NMR chemical shift and coupling constant patterns. For two compounds, **3b** in this work and a related species in ref 8a, the assignments were confirmed by ^1H,^{13}C COSY spectra. The requisite ^1H assignments were verified by ^1H,^1H COSY spectra.

(43) This coupling represents a satellite (d; ^{195}Pt = 33.8%) and is not reflected in the peak multiplicity given.

H, $2PCH_2CH_2$), 1.46−1.32 (m, 24 H, $12CH_2$); $^{13}C\{^1H\}$[39] 139.2 (s, *C*H═), 133.0 (virtual t,[40] J_{CP} = 5.8, *o*-Ph),[41] 130.9 (virtual t,[40] J_{CP} = 27.4, *i*-Ph),[41] 130.2 (s, *p*-Ph),[41] 127.9 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 114.1 (s, ═CH_2), 33.8 (s, CH_2CH═), 31.4 (virtual t,[40] J_{CP} = 7.5, $PCH_2CH_2CH_2$),[42] 29.4 (s, double intensity, $2CH_2$), 29.2 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 26.0 (virtual t,[40] J_{CP} = 17.0, PCH_2),[42] 25.6 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$ 17.3 (s, $^1J_{PPt}$ = 2659).[43] IR (cm^{-1}, powder film): 3076, 2926, 2853, 1502, 1463, 1436, 1104, 1058, 996, 957, 919, 803, 737, 691. MS:[38] 1073 (**3d**$^+$, 5%), 1038 ([**3d** − Cl]$^+$, 100%), 870 ([**3d** − Cl − C_6F_5]$^+$, 30%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_4CH$═$CH(CH_2)_4PPh_2$) (5a).** A two-necked flask was charged with **3a** (0.160 g, 0.171 mmol), Grubbs' catalyst **4** (ca. half of 0.007 g, 0.0086 mmol, 5 mol %), and CH_2Cl_2 (72 mL; the resulting solution is 0.0024 M in **3a**) and fitted with a condenser. The solution was refluxed. After 2.5 h, the remaining **4** was added. After 2.5 h, the solvent was removed by rotary evaporation and oil pump vacuum. $^{31}P\{^1H\}$ NMR of residue (δ, $CDCl_3$): 19.8 (s, $^1J_{PPt}$ = 2692,[43] 84%), 19.3 (s, 3%), 18.2 (s, 6%), 17.3 (s, 4%), 17.0 (s, 3%). Then CH_2Cl_2 was added, and the mixture was filtered through neutral alumina (5 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **5a** as a white powder (0.147 g, 0.162 mmol, 95%; *E*/*Z* 90:10). Anal. Calcd for $C_{40}H_{38}ClF_5P_2Pt$: C, 53.02; H, 4.23. Found: C, 52.92; H, 4.35. NMR (δ, $CDCl_3$): ^1H 8.05−8.03 (m, 4 H of 4Ph), 7.52−7.28 (m, 6 H of 4Ph), 7.13−6.92 (m, 10 H of 4Ph), 5.56−5.54/5.48−5.45 (m, 2 H, C*H*═C*H*, *E*/*Z* 90:10 (see text)), 2.80−2.74 (m, 4 H, $2CH_2$), 2.52−2.50 (m, 2 H, CH_2), 2.31−2.28 (m, 2 H, CH_2), 2.15−2.13, 2.05−2.03 (2 m, 4 H, $2CH_2$CH═, tentative), 1.73−1.46 (m, 4 H, $2CH_2$); $^{13}C\{^1H\}$[39] 134.7 (virtual t,[40] J_{CP} = 6.6, *o*-Ph),[41] 132.5 (virtual t,[40] J_{CP} = 26.5, *i*-Ph),[41] 131.5 (virtual t,[40] J_{CP} = 28.5, *i*-Ph′),[41] 131.0 (s, *p*-Ph),[41] 130.9 (s, *C*H═*C*H), 130.4 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 129.3 (s, *p*-Ph′),[41] 128.5 (virtual t,[40] J_{CP} = 5.6, *o*-Ph′),[41] 127.5 (virtual t,[40] J_{CP} = 4.6, *m*-Ph′),[41] 31.7 (s, CH_2CH═), 30.9 (virtual t,[40] J_{CP} = 8.6, $PCH_2CH_2CH_2$),[42] 27.0 (virtual t,[40] J_{CP} = 17.5, PCH_2),[42] 25.8 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$[44] 19.8 (s, $^1J_{PPt}$ = 2692,[43] 80%), 19.3 (s, 3%), 18.2 (s, $^1J_{PPt}$ = 2693,[43] 10%), 17.3 (s, 5%), 17.0 (s, 2%). IR (cm^{-1}, powder film): 2918, 2853, 1502, 1463, 1436, 1104, 1058, 957, 803, 737, 691. MS:[38] 905 (**5a**$^+$, < 5%), 870 ([**5a** − Cl]$^+$, 100%), 702 ([**5a** − Cl − C_6F_5]$^+$, 25%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_6CH$═$CH(CH_2)_6PPh_2$) (5b).**[6c,12] Anal. Calcd for $C_{44}H_{46}ClF_5P_2Pt$ (pale pink solid, 96%, *E*/*Z* 83:17, mp 193−195 °C): C, 54.92; H, 4.82. Found: C, 55.19; H, 5.00. NMR (δ): ^1H ($CDCl_3$) 7.46−7.40 (m, 8 H of 4Ph), 7.30−7.26 (m, 12 H of 4Ph), 5.38−5.27 (m, 2 H, C*H*═C*H*), 2.66−2.59 (m, 4 H, $2PCH_2$), 2.25 (m, 4 H, $2CH_2$CH═), 2.05 (m, 4 H, $2PCH_2CH_2$), 1.48−1.42 (m, 12 H, $6CH_2$) and (C_6D_6) 7.67−7.60 (m, 8 H of 4Ph), 7.03−6.99 (m, 12 H of 4Ph), 5.56−5.53/5.52−5.49 (2 m, C*H*═C*H*, *Z*/*E* 17:83 (see text)), 2.73−2.69 (m, 4 H, $2PCH_2$), 2.49 (m, 4 H, $2CH_2$CH═), 2.19−2.18 (m, 4 H, $2PCH_2CH_2$), 1.57−1.38 (m, 12 H, $6CH_2$); $^{13}C\{^1H\}$[39] ($CDCl_3$) 132.7 (virtual t,[40] J_{CP} = 5.5, *o*-Ph),[41] 131.8 (virtual t,[40] J_{CP} = 27.6, *i*-Ph),[41] 131.1 (s, *C*H═*C*H), 130.1 (s, *p*-Ph),[41] 128.0 (virtual t,[40] J_{CP} = 5.5, *m*-Ph),[41] 32.0 (s, CH_2CH═), 31.9 (virtual t,[40] J_{CP} = 9.2, $PCH_2CH_2CH_2$),[42] 28.9 (s, CH_2), 28.6 (s, CH_2), 27.2 (s, CH_2), 26.8 (virtual t,[40] J_{CP} = 16.6, PCH_2);[42] $^{31}P\{^1H\}$[44] ($CDCl_3$) 17.3 (s, $^1J_{PPt}$ = 2679,[43] 88%), 16.3 (s, $^1J_{PPt}$ = 2685,[43] 12%). IR (cm^{-1}, powder film): 3057, 2926, 2853, 1502, 1459, 1436, 1104, 1058, 957, 803, 737, 690. MS:[38] 961 (**5b**$^+$, 3%), 926 ([**5b** − Cl]$^+$, 55%), 757 ([**5b** − Cl − C_6F_5]$^+$, 20%), 566 ([**5b** − Cl − C_6F_5 − Pt]$^+$, 35%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_8CH$═$CH(CH_2)_8PPh_2$) (5c).** A two-necked flask was charged with **3c** (0.150 g, 0.143 mmol), **4** (ca. half of 0.006 g, 0.0073 mmol, 5 mol %), and CH_2Cl_2 (60 mL, the resulting solution is 0.0024 M in **3c**) and fitted with a condenser. The solution was refluxed. After 2 h, the remaining **4** was added. After 2 h, the solvent was removed by rotary evaporation and oil pump vacuum. $^{31}P\{^1H\}$ NMR of residue (δ, $CDCl_3$): 17.8 (s, 4%) 17.2 (s, $^1J_{PPt}$ = 2678,[43] 67%), 16.8 (s, $^1J_{PPt}$ = 2679,[43] 14%), 16.7 (s, 4%), 16.5 (s, $^1J_{PPt}$ = 2658,[43] 11%). Then CH_2Cl_2 was added, and the mixture was filtered through neutral alumina (5 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **5c** as a pale pink solid (0.131 g, 0.129 mmol, 90%; *E*/*Z* ca. 80:20). Anal. Calcd for $C_{48}H_{50}ClF_5P_2Pt$: C, 56.84; H, 4.97. Found: C, 56.96; H, 5.10. NMR (δ): ^1H ($CDCl_3$) 7.51−7.49 (m, 8 H of 4Ph), 7.33−7.24 (m, 12 H of 4Ph), 5.41−5.31 (m, 2 H, C*H*═C*H*), 2.70−2.65 (m, 4 H, $2PCH_2$), 2.29−2.26 (m, 4 H, $2CH_2CH$═), 2.06−2.05 (m, 4 H, $2PCH_2CH_2$), 1.57−1.53 (m, 4 H, $2PCH_2CH_2CH_2$), 1.46−1.28 (m, 16 H, $8CH_2$) and (C_6D_6) 7.63−7.54 (m, 8 H of 4Ph), 6.96−6.91 (m, 12 H of 4Ph), 5.52−5.47/5.43−5.38 (2 m, C*H*═C*H*, *Z*/*E* ca. 20:80 (see text)), 2.67−2.58 (m, 4 H, $2PCH_2$), 2.41 (m, 4 H, $2CH_2CH$═), 2.14−2.10 (m, 4 H, $2PCH_2CH_2$), 1.45−1.25 (m, 20 H, $10CH_2$); $^{13}C\{^1H\}$[39] ($CDCl_3$) 132.7 (virtual t,[40] J_{CP} = 5.8, *o*-Ph),[41] 131.7 (virtual t,[40] J_{CP} = 27.2, *i*-Ph),[41] 131.0 (s, *C*H═*C*H), 130.1 (s, *p*-Ph),[41] 128.0 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 32.1 (s, CH_2CH═), 31.9 (virtual t,[40] J_{CP} = 8.0, $PCH_2CH_2CH_2$),[42] 30.1 (s, CH_2), 29.7 (s, CH_2), 28.9 (s, CH_2), 28.4 (s, CH_2), 26.9 (s, CH_2), 26.7 (virtual t,[40] J_{CP} = 17.6, PCH_2);[42] $^{31}P\{^1H\}$[44] ($CDCl_3$) 17.8 (s, 4%) 17.2 (s, $^1J_{PPt}$ = 2678,[43] 67%), 16.8 (s, $^1J_{PPt}$ = 2679,[43] 14%), 16.7 (s, 4%), 16.5 (s, $^1J_{PPt}$ = 2658,[43] 11%). IR (cm^{-1}, powder film): 2926, 2853, 1502, 1463, 1436, 1104, 1058, 957, 803, 737, 695. MS:[38] 1017 (**5c**$^+$, 3%), 982 ([**5c** − Cl]$^+$, 100%), 813 ([**5c** − Cl − C_6F_5]$^+$, 45%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_9CH$═$CH(CH_2)_9PPh_2$) (5d).** A two-necked flask was charged with CH_2Cl_2 (66 mL), Grubbs' catalyst **4** (ca. half of 0.009 g, 0.011 mmol, 7 mol %), and **3d** (0.170 g, 0.158 mmol) and fitted with a condenser. The solution was refluxed. After 2 h, the remaining **4** was added. After 2 h, the solvent was removed by rotary evaporation and oil pump vacuum. $^{31}P\{^1H\}$ NMR of residue (δ, $CDCl_3$): 17.6 (s, $^1J_{PPt}$ = 2675,[43] 26%), 17.53 (s, < 2%), 17.5 (s, 10%), 17.4 (s, $^1J_{PPt}$ = 2670,[43] 48%), 17.2 (s, 16%). Then CH_2Cl_2 was added, and the mixture was filtered through neutral alumina (5 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **5d** as a pale pink solid (0.140 g, 0.134 mmol, 85%). Anal. Calcd for $C_{50}H_{58}ClF_5P_2Pt$: C, 57.39; H, 5.59. Found: C, 55.62; H, 5.73.[45] NMR (δ, $CDCl_3$): ^1H 7.48−7.45 (m, 8 H of 4Ph), 7.25−7.21 (m, 12 H of 4Ph), 5.38−5.27 (m, 2 H, C*H*═C*H*), 2.63−2.56 (m, 4 H, $2PCH_2$), 2.20−2.15 (m, ca. 1.3 H of 2 PCH_2CH_2), 2.07−1.99 (m, ca. 2.7 H of PCH_2CH_2 + 4 H of $2CH_2CH$═), 1.49−1.28 (m, 24 H, $12CH_2$); $^{13}C\{^1H\}$[39] 132.8 (virtual t,[40] J_{CP} = 5.8, *o*-Ph),[41] 132.7 (virtual t,[40] J_{CP} = 5.8, *o*-Ph),[41] 131.5 (virtual t,[40] J_{CP} = 27.2, *i*-Ph),[41] 130.7 (s, *C*H═*C*H), 130.2 (br s, *p*-Ph),[41] 128.0 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 31.9 (s, CH_2CH═), 31.5 (virtual t,[40] J_{CP} = 7.4, $PCH_2CH_2CH_2$),[42] 29.22 (s, CH_2), 29.16 (s, CH_2), 28.8 (s, double intensity, $2CH_2$), 27.9 (br s, CH_2), 26.5 (br s, CH_2), 25.7 (s, CH_2); $^{31}P\{^1H\}$[44] 17.6 (s, $^1J_{PPt}$ = 2675,[43] 29%), 17.53 (s, < 2%), 17.5 (s, 8%), 17.4 (s, $^1J_{PPt}$ = 2670,[43] 54%), 17.2 (s, 8%). IR (cm^{-1}, powder film): 2964, 2922, 2853, 1502, 1459, 1436, 1262, 1100, 1058, 1019, 953, 799, 737, 691. MS:[38] 1046 (**5d**$^+$, < 5%), 1011 ([**5d** − Cl]$^+$, 100%), 842 ([**5d** − Cl − C_6F_5]$^+$, 25%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_{10}PPh_2$) (6a).** A Schlenk flask was charged with **5a** (0.131 g, 0.145 mmol), 10% Pd/C (0.015 g, 0.015 mmol Pd), $ClCH_2CH_2Cl$ (7.5 mL), and ethanol (7.5 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 100 h. The solvent was removed by rotary evaporation and oil pump vacuum. Then CH_2Cl_2 was added, and the mixture filtered through neutral alumina (5 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was

(44) The additional signals were tentatively assigned to dimeric or oligomeric products derived from intermolecular alkene metathesis.

(45) A correct microanalysis could not be obtained for this compound.

removed by rotary evaporation and oil pump vacuum to give crude **6a** as a white powder (0.114 g, 0.126 mmol, 87%). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 20.5 (s, 9%), 18.7 (s, $^1J_{PPt}$ = 2693,[43] 87%), 16.5 (s, 4%). The sample was chromatographed on neutral alumina (8 × 2.5 cm column; eluted with 1:1 v/v CH_2Cl_2/hexanes) to give **6a** as a white powder (0.092 g, 0.101 mmol, 70%), mp 236−238 °C (capillary), 249 °C (DSC; $T_i/T_e/T_p/T_c/T_f$ 226.6/249.5/252.4/253.9/260.2 °C). TGA: onset of mass loss, 321.7 °C (T_e). Anal. Calcd for $C_{40}H_{40}ClF_5P_2Pt$: C, 52.90; H, 4.44. Found: C, 52.85; H, 4.58. NMR (δ): ^1H ($CDCl_3$) 8.06−8.05 (m, 4 H of 4Ph), 7.52−7.51 (m, 6 H of 4Ph), 7.14−6.91 (m, 10 H of 4Ph), 2.91−2.72 (m, 4 H, 2PC*H*H′C*H*H′),[46] 2.62−2.51 (m, 2 H, 2PCH*H*′),[46] 2.09 (m, 2 H, 2PCHH′C*H*H′),[46] 1.66−1.50 (m, 6 H, 2PCHH′CHH′C*HH*′C*H*H′),[46] 1.36−1.32 (m, 6 H, 2PCHH′CHH′CHH′CH*H*′C*HH*′)[46] and (toluene-d_8) 8.03−8.00 (m, 4 H of 4Ph), 7.15−7.05 (m, 8 H of 4Ph), 6.97−6.80 (m, 4 H of 4Ph), 6.70−6.61 (m, 4 H of 4Ph), 2.74−2.68 (m, 4 H, 2PC*H*H′H*H*′),[46] 2.25−2.19 (m, 2 H, 2PCH*H*′),[46] 2.06−2.03 (m, 2 H, 2PCHH′CH*H*′),[46] 1.57−1.43 (m, 12 H, 6CH_2); $^{13}C\{^1H\}$[39] ($CDCl_3$) 134.8 (virtual t,[40] J_{CP} = 6.6, *o*-Ph),[41] 132.4 (virtual t,[40] J_{CP} = 26.1, *i*-Ph),[41] 131.9 (virtual t,[40] J_{CP} = 27.0, *i*-Ph′),[41] 131.0 (s, *p*-Ph),[41] 130.4 (virtual t,[40] J_{CP} = 4.9, *m*-Ph),[41] 129.2 (s, *p*-Ph′),[41] 128.5 (virtual t,[40] J_{CP} = 5.5, *o*-Ph′),[41] 127.4 (virtual t,[40] J_{CP} = 4.6, *m*-Ph′),[41] 29.2 (virtual t,[40] J_{CP} = 8.3, $PCH_2CH_2CH_2$),[46] 27.1 (s, $PCH_2CH_2CH_2CH_2$), 26.7 (virtual t,[40] J_{CP} = 17.2, PCH_2),[46] 24.9 (s, double intensity, PCH_2CH_2 + $PCH_2CH_2CH_2CH_2CH_2$) and (toluene-d_8) 135.3 (virtual t,[40] J_{CP} = 6.7, *o*-Ph),[41] 133.1 (s, *i*-Ph),[41] 131.9 (virtual t,[40] J_{CP} = 27.0, *i*-Ph′),[41] 131.0 (s, *p*-Ph),[41] 130.8 (virtual t,[40] J_{CP} = 4.8, *m*-Ph),[41] 129.4 (s, *p*-Ph′),[41] 29.5 (virtual t,[40] J_{CP} = 8.1, $PCH_2CH_2CH_2$),[46] 27.5 (s, $PCH_2CH_2CH_2CH_2CH_2$), 27.2 (s, PCH_2), 25.4 (s, $PCH_2CH_2CH_2CH_2CH_2$); 25.2 (br s, $PCH_2CH_2CH_2$); $^{31}P\{^1H\}$ ($CDCl_3$) 18.9 (s, $^1J_{PPt}$ = 2694).[43] IR (cm^{-1}, powder film): 2934, 2860, 1502, 1463, 1436, 1104, 1058, 957, 803, 737, 691. MS:[38] 908 (**6a**$^+$, 20%), 872 ([**6a** − Cl]$^+$, 100%), 704 ([**6a** − Cl − C_6F_5]$^+$, 60%).

***trans*-(Cl)(C_6F_5)Pt(P$Ph_2(CH_2)_{14}$PPh_2) (6b).**[6c,12] Anal. Calcd for $C_{44}H_{48}ClF_5P_2Pt$ (white powder, 94%): C, 54.80; H, 5.02. Found: C, 54.91; H, 5.23. A chromatographic workup (Supporting Information) gave a sample (72%) that lacked the ^{31}P NMR impurity below, mp 162−164 °C (capillary), 170 °C (DSC; $T_i/T_e/T_p/T_c/T_f$ 150.0/169.6/172.2/174.0/190.4 °C). TGA: onset of mass loss, 317.0 °C (T_e). NMR (δ): ^1H ($CDCl_3$) 7.47−7.42 (m, 8 H of 4Ph), 7.31−7.27 (m, 12 H of 4Ph), 2.67−2.61 (m, 4 H, 2PCH_2), 2.13−2.10 (m, 4 H, 2PCH_2CH_2), 1.50−1.23 (m, 20 H, 10CH_2) and (THF-d_8) 7.59−7.55 (m, 8 H of 4Ph), 7.36−7.25 (m, 12 H of 4Ph), 2.78−2.72 (m, 4 H, 2PCH_2), 2.24−2.22 (m, 4 H, 2PCH_2CH_2), 1.59−1.33 (m, 20 H, 10CH_2); $^{13}C\{^1H\}$[39] ($CDCl_3$) 133.8 (virtual t,[40] J_{CP} = 5.4, *m*-Ph),[41] 131.4 (virtual t,[40] J_{CP} = 27.5, *i*-Ph),[41] 130.1 (s, *p*-Ph),[41] 127.9 (virtual t,[40] J_{CP} = 5.3, *m*-Ph),[41] 31.0 (virtual t,[40] J_{CP} = 7.6, $PCH_2CH_2CH_2$),[42] 27.7 (s, CH_2), 27.6 (s, CH_2), 27.2 (s, CH_2), 26.5 (s, CH_2), 26.2 (virtual t,[40] J_{CP} = 16.9, PCH_2),[42] 25.7 (s, PCH_2CH_2)[42] and (THF-d_8) 132.8 (virtual t,[40] J_{CP} = 5.7, *m*-Ph),[41] 132.7 (virtual t,[40] J_{CP} = 27.1, *i*-Ph),[41] 130.8 (s, *p*-Ph), 128.5 (virtual t,[40] J_{CP} = 5.0, *m*-Ph),[41] 31.8 (virtual t,[40] J_{CP} = 8.2, $PCH_2CH_2CH_2$),[42] 28.4 (s, double intensity, CH_2), 28.1 (s, CH_2), 27.3 (s, CH_2), 26.9 (virtual t,[40] J_{CP} = 18.0, PCH_2),[42] 26.6 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$ ($CDCl_3$) 17.1 (s, $^1J_{PPt}$ = 2670,[43] 94%), 16.7 (s, $^1J_{PPt}$ = 2663,[43] 6%).[44] IR (cm^{-1}, powder film): 3057, 2926, 2856, 1502, 1459, 1436, 1104, 1061, 957, 803, 741, 691. MS:[38] 964 ([**6b**]$^+$, 14%), 928 ([**6b** − Cl]$^+$, 100), 760 (50) ([**6b** − Cl − C_6F_5]$^+$, 50), 565 ([$Ph_2P(CH_2)_{14}PPh_2$]$^+$, 16%).

***trans*-(Cl)(C_6F_5)Pt(P$Ph_2(CH_2)_{18}$PPh_2) (6c).** A Schlenk flask was charged with **5c** (0.216 g, 0.212 mmol), 10% Pd/C (0.023 g, 0.022 mmol Pd), $ClCH_2CH_2Cl$ (12 mL), and ethanol (12 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 100 h. The solvent was removed by rotary evaporation and oil pump vacuum. Then CH_2Cl_2 was added, and the mixture filtered through neutral alumina (3 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was removed by rotary evaporation and oil pump vacuum to give crude **6c** as a white powder (0.190 g, 0.186 mmol, 88%). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 17.6 (s, 81%), 17.4 (s, 9%), 17.3 (s, 10%). The sample was chromatographed on neutral alumina (10 × 2.5 cm column) using CH_2Cl_2/hexanes (1:1 v/v). The solvent was removed from the product-containing fraction by rotary evaporation and oil pump vacuum to give **6c** as a white powder (0.127 g, 0.124 mmol, 59%), mp 196−198 °C (capillary), 200 °C (DSC; $T_i/T_e/T_p/T_c/T_f$ 178.6/200.2/202.7/204.0/220.6 °C). TGA: onset of mass loss, 322.0 °C (T_e). Anal. Calcd for $C_{48}H_{56}ClF_5P_2Pt$: C, 56.50; H, 5.53. Found: C, 56.29; H, 5.53. NMR (δ, $CDCl_3$): ^1H 7.52−7.49 (m, 8 H of 4Ph), 7.34−7.25 (m, 12 H of 4Ph), 2.68−2.63 (m, 4 H, 2PCH_2), 2.13−2.09 (m, 4 H, 2PCH_2CH_2), 1.55−1.49 (m, 4 H, 2P$CH_2CH_2CH_2$), 1.46−1.28 (m, 24 H, 12CH_2); $^{13}C\{^1H\}$[39] 132.8 (virtual t,[40] J_{CP} = 5.5, *o*-Ph),[41] 131.2 (virtual t,[40] J_{CP} = 27.4, *i*-Ph),[41] 130.1 (s, *p*-Ph),[41] 127.9 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 31.2 (virtual t,[40] J_{CP} = 7.8, $PCH_2CH_2CH_2$),[42] 28.72 (s, CH_2), 28.68 (s, CH_2), 28.3 (s, CH_2), 27.87 (s, CH_2), 27.84 (s, CH_2), 27.3 (s, CH_2), 26.1 (virtual t,[40] J_{CP} = 11.5, PCH_2),[42] 25.8 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$ 17.6 (s, $^1J_{PPt}$ = 2679).[43] IR (cm^{-1}, powder film): 3061, 2926, 2856, 1502, 1459, 1436, 1262, 1104, 1058, 1027, 957, 803, 737, 691. MS:[38] 1020 (**6c**$^+$, 20%), 984 ([**6c** − Cl]$^+$, 100%), 816 ([**6c** − Cl − C_6F_5]$^+$, 45%).

***trans*-(Cl)(C_6F_5)Pt(P$Ph_2(CH_2)_{20}$PPh_2) (6d).** A Schlenk flask was charged with **5d** (0.125 g, 0.119 mmol), 10% Pd/C (0.013 g, 0.011 mmol Pd), $ClCH_2CH_2Cl$ (6 mL), and ethanol (6 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 74 h. The solvent was removed by rotary evaporation and oil pump vacuum. Then CH_2Cl_2 was added, and the mixture filtered through neutral alumina (4 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was removed by rotary evaporation and oil pump vacuum to give crude **6d** as a white powder (0.095 g, 0.0906 mmol, 76%). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 16.8 (s, 8%), 16.6 (s, 86%), 16.5 (s, 6%). The sample was chromatographed on neutral alumina (7 × 2.5 cm column) using CH_2Cl_2/hexanes (1:1 v/v). The solvent was removed from the product-containing fraction by rotary evaporation and oil pump vacuum to give **6d** as a white powder (0.062 g, 0.0591 mmol, 50%), mp 122−124 °C (capillary), 139 °C (DSC, $T_i/T_e/T_p/T_c/T_f$ 137.7/138.9/143.9/146.0/147.8 °C). TGA: onset of mass loss, 321.7 °C (T_e). Anal. Calcd for $C_{50}H_{60}ClF_5P_2Pt$: C, 57.28; H, 5.77. Found: C, 57.09; H, 5.72. NMR (δ, $CDCl_3$): ^1H 7.51−7.45 (m, 8 H of 4Ph), 7.35−6.78 (m, 12 H of 4Ph), 2.68−2.62 (m, 4 H, 2PCH_2), 2.07−2.05 (m, 4 H, 2PCH_2CH_2), 1.55−1.29 (m, 32 H, 16CH_2); $^{13}C\{^1H\}$[39] 132.9 (virtual t,[40] J_{CP} = 5.7, *o*-Ph),[41] 131.3 (virtual t,[40] J_{CP} = 27.1, *i*-Ph),[41] 130.2 (s, *p*-Ph),[41] 127.9 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 31.4 (virtual t,[40] J_{CP} = 7.7, $PCH_2CH_2CH_2$),[42] 29.1 (s, CH_2), 29.0 (s, CH_2), 28.8 (s, CH_2), 28.5 (s, CH_2), 28.3 (s, CH_2), 27.9 (s, CH_2), 27.7 (s, CH_2), 26.2 (virtual t,[40] J_{CP} = 17.7, PCH_2),[42] 25.8 (s, PCH_2CH_2);[42] $^{31}P\{^1H\}$ 16.6 (s, $^1J_{PPt}$ = 2667).[43] IR (cm^{-1}, powder film): 2926, 2853, 1502, 1463, 1436, 1104, 1058, 957, 803, 737, 691. MS:[38] 1047 (**6d**$^+$, 10%), 1012 ([**6d** − Cl]$^+$, 100%), 843 ([**6d** − Cl − C_6F_5]$^+$, 80%).

Br(CH_2)$_2$C(CH_3)$_2$(CH_2)$_3$CH=CH_2 (1e). The dibromide Br(CH_2)$_2$C(CH_3)$_2$(CH_2)$_2$Br (6.45 g, 25.0 mmol)[21] was added to a THF solution of Li_2CuCl_4 (0.10 M, 49.8 mL; see General Data). The deep orange solution was cooled to 0 °C. Then $BrMgCH_2CH{=}CH_2$ (1 M in ether; 50 mL, 50 mmol) was added dropwise over 30 min with stirring. The mixture became deep green, then colorless, and finally black. After an additional hour, aqueous acetic acid (20 mL, 20%) was added. The sample was extracted with ether (3 × 70 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). The filtrate was cooled in ice while the solvent was removed

(46) The aliphatic ^1H NMR and ^{13}C NMR signals were assigned from a ^1H,^{13}C COSY spectrum.

by rotary evaporation. The oil was distilled (18 mbar, 40 °C) to give **1e** a colorless liquid (2.20 g, 10.0 mmol, 40%). NMR (δ, $CDCl_3$): ^{1}H 5.86−5.75 (m, 1 H, C*H*═), 4.99−4.92 (m, 2 H, ═CH_2), 3.38−3.34 (m, 2 H, BrCH_2), 2.08−1.98 (m, 2 H, CH_2-CH═), 1.88−1.81 (m, 2 H, $BrCH_2CH_2$), 1.33−1.27 (m, 2 H, CH_2), 1.21−1.15 (m, 2 H, CH_2), 0.88 (s, 6 H, 2CH_3); ^{13}C{^{1}H} 138.8 (s, *C*H═), 114.5 (s, ═*C*H_2), 45.5 (s, $BrCH_2CH_2$), 41.2 (s, $C(CH_3)_3CH_2CH_2CH_2$), 34.7 (s, *C*H_2CH═), 29.5 (s, $C(CH_3)_2$-$CH_2CH_2CH_2$), 27.2 (s, BrCH_2), 26.9 (s, double intensity, $C(CH_3)_2$), 23.3 (s, *C*$(CH_3)_2$). IR (cm^{-1}, $CDCl_3$): 3078, 2960, 2935, 2867, 1639, 1388, 1368, 651. MS:[38] 219 (**1e**$^+$, 100%).

$PPh_2(CH_2)_2C(CH_3)_2(CH_2)_3CH═CH_2$ (2e). A. A Schlenk flask was charged with **1e** (1.61 g, 7.34 mmol) and THF (10 mL) and cooled to 0 °C. Then $KPPh_2$ (0.5 M in THF, 14.7 mL, 7.34 mmol) was added dropwise with stirring over 0.5 h.[35] A white precipitate formed. After 1 h, the solvent was removed by oil pump vacuum. Then hexane was added, and mixture was filtered through neutral alumina (2.5 × 2.5 cm column; rinsed with hexanes). The solvent was removed by rotary evaporation. Distillation (9 × 10^{-3} mbar, 145 °C) gave **2e** as a colorless oil (0.977 g, 3.0 mmol, 41%). Anal. Calcd for $C_{22}H_{29}P$: C, 81.44; H, 9.01. Found: C, 81.48; H, 9.09. **B.** An otherwise identical reaction of **1e** (1.473 g, 6.723 mmol) and $KPPh_2$ (0.5 M in THF, 13.4 mL, 6.7 mmol) in which the alumina column was replaced by a simple filtration gave **2e** in 62% yield (1.350 g, 4.161 mmol). NMR (δ, $CDCl_3$): ^{1}H 7.46−7.38 (m, 4 H of 2Ph), 7.34−7.29 (m, 6 H of 2Ph), 5.82−5.71 (m, 1 H, C*H*═), 5.02−4.90 (m, 2 H, ═CH_2), 2.03−1.94 (m, 4 H, PCH_2 + CH_2CH═), 1.34−1.15 (m, 6 H, 3CH_2), 0.83 (s, 6 H, 2CH_3); ^{13}C{^{1}H} 139.2 (s, *C*H═), 138.9 (d, $^1J_{CP}$ = 13.0, *i*-Ph),[36] 132.7 (d, $^2J_{CP}$ = 18.2, *o*-Ph),[36] 128.5 (s, *p*-Ph),[36] 128.4 (d, $^3J_{CP}$ = 6.5, *m*-Ph),[36] 114.3 (s, ═*C*H_2), 40.9 (s, *C*$H_2CH_2CH_2CH$═), 37.7 (d, J_{CP} = 16.8, *C*H_2), 34.6 (s, *C*H_2CH═), 33.3 (d, J_{CP} = 13.1, *C*H_2), 26.9 (s, double intensity, $C(CH_3)_2$), 23.3 (s, *C*H_2-CH_2CH═); 22.5 (d, $^3J_{CP}$ = 10.5, *C*$(CH_3)_2$);[47] ^{31}P{^{1}H} −13.6 (s). IR (cm^{-1}, $CDCl_3$): 3074, 2958, 2936, 2867, 1434, 1386, 1365. MS:[38] 325 (**2e**$^+$, 100%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_2C(CH_3)_2(CH_2)_3CH═CH_2$)$_2$ (3e).** A Schlenk flask was charged with [Pt(μ-Cl)-(C_6F_5)(S(CH_2CH_2−)$_2$)]$_2$ (0.243 g, 0.251 mmol),[14] **2e** (0.325 g, 1.002 mmol), and CH_2Cl_2 (13 mL). The mixture was stirred (16 h), and the solvent was removed by oil pump vacuum. The residue was chromatographed on alumina (11 × 2.5 cm column) using CH_2Cl_2/hexanes (1:2 v/v). The solvent was removed from the product fraction to yield **3e** as a colorless oil (0.330 g, 0.315 mmol, 63%), which solidified after several days. Anal. Calcd for $C_{50}H_{58}ClF_5P_2Pt$: C, 57.39; H, 5.59. Found: C, 57.25; H, 5.31. NMR (δ, $CDCl_3$): ^{1}H 7.50−7.46 (m, 8 H of 4Ph), 7.33−7.22 (m, 12 H of 4Ph), 5.83−5.73 (m, 2 H, 2C*H*═), 5.00−4.91 (m, 4 H, 2 ═CH_2), 2.55−2.52 (m, 4 H, 2PCH_2), 2.01−1.98 (m, 4 H, 2CH_2CH═), 1.92−1.90 (m, 4 H, 2PCH_2CH_2), 1.52−1.41 (m, 4 H, 2CH_2), 1.33−1.21 (m, 4 H, 2CH_2), 0.90 (s, 12 H, 4CH_3); ^{13}C{^{1}H}[39] 138.9 (s, *C*H═), 132.8 (virtual t,[40] J_{CP} = 6.0 Hz, *o*-Ph),[41] 131.1 (virtual t,[40] J_{CP} = 26.7 Hz, *i*-Ph),[41] 130.1 (s, *p*-Ph),[41] 127.8 (virtual t,[40] J_{CP} = 5.1 Hz, *m*-Ph),[41] 114.3 (s, ═*C*H_2), 41.1 (s, *C*H_2), 37.4 (s, *C*H_2), 34.6 (s, *C*H_2CH═), 33.7 (virtual t,[40] J_{CP} = 7 Hz, *C*H_2), 26.8 (s, double intensity, $C(CH_3)_2$), 23.4 (s, *C*H_2CH_2CH═), 21.3 (br s, *C*$(CH_3)_2$);[47] ^{31}P{^{1}H} 18.0 (s, $^1J_{PPt}$ = 2427 Hz).[43] IR (cm^{-1}, powder film): 2961, 2934, 2864, 1502, 1463, 1436, 1104, 1058, 957, 911, 807, 737, 691 cm^{-1}. MS:[38] 1046 (**3e**$^+$, 3%), 1010 ([**3e** − Cl]$^+$, 100%), 842 ([**3e** − Cl − C_6F_5]$^+$, 20%), 517 ([**3e** − Cl − C_6F_5 − PR_3]$^+$, 30%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_2C(CH_3)_2(CH_2)_3CH═CH(CH_2)_3C(CH_3)_2(CH_2)_2PPh_2$) (5e).** A two-necked flask was charged with **4** (ca. half of 0.009 g, 0.011 mmol, 10 mol %), **3e** (0.120 g, 0.115 mmol), and CH_2Cl_2 (46 mL, the resulting solution is 0.0025 M in **3e**) and fitted with a condenser. The solution was refluxed. After 2 h, the remaining **4** was added. After 3 h, the solvent was removed by rotary evaporation. ^{31}P{^{1}H} NMR of residue (δ, $CDCl_3$): 18.3 (s, $^1J_{PPt}$ = 2673,[43] 91%), 17.3 (s, 9%). Then CH_2Cl_2 was added, and the residue was filtered through neutral alumina (5 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **5e** as a pale pink solid (0.091 g, 0.0893 mmol, 78%; *E*/*Z* 88:12). Anal. Calcd for $C_{48}H_{54}ClF_5P_2Pt$: C, 56.61; H, 5.34. Found: C, 56.59; H, 5.47. NMR (δ, $CDCl_3$): ^{1}H 7.52−7.49 (m, 8 H of 4Ph), 7.34−7.19 (m, 12 H of 4Ph), 5.50−5.47/5.43−5.40 (m, 2 H, C*H*═C*H*, *E*/*Z* 88:12 (see text)), 2.69−2.65 (m, 4 H, 2PCH_2), 2.02−2.01 (m, 4 H, 2CH_2CH═), 1.95−1.91 (m, 4 H, 2PCH_2CH_2), 1.42−1.28 (m, 8 H, 4CH_2), 0.94 (s, 12 H, 4CH_3); ^{13}C{^{1}H}[39] 132.9 (virtual t,[40] J_{CP} = 6.8, *o*-Ph),[41] 131.2 (virtual t,[40] J_{CP} = 27.6, *i*-Ph),[41] 131.0 (s, *C*H═*C*H), 130.1 (s, *p*-Ph),[41] 127.9 (virtual t,[40] J_{CP} = 5.1, *m*-Ph),[41] 40.5 (s, *C*H_2), 36.7 (s, *C*H_2), 33.7 (virtual t,[40] J_{CP} = 7.1, *C*H_2), 32.7 (s, *C*H_2CH═), 27.0 (s, double intensity, $C(CH_3)_2$), 23.6 (s, *C*H_2), 20.8 (br s, *C*$(CH_3)_2$);[47] ^{31}P{^{1}H}[44] 18.3 (s, $^1J_{PPt}$ = 2671,[43] 91%), 17.3 (s, 9%). IR (cm^{-1}, powder film): 2922, 2845, 1502, 1463, 1436, 1100, 1058, 957, 807, 726, 691. MS:[38] 1018 (**5e**$^+$, <2%), 982 ([**5e** − Cl]$^+$, 100%), 813 ([**5e** − Cl − C_6F_5]$^+$, 80%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_2C(CH_3)_2(CH_2)_8C(CH_3)_2(CH_2)_2PPh_2$) (6e).** A Schlenk flask was charged with **5e** (0.076 g, 0.0746 mmol), 10% Pd/C (0.008 g, 0.008 mmol Pd), $ClCH_2CH_2Cl$ (4.5 mL), and ethanol (4.5 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 48 h. The solvent was removed by rotary evaporation. Then CH_2Cl_2 was added, and the mixture filtered through neutral alumina (3 × 2.5 cm column; rinsed with CH_2Cl_2). The solvent was removed by rotary evaporation and oil pump vacuum to give the crude **6e** as a white powder (0.050 g, 0.0489 mmol, 66%). The sample was chromatographed on neutral alumina (9 × 2.5 cm column) using CH_2Cl_2/hexanes (1:1 v/v). The solvent was removed from the product-containing fraction by rotary evaporation and oil pump vacuum to give **6e** as a white powder (0.041 g, 0.0402 mmol, 54%), mp 175−177 °C (capillary). Anal. Calcd for $C_{48}H_{56}ClF_5P_2Pt$: C, 56.50; H, 5.53. Found: C, 56.59; H, 5.69. NMR (δ, $CDCl_3$): ^{1}H 7.53−7.50 (m, 8 H of 4Ph), 7.36−7.26 (m, 12 H of 4Ph), 2.70−2.65 (m, 4 H, 2PCH_2), 1.86−1.82 (m, 4 H, 2PCH_2CH_2), 1.34−1.29 (m, 16 H, 8CH_2), 0.93 (s, 12 H, 4CH_3); ^{13}C{^{1}H}[39] 133.1 (virtual t,[40] J_{CP} = 5.9, *o*-Ph),[41] 130.7 (virtual t,[40] J_{CP} = 27.1, *i*-Ph),[41] 130.2 (s, *p*-Ph),[41] 127.9 (virtual t,[40] J_{CP} = 5.0, *m*-Ph),[41] 40.2 (s, *C*H_2), 35.1 (s, *C*H_2), 33.6 (virtual t,[40] J_{CP} = 6.6, *C*H_2), 29.4 (s, *C*H_2), 28.0 (s, *C*H_2), 27.8 (s, double intensity, $C(CH_3)_2$), 22.7 (s, *C*H_2), 20.6 (virtual t,[40] J_{CP} = 17.6, *C*$(CH_3)_2$);[47] ^{31}P{^{1}H}[44] 17.5 (s, 11%), 16.4 (s, $^1J_{PPt}$ = 2671,[43] 89%). IR (cm^{-1}, powder film): 2930, 2853, 1502, 1463, 1436, 1104, 1061, 957, 803, 737, 691. MS:[38] 1019 (**6e**$^+$, 10%), 984 ([**6e** − Cl]$^+$, 100%), 816 ([**6e** − Cl − C_6F_5]$^+$, 80%).

Crystallography. Toluene solutions of **6a**,**c**,**d** were layered with ethanol and kept at −18 °C (3 days to one month). The resulting colorless prisms were taken directly to a Nonius Kappa CCD diffractometer for data collection as outlined in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with 16 830, 10 708, and 11 638 reflections, respectively. Lorentz, polarization, and absorption corrections were applied.[48] The space groups were determined from systematic absences and subsequent least-squares refinement. The structures were solved by direct methods. The parameters were refined with all data by full-matrix least-squares on F^2 using SHELXL-97.[49] Non-hydrogen atoms were

(47) The least intense of the aliphatic ^{13}C NMR signals was assigned to the quaternary carbon.

(48) (a) "Collect" data collection software, Nonius B.V., 1998. (b) "Scalepack" data processing software: Otwinowski, Z.; Minor, W. In *Methods Enzymol.* **1997**, *276* (Macromolecular Crystallography, Part A), 307.

(49) Sheldrick, G. M. *SHELX-97*, Program for refinement of crystal structures; University of Göttingen, 1997.

refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from the literature.[50] Two independent molecules were found in the unit cell of **6a**. The methyl groups of the solvate in **6d**·(toluene)$_{0.5}$ were disordered, but refined to a 50:50 occupancy ratio. Disorder was also apparent within the aliphatic chain, but could not be resolved due to the data set quality.

(50) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG, GL 300/1-2) and Johnson Matthey PMC (platinum and ruthenium loans) for support, and Dr. Wolfgang Mohr for the synthesis of phosphine **1d**.

Supporting Information Available: Full experimental procedures for previously reported compounds (**b** series)[6c,12] and additional crystallographic data for **6a**,**c**,**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034121U