

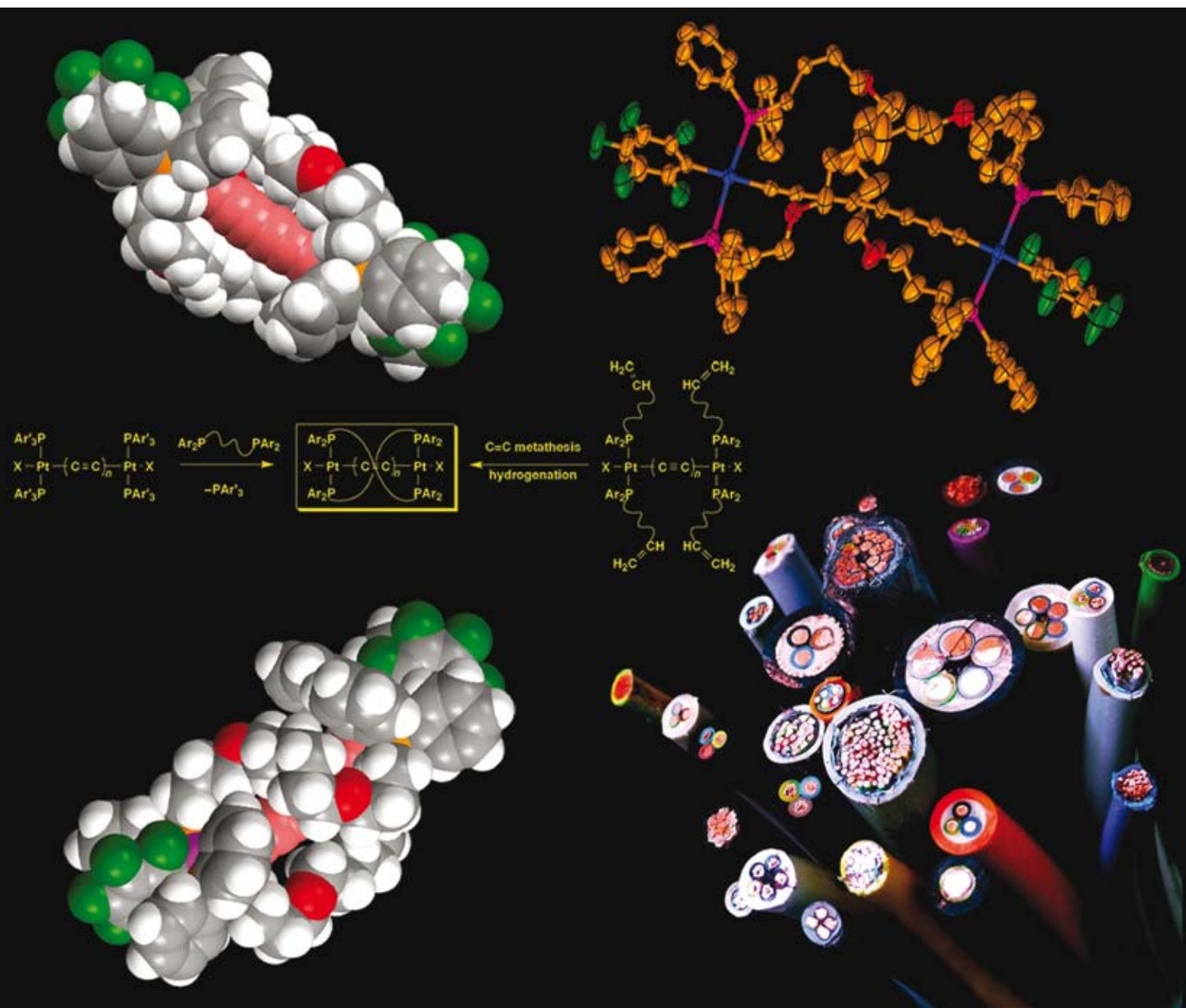
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sp Carbon chains surrounded by sp³ carbon double helices: wire-like Pt(C≡C)_nPt moieties that are spanned by two α,ω-diphosphines that bear heteroatoms or alkyl substituents

Laura de Quadras,^a Eike B. Bauer,^a Jürgen Stahl,^a Fedor Zhuravlev,^a Frank Hampel^a and John A. Gladysz^{*ab}

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Reactions of *trans*-(C₆F₅)L₂PtCl (**2**, L = Ph₂P(CH₂)₄O(CH₂)₂CH=CH₂; **6**, L = Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₃CH=CH₂) and H(C≡C)₂H (HNEt₂, cat. CuI) give *trans*-(C₆F₅)L₂Pt(C≡C)₂H (**3**, **7**; 86–97%). Oxidative homocouplings (O₂, cat. CuCl/TMEDA, acetone) yield *trans,trans*-(C₆F₅)L₂Pt(C≡C)₄PtL₂(C₆F₅) (**4**, **8**; 75–86%). Reactions with Grubbs' catalyst, followed by hydrogenation, give mainly *trans,trans*-(C₆F₅)-(Ph₂P(CH₂)₄O(CH₂)₆O(CH₂)₄PPh₂)Pt(C≡C)₄Pt(Ph₂P(CH₂)₄O(CH₂)₆O(CH₂)₄PPh₂)(C₆F₅) (**5**), with termini-spanning diphosphines, and *trans,trans*-(C₆F₅)-(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂)Pt(C≡C)₄-Pt(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂)(C₆F₅) (**9**), with *trans*-spanning diphosphines, respectively. Reactions of *trans,trans*-(C₆F₅)(*p*-tol₃P)₂Pt(C≡C)₄Pt(*p*-tol₃)₂(C₆F₅) with Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂ and *p*-tol₂P(CH₂)₃(CF₂)₈(CH₂)₃*p*-tol₂ give **10** (70%), the isomer of **9** with termini-spanning diphosphines, and the analogous adduct of the fluorinated diphosphine. However, the latter oligomerizes upon attempted workup. The crystal structure of **5** shows that the sp³ chains adopt a chiral double-helical conformation about the sp chain, with the endgroups defining a 164.1° angle. Additional conformational properties of the preceding complexes are analyzed in detail, and dynamic properties are probed by low temperature NMR experiments.

Introduction

In previous full papers, we have described two effective syntheses of diplatinum polyynediyl or Pt(C≡C)_nPt complexes in which two α,ω-bis(diarylphosphino)alkane ligands Ar₂P(CH₂)_mAr₂ span the platinum termini.^{1–3} One involves four-fold monophosphine ligand substitution, or coordination-driven self-assembly. The other involves alkene metatheses of precursors with four ligands of the formula Ar₂P(CH₂)_mCH=CH₂ (*m* = 2*m*' + 2), and subsequent hydrogenations. The sp³ carbon chains of the diphosphine ligands sterically protect the sp carbon chains. When the sp³/sp carbon atom ratios are sufficient, the molecules can adopt chiral double-helical conformations of idealized D₂ symmetry, as illustrated by the enantiomers **A** and **A'** in Scheme 1. These can interconvert *via* achiral conformations of the type **B**, which dominate at lower sp³/sp ratios.

The double helices **A/A'** are unique in the absence of bonding interactions or complementarity between the strands.⁴ The sp chain can be viewed as a beanpole-like

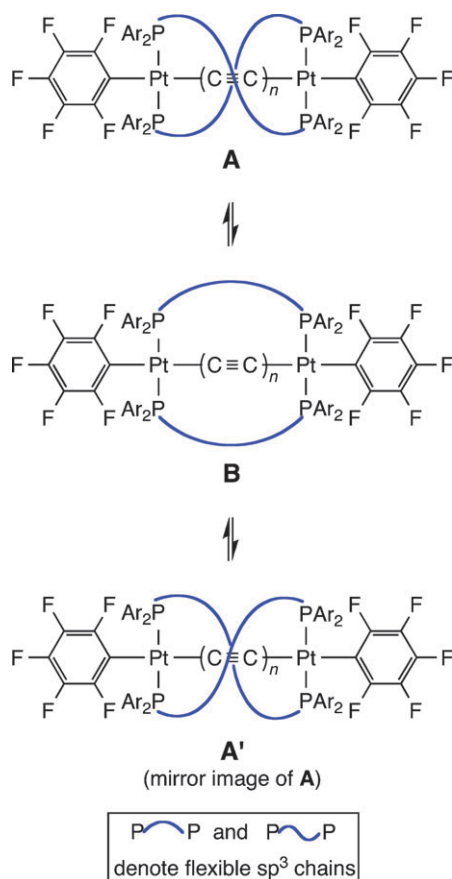
mechanical support, without which the helical conformations would not be energetically competitive. Given that two redox active termini are connected by an unsaturated bridging ligand, such assemblies can be viewed as insulated molecular wires.⁵ Only a few other systems are known in which unsaturated assemblies that span electroactive endgroups are similarly shielded.⁵

We sought to further probe the accessibilities and properties of such complexes, particularly with respect to modifications in the sp³ chains. One question is whether functional groups or substituents can be introduced into the diphosphine backbones. Functional groups might be employed to construct multidimensional arrays, such as “bundles” of parallel wires.⁶ Fluorine substituents or difluoromethylene segments—the ground state conformations of which are also helical⁷—could give “fluorous”⁸ or “Teflon[®]-coated” wires. Note that *geminal* substituents avoid the generation of new stereocenters that might lead to difficultly separable isomer mixtures.

Geminal *dialkyl* substituents would be of interest with respect to unsolved questions of dynamics. As detailed in previous papers,^{1,2} the enantiomeric double helices **A/A'** appear to interconvert rapidly on the NMR time scale in solution, even at very low temperatures. Said differently, it has not yet proved possible to detect separate signals for the many diastereotopic geminal groups (aryl, *CHH'*, etc.), which undergo net exchange when **A** untwists to **B** and further twists

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Scheme 1 Limiting structures for complexes derived from $C_6F_5Pt(C\equiv C)_nPtC_6F_5$ units and α,ω -diphosphines $Ar_2P(CH_2)_mPAr_2$ or functionalized analogs.

to A'. The sp^3 chains feature a number of *gauche* RCH_2CH_2R segments, which are chiral as illustrated by C/C' in Scheme 2. For A to become A', the configurations of all of these segments must invert. This involves rotation about the RCH_2-CH_2R bonds and transition states with two eclipsed R/H moieties.⁹

Geminal dialkyl groups can have a profound effect upon conformational equilibria, and generally raise the barriers for such bond rotations.¹⁰ As illustrated in Scheme 2 for *gauche*

segments with dimethyl groups (E/E'), the analogous transition states now feature R/Me, R/H, and Me/H eclipsing interactions. Thus, it might be expected that complexes A/A' in which geminal dialkyl groups have been incorporated into the diphosphine backbones would exhibit higher interconversion barriers. However, there is an important caveat. Geminal dialkyl groups could also in principle sterically destabilize the helical conformations. Hence, it is essential that the transition state destabilization be greater than any ground state destabilization. For this reason, the smallest possible alkyl group (methyl) was selected for this study.

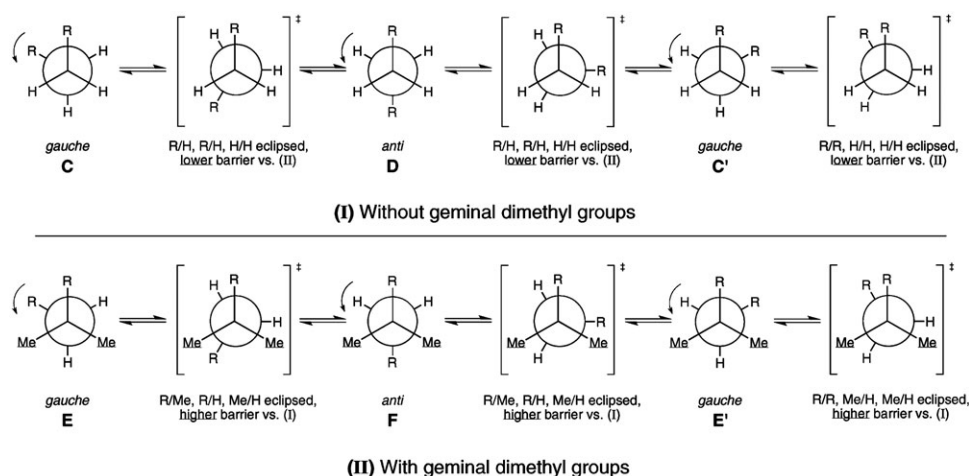
In this paper, we report syntheses of oxygen-containing and polydimethylated derivatives of complexes of the types A/A' using both phosphine ligand substitutions and alkene metathesis/hydrogenation sequences. Structural and dynamic data, as well as efforts to introduce fluorinated sp^3 chains, are also described. A portion of this work has been communicated,^{3c} and additional details are supplied elsewhere.¹¹

Results

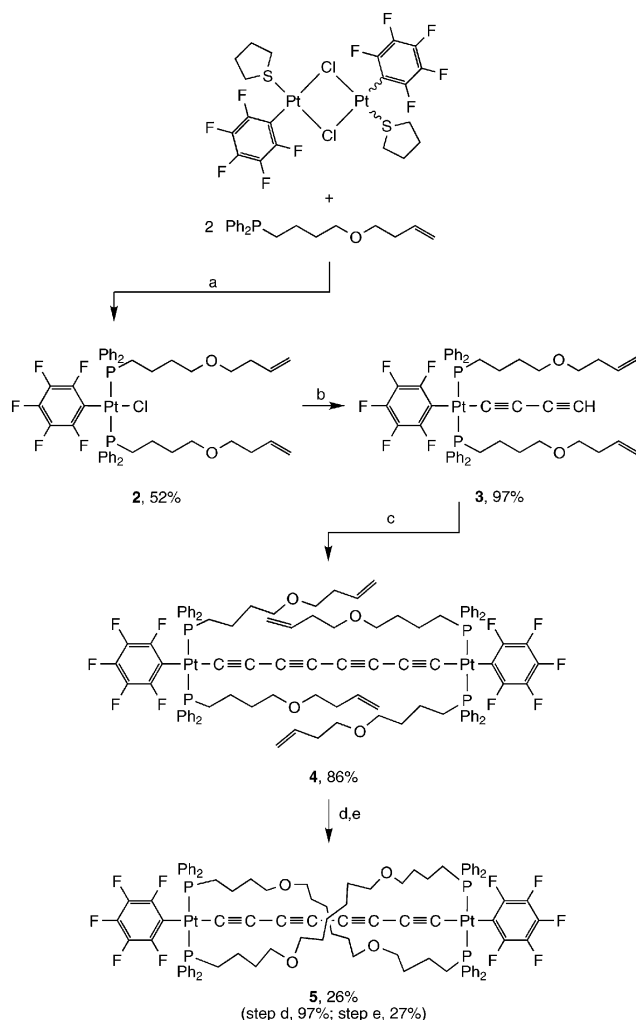
1. Oxygen-containing sp^3 chains

As shown in Scheme 3, a diplatinum di(tetrahydrothiophene) complex¹² was treated with *ca.* four equivalents of the ethereal alkene-containing phosphine $Ph_2P(CH_2)_4O(CH_2)_2CH=CH_2$ (1).¹³ Workup gave the *trans* monoplutonium bis(phosphine) chloride complex 2 as a colorless oil in 52% yield. This was treated with $H(C\equiv C)_2H/HNEt_2$ in the presence of a catalytic amount of CuI to yield the butadiynyl complex 3 (97%). Subsequent Hay oxidative coupling afforded the desired diplatinum octatetraynediyl complex 4 as a yellow oil (86%). Each of these steps proceeded with approximately the same rate and yield as for related complexes without the ether linkages.^{1,2,13–16}

All platinum complexes were characterized by NMR (1H , ^{13}C , ^{31}P) and IR spectroscopy and mass spectrometry, as summarized in the experimental section. In general, properties were very similar to those of related complexes described in earlier papers.^{1,2,13–16} In most cases, correct microanalyses were also obtained. All ^{31}P NMR spectra exhibited $^{31}P-^{195}Pt$



Scheme 2 Effect of geminal dimethyl groups on energy barriers for interconversions of *gauche*/anti conformers.



Scheme 3 Syntheses of oxygen-containing platinum complexes. Conditions: (a) CH₂Cl₂; (b) H(C≡C)₂H, cat. CuI, HNEt₃; (c) O₂, cat. CuCl/TMEDA, acetone; (d) 6 mol% Grubbs' second generation H₂IMes catalyst; (e) 10% Pd/C, 1 atm H₂.

couplings, the magnitudes of which (2658–2566 Hz) require *trans* P–Pt–P linkages.¹⁷ These couplings furthermore indicate the absence of any equilibria involving rapid phosphine dissociation.

Dilute CH₂Cl₂ solutions of the tetraalkene **4** (0.0011–0.0007 M) were treated with alkene metathesis catalysts. In contrast to the non-ethereal educts in the previous paper,² reactions of **4** and Grubbs' catalyst were sluggish; complete conversions required multiple charges. However, Grubbs' second generation H₂IMes catalyst was much more effective. As shown in Scheme 3, the crude products were hydrogenated over Pd/C. Chromatography gave the target complex **5**, with terminispanning diphosphine ligands, as a yellow powder in 26% overall yield. Later fractions contained only small amounts of non-oligomeric products. Although constitutional isomers with *trans*-spanning diphosphine ligands were not noted, yields of <5% would have escaped detection.

The phosphorus atoms that anchor the flexible sp³ chains in **5** are bridged by sixteen atoms. The crystal structure of a solvate was determined as summarized in Table 1 and the experimental section. Selected metrical parameters are pro-

Table 1 Summary of crystallographic data for **5**·MeOH

Empirical formula	C ₉₇ H ₁₀₀ F ₁₀ O ₅ P ₄ Pt ₂
Formula weight	2049.83
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions:	
<i>a</i> [Å]	21.4114(3)
<i>b</i> [Å]	17.9695(3)
<i>c</i> [Å]	24.2342(3)
α [°]	90
β [°]	101.855(1)
γ [°]	90
<i>V</i> [Å ³]	9125.3(2)
<i>Z</i>	4
ρ_{calcd} [Mg m ⁻³]	1.492
μ [mm ⁻¹]	3.204
<i>F</i> (000)	4112
Crystal size, mm	0.15 × 0.15 × 0.15
θ range	2.06 to 27.49
Index ranges (<i>h,k,l</i>)	−27,27; −23,23; −31,31
Reflections collected	39 762
Independent reflections	20 905 [<i>R</i> (int) = 0.0497]
Reflections [<i>I</i> > 2 σ (<i>I</i>)	13 238
Completeness to θ = 27.49°	99.7%
Data/restraints/parameters	20 905/0/1063
Goodness-of-fit on <i>F</i> ²	0.966
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)	<i>R</i> 1 = 0.0421 <i>wR</i> 2 = 0.0848
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0886 <i>wR</i> 2 = 0.0979
Largest diff. peak and hole [e Å ⁻³]	1.123 and −0.956

vided in Tables 2 and 3. As depicted in Fig. 1, a double-helical conformation was found, with both enantiomers in the unit cell. The endgroups or two P–Pt–P/Pt planes defined an angle of 164.1°—somewhat less than a half twist. This is less than the range of values for four crystalline analogs with Ar₂P(CH₂)₁₄–PAr₂ ligands, which feature fourteen atoms in the diphosphine backbones (189.3–196.5°).¹ Thus, the degree of twisting is not a simple function of the number of atoms that bridge the phosphorus atoms. Additional features are analyzed below.

A cyclic voltammogram of **5** was recorded under conditions analogous to those used for related compounds in the preceding papers.^{1,2} A partially reversible oxidation was observed (*E*_{p,a}, 1.304 V; *E*_{p,c}, 1.231 V; *E*^o, 1.268 V; ΔE 73 mV; *i*_{c/a}, 0.75). The *i*_{c/a} value was very close to those of analogous complexes with Ar₂P(CH₂)₁₄PAr₂ (0.71–0.78; *E*^o 1.203–1.265 V)¹ and Ph₂P(CH₂)₁₆PPh₂ (0.80; *E*^o 1.260 V)² bridges. The *E*^o value appeared slightly more positive, indicating a thermodynamically more difficult oxidation and consistent with an electron-withdrawing effect of the oxygen atoms.

The DSC trace of **5** showed an endotherm at 203.7 °C (*T*_c), likely indicative of a phase transition. A TGA trace showed mass loss commencing at 265 °C. Low temperature ¹H NMR spectra of **5** were recorded in CDFCl₂.¹⁸ At −115 °C, no decoalescence phenomena involving any of the diastereotopic geminal groups were apparent. Only slightly broadened peaks were observed, including the well-separated PCH₂ and OCH₂ signals.

2. Geminally dimethylated sp³ chains

The monoplatinum chloride complex **6** shown in Scheme 4 was prepared earlier, together with the homolog without geminal

Table 2 Key crystallographic distances [Å] and angles (°) for **5**·MeOH

Pt...Pt	12.7478(3)
Sum of bond lengths, Pt1 to Pt2	12.890
Pt1–C1	1.975(5)
C1–C2	1.216(7)
C2–C3	1.367(7)
C3–C4	1.207(7)
C4–C5	1.346(7)
C5–C6	1.227(7)
C6–C7	1.368(7)
C7–C8	1.205(7)
C8–Pt2	1.979(5)
Pt1–C1–C2	174.7(4)
C1–C2–C3	175.1(6)
C2–C3–C4	177.4(6)
C3–C4–C5	175.8(6)
C4–C5–C6	174.4(6)
C5–C6–C7	178.9(6)
C6–C7–C8	177.3(6)
C7–C8–Pt2	175.1(4)
Average Pt–C _{sp} –C _{sp}	174.9
Average C _{sp} –C _{sp} –C _{sp}	176.5
Average sp ³ /sp ³ distance ^a	4.279
Average π stacking ^b	3.77
P–Pt–P/Pt angle ^c	164.1
Pt + P + P + C _i + C _i angle ^c	150.6

^a Average distance from every oxygen or CH₂ carbon atom to the Pt–Pt vector. ^b Average distance between midpoints of the C₆F₅ and C₆H₅ rings. ^c Angle between planes defined by these atoms on each endgroup.

dimethyl groups.^{14a} Both underwent ring-closing alkene metatheses to give products with *trans*-spanning diphosphine ligands and seventeen-membered macrocycles.^{14a} For the present study, **6** was elaborated to the butadiynyl complex **7** (86% after workup) and the diplatinum octatetraynediyl complex **8** (75%), analogously to the oxygen-containing complexes in Scheme 3. The ¹H and ¹³C NMR spectra of all of these species exhibited, as expected, one sharp singlet for the enantiotopic methyl groups (experimental section).

Table 3 Torsion angles [°] involving the flexible sp³ chain in **5**·MeOH^a

P–C1–C2–C3	169.3(4)	167.5(4)
C1–C2–C3–C4	51.3(8)	–74.3(8)
C2–C3–C4–O5	61.4(8)	–177.8(6)
C3–C4–O5–C6	–160.6(7)	–175.9(7)
C4–O5–C6–C7	–68.1(10)	–75.6(9)
O5–C6–C7–C8	–179.3(8)	–165.5(7)
C6–C7–C8–C9	–164.0(11)	–179.3(7)
C7–C8–C9–C10	–178.3(9)	60.6(10)
C8–C9–C10–C11	–74.8(13)	59.9(10)
C9–C10–C11–O12	–166.5(8)	61.8(9)
C10–C11–O12–C13	–178.6(6)	178.1(6)
C11–O12–C13–C14	178.5(5)	–178.9(5)
O12–C13–C14–C15	–71.9(6)	–59.2(6)
C13–C14–C15–C16	–79.4(6)	–65.2(6)
C14–C15–C16–P	173.6(4)	177.9(4)

^a The torsion angles for both chains are presented starting from the same platinum atom.

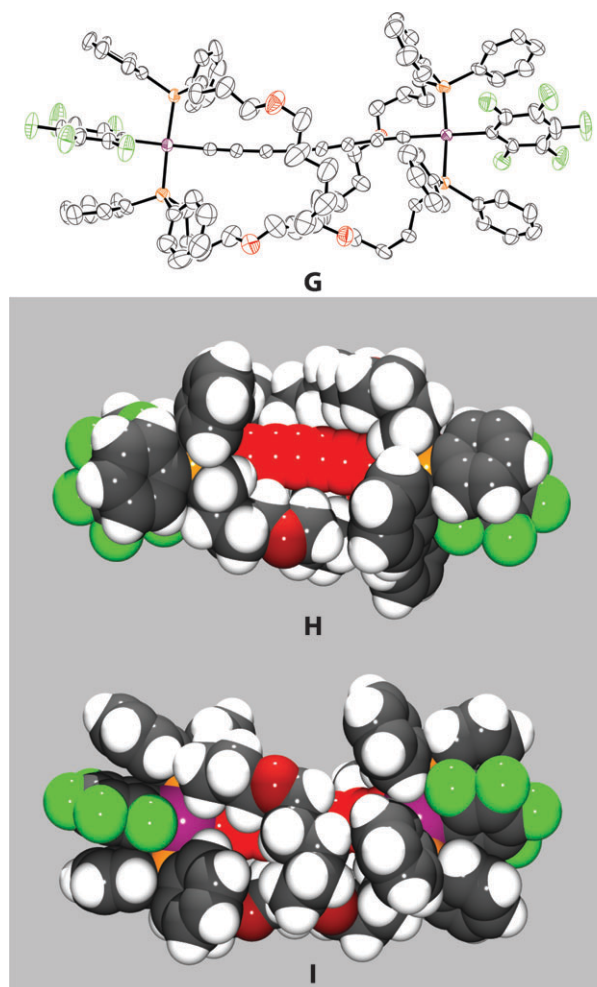
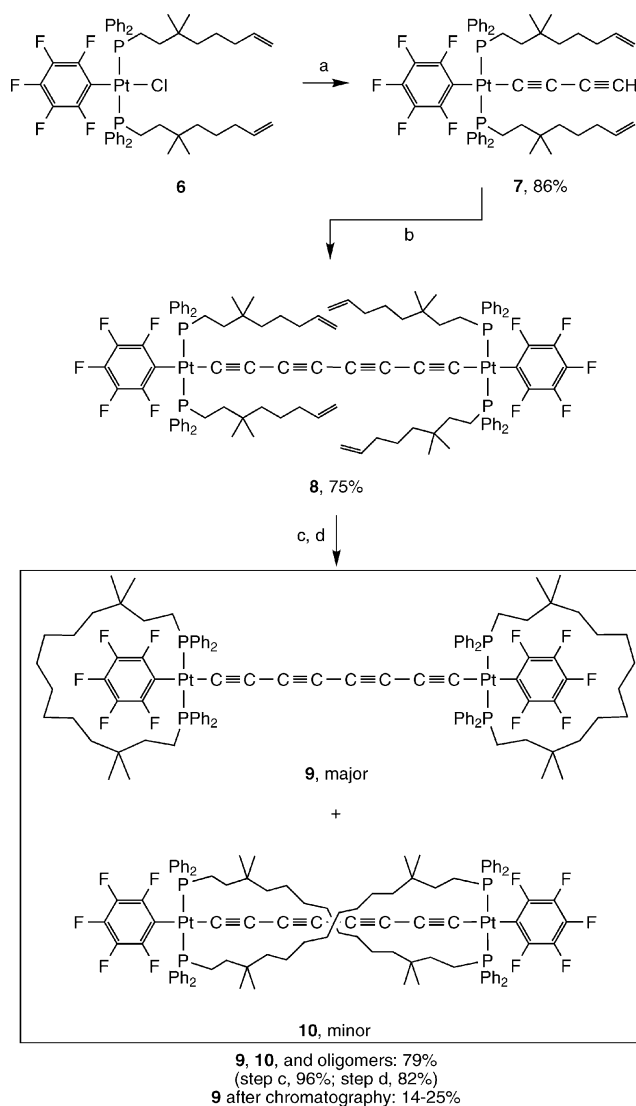


Fig. 1 Structures of **5**·MeOH with the solvate molecule omitted: **G**, thermal ellipsoid plot (50% probability level) with hydrogen atoms omitted; **H**, **I**, views parallel and perpendicular to the planes of the C₆F₅ ligands with atoms at van der Waals radii.

A dilute CH₂Cl₂ solution of **8** (0.00095 M) was treated with Grubbs' catalyst. Workup gave the crude metathesis products in 96% yield. A ³¹P NMR spectrum showed a 76 : 16 : 8 ratio of three peaks, the first of which had two shoulders, thus indicating at least five components. The sample was hydrogenated under standard conditions (Scheme 4). The crude product was isolated in 82% yield after alumina filtration, and a ³¹P NMR spectrum showed a 41 : 16 : 14 : 12 : 11 : 6 ratio of six peaks. The first (major) peak could be assigned to **9**, with *trans*-spanning diphosphine ligands. Based upon an independent synthesis (below), the last (minor) peak could be assigned to **10**, with termini-spanning diphosphine ligands that feature fourteen atoms in the backbone.

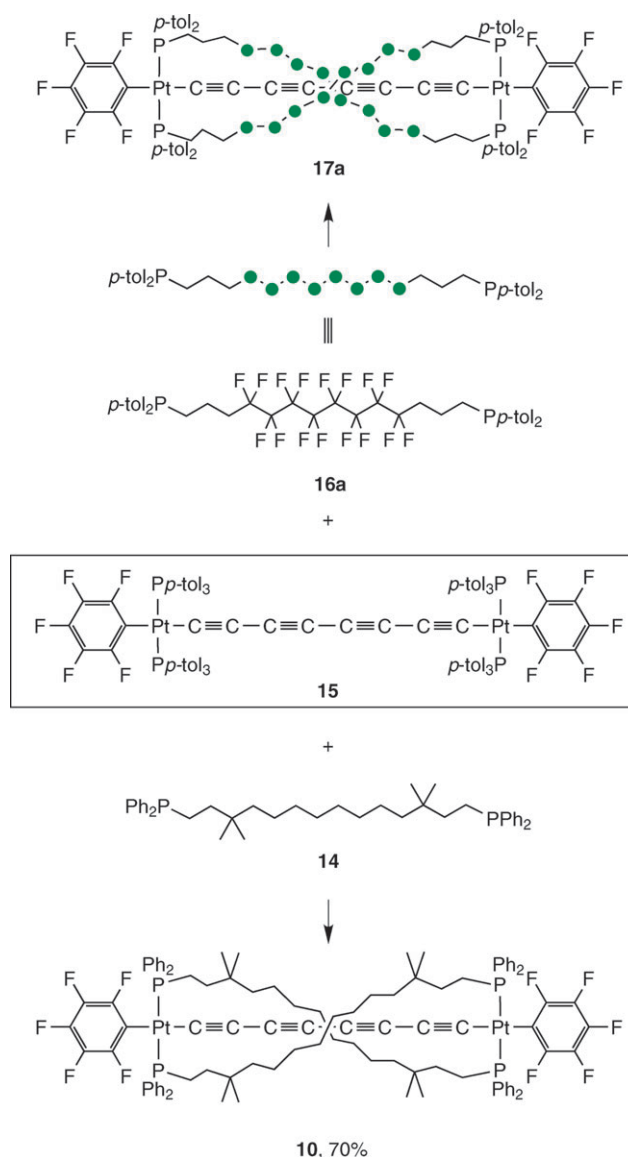
Chromatographic workups gave **9** as a yellow powder in 14–25% yields. The spectroscopic properties were very similar to those of related complexes lacking methyl groups in the previous full paper.² The DSC trace showed an endotherm at 175.3 °C (*T_c*), and a TGA trace showed the onset of mass loss at 289.6 °C. The ¹H and ¹³C NMR spectra exhibited two singlets for the now-diastereotopic methyl groups, as well as other “doubled” resonances. Crystallographic data establish



Scheme 4 Syntheses of platinum complexes containing geminal dimethyl groups. Conditions: (a) $\text{H}(\text{C}\equiv\text{C})_2\text{H}$, cat. CuI , HNEt_2 ; (b) O_2 , cat. CuCl/TMEDA , acetone; (c) 8 mol% Grubbs' catalyst; (d) 10% Pd/C , 1 atm H_2 .

that the pentafluorophenyl ligands are too large to pass through seventeen-membered macrocycles,^{2,19} which as detailed elsewhere^{2,11b,14,19} would exchange the various diastereotopic groups. An identical sequence starting with the homolog of **8** without geminal dimethyl groups gives mainly a termini-spanning diphosphine complex similar to **10**.² Hence, the geminal dimethyl groups invert the dominant mode of ring closing metathesis.

In order to definitively assign the minor ^{31}P NMR signal to **10**, an authentic sample was required. Thus, the bis(geminally disubstituted) phosphine **14** shown in Scheme 5 (bottom) was prepared as described elsewhere.¹³ Using conditions similar to those employed for related diphosphines in a previous paper,¹ a dilute CH_2Cl_2 solution of **14** (0.001 M) was added to a dilute CH_2Cl_2 solution of the octatetraynediyl complex **15** (0.0005 M).¹⁵ A precipitation step gave spectroscopically pure **10** in 70% yield. Complex **9** was not detected. A small portion of the isolated material did not redissolve, suggesting the formation



Scheme 5 Reactions of $\text{Pt}(\text{C}\equiv\text{C})_4\text{Pt}$ complex **15** and α,ω -diphosphines; improved synthesis of **10**.

of some oligomer. Extensive attempts to grow crystals were unsuccessful.

Room temperature NMR spectra of **10** did not show any diastereotopic groups, indicating the rapid interconversion of any enantiomeric helical conformers **A/A'** (Scheme 1). When ^1H NMR spectra were recorded at -90 to -110°C in CD_2Cl_2 or CDFCl_2 ,¹⁸ no decoalescence phenomena were observed.

3. sp^3 Chains with $(\text{CF}_2)_m$ segments

Although phosphines with perfluoro-*n*-alkyl groups are readily available,²⁰ diphosphines of the formula $\text{Ar}_2\text{P}(\text{CF}_2)_m\text{PAR}_2$ would be too weakly nucleophilic and basic to displace the *Pp*-tol₃ ligands in the octatetraynediyl complex **15**.²¹ Thus, the diphosphines $\text{R}_2\text{P}(\text{CH}_2)_3(\text{CF}_2)_8(\text{CH}_2)_3\text{PR}_2$ (**16**; $\text{R} = \text{a}, p\text{-tol}$; **b**, *t*-Bu; **c**, *o*-tol), which feature insulating trimethylene spacers, were synthesized as described elsewhere.¹³ As with **14**, the phosphorus atoms are bridged by fourteen carbon atoms.

Importantly, **16a** would yield a highly fluorinated analog of a complex reported earlier.¹

As shown in Scheme 5 (top), a dilute CH₂Cl₂ solution of **16a** (0.001 M) was slowly added to a dilute CH₂Cl₂ solution of **15** (0.001 M). Substitution was complete within minutes, as assayed by a ³¹P NMR spectrum of an aliquot (30.69 (minor), 14.94 (minor), 14.55 (dominant; ¹J_{PPt} = 2585), 14.10 (minor), −7.47 (Pp-tol₃) ppm). The chemical shift and coupling constant of the dominant signal were characteristic of complexes of the type A/A'.^{1,2} Hence, the experiment was interpreted as providing the target molecule **17a** in high spectroscopic yield.

However, solvent evaporation always gave an appreciable amount of material that would not redissolve, even in the same solvent. After several such cycles, samples became totally insoluble. Hence, **17a** is presumed to be unstable with respect to oligomerization, a side reaction that especially plagues reactions of **15** and longer-chain α,ω-diphosphines.¹ All attempts to crystallize **17a** were unsuccessful. The bulkier diphosphines **16b,c** did not react with **15**, even at temperatures of > 100 °C (**16b**: toluene, 105 °C, 20 h or melt, 206 °C; **16c**: DMF, 140 °C).

An NMR tube was charged with **15**, **16a**, and THF-*d*₈, and cooled to −100 °C in a NMR probe. Both ¹H and ³¹P NMR spectra showed the somewhat cleaner generation of **17a**, and the concomitant formation of Pp-tol₃. However, no decoalescence phenomena were apparent. As with the analogous non-fluorinated complex,¹ only a single *p*-tolyl methyl resonance was observed. Thus, as for **10**, the interconversion of any helical conformers A/A' remains rapid on the NMR time scale.

Discussion

1. Syntheses

Schemes 3 and 5 establish that it is possible to extend the syntheses previously developed for complexes of the types A/A' (Scheme 1) to sp³ chains that bear heteroatoms and alkyl substituents. The heteroatoms may be located within the chain (**5**), or exo to it (**17a**). These adducts represent a conceptual advance in the direction of more complex architectures or supramolecular assemblies, for which suitable functionality is required. For example, non-covalent interactions might be used to template “multi-stranded” molecular wires,²² which offer obvious advantages over assemblies with a single unsaturated bridge and one-atom terminal contacts.

The oxygen-containing complex **5** was prepared by the more reliable alkene metathesis/hydrogenation sequence (Scheme 3). We have not attempted to access this or related ethereal derivatives *via* substitution reactions involving α,ω-diphosphines. However, a wide variety of polyoxygenated diphosphines are readily available, including Ph₂PCH₂(CH₂OCH₂)₄CH₂PPh₂, which features a fourteen-atom backbone.²³ Such ligands have an extensive coordination chemistry, yielding “metallacrown ethers” that can bind to alkali metal cations and other species.²⁴ Cationic guests might be employed to direct conformational equilibria of the type A/B. Analogs with more basic nitrogen and sulfur atoms would also have obvious applications, and their syntheses are under active investigation.²⁵

Unexpected results were encountered *en route* to the polymethylated complex **10**. The metathesis/hydrogenation sequence in Scheme 4 affords mainly the product derived from cyclization of the *trans* phosphine ligands (**9**), as opposed to that from ligands on opposite platinum termini (**10**). This is in contrast to the many examples in the previous paper,² including the exact analog without the geminal dimethyl groups. However, **10** could be readily synthesized by a substitution reaction involving the corresponding diphosphine **14** (Scheme 5). In most ring closing metatheses of platinum complexes that we have studied, we believe that the product distributions are kinetic, or at the very least that not all possible products are thermodynamically sampled.²⁶ Thus, perhaps the geminal dimethyl groups increase the strain associated with the transition state leading to **10** more than that to **9**. Although we presently have no measure of the relative thermodynamic stabilities of **9** and **10**, it is possible that catalytic conditions that promote higher turnover numbers may give altered selectivities.

Our inability to isolate the fluorinated complex **17a** represents a major disappointment, especially in view of the gently twisting helical ground states of perfluoro-*n*-alkanes.⁷ However, the energy barriers associated with interconverting enantiomeric *gauche* conformations are not higher than with *n*-butane (*ca.* 2.7 kcal mol^{−1}).^{7a,c} Also, in accord with the underlying principles of fluorous biphasic catalysis,⁸ there would be advantages to conformations in which the CF₂ groups more strongly interact with each other, as opposed to being splayed along the sp carbon chain. Furthermore, the van der Waals radius of fluorine is greater than that of hydrogen (1.47 Å vs. 1.20 Å).²⁷ All of these factors may contribute to the apparently low barrier for the interconversion of the enantiomeric helical conformations of **17a**, as well as its facile decomposition to oligomeric material. However, double helices derived from two (CF₂)₈ moieties have recently been observed in the solid state.^{7d,e}

2. Spectroscopic and structural properties

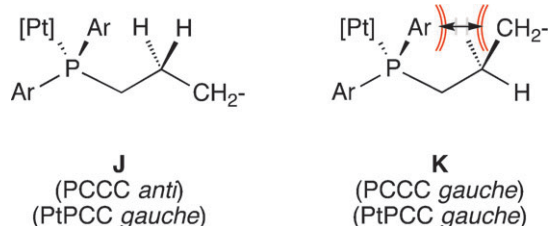
Although the spectroscopic features of the title complexes do not break any new ground, several merit emphasis. First, the UV-visible and IR spectra of ether-containing **5** are very similar to analogs without the oxygen atoms.^{1,2} Second, the ¹³C NMR chemical shifts of the sp carbon atoms also show virtually no effect (PtC≡CC≡C at 100.1/94.3/63.8/58.3 vs. 99.3/94.0/63.7/57.8 ppm for the analog with eight and sixteen sp and sp³ carbon atoms).² Third, the ³¹P NMR chemical shifts of the isomers **9** and **10** differ more than those of the analogs without the methyl groups (1.6 ppm vs. <0.5 ppm).² However, the ¹³C NMR chemical shifts of the sp carbon atoms are very similar.

The bond lengths and angles associated with the crystal structure of **5** (Table 2) are routine. However, the conformations of the sp³ chains exhibit several interesting features. A regular cylindrical helix is characterized by a radius, which for **5** can be approximated by calculating the average distance from the non-phosphorus atoms of the sp³ chain to the Pt–Pt vector. The value (4.28 Å) is greater than those of analogous complexes with Ar₂P(CH₂)₁₄PAr₂ bridges (3.76–4.04 Å). This

logically follows from the combination of (a) the lower degree of twisting as noted above, and (b) the two extra atoms in each sp^3 chain, which given the diminished twisting can only be accommodated by a radial extension.

As illustrated in Fig. 1, the lone pairs of the oxygen atoms point conspicuously away from the sp chain. This may reflect the avoidance of repulsive filled/filled orbital interactions, and/or attractive interactions of the π system with the positive ends of the carbon–oxygen bond dipoles. The former would destabilize **A/A'** relative to **B**, lowering the energy barrier for the interconversion of enantiomeric double helices. However, complexes with electron-deficient segments or Lewis acidic atoms in the flexible chain might exhibit enhanced barriers (stabilization of **A/A'** relative to **B**). This represents another strategy worthy of future attention.

The torsion angles associated with the sp^3 chain (Table 3) show that $Ar_2PCH_2CH_2CH_2$ and immediately adjacent $CH_2CH_2CH_2CH_2$ segments exhibit *anti* and *gauche* conformations, respectively. The $PtPCH_2CH_2$ segments also exhibit *gauche* conformations. Analogous features are found in all related double-helical complexes.^{1,2} As illustrated by **J** and **K**, the *anti* $Ar_2PCH_2CH_2CH_2$ segments avoid 1,5-synperiplanar interactions²⁸ with the PAR_2 groups and/or platinum fragment. The *gauche* segments represent the onset of helical chirality. One of the sp^3 chains exhibits seven *gauche* segments comprised of carbon and/or oxygen atoms, and the other six. Interestingly, these *gauche* segments are not all of the same chirality. For example, in one chain there are four negative *gauche* torsion angles followed by two that are positive.



We rationalize this behavior as follows. If the endgroup planes were twisted to the maximum degree allowed by the sp^3 chain lengths, all *gauche* segments should have the same helical chirality. However, as noted above, the endgroups in **5**·MeOH are distinctly less twisted than those in analogous $Ar_2P(CH_2)_{14}PAR_2$ complexes, which have two fewer atoms in each sp^3 chain. Hence, there is “play” in the sp^3 chains of **5**·MeOH, as reflected by a greater average sp^3/sp chain distance. Thus, if there are too many *gauche* segments of the same chirality, the sp^3 chains can “overshoot” the plane of the endgroup, and must “double back” by means of *gauche* segments of the opposite chirality.

3. Conclusions

This study has established routes to complexes of the types **A/A'** with several types of functionality in the flexible sp^3 chains. In the case of the polyether **5**, a double-helical conformation has been confirmed in the solid state. In the case of the polymethylated and polyfluorinated derivatives **10** and **17a**, no structural data could be obtained. With the latter, this reflects the tendency of the complex to oligomerize.

However, for all three complexes, the NMR data indicate that **A/A'** rapidly interconvert in solution, even at $-100\text{ }^\circ\text{C}$. Although our present data do not exclude the possibility that achiral conformations of the type **B** dominate in solution, we believe this to be unlikely, as discussed in detail elsewhere.^{1,2}

Regardless, the importance of this study resides in the creation of functional building blocks that can potentially be elaborated to more complex assemblies, such as multistranded molecular wires.²² In future work, attention will be directed at coupling reactions other than alkene metathesis. For example, a precursor analogous to **4** or **8** but with four phosphine ligands of the formula $Ph_2P(CH_2)_mX$ might be treated with malonate anions. This could lead to species of the type **A/A'** with odd-carbon sp^3 chains, and four functional groups. These and other new directions noted above are under investigation, and the results will be reported in due course.^{25,29}

Experimental

1. General

Instrumentation, and methods for recording or treating DSC/TGA and cyclic voltammetry data, were identical to those in previous papers.^{1,2} Chemicals were used as follows: CH_2Cl_2 , distilled from CaH_2 ; acetone, distilled from K_2CO_3 ; $HNEt_2$, distilled from KOH; toluene, ethyl acetate, ethanol, methanol, and TMEDA (Aldrich), distilled; Grubbs' catalyst (Strem), Grubbs' second generation catalyst ($Ru(=CHPh)(H_2IMes)(PCy_3)(Cl)_2$; Aldrich), 10% Pd/C (Acros), CuI (Aldrich, 99.999%), CuCl (Aldrich, 99.99%), $ClCH_2CH_2Cl$ (Fluka, 98%), and other materials, used as received unless noted.

2. Synthesis

Trans-(C₆F₅)(Ph₂P(CH₂)₄O(CH₂)₂CH=CH₂)₂PtCl (2). A Schlenk flask was charged with $[Pt(\mu-Cl)(C_6F_5)(tht)]_2$ (0.721 g, 0.752 mmol; tht = tetrahydrothiophene)¹² and CH_2Cl_2 (30 mL), and $Ph_2P(CH_2)_4O(CH_2)_2CH=CH_2$ (**1**; 1.032 g, 3.304 mmol) was added with stirring. After 20 h, the sample was filtered through a Celite/decolorizing carbon pad. The solvent was removed by rotary evaporation. The residue was chromatographed on an alumina column (20 × 2.0 cm, 90 : 10 v/v hexanes–ethyl acetate). The solvent was removed from the product-containing fractions by oil pump vacuum to give **2** as a colorless oil (0.795 g, 0.803 mmol, 52%). Calcd for $C_{46}H_{50}ClF_5O_2P_2Pt$: C, 54.04; H, 4.93. Found: C, 54.10; H, 5.02%.

NMR (δ , $CDCl_3$), 1H 7.52–7.41 (m, 8H of 4 Ph), 7.34–7.32 (m, 4H of 4 Ph), 7.27–7.26 (m, 8H of 4 Ph), 5.84–5.76 (m, 2H, CH=), 5.07 (br d, 2H, $^3J_{HHtrans} = 17.2$ Hz, $=CH_EH_Z$), 5.00 (br d, 2H, $^3J_{HHcis} = 10.2$ Hz, $=CH_EH_Z$), 3.48–3.45 (m, 8H, CH_2OCH_2), 2.65–2.64 (m, 4H, PCH_2), 2.35–2.31 (m, 4H, $CH_2CH=$), 1.98–1.97 (m, 4H, PCH_2CH_2), 1.74–1.73 (m, 4H, $PCH_2CH_2CH_2$); $^{13}C\{^1H\}$ ^{30,31} 135.7 (s, CH=), 133.5 (virtual t, $J_{CP} = 5.7$ Hz, *o* to P), 131.0 (virtual t, $J_{CP} = 27.3$ Hz, *i* to P), 130.7 (s, *p* to P), 128.4 (virtual t, $J_{CP} = 5.0$ Hz, *m* to P), 116.7 (s, $=CH_2$), 70.6 and 70.5 (2 s, CH_2OCH_2), 34.7 (s, $CH_2CH=$), 31.5 (virtual t, $J_{CP} = 7.4$ Hz, $PCH_2CH_2CH_2$), 26.0 (virtual t, $J_{CP} = 16.9$ Hz, PCH_2), 22.7 (s, PCH_2CH_2); $^{31}P\{^1H\}$ 16.5 (s, $^1J_{PPt} = 2658$ Hz).³² IR (cm^{-1} , oil film), 3078

(vw), 3060 (vw), 2935 (w), 2912 (w), 2860 (w), 1640 (w), 1501 (s), 1461 (s), 1436 (ms), 1364 (w), 1104 (s), 1059 (m), 957 (vs), 915 (m), 805 (m), 739 (s), 691 (vs); MS,³³ 986 $[(2 - \text{Cl})^+]$, 100%), 818 $[(2 - \text{Cl} - \text{C}_6\text{F}_5)^+]$, 18%), and other ions.

Trans-(C₆F₅)(Ph₂P(CH₂)₄O(CH₂)₂CH=CH₂)₂Pt(C≡C)₂H (3). A Schlenk flask was charged with **2** (0.765 g, 0.269 mmol), CuI (0.285 g, 0.149 mmol), and HNET₂ (70 mL) with stirring, and cooled to −45 °C. Then H(C≡C)₂H (9.0 mL, 15.3 mmol, *ca.* 1.7 M in THF)³⁴ was added *via* syringe. The mixture turned yellow. After 3 h, the cold bath was removed. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with toluene–ethyl acetate (50 : 50 v/v). The extract was chromatographed on an alumina column (10 × 2.0 cm, 50 : 50 v/v hexanes–ethyl acetate). The solvent was removed from the product-containing fractions by oil pump vacuum to give **3** as a yellow oil (0.752 g, 0.261 mmol, 97%). Calcd for C₅₀H₅₁F₅O₂P₂Pt: C, 57.97; H, 4.96. Found: C, 58.16; H, 5.06%.

NMR (δ , CDCl₃), ¹H 7.49–7.46 (m, 8H of 4 Ph), 7.34–7.32 (m, 4H of 4 Ph), 7.28–7.24 (m, 8H of 4 Ph), 5.79 (ddt, 2H, ³J_{HHtrans} = 17.1 Hz, ³J_{HHcis} = 10.3 Hz, ³J_{HH} = 6.7 Hz, CH=), 5.06 (br d, 4H, ³J_{HHtrans} = 17.2 Hz, =CH_EH_Z), 4.99 (br d, 4H, ³J_{HHcis} = 10.7 Hz, =CH_EH_Z), 3.46–3.42 (m, 8H, CH₂OCH₂), 2.65–2.63 (m, 4H, PCH₂), 2.32–2.29 (m, 4H, CH₂CH=), 1.86–1.85 (m, 4H, PCH₂CH₂), 1.72–1.66 (m, 4H, PCH₂CH₂CH₂), 1.66 (s, 1H, ≡CH); ¹³C{¹H}^{30,31} 135.3 (s, CH=), 133.1 (virtual t, J_{CP} = 5.9 Hz, *o* to P), 131.0 (virtual t, J_{CP} = 27.9 Hz, *i* to P), 130.3 (s, *p* to P), 127.9 (virtual t, J_{CP} = 5.1 Hz, *m* to P), 116.2 (s, =CH₂), 92.4 (s, PtC≡C), 72.3 (s, C≡CH), 70.1, 70.0 (2 s, CH₂OCH₂), 58.9 (s, ≡CH), 34.1 (s, CH₂CH=), 31.0 (virtual t, J_{CP} = 7.4 Hz, PCH₂CH₂CH₂), 27.9 (virtual t, J_{CP} = 17.9 Hz, PCH₂), 22.2 (s, PCH₂CH₂); ³¹P{¹H} 14.0 (s, ¹J_{PPt} = 2569 Hz).³² IR (cm^{−1}, oil film), ν_{CH} 3308 (w), $\nu_{\text{C}\equiv\text{C}}$ 2150 (m); MS,³³ 1037 (**3**⁺, 33%), 986 $[(3 - \text{C}_4\text{H})^+]$, 100%), and other ions.

Trans,trans-(C₆F₅)(Ph₂P(CH₂)₄O(CH₂)₂CH=CH₂)₂Pt(C≡C)₄Pt(Ph₂P(CH₂)₄O(CH₂)₂CH=CH₂)₂(C₆F₅) (4). A three-necked flask was charged with **3** (0.205 g, 0.200 mmol) and acetone (20 mL), and fitted with a gas inlet needle and a condenser. A Schlenk flask was charged with CuCl (0.090 g, 0.091 mmol) and acetone (20 mL), and TMEDA (0.180 mL, 1.08 mmol) was added with stirring. After 0.5 h, stirring was halted (blue supernatant/yellow-green solid). Then O₂ was bubbled through the three-necked flask with stirring, and the solution was heated to 60 °C. The blue supernatant was added in portions. After 4 h, the solvent was removed by rotary evaporation and oil pump vacuum. The residue was extracted with ethyl acetate. The extract was filtered through an alumina column. The solvent was removed from the filtrate by rotary evaporation to give **4** as a yellow oil (0.177 g, 0.855 mmol, 86%).

NMR (δ , CDCl₃), ¹H 7.48–7.45 (m, 16H of 8 Ph), 7.42–7.38 (m, 8H of 8 Ph), 7.34–7.31 (m, 16H of 8 Ph), 5.80 (ddt, 4H, ³J_{HHtrans} = 17.1 Hz, ³J_{HHcis} = 10.3 Hz, ³J_{HH} = 6.7 Hz, CH=), 5.06 (br d, 2H, ³J_{HHtrans} = 17.2 Hz, =CH_EH_Z), 4.99 (br d, 2H, ³J_{HHcis} = 10.2 Hz, =CH_EH_Z), 3.43–3.40 (m, 16H, CH₂OCH₂), 2.61–2.59 (m, 8H, PCH₂), 2.32–2.29 (m, 8H,

CH₂CH=), 1.85–1.83 (m, 8H, PCH₂CH₂), 1.69–1.65 (m, 8H, PCH₂CH₂CH₂); ¹³C{¹H}^{30,31} 135.4 (s, CH=), 133.0 (virtual t, J_{CP} = 5.8 Hz, *o* to P), 131.0 (virtual t, J_{CP} = 27.9 Hz, *i* to P), 130.3 (s, *p* to P), 127.9 (virtual t, J_{CP} = 5.0 Hz, *m* to P), 116.2 (s, =CH₂), 94.1 (s, PtC≡C), 70.1 and 70.0 (2 s, CH₂OCH₂), 63.7 (s, PtC≡CC), 58.1 (s, PtC≡CC≡C), 34.2 (s, CH₂CH=), 30.9 (virtual t, J_{CP} = 7.5 Hz, PCH₂CH₂CH₂), 27.9 (virtual t, J_{CP} = 17.9 Hz, PCH₂), 22.2 (s, PCH₂CH₂); ³¹P{¹H} 14.0 (s, ¹J_{PPt} = 2569 Hz).³² IR (cm^{−1}, oil film), $\nu_{\text{C}\equiv\text{C}}$ 2142 (m), 2001 (w); MS,³³ 2068 (**4**⁺, 40%), 1396 $[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2)_2\text{PtC}_8\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2)_2]$, 100%), 985 $[(\text{Pt}(\text{C}_6\text{F}_5)(\text{PPh}_2(\text{CH}_2)_4\text{O}(\text{CH}_2)_2\text{CH}=\text{CH}_2)_2)^+]$, 80%), and other ions.

Alkene metathesis of 4. A. A two-necked Schlenk flask was charged with **4** (0.211 g, 0.102 mmol), Grubbs' catalyst (*ca.* half of 0.006 g, 0.006 mmol), and CH₂Cl₂ (150 mL), and fitted with a condenser. The solution was refluxed. After 2 h, the remaining catalyst was added. After an additional 2 h, the solvent was removed by oil pump vacuum, and CH₂Cl₂ was added. The sample was filtered through an alumina column (4 × 2 cm), which was eluted with CH₂Cl₂ until UV monitoring showed no absorbing material. A ¹H NMR spectrum showed 44% conversion. The sample was dissolved in CH₂Cl₂ (150 mL), and refluxed with additional Grubbs' catalyst (0.012 g, 0.010 mmol; added in three portions over 6 h). An analogous workup and analysis showed 80% conversion. A third cycle (0.006 g, 0.006 mmol of Grubbs' catalyst) gave a mixture of cyclized products as a yellow oil (0.198 g, 0.0972 mmol, 96%). ³¹P{¹H} NMR (δ , CDCl₃) 16.6 (s), 16.5 (s), 16.3 (s), 14.2 (s), 14.12 (s, ¹J_{PPt} = 2569 Hz, major),³² 14.05 (s), 14.0 (s).

B. A two-necked Schlenk flask was charged with **4** (0.278 g, 0.134 mmol), Grubbs' second generation catalyst (*ca.* half of 0.007 g, 0.008 mmol), and CH₂Cl₂ (125 mL), and fitted with a condenser. The solution was refluxed. After 2 h, the remaining catalyst was added. After an additional 3 h, the solvent was removed by oil pump vacuum, and CH₂Cl₂ was added. The sample was filtered through an alumina column (4 × 2.5 cm), which was rinsed with CH₂Cl₂ until UV monitoring showed no absorbing material. The solvent was removed from the filtrate by oil pump vacuum to give a mixture of cyclized products as a yellow oil (0.261 g, 0.130 mmol, 97%).

³¹P{¹H} NMR (δ , CDCl₃) 14.2 (s, ¹J_{PPt} = 2571 Hz, major),³² 14.1 (s), 14.02 (s), 13.98 (s).

Trans,trans-(C₆F₅)(Ph₂P(CH₂)₄O(CH₂)₆O(CH₂)₄PPh₂)-Pt(C≡C)₄Pt(Ph₂P(CH₂)₄O(CH₂)₆O(CH₂)₄PPh₂)(C₆F₅) (5).

A Schlenk flask was charged with metathesized **4** (0.261 g, 0.130 mmol), 10% Pd/C (0.028 g, 0.026 mmol), ClCH₂CH₂Cl (15 mL), and ethanol (10 mL), flushed with H₂, and fitted with a balloon filled with H₂. The mixture was stirred for 14 d. The solvent was removed by oil pump vacuum. The residue was extracted with CH₂Cl₂. The extract was filtered through an alumina column (2 × 2 cm), which was rinsed with ethyl acetate. The solvent was removed from the filtrate by oil pump vacuum. The residue was chromatographed on an alumina column (15 × 5 cm, 80 : 20 v/v hexanes–ethyl acetate). The solvent was removed from the first product-containing

fraction by oil pump vacuum to give **5** as a yellow solid (0.070 g, 0.039 mmol, 27%). Calcd for $C_{96}H_{96}F_{10}O_4P_4Pt_2$: C, 57.14; H, 4.79. Found: C, 56.25; H, 4.65%. DSC: endotherm with T_i , 175.4 °C; T_e , 203.7 °C; T_c , 215.1 °C; T_f , 228.1 °C. TGA: weight loss 42%, 265–410 °C.

NMR (δ , $CDCl_3$), 1H 7.41–7.37 (m, 16H of 8 Ph), 7.33–7.26 (m, 8H of 8 Ph), 7.26–7.20 (m, 16H of 8 Ph), 3.49 (t, 8H, $^3J_{HH}$ = 6.5 Hz, $PCH_2CH_2CH_2CH_2O$), 3.38 (t, 8H, $^3J_{HH}$ = 6.7 Hz, $OCH_2CH_2CH_2$), 2.75–2.71 (m, 8H, PCH_2), 2.05–2.03 (m, 8H, PCH_2CH_2), 1.80–1.77 (m, 8H, $PCH_2CH_2CH_2$), 1.49–1.46 (m, 8H, $OCH_2CH_2CH_2$), 1.29–1.24 (m, 8H, $OCH_2CH_2CH_2$); $^{13}C\{^1H\}^{31}$ 145.8 (dm, $^1J_{CF}$ = 224 Hz, o to Pt), 136.4 (dm, $^1J_{CF}$ = 233 Hz, m/p to Pt), 132.8 (br s, o to P), 131.2 (virtual t, J_{CP} = 27.5 Hz, i to P), 130.3 (s, p to P), 127.9 (br s, m to P), 100.1 (s, $PtC\equiv$), 94.3 (s, $PtC\equiv C$), 70.6 and 70.1 (2 s, CH_2OCH_2), 63.8 (s, $PtC\equiv CC$), 58.3 (s, $PtC\equiv CC\equiv C$), 30.8 (virtual t, J_{CP} = 7.6 Hz, $PCH_2CH_2CH_2$), 29.4 (s, $OCH_2CH_2CH_2$), 28.0 (virtual t, J_{CP} = 17.5 Hz, PCH_2), 25.4 (s, $OCH_2CH_2CH_2$), 22.7 (s, PCH_2CH_2); $^{31}P\{^1H\}$ 14.1 (s, $^1J_{PPT}$ = 2566 Hz).³² IR (cm^{-1} , powder film), $\nu_{C\equiv C}$ 2142 (m), 2001 (w); UV-Vis (nm (ϵ , $M^{-1}cm^{-1}$), 1.25×10^{-5} M in CH_2Cl_2), 263 (8500), 291 (104 000), 320 (127 000), 353 (7000), 379 (5900), 411 (3400); MS,³³ 2017 (5^+ , 100%).

Trans-(C₆F₅)(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₃CH=CH₂)₂Pt-(C \equiv C)₂H (7**).** A Schlenk flask was charged with **6** (0.338 g, 0.323 mmol),¹⁵ CuI (0.012 g, 0.065 mmol), CH_2Cl_2 (3 mL), and $HNEt_2$ (20 mL), and cooled to –45 °C. Then $H(C\equiv C)_2H$ (0.258 g, 5.17 mmol, *ca.* 1 M in THF)³⁴ was added with stirring. The mixture turned light yellow. The cold bath was allowed to warm to 10 °C over the course of 3 h, and then removed. After an additional 2.5 h (orange supernatant/white precipitate), the solvent was removed by oil pump vacuum. The tan residue was extracted with toluene (3 \times 3 mL). The combined extracts were filtered through an alumina column (4 \times 2.5 cm, toluene rinses). The solvent was removed from the filtrate by oil pump vacuum to give **7** as a yellow-tan oil (0.293 g, 0.276 mmol, 86%). Calcd for $C_{54}H_{59}F_5P_2Pt$: C, 61.18; H, 5.61. Found: C, 61.44; H, 5.43%.

NMR (δ , $CDCl_3$), 1H 7.54–7.51 (m, 8H of 4 Ph), 7.37–7.27 (m, 12H of 4 Ph), 5.87–5.80 (m, 2H, $CH=$), 5.05–4.95 (m, 4H, $=CH_2$), 2.64–2.61 (m, 4H, PCH_2), 2.07–2.05 (m, 4H, $CH_2CH=$), 1.86–1.82 (m, 4H, PCH_2CH_2), 1.36–1.26 (m, 8H, CH_2), 0.94 (s, 12H, CH_3); $^{13}C\{^1H\}^{30,31}$ 146.1 (dm, $^1J_{CF}$ = 268 Hz, o to Pt), 139.1 (s, $CH=$), 136.5 (dm, $^1J_{CF}$ = 239 Hz, m/p to Pt), 133.0 (virtual t, J_{CP} = 5.8 Hz, o to P), 131.6 (virtual t, J_{CP} = 27.8 Hz, i to P), 130.2 (s, p to P), 127.9 (virtual t, J_{CP} = 5.2 Hz, m to P), 114.3 (s, $=CH_2$), 93.0 (s, $PtC\equiv C$), 72.4 (s, $PtC\equiv CC$), 59.8 (s, $PtC\equiv CC\equiv C$), 41.0 (s, CH_2), 37.1 (s, CH_2), 34.6 (s, $CH_2CH=$), 33.3 (virtual t, J_{CP} = 7.5 Hz, PCH_2CH_2C), 26.7 (s, double intensity, CH_3), 23.34 (s, CH_2), 23.30 (virtual t, J_{CP} = 17.5 Hz, PCH_2); $^{31}P\{^1H\}$ 15.0 (s, $^1J_{PPT}$ = 2583 Hz).³² IR (cm^{-1} , oil film), $\nu_{=CH}$ 3309 (w), $\nu_{C\equiv C}$ 2150 (m); MS,³³ 1060 (7^+ , 10%), 1010 ($[7 - C_4H]^+$, 20%), 841 ($[7 - C_4H - C_6F_5]^+$, 8%), 373 (PPh_2R^+ , 100%).

Trans,trans-(C₆F₅)(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₃CH=CH₂)₂Pt-(C \equiv C)₄Pt(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₃CH=CH₂)₂(C₆F₅) (8**).** A three-necked flask was charged with **7** (0.280 g,

0.264 mmol) and acetone (6 mL), and fitted with a gas inlet needle and a condenser. A Schlenk flask was charged with CuCl (0.050 g, 0.51 mmol) and acetone (15 mL), and TMEDA (0.020 mL, 0.13 mmol) was added with stirring. After 0.5 h, stirring was halted (blue supernatant/green solid). Then O_2 was bubbled through the three-necked flask with stirring, and the solution was heated to 65 °C. The blue supernatant was added in portions over 1.5 h (aspirated acetone was replenished). After an additional 0.5 h, the solvent was removed from the green-yellow solution by rotary evaporation and oil pump vacuum. Toluene was added (2 \times 3 mL), and the mixture was transferred to an alumina column (4 \times 2.5 cm). The column was eluted with toluene until UV monitoring showed no absorbing material (*ca.* 30 mL). The solvent was removed by rotary evaporation and oil pump vacuum to give **8**·toluene as a slightly yellow oil (0.220 g, 0.0995 mmol, 75%) that solidified after several weeks, mp 108–110 °C. Calcd for $C_{108}H_{116}F_{10}P_4Pt_2 \cdot C_7H_8$: C, 62.49; H, 5.65. Found: C, 62.42; H, 5.50%.

NMR (δ , $CDCl_3$), 1H 7.50–7.46 (m, 12H of 8 Ph), 7.37–7.26 (m, 33H of 8 Ph and 1 toluene), 5.84–5.77 (m, 4H, $CH=$), 5.02–4.92 (m, 8H, $=CH_2$), 2.56–2.53 (m, 8H, PCH_2), 2.39 (s, 3H, toluene), 2.04–2.02 (m, 8H, $CH_2CH=$), 1.86–1.82 (m, 8H, PCH_2CH_2), 1.36–1.26 (m, 16H, CH_2), 0.89 (s, 24H, CH_3); $^{13}C\{^1H\}^{30,31}$ 146.0 (dm, $^1J_{CF}$ = 258 Hz, o to Pt), 139.1 (s, $CH=$), 137.8 (s, toluene), 136.5 (dm, $^1J_{CF}$ = 236 Hz, m/p to Pt), 133.0 (virtual t, J_{CP} = 5.7 Hz, 31 o to P), 131.6 (virtual t, J_{CP} = 27.9 Hz, i to P), 130.2 (s, p to P), 129.0 (s, toluene), 128.2 (s, toluene), 127.9 (virtual t, J_{CP} = 5.1 Hz, m to P), 125.3 (s, toluene), 114.3 (s, $=CH_2$), 94.6 (s, $PtC\equiv C$), 63.6 (s, $PtC\equiv CC$), 58.1 (s, $PtC\equiv CC\equiv C$), 41.1 (s, CH_2), 37.2 (s, CH_2), 34.5 (s, $CH_2CH=$), 33.3 (virtual t, J_{CP} = 6.9 Hz, PCH_2CH_2C), 26.7 (s, double intensity, CH_3), 23.34 (s, CH_2), 23.32 (virtual t, J_{CP} = 15.6 Hz, PCH_2), 21.4 (s, toluene); $^{31}P\{^1H\}$ 15.0 (s, $^1J_{PPT}$ = 2577 Hz).³² IR (cm^{-1} , powder film), $\nu_{C\equiv C}$ 2143 (m); MS,³³ 2117 (8^+ , 30%), 1010 ($[(C_6F_5)Pt(PPh_2R)_2]^+$, 100%), 840 ($[Pt(PPh_2R)_2]^+$, 50%).

Alkene metathesis of 8. A two-necked flask was charged with **8**·toluene (0.209 g, 0.0946 mmol), Grubbs' catalyst (*ca.* half of 0.006 g, 0.008 mmol), and CH_2Cl_2 (100 mL), and fitted with a condenser. The solution was refluxed. After 2 h, the remaining catalyst was added. After 3 h, the solvent was removed by oil pump vacuum, and CH_2Cl_2 (2 \times 3 mL) was added. The sample was transferred in two portions to an alumina column (4 \times 2.5 cm), which was eluted with CH_2Cl_2 until UV monitoring showed no absorbing material (*ca.* 30 mL). The solvent was removed by rotary evaporation and oil pump vacuum to give a mixture of cyclized products as a tan solid (0.188 g, 0.0912 mmol, 96%).

NMR (δ , $CDCl_3$), 1H 7.90 (m, 4H of 8Ph), 7.47–7.41 (m, 12H of 8Ph), 7.27–7.15 (m, 24H of 8Ph), 5.46–5.45 (m, 4H, $CH=$), 2.73–2.62 (m, 8H, CH_2), 2.35–2.32 (m, 4H, CH_2), 2.04 (m, 12H, CH_2), 1.42–1.26 (m, 16H, CH_2), 0.90, 0.88, and 0.85 (3 s, 24H, CH_3); $^{31}P\{^1H\}$, 15.1 (s, $^1J_{PPT}$ = 2575 Hz, 76%),³² 14.9 (s, 16%), 14.4 (s, 8%). MS,³³ 2060 ($[M - H]^+$, 20%), 1893 ($[M - H - C_6F_5]^+$, <3%), 982 ($[(C_6F_5)Pt(Ph_2P(CH_2)_2C(CH_3)_2(CH_2)_3CH=CH(CH_2)_3C(CH_3)_2(CH_2)_2PPh_2)]^+$, 20%), 815 ($[Pt(Ph_2P(CH_2)_2C(CH_3)_2(CH_2)_3CH=CH(CH_2)_3C(CH_3)_2(CH_2)_2PPh_2)]^+$, 100%).

***Trans,trans*-(C₆F₅)(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂-(CH₂)₂PPh₂)Pt(C≡C)₄Pt(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂)(C₆F₅) (9).** A Schlenk flask was charged with metathesized **8** (0.400 g, 0.194 mmol), 10% Pd/C (0.021 g, 0.021 mmol), ClCH₂CH₂Cl (13 mL), and ethanol (13 mL), flushed with H₂, and fitted with a balloon filled with H₂. The mixture was stirred for 14 d. The solvent was removed by oil pump vacuum. The residue was extracted with CH₂Cl₂ (2 × 3 mL). The extract was eluted through an alumina column (4 × 2.5 cm), which was rinsed with CH₂Cl₂ until UV monitoring showed no absorbing material (*ca.* 30 mL). The solvent was removed by oil pump vacuum to give a mixture of cyclized products (0.329 g, 0.159 mmol, 82%).

NMR (δ, CDCl₃), ¹H 7.90 (m, 4H of 8 Ph), 7.48–6.89 (m, 36H of 8 Ph), 2.67–2.65 (m, 8H, CH₂), 2.04–1.98 (m, 8H, CH₂), 1.42–1.26 (m, 32H, CH₂), 0.92, 0.90, and 0.89 (3 s, 24H, CH₃); ³¹P{¹H} 16.4 (s, ¹J_{PPt} = 2665 Hz, 14%), ³² 15.4 (s, 6%, **10**), 15.1 (s, 12%), 15.0 (s, 16%), 14.9 (s, 11%), 13.8 (s, ¹J_{PPt} = 2570 Hz, 41%, **9**).³²

An analytical sample of **9** was isolated by column chromatography (12 × 2.5 cm Al₂O₃, 25 : 75 v/v hexanes–CH₂Cl₂) and dried by oil pump vacuum, giving a yellow powder (0.055 g, 0.0266 mmol, 14%), mp 217–220 °C. Calcd for C₁₀₄H₁₁₂F₁₀P₄Pt₂: C, 60.46; H, 5.46. Found: C, 59.93; H, 5.48%. DSC: endotherm with T_i, 162.3 °C; T_e, 175.3 °C; T_p, 186.7 °C; T_c, 210.9 °C; T_f, 214.9 °C. TGA: onset of mass loss, 289.6 °C (T_e).

NMR (δ, CDCl₃), ¹H 7.70–7.68 (m, 8H of 8 Ph), 7.49–7.37 (m, 12H of 8 Ph), 7.36–7.26 (m, 20H of 8 Ph), 2.63 (m, 8H, PCH₂), 1.89 (m, 4H, PCH₂CHH'), 1.51 (m, 4H, PCH₂CHH'), 1.28–1.02 (m, 32H, CH₂), 0.90 (s, 12H, CH₃), 0.89 (s, 12H, CH₃); ¹³C{¹H} ^{30,31} 146.0 (dm, ¹J_{CF} = 224 Hz, *o* to Pt), 136.6 (dm, ¹J_{CF} = 237 Hz, *m/p* to Pt), 134.2 (virtual t, J_{CP} = 6.3 Hz, *o* to P), 131.8 (virtual t, J_{CP} = 5.3 Hz, *o* to P), 131.3 (virtual t, J_{CP} = 27.1 Hz, *i* to P), 130.8 (s, *p* to P), 130.5 (virtual t, J_{CP} = 26.9 Hz, *i* to P), 129.7 (s, *p* to P), 128.1 (virtual t, J_{CP} = 5.3 Hz, *m* to P), 127.6 (virtual t, J_{CP} = 4.7 Hz, *m* to P), 95.0 (s, PtC≡C), 63.7 (s, PtC≡CC), 58.8 (s, PtC≡CC≡C), 40.5 (s, CH₂), 35.3 (s, CH₂), 33.3 (virtual t, J_{CP} = 6.7 Hz, PCH₂CH₂C), 29.3 (s, CH₂), 28.0 (s, CH₃), ³⁵ 27.8 (s, CH₂), 27.2 (s, CH₃), ³⁵ 23.4 (virtual t, J_{CP} = 18.4 Hz, PCH₂), 22.7 (s, CH₂); ³¹P{¹H} 13.9 (s, ¹J_{PPt} = 2571 Hz).³² IR (cm⁻¹, powder film), ν_{C≡C} 2142 (m); MS, ³³ 2065 ([**9** – H]⁺, 60%), 1898 ([**9** – C₆F₅]⁺, 5%), 984 ([C(C₆F₅)Pt(Ph₂P(CH₂)₂C(CH₃)₂-(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂)]⁺, 100%), 815 ([Pt(Ph₂P(CH₂)₂-C(CH₃)₂(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂)]⁺, 60%).

***Trans,trans*-(C₆F₅)(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂-(CH₂)₂PPh₂)Pt(C≡C)₄Pt(Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂)(C₆F₅) (10).** A Schlenk flask was charged with *trans,trans*-(C₆F₅)(*p*-tol₃P)₂Pt(C≡C)₄Pt(*Pp*-tol₃)₂(C₆F₅) (**15**;¹⁵ 0.102 g, 0.050 mmol) and CH₂Cl₂ (100 mL). A solution of Ph₂P(CH₂)₂C(CH₃)₂(CH₂)₈C(CH₃)₂(CH₂)₂PPh₂ (**14**;¹³ 0.075 g, 0.12 mmol) in CH₂Cl₂ (120 mL) was passed through a silica gel pad (2 cm) directly into the Schlenk flask with stirring. After 2 h, the mixture was concentrated by 50% and ethanol (50 mL) was added. This procedure was repeated two

times. The yellow solid was collected by filtration, washed with ethanol (2 × 20 mL), and dried by oil pump vacuum to give **10** (0.073 g, 0.035 mmol, 70%).

NMR (δ, CDCl₃), ¹H 7.42 (m, 16H of 8 Ph), 7.27 (m, 8H of 8 Ph), 7.19 (m, 16H of 8 Ph), 2.65 (m, 8H, PCH₂), 2.16 (m, 8H, PCH₂CH₂), 1.43–1.15 (m, 32H, CH₂), 1.05 (s, 24H, CH₃); ¹³C{¹H} ^{30,31} 145.5 (dm, ¹J_{CF} = 228 Hz, *o* to Pt), 136.3 (dm, ¹J_{CF} = 245 Hz, *m/p* to Pt), 133.0 (virtual t, J_{CP} = 5.8 Hz, *o* to P), 130.6 (virtual t, J_{CP} = 27.1 Hz, *i* to P), 130.2 (s, *p* to P), 127.9 (virtual t, J_{CP} = 5.0 Hz, *m* to P), 95.7 (s, PtC≡C), 63.6 (s, PtC≡CC), 59.0 (s, PtC≡CC≡C), 40.2 (s, CH₂), 35.0 (s, CH₂), 33.6 (virtual t, J_{CP} = 6.6 Hz, PCH₂CH₂C), 29.3 (s, CH₂), 28.0 (s, CH₂), 27.8 (s, CH₃), 22.7 (s, CH₂), 20.5 (virtual t, J_{CP} = 17.3 Hz, PCH₂); ³¹P{¹H} 15.5 (s, ¹J_{PPt} = 2584 Hz).³² IR (cm⁻¹, powder film), ν_{C≡C} 2146 (m), 2003 (w); MS, ³³ 2065 ([**10** – H]⁺, 100%), 2051 ([**10** – CH₃]⁺, 68%), 2037 ([**10** – 2CH₃ + H]⁺, 68%), no other significant peaks with *m/z* > 975.

***Trans,trans*-(C₆F₅)(*p*-tol₂P(CH₂)₃(CF₂)₈(CH₃)₃*Pp*-tol₂)-Pt(C≡C)₄Pt(*p*-tol₂P(CH₂)₃(CF₂)₈(CH₃)₃*Pp*-tol₂)(C₆F₅)**

(**17a**). A 5 mm NMR tube was charged with **15** (0.0193 g, 0.00972 mmol), **16a** (0.0177 g, 0.0194 mmol), and THF-*d*₈ (0.6 mL; freshly dried and deoxygenated by pre-treatment with CaH₂, heating with Na/benzophenone, and vacuum transfer). The sample was immediately transferred to a –100 °C NMR probe. Data: see text.

3. Crystallography

A CH₂Cl₂ solution of **5** was layered with methanol. After one week, yellow prisms of **5**·MeOH were obtained. Data were collected on a Nonius KappaCCD diffractometer as outlined in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and were refined with 20654 reflections. Lorentz, polarization, and absorption corrections³⁶ were applied. The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on *F*² using SHELXL-97.³⁷ Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from the literature.³⁸ The solvate molecule was disordered and could only be poorly resolved. Per the preliminary communication of this structure in ref. 3d, additional data are available from the Cambridge Crystallographic Data Center via the CCDC number 295841.

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