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Platinum(II) alkyl complexes of chelating dibridgehead diphosphines $P((CH_2)_n)_3P$ (n = 14, 18, 22); facile *cis/trans* isomerizations interconverting gyroscope and parachute like adducts

The dibridgehead diphosphines $P((CH_2)_n)_3P$ can serve either as *cis* or *trans* spanning chelate ligands, termed "parachute" and "gyroscope" systems, respectively. This work examines the dependence of the ancillary ligands upon this equilibrium, using both experimental and computational probes. The diphosphines ligands in the *cis* isomers are intrinsically more strained, but they are nonetheless favoured with strong sigma donor ligands such as *n*-alkyl.

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Platinum(II) alkyl complexes of chelating dibridgehead diphosphines P((CH$_2$)$_n$)$_3$P (*n* = 14, 18, 22); facile *cis/trans* isomerizations interconverting gyroscope and parachute like adducts†

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The gyroscope like dichloride complexes *trans*-Pt(Cl)$_2$(P((CH$_2$)$_n$)$_3$P) (*trans*-**2**; *n* = **c**, 14; **e**, 18; **g**, 22) and MeLi (2 equiv.) react to yield the parachute like dimethyl complexes *cis*-Pt(Me)$_2$(P((CH$_2$)$_n$)$_3$P) (*cis*-**4c,e,g**, 70−91%). HCl (1 equiv.) and *cis*-**4c** react to give *cis*-Pt(Cl)(Me)(P((CH$_2$)$_{14}$)$_3$P) (*cis*-**5c**, 83%), which upon stirring with silica gel or crystallization affords *trans*-**5c** (89%). Similar reactions of HCl and *cis*-**4e,g** give *cis/trans*-**5e,g** mixtures that upon stirring with silica gel yield *trans*-**5e,g**. A parallel sequence with *trans*-**2c**/EtLi gives *cis*-Pt(Et)$_2$(P((CH$_2$)$_{14}$)$_3$P) (*cis*-**6c**, 85%) but subsequent reaction with HCl affords *trans*-Pt(Cl)(Et)(P((CH$_2$)$_{14}$)$_3$P) (*trans*-**7c**, 45%) directly. When previously reported *cis*-Pt(Ph)$_2$(P((CH$_2$)$_{14}$)$_3$P) is treated with HCl (1 equiv.), *cis*- and *trans*-Pt(Cl)(Ph)(P((CH$_2$)$_{14}$)$_3$P) are isolated (44%, 29%), with the former converting to the latter at 100 °C. Reactions of *trans*-**5c** and LiBr or NaI afford the halide complexes *trans*-Pt(X)(Me)(P((CH$_2$)$_{14}$)$_3$P) (*trans*-**9c**, 88%; *trans*-**10c**, 87%). Thermolyses and DFT calculations that include acyclic model compounds establish *trans* > *cis* stabilities for all except the dialkyl complexes, for which energies can be closely spaced. The σ donor strengths of the non-phosphine ligands are assigned key roles in the trends. The crystal structures of *cis*-**4c**, *trans*-**5c**, *trans*-**7c**, and *trans*-**10c** are determined and analyzed together with the computed structures.

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Introduction

The broad field of molecular rotors is highly relevant to several types of molecular machines, and in lieu of an extensive list of primary research articles, readers are referred to three expansive reviews.[1–3] We have had an ongoing interest in the subnanoscale miniaturization of various macroscopic devices, and this has driven the synthesis and intensive study of two classes of metal complexes in our group. The first, exemplified by *trans*-**II** in Scheme 1, has been termed "gyroscope like" due to the obvious geometric resemblance.[3] Such species can be accessed *via* three-fold ring closing metathesis/hydrogenation sequences involving complexes with *trans* phosphine ligands of the formula P((CH$_2$)$_m$CH=CH$_2$)$_3$ (*trans*-**I**).[3–7] This affords adducts of cage like dibridgehead diphosphines with three

connecting (CH$_2$)$_n$ bridges (*n* = 2*m* + 2). Depending upon the lengths of the methylene segments and the sizes of the ligands, the ML$_y$ rotators may be capable of rotation, exchanging the positions of the ligands or (equivalently) the (CH$_2$)$_n$ bridges.
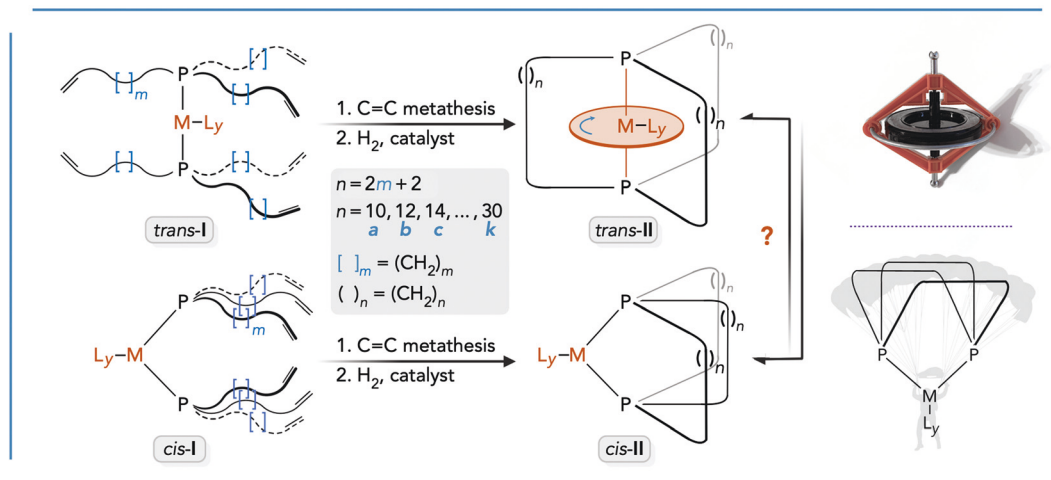
When such sequences are carried out with analogous *cis* complexes (*e.g.*, *cis*-**I**, Scheme 1), the same diphosphine ligands can be generated, but now with the donor atoms connecting *cis* positions.[8] When accessed in square planar geometries, one (CH$_2$)$_n$ bridge can be visualized as lying in the coordination plane, the second above, and the third below. Depending upon the lengths of the methylene segments and the sizes of the ligands, the bridges may be capable of "jump rope" dynamic processes that exchange their positions. When square planar versions of *cis*-**II** are viewed from appropriate perspectives, there is some resemblance to a parachutist, so they are often termed "parachute like".

In analyzing the dynamic behavior of both classes of complexes, it has been important to exclude alternative mechanisms for exchanging the positions of ligands or (CH$_2$)$_n$ bridges.[9] Specifically, any facile *trans/cis* isomerization could open up new pathways. In one embodiment, gyroscope like *trans*-**II** might first undergo a hypothetically endergonic iso-

Scheme 1 Generalized syntheses of gyroscope like (*trans*-II) and parachute like (*cis*-II) metal complexes.

merization to parachute like *cis*-**II**, where $(CH_2)_n$ exchange might be more rapid than in *trans*-**II** ("jump rope" rate > ML_y rotation). Alternatively, one can play the devil's advocate in the opposite direction. Thus, we have sought to probe the relative stabilities of *cis/trans*-**II** and their thermal interconversion both experimentally and computationally.

In earlier studies, we examined these issues with a series of platinum dichloride complexes, *cis*- and *trans*-Pt $(Cl)_2(P((CH_2)_n)_3P)$ (*cis*- and *trans*-**2**).[4c,8] As shown in Scheme 2, temperatures of 150–185 °C were required to effect equilibrations on reasonable time scales from either direction. In all cases, the gyroscope like *trans* isomers were favored. To facilitate comparisons with earlier papers, the same letter indices have been employed for n ($n = 10$, **a**; 12, **b**; 14, **c**; *etc*.). Computationally, as one goes from $(CH_2)_{10}$ (**2a**) to $(CH_2)_{22}$ (**2g**), or 13- to 25-membered macrocycles, the gyroscope like *trans*-**2** ranges from 5.1 to 9.2 kcal mol^{-1} more stable than the parachute like *cis*-**2**.[8,10]

The acyclic precursor complexes *cis*- and *trans*-Pt $(Cl)_2(P((CH_2)_mCH=CH_2)_3)_2$ (*cis*- and *trans*-**1**) could also be thermally equilibrated.[4c] Here, in line with literature precedent,[11,12] there is a significant effect of solvent polarity that tracks the dipole moments (*cis* > *trans*; more polar CH_2Cl_2: appreciable amounts of both isomers; less polar toluene: >95% *trans*).[13] Other reactivity data are relevant. As shown in Scheme 3, the dichloride complexes **2** and Ph_2Zn react at room temperature to give the diphenyl complexes Pt $(Ph)_2(P((CH_2)_n)_3P)$ (**3**).[4] Since *cis*-**2c,d** and *trans*-**2c,e** afford *cis*-**3c,d** and *trans*-**3c,e**, respectively, these fit the textbook definition of stereospecific reactions.[14] Furthermore, the stereospecificity excludes *cis/trans* isomerization at any stage of the reaction coordinates.

In this paper, we report the surprising observation of much lower energy pathways for the interconversion of *trans*-**II** and *cis*-**II** when the chloride ligands in **2** are replaced by one or more alkyl groups. Since these isomerizations impinge upon a number of mechanistic questions, even beyond those
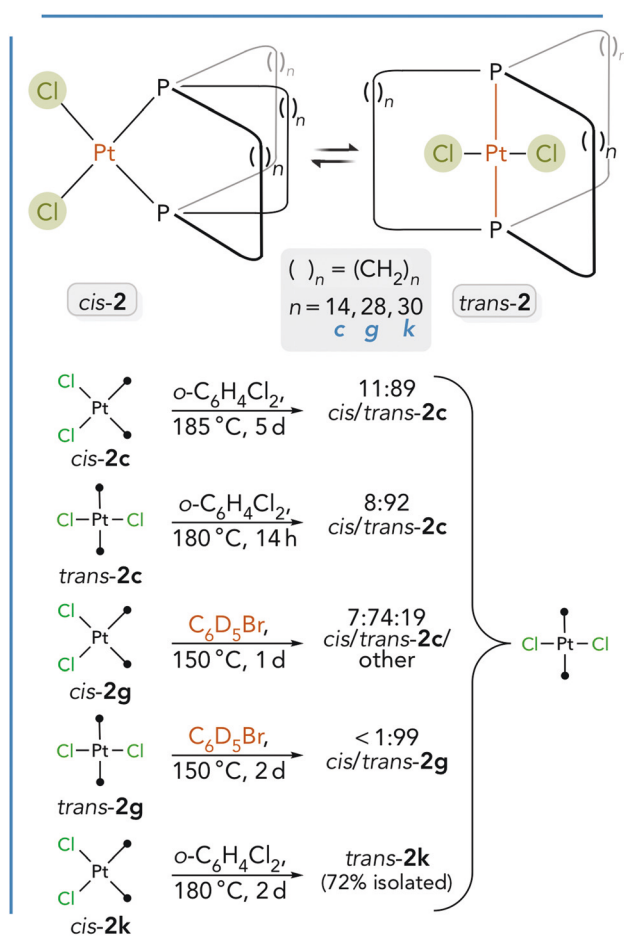
Scheme 2 Previously studied isomerizations of parachute and gyroscope like complexes.

expressed above, it was imperative to bring definition to the phenomena. Accordingly, a variety of synthetic, structural, thermolytic, and computational experiments have been carried
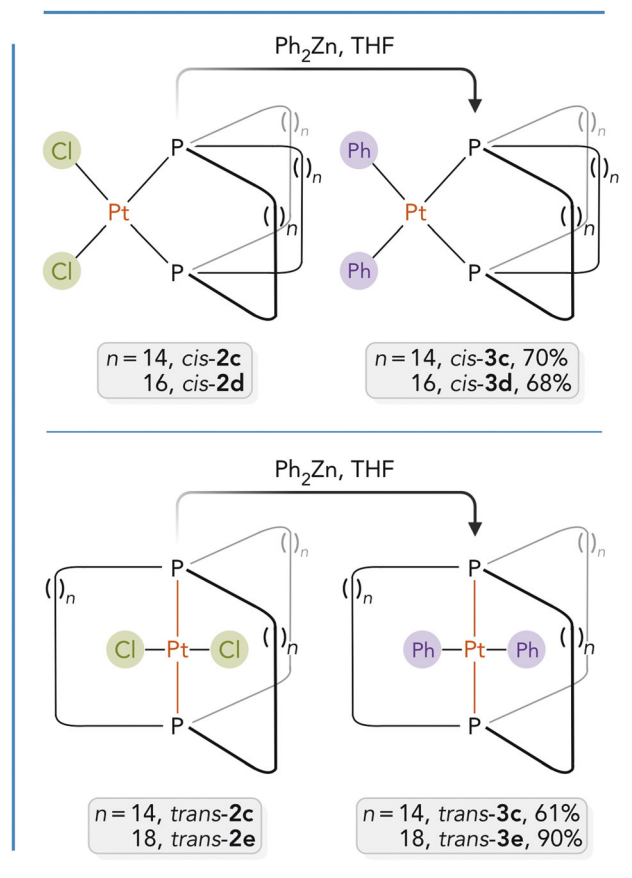
Scheme 3 Stereospecific substitution of chloride ligands by phenyl ligands in *trans* and *cis* platinum complexes.
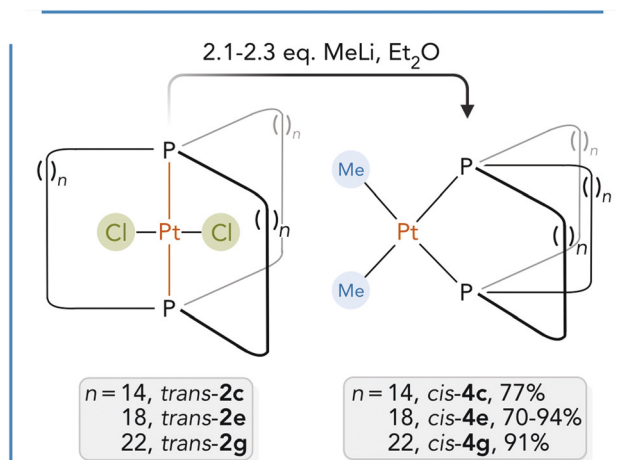

Scheme 4 Substitution of the chloride ligands in *trans*-**2c,e,g** by methyl ligands with isomerization.

out, as detailed in the narrative below. None of these data have been previously communicated.

Results

Syntheses and NMR characterization

As shown in Scheme 4, the gyroscope like platinum dichloride complexes *trans*-**2c,e,g**[4a] were treated with diethyl ether solutions of MeLi (2.1–2.3 equiv.). Workups gave the new parachute like dimethyl complexes *cis*-Pt(Me)$_2$(P((CH$_2$)$_n$)$_3$P) (*cis*-**4c, e,g**) in 70–94% yields as air stable white solids. When the first such reaction was conducted, the *trans/cis* isomerization was considered surprising. Thus, the neutral alumina columns used in initial experiments were omitted. However, identical results were obtained.

These and all other new complexes below were characterized by NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) and microanalyses, as summarized in the Experimental section. The *cis* stereochemistry was evidenced by a number of features, such as the lower $^1J_{PPt}$ values (1853–1886 Hz *vs.* 2389–2398 Hz for *trans*-**2c,e,g**).[15] Each ^{13}C{^{1}H} NMR spectrum showed a doublet of doublets for the methyl groups ($^2J_{CP(trans)}$ = 101.7–101.1 Hz, $^2J_{CP(cis)}$ = 9.9–10.0 Hz). Each ^{1}H NMR spectrum also showed a

doublet of doublets ($^3J_{HP(trans)}$ = 7.3–6.7 Hz, $^3J_{HP(cis)}$ = 6.1–5.7 Hz), and platinum satellites were usually visible ($^2J_{HPt}$ = 66–65 Hz). The ^{1}H and ^{31}P NMR properties were very similar to those reported for the related acyclic complexes *cis*-Pt (Me)$_2$(PR$_3$)$_2$.[16,17]

A reaction of *trans*-**2c** and only 1.1 equiv. of MeLi was similarly conducted. A ^{31}P{^{1}H} NMR spectrum of the crude reaction mixture showed 40–50% conversion to the dimethyl complex *cis*-**4c**. The only other signal detected was that of the starting material *trans*-**2c**. Thus, it was not possible to interrogate the stereochemistry of the presumed intermediate, the methyl chloride complex Pt(Cl)(Me)(P((CH$_2$)$_{14}$)$_3$P) (**5c**). When the reaction of *trans*-**2c** and 2.2 equiv. of MeLi (Scheme 4) was repeated at 0 °C, the result was the same as at room temperature.

As shown in Scheme 5, CH$_2$Cl$_2$ solutions of *cis*-**4c,e,g** were treated with 1.0 equiv. of HCl. In some cases the HCl was generated *in situ* from acetyl chloride (1.0 equiv.) and excess methanol, and in other cases 2.0 M Et$_2$O solutions were used. With *cis*-**4c**, a chromatographic workup (neutral alumina) gave parachute like *cis*-Pt(Cl)(Me)(P((CH$_2$)$_{14}$)$_3$P) (*cis*-**5c**) in 83% yield. The lower symmetry was evidenced by doubled ^{31}P NMR signals, and Pt$C\underline{H}_3$ ^{1}H and ^{13}C NMR signals that were now doublets of doublets. Analogous patterns have been noted for the related complexes *cis*-Pt(Cl)(Me)(PR$_3$)$_2$.[17,18]

The stereochemical homogeneity of *cis*-**5c** was quickly found to be tied to a hair trigger. Either exposure to silica gel (in the form of a column or slurry) or crystallization (Et$_2$O/ methanol or Et$_2$O/ethanol) afforded gyroscope like *trans*-**5c** (≥89%). Even CH$_2$Cl$_2$ solutions of the dimethyl complex *cis*-**4c**, when slurried with silica gel, gave *trans*-**5c** (70%). The NMR properties of *trans*-**5c** were similar to those of the dichloride complex *trans*-**2c**, with the ^{1}H and ^{13}C NMR spectra showing triplets for the Pt$C\underline{H}_3$ group.

With *cis*-**4e,g**, the analogous methyl chloride complexes *cis*-**5e,g** could be detected "on the fly", but isolated samples always contained significant amounts of *trans*-**5e,g**. These mix-
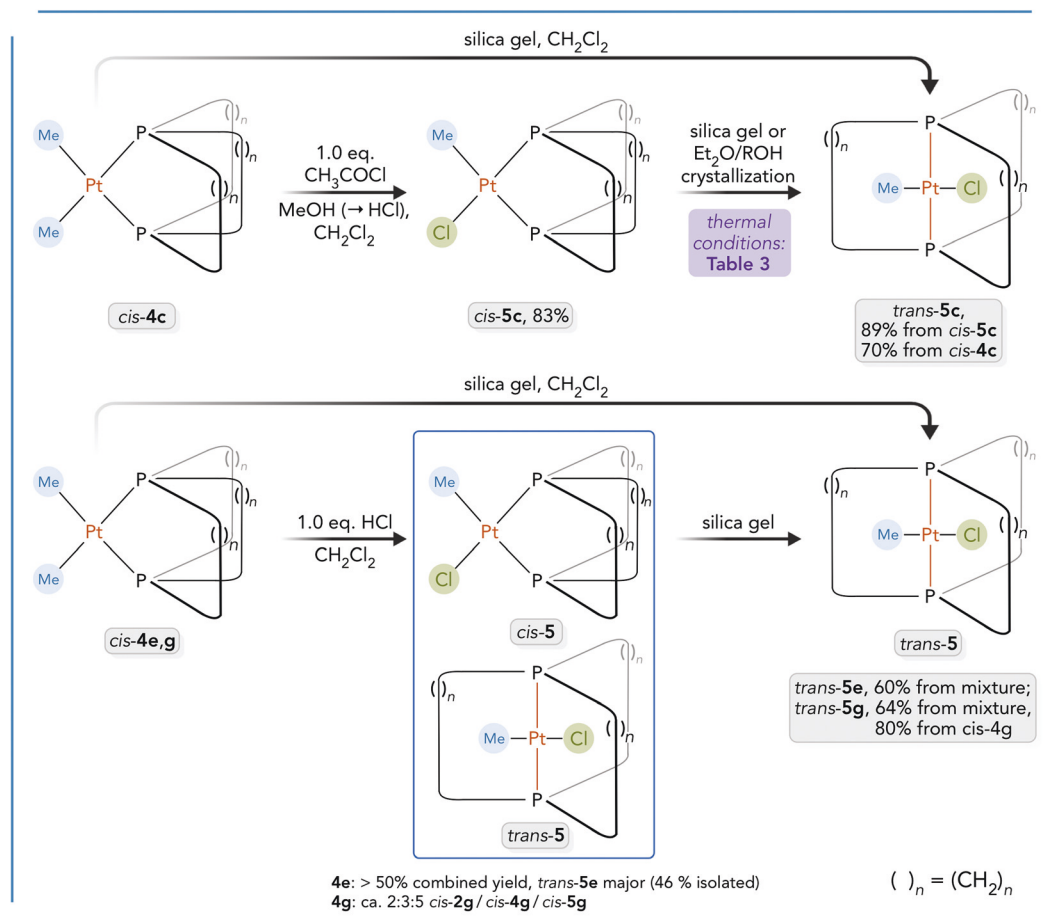
Scheme 5 Introduction of halide ligands and attendant isomerization.

tures were further slurried with silica gel to give pure *trans*-**5e**, **g** (60–64%). Additional details can be found in the Experimental section. The NMR properties were similar to those of *trans*-**5c**, and all three complexes exhibited $^1J_{PPt}$ values (2824–2796 Hz) that were diagnostic of the *trans* stereochemistry.[15] Given the modest dependence of the chemistry in Schemes 3–5 upon the lengths of the $(CH_2)_n$ bridges, subsequent experiments were confined to $(CH_2)_{14}$ systems ("**c** series").

As depicted in Scheme 6, a parallel sequence was carried out with *trans*-**2c** and EtLi in place of MeLi. The parachute like diethyl complex *cis*-Pt(Et)$_2$(P((CH$_2$)$_{14}$)$_3$P) (*cis*-**6c**) was isolated in 85% yield. NMR spectra showed a $^1J_{PPt}$ value of 1746 Hz, and PtC$\underline{H_2}$C$\underline{H_3}$ ^{1}H signal patterns similar to those of related acyclic complexes *cis*-Pt(Et)$_2$(PR$_3$)$_2$.[16] Next, *cis*-**6c** was treated with HCl analogously to the dimethyl complex *cis*-**4c** in Scheme 5. However, the same chromatographic workup (neutral alumina) afforded only gyroscope like *trans*-**7c** (45%). Accordingly, the
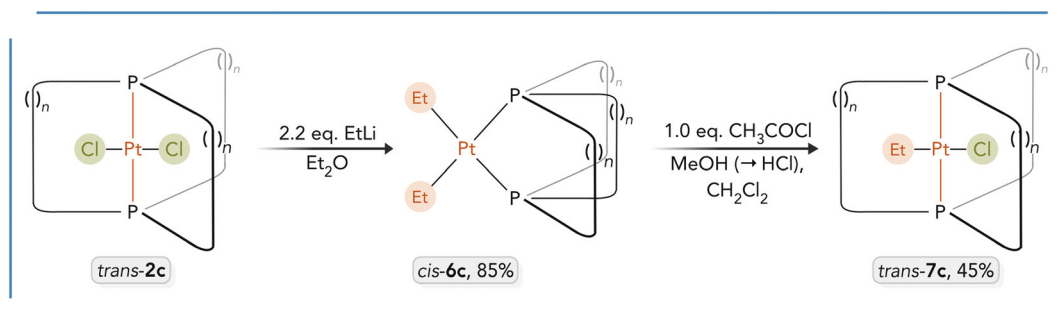
Scheme 6 Substitution and isomerization reactions involving ethyl ligands.

NMR spectra now showed a $^1J_{PPt}$ value of 3002 Hz, and PtC$\underline{H}_2$C$\underline{H}_3$ ^{1}H signal patterns similar to those of other complexes of the type *trans*-Pt(Cl)(Et)(PR$_3$)$_2$.[19] No significant amounts of byproducts were noted when crude reaction mixtures were assayed by ^{31}P NMR.

The main difference between the substitution reactions of the gyroscope like dichloride complex *trans*-**2c** in Schemes 4 and 6 and that in Scheme 3 is the use of alkyl lithium *versus* aryl zinc nucleophiles. Thus, as shown in Scheme 7 (top), *trans*-**2c** was treated with PhLi in a procedure analogous to that in Scheme 6. Workup gave the gyroscope like diphenyl complex *trans*-**3c** in 85% yield. All of the syntheses in this report have been reproduced several times, often by different coworkers. However, in one case this same reaction gave, under essentially identical conditions, *trans*-**3c** and *cis*-**3c** in 50% and 29% isolated yields, respectively. Regardless, the chloride/phenyl ligand substitution is not accompanied by the same degree of isomerization as chloride/alkyl ligand substitution.

In previous work, the gyroscope like diphenyl complexes *trans*-Pt(Ph)$_2$(P((CH$_2$)$_n$)$_3$P) (*trans*-**3c,e**) had been shown to react with 1.0 equiv. of HCl to give the gyroscope like phenyl chloride complexes *trans*-Pt(Cl)(Ph)(P((CH$_2$)$_n$)$_3$P) (*trans*-**8c,e**) in 93–98% yields after workup. This is exemplified with *trans*-**3c** in Scheme 7 (top). However, analogous substitution reactions with parachute like *cis*-**3** had not been investigated. Thus, *cis*-**3c** and HCl were similarly combined (Scheme 7, bottom). A chromatographic workup (neutral alumina) gave the easily separated products *cis*-**8c** (44%) and *trans*-**8c** (29%). The structure of the former, a new compound, followed readily from the types of NMR properties detailed above.

In connection with thermolyses described below, authentic samples of platinum bromide and iodide complexes became of interest. Thus, as shown in Scheme 8, the gyroscope like chloride complex *trans*-**5c** was treated (in separate reactions) with LiBr or NaI. Workups gave the gyroscope like halide complexes *trans*-Pt(X)(Me)(P((CH$_2$)$_{14}$)$_3$P) (X = Br, *trans*-**9c**; Cl, *trans*-**10c**) in 87–88% yields. The structure and stereochemistry followed readily from the NMR properties, as well as a crystal structure in the following section.

Crystallographic characterization

Due to the varied stereochemical issues involving the preceding complexes, crystal structures were sought wherever poss-
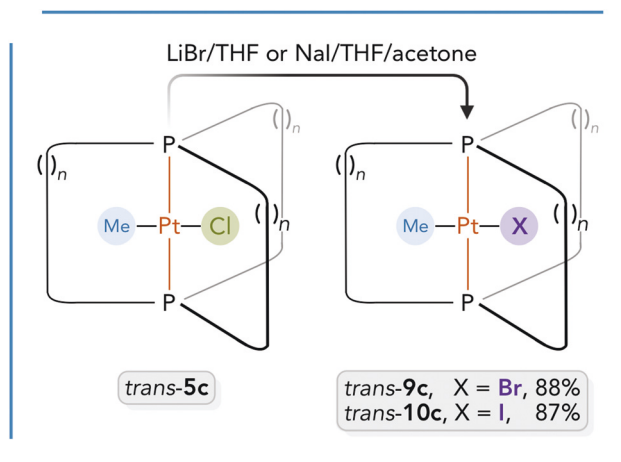
Scheme 8 Halide substitution reactions.
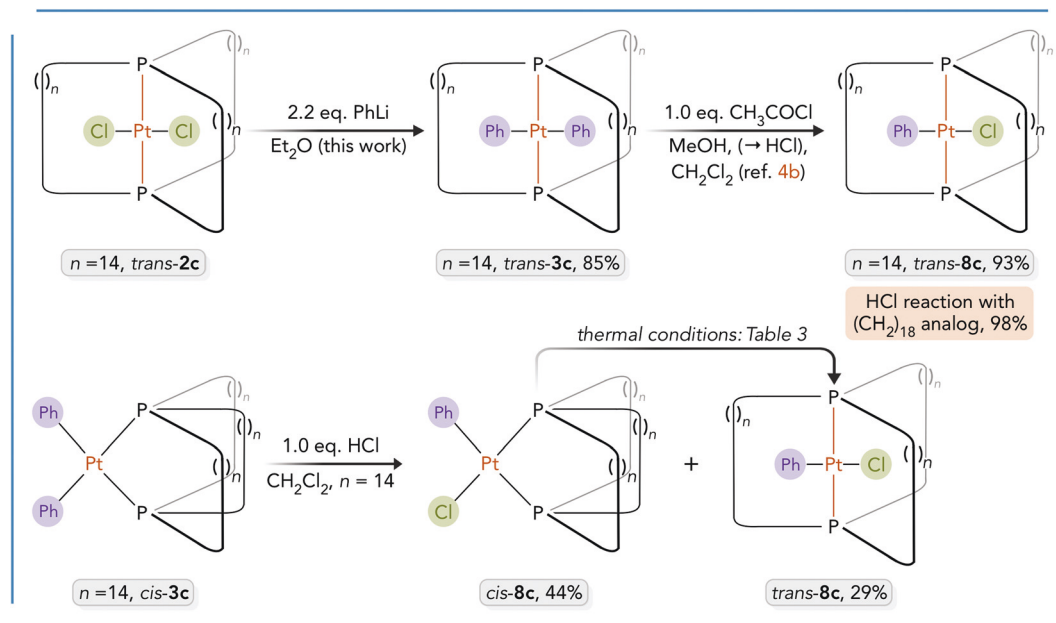
Scheme 7 Substitution and isomerization reactions involving phenyl ligands.

ible. Single crystals of *cis*-**4c**, *trans*-**5c**, *trans*-**7c**, and *trans*-**10c** could be obtained, and the X-ray structures were determined as described in the Experimental section and Table 1. Key metrical parameters are summarized in Table 2. Thermal ellipsoid plots are depicted in Fig. 1–4. All of the structures exhibited disorder that could easily be modeled (Me/X positions in *trans*-**5c** and *trans*-**10c**; certain $(CH_2)_n$ segments in *cis*-**4c**, *trans*-**5c**, and *trans*-**7c**). Data are given only for the dominant conformation.

As shown in Fig. 1, the dimethyl complex *cis*-**4c** exhibits, as with other parachute like adducts structurally characterized earlier,[8] one macrocycle in which the proximal CH_2 groups lie close to the coordination plane, and two in which the proximal CH_2 groups lie in roughly perpendicular planes. With the gyroscope like ethyl chloride complex *trans*-**7c**, three independent molecules were found in the unit cell. Since these involved rather minor conformational differences, only one is depicted in Fig. 3, but all are illustrated in the ESI.†

The views of the iodide complex *trans*-**10c** in Fig. 4 and the analogous chloride complex *trans*-**5c** in Fig. 2 have been arranged as closely as possible. While these adducts clearly pass the "eye test" as isostructural, the space groups are not identical (*Pbca* vs. *P*12₁/*n*1) and the crystal lattices differ.

Additional characterization of equilibria

Attention was turned to addressing certain gaps in the preceding preparative data. Although the reactions in Scheme 5 convincingly show that for the methyl chloride complexes **5c,e,g**, the *trans*/gyroscope isomers are more stable than the *cis*/parachute isomers, purely thermal conversions of purified samples were lacking. Accordingly, when o-$C_6H_4Cl_2$ or C_6D_5Br solutions of *cis*-**5c** were kept at 100–110 °C for 3–7 h, or toluene solutions kept at 80 °C for 72 h, or mesitylene solutions kept at 140 °C for 0.5 h, >99% conversions to *trans*-**5c** were observed, as assayed by $^{31}P\{^1H\}$ NMR. These data are from entries 9–13 of Table 3.

The previously reported thermolyses in Scheme 2 unambiguously show that the gyroscope like dichloride complexes *trans*-**2** are more stable than the parachute like *cis*-**2**. Since the procedures for isolating the latter did not involve silica gel (found to promote *cis*/*trans* isomerization in Scheme 5), it was of interest to see if conversion to *trans*-**2c** might be effected in slurries. However, no reaction occurred when *cis*-**2c** was combined with silica gel for 24 h at room temperature in toluene-d_8 or $CDCl_3$ (entry 1, Table 3).

The workups for isolating the analogous diphenyl complexes *cis*-**3c,d** (Scheme 3) did involve silica gel.[8] Nonetheless,

Table 1 Summary of crystallographic data

	cis-**4c**	*trans*-**5c**	*trans*-**7c**	*trans*-**10c**
Empirical formula	$C_{44}H_{90}P_2Pt$	$C_{43}H_{87}ClP_2Pt$	$C_{44}H_{89}ClP_2Pt$	$C_{43}H_{87}IP_2Pt$
Formula weight	876.18	896.60	910.63	988.05
Temperature [K]	110(2)	110(2)	110(2)	110(2)
Diffractometer	Quest	Quest	APEX II	APEX II
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*P*12₁/*c*1	*P*12₁/*n*1	*P*12₁/*c*1	*Pbca*
Unit cell dimensions:				
a [Å]	10.3514(4)	16.2658(9)	38.540(7)	20.481(6)
b [Å]	15.4895(6)	13.6513(8)	14.255(3)	13.685(4)
c [Å]	28.4607(12)	19.9653(11)	25.681(4)	33.232(10)
α [°]	90	90	90	90
β [°]	95.7670(10)	90.909(2)	91.995(2)	90
γ [°]	90	90	90	90
V [Å³]	4540.2(3)	4432.7(4)	14 100(4)	9314(5)
Z	4	4	12	8
ρ_{calc} [Mg m⁻³]	1.282	1.344	1.287	1.409
μ [mm⁻¹]	3.188	3.325	3.137	3.770
$F(000)$	1848	1880	5736	4048
Crystal size [mm³]	0.441 × 0.207 × 0.182	0.493 × 0.475 × 0.292	0.10 × 0.10 × 0.10	0.56 × 0.16 × 0.12
Θ limit [°]	1.949 to 24.999	1.948 to 27.496	1.66 to 27.50	2.336 to 27.497
Index range (h, k, l)	−12, 12; −18, 18; −33, 33	−21, 21; −17, 17; −25, 25	−50, 50; −18, 18; −33, 33	−26, 26; −17, 17; −43, 43
Reflections collected	102 005	173 120	154 056	97 076
Independent reflections	7997	10 146	32 379	10 629
R(int)	0.0451	0.0537	0.0930	0.0463
Completeness to Θ	99.9	99.8	99.9	99.6
Max. and min. transmission	0.4291 and 0.1274	0.2616 and 0.0906	0.7457 and 0.4356	0.7456 and 0.4890
Data/restraints/parameters	7997/801/566	10 146/123/459	32 379/1956/1676	10 629/3/426
Goodness-of-fit on F^2	1.073	1.056	1.056	1.076
R indices (final) $[I > 2\sigma(I)]$				
R_1	0.0331	0.0183	0.0585	0.0353
wR_1	0.0695	0.0387	0.1194	0.0837
R indices (all data)				
R_2	0.0378	0.0226	0.0934	0.0493
wR_2	0.0732	0.402	0.1364	0.0918
Largest diff. peak and hole [e Å⁻³]	2.107 and −2.309	0.683 and −0.795	1.927 and −1.925	2.037 and −1.132

Table 2 Key crystallographic bond lengths [Å] and angles [°]

	cis-4c	trans-5c [a]	trans-7c (1) [b]	trans-7c (2) [b]	trans-7c (3) [b]	trans-10c [a]
Pt–P	2.2844(11)	2.2810(5)	2.2887(16)	2.2848(19)	2.284(2)	2.2946(12)
	2.2818(11)	2.2920(5)	2.3089(16)	2.3037(19)	2.285(2)	2.3032(13)
Pt–C	2.105(4)	2.074(7)	2.102(6)	2.093(8)	2.104(8)	2.179(5)
	2.106(5)					
Pt–Cl or I	—	2.4020(6)	2.4052(16)	2.401(2)	2.408(2)	2.6864(8)
P–Pt–P	104.15(4)	176.055(17)	172.37(6)	177.07(7)	172.97(9)	175.55(4)
P–Pt–C	86.76(16)					
	167.83(15)	88.0(3)	87.77(17)	88.1(2)	91.5(2)	87.66(16)
	87.06(17)	90.7(3)	90.75(17)	91.6(2)	87.1(2)	90.56(16)
	167.78(17)					
C–Pt–C	82.6(2)	—	—	—	—	—
P–Pt–Cl or I	—	92.74(2)	91.60(6)	92.29(7)	90.03(9)	93.77(3)
		88.70(2)	90.31(6)	88.21(7)	91.85(8)	88.46(3)
C–Pt–Cl or I	—	177.7(3)	176.6(2)	176.6(3)	176.0(3)	173.42(16)

[a] Values for the dominant X-Pt-CH$_3$ orientation. [b] Values for the three independent molecules in the unit cell.
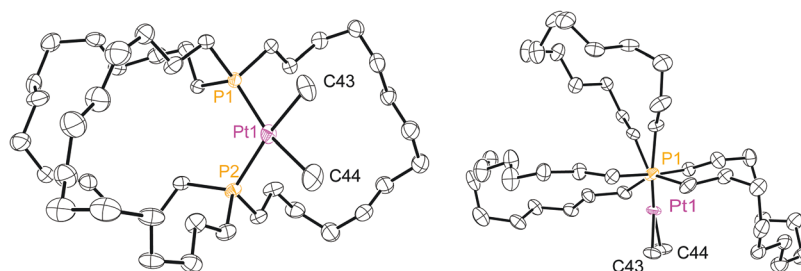
Fig. 1 Thermal ellipsoid plots of the molecular structure of cis-**4c** (50% probability level, dominant conformation).
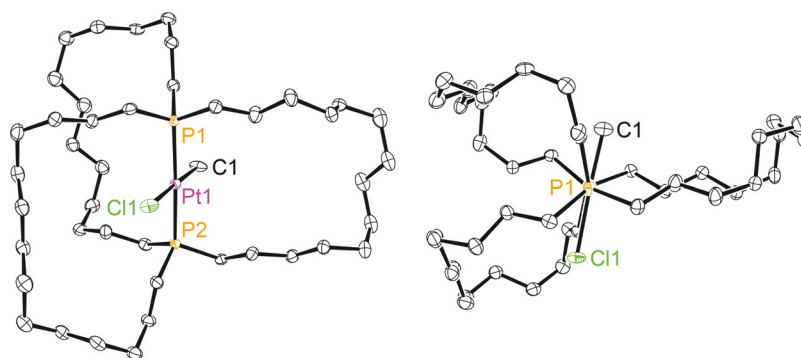
Fig. 2 Thermal ellipsoid plots of the molecular structure of trans-**5c** (50% probability level, dominant conformation).

cis-**3c** was slurried with the same batch used in Scheme 5. No reaction was observed after 5 h at room temperature or 24 h at 80 °C (entry 4, Table 3). When a mesitylene solution of cis-**3c** was kept at 140 °C for 30 h (entry 3, Table 3), ^{31}P{^{1}H} NMR spectra showed the gradual conversion to two new species, neither of which was trans-**3c** (δ/ppm 7.4 (s, 84%) and 4.3 (s, 16%)).[20]

When a toluene-d_8 solution of the parachute like dimethyl complex cis-**4c** was kept at 80 °C for 10 h (entry 5, Table 3) or slurried at room temperature with silica gel for 24 h (entry 7, Table 3), no reaction was observed. However, when slurried at 80 °C for 24 h (entry 8, Table 3), complete conversion to two unknown species occurred (δ/ppm 11.4 (s, 76%) and 6.2 (s,
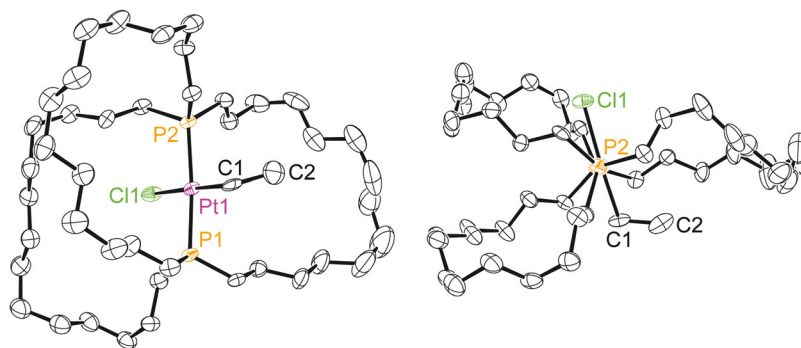
Fig. 3 Thermal ellipsoid plots of the molecular structure of *trans*-**7c** (50% probability level, one of three independent molecules).
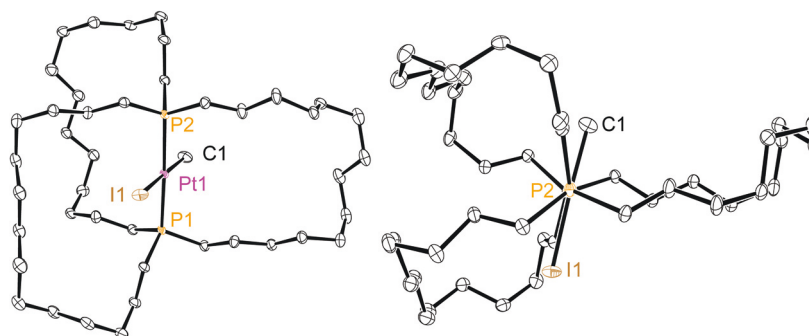

Fig. 4 Thermal ellipsoid plots of the molecular structure of *trans*-**10c** (50% probability level, dominant conformation).

24%)).[20] When a mesitylene solution of *cis*-**4c** was kept at 140 °C for 30 h, there was *ca.* 16% conversion to an unknown new species.

When a mesitylene solution of the gyroscope like methyl chloride complex *trans*-**5c** was kept at 140 °C for 30 h (entry 14, Table 3), most of the *trans*-**5c** remained, with 13% conversion to an unknown species (7.3 ppm; no detectable *cis*-**5c**). However, an analogous experiment with the corresponding ethyl chloride complex *trans*-**7c** (entry 15, Table 3) showed the gradual conversion to an unknown product (^{31}P{^{1}H} NMR: 7.4 ppm, s, $^{1}J_{PPt}$ = 2447 Hz),[20] with one main intermediate (18.3 ppm), the NMR properties of which (Experimental section) indicated a platinum hydride complex (^{1}H NMR: −16.78 ppm, t, $^{2}J_{HP}$ = 13.8 Hz).

Next, *o*-$C_6H_4Cl_2$ solutions of the new parachute like phenyl chloride complex *cis*-**8c** (Scheme 7) were kept at 100 °C for 6 h or 140 °C for 0.5 h (entries 16 and 17, Table 3). In both cases, >99% conversion to gyroscope like *trans*-**8c** was observed. Thus, the relative thermodynamic stabilities of the phenyl chloride complexes are analogous to those of the alkyl chloride complexes.

Some attempted thermal equilibrations gave well defined alternative reactions. As shown in Scheme 9, a C_6D_5Br solution of the parachute like dimethyl complex *cis*-**4c** was kept at 110 °C for 7 h (little change) and then 140 °C for 6 h. The higher temperature gave complete conversion to the gyroscope like methyl bromide complex *trans*-**9c**, as confirmed by ^{31}P and

^{1}H NMR. Toluene-d_5 was also detected. An analogous reaction of the diethyl complex *cis*-**6c** (140 °C) initially gave what was assigned as the ethyl bromide complex *trans*-Pt(Br)(Et) (P((CH$_2$)$_{14}$)$_3$P) based upon the similar $^{1}J_{PPt}$ value (2771 *vs.* 2806 Hz). With time, this further converted to the previously isolated dibromide complex *trans*-Pt(Br)$_2$(P((CH$_2$)$_{14}$)$_3$P) ($^{1}J_{PPt}$ 2347 *vs.* 2344 [4a] Hz). In another example, an *o*-$C_6H_4Cl_2$ solution of *cis*-**4c** was kept at 140 °C for 12 h. Complete conversion to the gyroscope like methyl chloride complex *trans*-**5c** occurred. In this case, an unknown intermediate could be seen by ^{31}P NMR (8.9 ppm, s).

Computational data

In order to better interpret the preceding isomerizations, molecular dynamics simulations followed by DFT optimizations were carried out for all complexes with (CH$_2$)$_{14}$ bridges ("**c** series") along the lines reported earlier.[8] The molecular dynamics annealing simulations were run to maximize the likelihood of correctly identifying the lowest energy conformer.[21] The ten lowest conformations from each trajectory were extracted and "cleaned up" using a semi-empirical method (PM7) followed by DFT optimizations (in the gas phase at 25 °C or 298 K).[22] The computed relative energies of these species are shown in Fig. 5. It was critical to incorporate dispersion corrections in order to obtain appropriately folded (CH$_2$)$_{14}$ bridges. Subsequently, single point corrections were performed using an implicit solvation model for two typical

Table 3 Summary of thermolysis experiments

Entry	Starting material		Solvent	Temperature (°C)	Time (h)	Result[a]
1		cis-**2c**	Toluene-d_8 or CDCl$_3$/silica get	25	24	>99 : 1 cis/trans-**2c**
2		cis-**3c**	Toluene-d_8	80	10	>99 : 1 cis/trans-**3c**
3			Mesitylene	140	30	>99% conv. unknown species[b]
4			Toluene-d_8/silica gel	25, then 80	5, then 24	>99 : 1 cis/trans
5		cis-**4c**	Toluene-d_8	80	10	>99 : 1 cis/trans-**4c**
6			Mesitylene	140	30	16% conv. unknown species[b]
7			Toluene-d_8/silica gel	25	24	>99 : 1 cis/trans
8			Toluene-d_8/silica gel	25, then 80	5, then 24	>99% conv. unknown species[b]
9		cis-**5c**	Toluene-d_8 or toluene-d_0	80	10 or 72	86 : 14 or <1 : >99 cis/trans-**5c**
10			o-C$_6$H$_4$Cl$_2$	100	3	<1 : 99 cis/trans-**5c**
11			o-C$_6$H$_4$Cl$_2$	140	0.5	<1 : 99 cis/trans-**5c**
12			C$_6$D$_5$Br	110	7	<1 : 99 cis/trans-**5c**
13			Mesitylene	140	0.5	<1 : 99 cis/trans-**5c**
14		trans-**5c**	Mesitylene	140	30	13% conv. unknown species[b]
15		trans-**7c**	Mesitylene	140	30	>99% conv. unknown species[b,c]
16		cis-**8c**	o-C$_6$H$_4$Cl$_2$	100	6	<1 : 99 cis/trans-**8c**
17			o-C$_6$H$_4$Cl$_2$	140	0.5	<1 : 99 cis/trans-**8c**
18		trans-**8c**	Mesitylene	140	30	<1 : 99 cis/trans-**8c**

[a] Assayed by ^{31}P NMR as detailed in the Experimental section. [b] Chemical shifts are provided in the Experimental section; when only 13–16% conversion is noted, the remaining material is the educt. [c] A platinum hydride intermediate can be observed by ^{1}H NMR; see text and Experimental section.
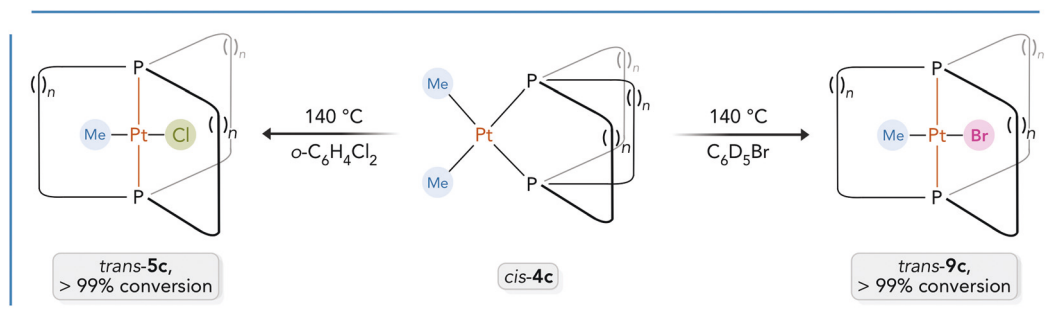
Scheme 9 Thermolyses that afford well defined complex/solvent reactions.
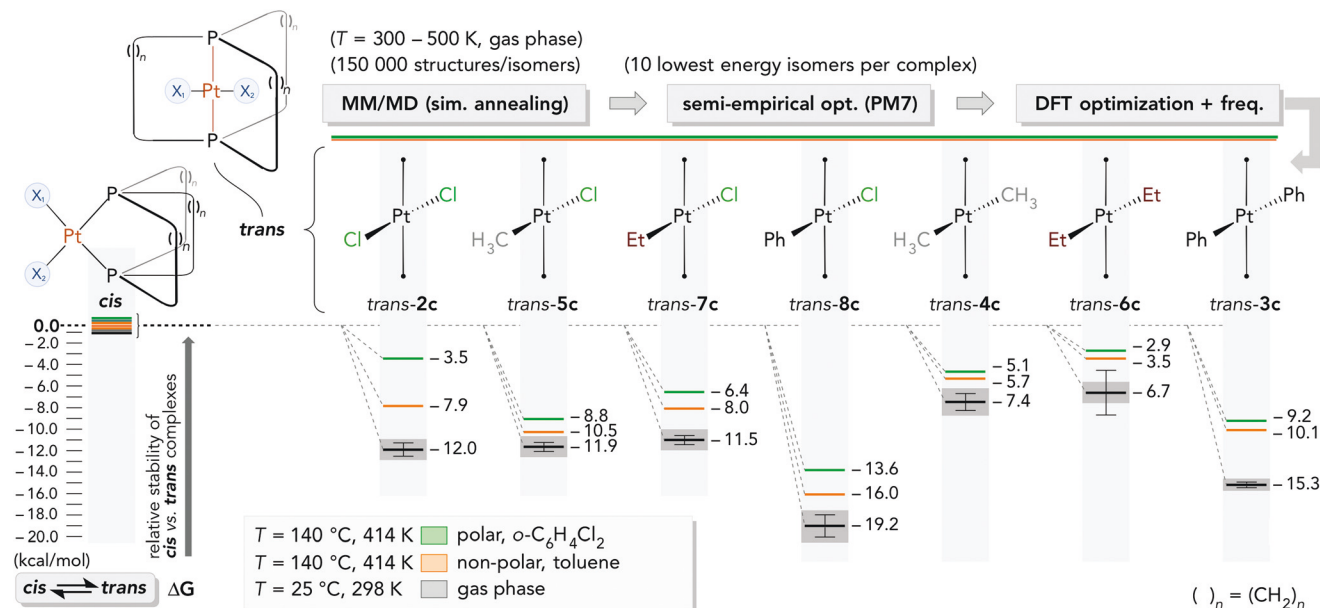
Fig. 5 Relative energies (ΔG, kcal mol^{-1}) of isomeric *cis*/parachute and *trans*/gyroscope platinum complexes as computed by DFT (gas phase or toluene or *o*-C$_6$H$_4$Cl$_2$ solutions) preceded by molecular dynamics and semi-empirical (PM7) computations.

solvents from Table 3 (*o*-C$_6$H$_4$Cl$_2$, toluene).[23] Frequency calculations were also performed to confirm that minimum structures were obtained and further to afford temperature corrections to the Gibbs energy at a representative temperature from Table 3 (140 °C or 414 K).

It was also sought to compare the relative energies of acyclic model complexes, which would not be subject to possible ring strain effects derived from the dibridgehead diphosphine ligands. For this purpose, PEt$_3$ as opposed to PMe$_3$ was selected for the phosphine ligands, as the former better mimics the electronic effect exerted by the three (CH$_2$)$_{14}$ bridges.[24] These species are designated with double primes; for example *trans*-2″ represents *trans*-Pt(Cl)$_2$(PEt$_3$)$_2$, the analog of the gyroscope like dichloride complex *trans*-2c.

In Fig. 5 and 6, the energies of the *trans* isomers are displayed relative to those of the *cis* isomers symbolized in the columns at the far left. In Fig. 5, most of the gyroscope isomers are 11.5–19.2 kcal mol^{-1} more stable than the parachute isomers in the gas phase. However, the energies of the two dialkyl complexes *cis/trans*-4c and *cis/trans*-6c are closer, with the *trans* isomers 6.7–7.4 kcal mol^{-1} more stable. Fig. 5 also shows the energy differences for the dichloride complexes *cis/trans*-2c. This system was also examined by DFT earlier,[8] with the important result that the *trans* isomers were more stable for all the (CH$_2$)$_n$ bridge lengths examined (*n* = 10, 12, 14, 16, 18, 20, 22).[10] All bond lengths and angles about platinum nicely model those determined crystallographically (Table 2 and earlier papers for *trans*-2c,[4a] *cis*-2c,[8] *trans*-3c,[4a] *cis*-3c,[8] and *trans*-8c[4b]), and some are depicted in the graphics below.

In Fig. 6, the results for the PEt$_3$ substituted acyclic model compounds are presented. Here, the gas phase energy differences closely (albeit not perfectly) follow the pattern in Fig. 5,

but average 6.6 kcal mol^{-1} lower. This suggests that the *cis*/parachute isomers in Fig. 5 are *ca.* 6.6 kcal mol^{-1} destabilized relative to the *trans*/gyroscope isomers (and/or that the latter are in some manner stabilized). In any case, the *cis* and *trans* dialkyl complexes Pt(R)$_2$(PEt$_3$)$_2$ are rendered approximately equal in energy.

In response to a reviewer inquiry regarding the origin of the 6.6 kcal mol^{-1} difference, the PtX$_2$ or PtXX′ fragments were excised from the structures of all *cis*/parachute and *trans*/gyroscope complexes in Fig. 5, in each case taking the most favorable of the ten conformations analyzed. Single point calculations were carried out on the remaining dibridgehead diphosphines, a process that freezes the phosphorus–phosphorus distances (3.4–3.5 *vs.* 4.5–4.6 Å) and all other atoms. In all cases, the gas phase energies of the gyroscope derived diphosphines were lower (2.8–7.3 kcal mol^{-1}). Next, the diprimary and disecondary diphosphines H$_2$P(CH$_2$)$_{14}$PH$_2$ and HP((CH$_2$)$_{14}$)$_2$PH, derived by deleting two and one (CH$_2$)$_{14}$ bridges, respectively, were similarly examined. A detailed analysis of the results (see highlights in the ESI†) suggests that bridge/bridge interactions provide stabilization in the *trans*/gyroscope systems. Torsional interactions and angle strain (*e.g.*, at phosphorus) seemingly have subordinate roles in the energy differences. Further analysis is provided below and in the ESI.†

Discussion

Preliminary remarks

Schemes 3–8 diagram a number of substitution reactions involving gyroscope and parachute like complexes. Although this study is concerned with general isomerization rates and
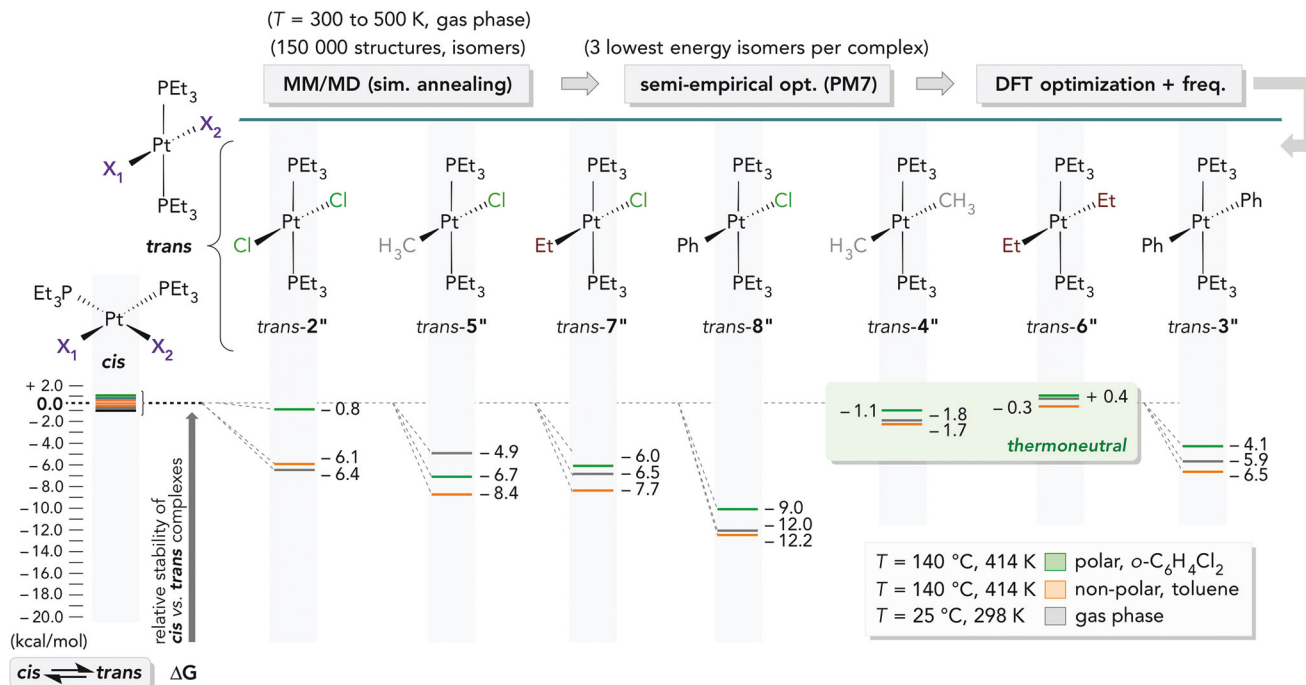
Fig. 6 Relative energies (ΔG, kcal mol^{-1}) of isomeric *cis* and *trans* platinum complexes with acyclic triethylphosphine ligands as computed by DFT (gas phase or toluene or o-C$_6$H$_4$Cl$_2$ solutions) preceded by molecular dynamics and semi-empirical (PM7) computations.

equilibria as opposed to mechanism, it should be noted that substitution mechanisms of square planar platinum(II) complexes have been extensively studied, going back more than 60 years.[25,26] However, the gyroscope like complexes may have

pathways available that lack counterparts in classical complexes. For example, equilibria exist that allow the ML$_y$ rotators to "escape" from their cages.[4a,5c,27,28] A possible initial step is shown in Scheme 10 (*trans*-**II** → **V**). This entails the cleavage of
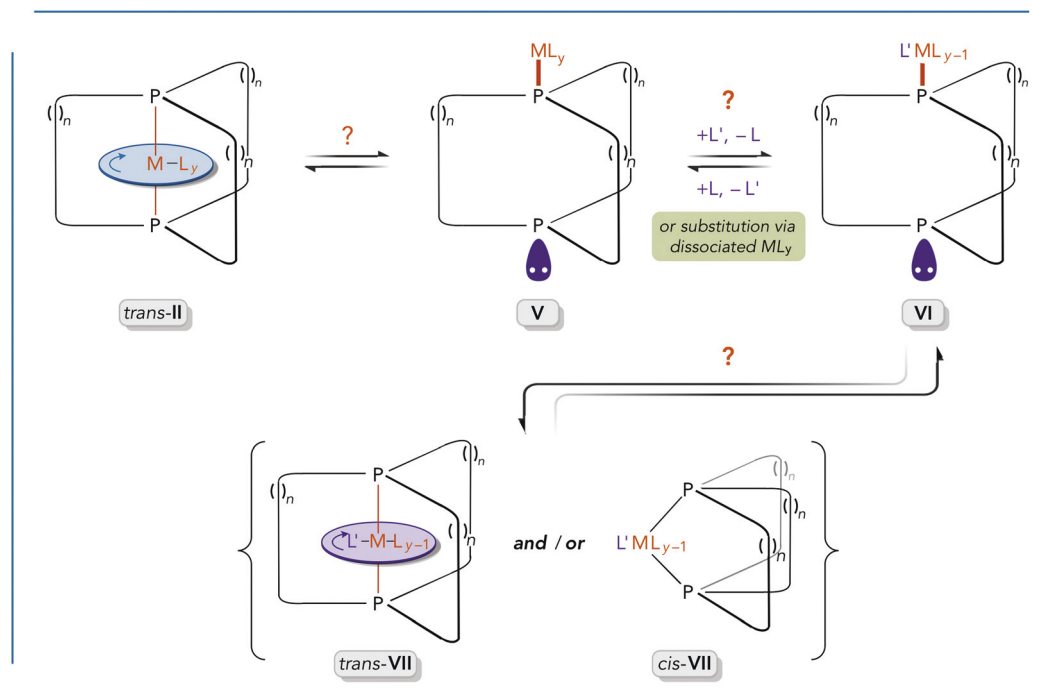
Scheme 10   Potential equilibria that may play a role in substitution reactions.

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one metal–phosphorus bond and isomerization of the dibridgehead diphosphine ligand from an "*in/in*" to an "*out/out*" geometry.[29] Such isomerizations are facile with the free diphosphines.[28]

Thus, there exists the possibility that substitution occurs external to the cage, perhaps involving **V** directly, or another transient species. Furthermore, as shown in Scheme 10, either gyroscope (*trans*-**VII**) or parachute (*cis*-**VII**) products could be preferred kinetically. Also, per studies of related acyclic platinum(ii) complexes, mechanisms would be expected to differ depending upon the attacking group, especially for nucleophilic or organometallic agents such as RLi *versus* electrophilic agents such as HCl.[17] Finally, although purely thermal *cis/trans* isomerizations of platinum(ii) complexes have been established, a wide variety of catalysts have been documented.[11,30–32] To sum, this digression conveys the diversity of phenomena that might play roles in Schemes 3–8, but are beyond the scope of the present investigation.

Coordination geometries: *trans*/gyroscope *versus* cis/parachute

One starting point for analysis involves the gyroscope and parachute like dichloride complexes *trans*-**2** and *cis*-**2** (Scheme 2). As reported earlier,[8] both DFT and thermolysis data (Scheme 2) show the former to be more stable, at least for $(CH_2)_n$ bridges with $n \geq 10$. In syntheses where the educts cannot bias the stereochemical outcome – for example,[27] $PtCl_2$ and the dibridgehead diphosphine $P((CH_2)_{14})_3P$ – *trans*-**2** is always the exclusive product. The new computational data in Fig. 5 and 6 establish an intrinsic energetic preference for the gyroscope like isomers (*ca.* 6.6 kcal mol^{-1} with $(CH_2)_{14}$ bridges). The single point calculations with $P((CH_2)_{14})_3P$ localize the principal origin of the energy differences within the diphosphine ligands. The additional calculations with HP $((CH_2)_{14})_2PH$ and $H_2P((CH_2)_{14})PH_2$ point to non-covalent chain/chain interactions, and any attendant dispersion forces, as stabilizing factors in the gyroscope systems. Efforts to identify destabilizing steric features unique to the parachute systems have so far not been successful.

Computations have previously been carried out with related phosphite complexes, for which only parachute like *cis* isomers have been synthetically accessed.[8] Here the DFT data show the *cis* isomers to be considerably more stable. Since phosphite ligands are stronger π acceptors than phosphine ligands,[33,34] geometries in which the π donor chloride ligands[35] are *trans* to the phosphorus donor atoms become preferred. In other words, this favorable electronic interaction dominates over any steric factors that may prefer gyroscope like dibridgehead diphosphite complexes.

Alkyl ligands are considered to be strong σ donors – indeed, the strongest among the ligands in this study[34] – and in the context of the *trans* influence (*vide infra*), *trans* geometries are considered to be particularly unfavorable. From this perspective, the formation of the parachute like dialkyl complexes *cis*-**4c,e,g** and *cis*-**6c** in Schemes 4 and 6 is less surprising. However, we were unable to access any of the corresponding *trans* isomers, precluding an experimental confirmation of the relative stabilities. Thus, two scenarios remain in play: (a) *cis*-**4c,e,g** and *cis*-**6c** represent kinetically but not thermodynamically favored substitution products and conditions for isomerizations to *trans*-**4c,e,g** and *trans*-**6c** remain to be developed, or (b) *cis*-**4c,e,g** and *cis*-**6c** represent thermodynamically favored substitution products, either produced directly (kinetic products) or *via* transient *trans* isomers.

In our opinion, the computational data fit best with the latter. Although parachute like *cis*-**4c** and *cis*-**6c** remain 7.4–6.7 kcal mol^{-1} less stable than gyroscope like *trans*-**4c** and *trans*-**6c** in the gas phase (Fig. 5), these differences narrow to 5.7–2.9 kcal mol^{-1} in toluene or o-$C_6H_4Cl_2$, with the diminution always more pronounced in the more polar dichlorinated solvent. For the acyclic model compounds **4″** and **6″** (Fig. 6), the *cis* and *trans* isomers have essentially equal energies. In addition, ethyl is a stronger σ donor than methyl,[36] further destabilizing the *trans* isomers. In any case, Fig. 5 reproduces the relative trends in our data, although *trans*-**4c** and *trans*-**6c** appear overstabilized compared to their *cis* isomers.[37]

Consider next the diphenyl complexes **3** introduced in Scheme 3. The computations in Fig. 5 indicate much greater stabilities for the *trans*/gyroscope *versus* cis/parachute isomers as compared to the dialkyl analogs. The same trend is seen with the acyclic analogs in Fig. 6. The ligating sp^2 carbon atom of a phenyl ligand constitutes a weaker σ donor than the sp^3 carbon atom of an alkyl ligand,[36] attenuating the electronic mismatch in the *trans* isomers.[38] However, numerous experimental attempts to establish equilibria (Table 3) have been unsuccessful. Regardless, it can be concluded that the reaction of *cis*-**2c** and Ph_2Zn to give *cis*-**3c** (Scheme 3) is under kinetic control.

The remaining equilibrium issues in Schemes 3–8 are quite clear cut. In all cases, it can be shown experimentally that the *trans*/gyroscope methyl or phenyl chloride complexes **5c,e,g** and **8c** are much more stable than the *cis*/parachute analogs (Schemes 5 and 7), and the same can be presumed for the ethyl chloride complex **7c** (Scheme 6). These trends are fully supported by the computations. In all cases the weak σ donor chloride ligand is preferentially directed opposite to the stronger alkyl or phenyl σ donor.[34]

There still remain various open questions. For example, a reviewer inquired regarding the mechanism of the *cis/trans* isomerizations that take place over silica gel in Scheme 5. Silica gel promotes or catalyzes quite a broad spectrum of organic reactions,[39] but to the authors' knowledge has not been previously observed to effect geometric isomerizations of metal complexes. Nonetheless, given the plethora of *cis/trans* equilibration mechanisms established for square planar platinum(ii) complexes,[11,30–32] many possible roles are easily envisioned. Since isomerization also occurs upon attempted Et_2O/ROH crystallization, perhaps the hydroxyl groups associated with silica are involved.

Further electronic and structural considerations

The preceding analysis made little reference to the "*trans* influence", which is considered the thermodynamic counterpart of

the "*trans* effect".[25,26,40,41] There have been extensive studies of these phenomena in platinum(II) chemistry. For the ligands of interest in this paper, the *trans* influence increases in the order $Cl^- < I^- < Ph^- < PR_3 < Me^- < Et^-$.[36,41c] However, these concepts are often applied rather simplistically, although even in early studies it was appreciated that the trends represent a complex mash-up of σ and π donor/acceptor effects, the relative importance of which can vary from substrate to substrate.[42] Accordingly, correlations with the equilibria established above are not attempted.

Much work involving the *trans* influence has been focused upon structural trends – specifically, the effect of a series of *trans* ligands upon a metal–ligand bond distance. A longer bond *trans* to the ligand of interest is taken as evidence of destabilization, and a shorter bond is taken as evidence for stabilization.[36,40,41] One question is whether our computed structures, excerpted in Fig. 7, conform to these expectations.

For example, with the chloride substituted gyroscope like complexes *trans*-**7c**, *trans*-**5c**, *trans*-**8c**, and *trans*-**2c**, the platinum–chlorine bond lengths (2.47, 2.46, 2.44, 2.35 Å) contract as the *trans* influences of the ethyl, methyl, phenyl, and chloride ligands decrease. The same trend holds for the platinum–carbon bond lengths in the diethyl, dimethyl, and diphenyl complexes *trans*-**6c**, *trans*-**4c**, and *trans*-**3c** (2.16, 2.15, 2.09 Å). With the *cis*/parachute complexes, the platinum–phosphorus bond lengths do not change as much as the *trans* ligand is varied, except in the case of the dichloride complex *cis*-**2c** (2.28 Å *vs.* 2.38–2.39 Å for *trans* ethyl, methyl, and phenyl ligands). However, the platinum–carbon bond lengths follow the same trends as in the *trans* complexes. They are (as compared to *trans* complexes) uniformly longer in *cis*-**5c**, *cis*-**7c**, and *cis*-**8c** (all bonds *cis* to chloride), and shorter in *cis*-**4c**, *cis*-**6c**, and *cis*-**3c** (all bonds *cis* to alkyl).

The experimental structural data for *cis*-**4c**, *trans*-**5c**, and *trans*-**7c** (Table 2) are in excellent agreement with the bond lengths in Fig. 7 and other computed metrical parameters. All values are in the normal ranges for square planar platinum(II) complexes.[43–45] The analogous methyl and ethyl chloride complexes *trans*-**5c** and *trans*-**7c** exhibit bond lengths and angles about platinum that are within experimental error. In the

methyl chloride and iodide complexes *trans*-**5c** and *trans*-**10c**, the platinum–carbon bonds lengthen from 2.074(7) Å to 2.179 (5) Å. This can be attributed to the greater *trans* influence of the iodide ligand noted above.[25,41c]

Additional properties of new complexes

Although this study is not concerned with the dynamic properties of the complexes in Schemes 3–8, certain features are apparent from the ^{13}C NMR spectra. Specifically, all of the *trans*/gyroscope complexes in the "**c** series" exhibit only seven signals. This indicates that rapid ML_y rotation (or $(CH_2)_{14}$ bridge exchange) takes place on the NMR time scale at room temperature (with the number of signals, 14/2, reflecting the formal horizontal mirror plane). Similar behavior has been observed with other methyl substituted rotors,[5c,7] but *trans*-**7c** represents the first case with a larger ethyl ligand. The analogs with longer $(CH_2)_n$ bridges, *trans*-**4e,g**, also gave the minimum number of ^{13}C NMR signals. These processes have been analyzed in depth in a recent review that collects all available activation parameters.[3] A key consideration involves the van der Waals radii of the ML_y rotators *versus* the clearance allowed by the $(CH_2)_n$ bridges.

In contrast, the parachute like complex *cis*-**3c** exhibits eleven CH_2 ^{13}C NMR signals, indicating that the "jump rope" process is slow on the NMR time scale at room temperature. In theory, two sets of seven signals with a *ca.* 2 : 1 intensity ratio should be observable, but sufficient resolution was not available at 126 MHz. As reported earlier, the corresponding dichloride complex *cis*-**2c** exhibits twelve signals.[8] The higher homologs *cis*-**3e,g** give the minimum number of signals (nine and eleven), indicative of rapid jump rope processes.

The thermolyses in Scheme 9 convert the parachute like dimethyl complex *cis*-**4c** to the gyroscope like methyl halide complexes *trans*-**5c** and *trans*-**9c**. This suggests an initial oxidative addition of the high boiling haloarene solvent to give a platinum(IV) species, a type of reaction with significant precedent.[46] Indeed, toluene-d_5 can be identified as a product in the reaction with bromobenzene-d_5. Evidence has also been obtained from related reactions for the formation of species with new platinum–carbon bonds. Another fascinating lead
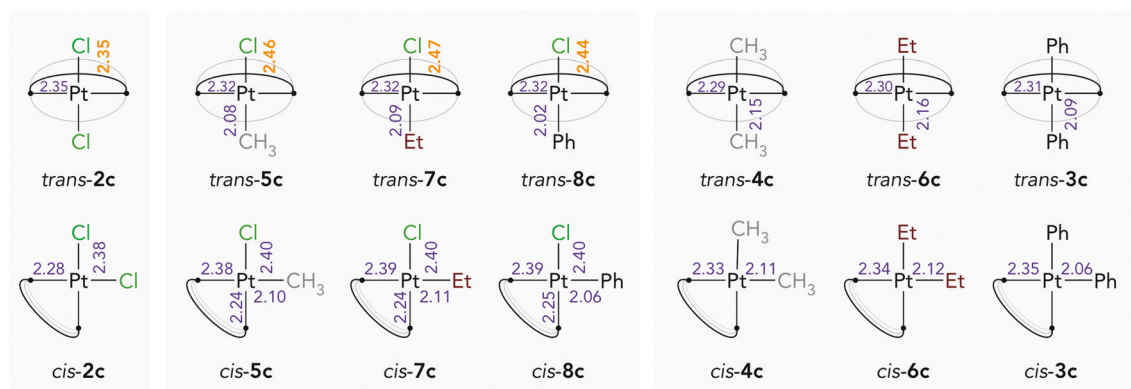

Fig. 7 Platinum−ligand bond lengths (Å) for computed *trans*/gyroscope and *cis*/parachute complexes.

only briefly mentioned above is the apparent formation of a platinum bis(phosphine) hydride intermediate upon attempted isomerization of the ethyl chloride complex *trans*-**5c**. All of these transformations and the mesitylene-derived products in Table 3 remain under active investigation.

Summary

With respect to the gyroscope like dichloride complexes *trans*-**2c,e,g**, this study has established that isomerization normally accompanies reactions with alkyl lithium reagents to give the dialkyl complexes *cis*-**4c,e,g** and *cis*-**6c** (Schemes 4 and 6). In contrast, phenyl nucleophiles normally afford *trans* diphenyl complexes, although lesser amounts of *cis* adducts are sometimes observed in reactions with PhLi. Subsequent reactions of *cis*-**4c,e,g** and HCl (1.0 equiv.) give detectable quantities of *cis* alkyl chloride complexes that easily convert (over silica gel or at ∼100 °C) to the gyroscope like isomers *trans*-**5c,e,g**. The *cis* phenyl chloride complex *cis*-**8c** undergoes an analogous thermal isomerization to *trans*-**8c**. DFT calculations indicate that the *trans*/gyroscope complexes always have lower energies than the *cis*/parachute complexes in the gas phase. However, isomeric dimethyl and diethyl complexes have nearly the same energies in o-$C_6H_4Cl_2$.[37] With acyclic model compounds the energy differences are much less, and the isomeric dimethyl and diethyl complexes exhibit essentially equal energies.

Overall, this work has bought several concepts from traditional platinum(II) coordination chemistry into the modern context of the chelating and potentially *trans* spanning dibridgehead diphosphine ligands $P((CH_2)_n)_3P$. These data greatly enhance the confidence with which the NMR data associated with various dynamic processes can be interpreted. These include ML_y rotation in the gyroscope like complexes and the "jump rope" $(CH_2)_n$ exchange in the parachute like complexes, both of which will be topics of future reports.

Experimental section

General

Reactions were conducted under nitrogen atmospheres unless noted. Materials were utilized as follows: Et_2O, CH_2Cl_2, and THF, purified by a Glass Contour system; hexanes (98.5%, Sigma-Aldrich), EtOAc (99.5%, Sigma-Aldrich), methanol (99.8%, Sigma-Aldrich), benzene (99.88%, Sigma-Aldrich), mesitylene (97%, TCI), o-$C_6H_4Cl_2$ (99%, Sigma-Aldrich), $CDCl_3$, C_6D_6, toluene-d_8, C_6D_5Br (4 × Cambridge Isotopes), MeLi (1.6 M in Et_2O, Sigma-Aldrich), EtLi (0.50 M in benzene, Sigma-Aldrich), PhLi (1.8 M in Bu_2O, Sigma-Aldrich), CH_3COCl (98%, Alfa-Aesar), HCl (2.0 M in Et_2O, Alfa-Aesar), Et_3N (99%, Alfa-Aesar), LiBr (99.99%, Alfa-Aesar), NaI (99%, EMD), celite (EMD), silica gel (40–63 μm, 230–400 mesh, Silicycle), and neutral alumina (Brockmann I, for chromatography, 40–300 μm, 60A, Acros), used as received.

NMR spectra were recorded on standard 500 MHz FT spectrometers at ambient probe temperatures and referenced as follows (δ, ppm): [1]H: residual internal $CHCl_3$ (7.26) or C_6D_5H (7.16); [13]C{[1]H}: internal $CDCl_3$ (77.16) or C_6D_6 (128.06); [31]P{[1]H}: external 85% H_3PO_4 (0.00). Melting points were determined on a Stanford Research Systems (SRS) MPA100 (Opti-Melt) automated device. Microanalyses were conducted by Atlantic Microlab.

cis-Pt(Me)$_2$(P((CH$_2$)$_{14}$)$_3$P) (cis-4c). A Schlenk flask was charged with *trans*-Pt(Cl)$_2$(P((CH$_2$)$_{14}$)$_3$P) (*trans*-**2c**;[4a] 0.2242 g, 0.2445 mmol) and Et_2O (12 mL). Then MeLi (1.6 M in Et_2O, 0.330 mL, 0.528 mmol) was added with stirring (rt). After 12 h, the mixture was exposed to air. After 1 h, the sample was filtered through celite, which was washed with Et_2O (10–20 mL). The solvent was removed from the filtrate by rotary evaporation. The residue was chromatographed on neutral alumina (1 : 0.005 v/v hexanes/Et_3N). The solvent was removed from the product containing fractions (TLC monitoring) by rotary evaporation. The oil was kept at 4 °C, and after 2 d gave *cis*-**4c** as a white solid (0.1645 g, 0.1877 mmol, 77%), mp (open capillary) 80–83 °C. Anal. Calcd for $C_{44}H_{90}P_2Pt$ (876.21): C, 60.31; H, 10.35. Found: C, 60.59; H, 10.55. MS (MALDI-TOF, m/z, relative intensity): 875.6 ([M]$^+$, 19%), 860.6 ([M − CH_3]$^+$, 100%).

NMR ($CDCl_3$, δ/ppm):[47] [1]H (500 MHz) 1.90–1.78 (br m, 4H, PC$\underline{H}_2$), 1.72–1.50 (br m, 12H, C$\underline{H}_2$), 1.50–1.21 (br m, 68H, remaining C$\underline{H}_2$), 0.30 (dd, 6H, $^3J_{HP(trans)}$ = 7.1 Hz, $^3J_{HP(cis)}$ = 6.1 Hz, $^2J_{HPt}$ = 66 Hz,[48] PtC$\underline{H}_3$); [13]C{[1]H} (126 MHz) 31.1 (virtual t,[49] J_{CP} = 4.2 Hz, PCH$_2$CH$_2$C$\underline{H}_2$), 30.5 (virtual t,[49] J_{CP} = 6.6 Hz, PCH$_2$C$\underline{H}_2$CH$_2$), 28.3 (s, $\underline{C}$H$_2$), 27.52 (s, $\underline{C}$H$_2$), 27.46 (s, $\underline{C}$H$_2$), 27.2 (s, $\underline{C}$H$_2$), 26.9 (s, $\underline{C}$H$_2$), 26.5 (s, $\underline{C}$H$_2$), 26.4 (s, $\underline{C}$H$_2$), 24.8 (virtual t,[49] J_{CP} = 10.5 Hz, PCH$_2$C$\underline{H}_2$), 23.3 (apparent br m, P$\underline{C}$H$_2$), 2.8 (dd, $^2J_{CP(trans)}$ = 101.7 Hz, $^2J_{CP(cis)}$ = 9.9 Hz, PtC$\underline{H}_3$); [31]P{[1]H} (202 MHz) 6.9 (s, $^1J_{PPt}$ = 1886 Hz).[48]

cis-Pt(Me)$_2$(P((CH$_2$)$_{18}$)$_3$P) (cis-4e). *A.* A Schlenk flask was charged with *trans*-Pt(Cl)$_2$(P((CH$_2$)$_{18}$)$_3$P) (*trans*-**2e**;[4a] 0.1239 g, 0.1142 mmol) and Et_2O (20 mL). Then MeLi (1.6 M in Et_2O, 0.160 mL, 0.256 mmol) was added with stirring (rt). After 12 h, the mixture was exposed to air. After 1 h, the sample was filtered through celite, which was washed with diethyl ether (10–20 mL). The solvent was removed from the filtrate by rotary evaporation. The residue was chromatographed on neutral alumina (1 : 0.005 v/v hexanes/Et_3N). The solvent was removed from the product containing fractions (TLC monitoring) by rotary evaporation to give *cis*-**4e** as a colorless oil (0.0838 g, 0.0802 mmol, 70%). *B.* A Schlenk flask was charged with *trans*-**2e** (0.1436 g, 0.1323 mmol) and Et_2O (25 mL). Then MeLi (1.6 M in Et_2O, 0.210 mL, 0.336 mmol) was added with stirring (rt). After 12 h, the mixture was exposed to air. After 1 h, the sample was filtered through celite, which was washed with Et_2O (10–20 mL). The solvent was removed from the filtrate by rotary evaporation to give *cis*-**4e** as a beige oil (0.1298 g, 0.1243 mmol, 94%), which solidified after 4 d, mp (open capillary) 48–51 °C. Anal. Calcd for $C_{56}H_{114}P_2Pt$ (1044.53): C, 64.39; H, 11.00. Found: C, 64.69; H, 11.19.

NMR ($CDCl_3$, δ/ppm):[47] [1]H (500 MHz) 1.77–1.64 (br m, 12H, PC$\underline{H}_2$), 1.48–1.39 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.39–1.33 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.33–1.18 (br m, 72H, remaining C$\underline{H}_2$), 0.33 (dd, 6H, $^3J_{HP(trans)}$ = 6.7 Hz, $^3J_{HP(cis)}$ = 5.7 Hz, $^2J_{HPt}$ = 65 Hz,[48]

PtC$\underline{H}_3$); ^{13}C$\{^1$H$\}$ (126 MHz) 31.5 (virtual t,[49] J_{CP} = 5.9 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 29.3 (s, $\underline{C}$H$_2$), 29.0 (s, $\underline{C}$H$_2$), 28.5 (s, $\underline{C}$H$_2$), 27.9 (s, $\underline{C}$H$_2$), 27.6 (s, $\underline{C}$H$_2$), 27.2 (s, $\underline{C}$H$_2$), 24.74 (apparent br m, PCH$_2$$\underline{C}H_2$), 24.67 (s, P$\underline{C}H_2$), 2.6 (dd, $^2J_{CP(trans)}$ = 101.1 Hz, $^2J_{CP(cis)}$ = 10.0 Hz, Pt$\underline{C}$H$_3$); ^{31}P$\{^1$H$\}$ (202 MHz) 4.5 (s, $^1J_{PPt}$ = 1860 Hz).[48]

cis-Pt(Me)$_2$(P((CH$_2$)$_{22}$)$_3$P) (_cis_-4g). A Schlenk flask was charged with _trans_-Pt(Cl)$_2$(P((CH$_2$)$_{22}$)$_3$P) (_trans_-2g;[4c] 0.1469 g, 0.1172 mmol) and Et$_2$O (20 mL). Then MeLi (1.6 M in Et$_2$O, 0.170 mL, 0.272 mmol) was added with stirring (rt). After 12 h, the mixture was exposed to air. After 1 h, the sample was filtered through celite, which was washed with Et$_2$O (10–20 mL). The solvent was removed from the filtrate by rotary evaporation. The residue was dissolved in benzene and sample freeze dried to give _cis_-4g as a white powder (0.1294 g, 0.1067 mmol, 91%), mp (open capillary) 55–60 °C. Anal. Calcd for C$_{68}$H$_{138}$P$_2$Pt (1212.84): C, 67.34; H, 11.47. Found: C, 67.61; H, 11.64.

NMR (C$_6$D$_6$, δ/ppm):[47] ^{1}H (500 MHz) 1.90–1.79 (br m, 12H, PC$\underline{H}_2$), 1.70–1.58 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.49–1.42 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$) 1.42–1.32 (br m, 96H, remaining C$\underline{H}_2$), 1.08 (dd, 6H, $^3J_{HP(trans)}$ = 7.3 Hz, $^3J_{HP(cis)}$ = 6.1 Hz, $^2J_{HPt}$ = 66 Hz,[48] PtC$\underline{H}_3$); ^{13}C$\{^1$H$\}$ (126 MHz) 32.0 (virtual t,[49] J_{CP} = 5.8 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 29.98 (s, $\underline{C}$H$_2$), 29.97 (s, $\underline{C}$H$_2$), 29.85 (s, $\underline{C}$H$_2$), 29.5 (s, $\underline{C}$H$_2$), 29.0 (s, $\underline{C}$H$_2$), 28.5 (s, $\underline{C}$H$_2$), 28.2 (s, $\underline{C}$H$_2$), 27.9 (s, $\underline{C}$H$_2$), 25.4 (apparent br m, PCH$_2$$\underline{C}H_2$), 25.2 (virtual t,[49] J_{CP} = 9.3 Hz, P$\underline{C}$H$_2$), 3.9 (dd, $^2J_{CP(trans)}$ = 101.7 Hz, $^2J_{CP(cis)}$ = 10.0 Hz, Pt$\underline{C}$H$_3$); ^{31}P$\{^1$H$\}$ (202 MHz) 4.6 (s, $^1J_{PPt}$ = 1853 Hz).[48]

cis-Pt(Cl)(Me)(P((CH$_2$)$_{14}$)$_3$P) (_cis_-5c). Under air, a round bottom flask was charged with _cis_-3c (0.4007 g, 0.4573 mmol), CH$_2$Cl$_2$ (10 mL), and methanol (1.0 mL). Then CH$_3$COCl (0.0344 mL, 0.4865 mmol) was added with stirring. After 0.5 h, the solvent was removed by rotary evaporation. The white solid was chromatographed on neutral alumina (25 : 1 : 0.2 v/v/v hexanes/EtOAc/Et$_3$N). The solvent was removed from the product containing fractions (TLC monitoring) by rotary evaporation to give _cis_-5c as a white solid (0.3610 g, 0.4026 mmol, 83%), mp (open capillary) 122–127 °C. Anal. Calcd for C$_{43}$H$_{87}$ClP$_2$Pt (896.63): C, 57.60; H, 9.78. Found: C, 57.80; H, 10.00.

NMR (CDCl$_3$, δ/ppm):[47] ^{1}H (500 MHz) 2.42–2.33 (br m, 2H, PC$\underline{H}_2$), 1.92–1.83 (br m, 2H, C$\underline{H}_2$), 1.82–1.68 (br m, 6H, C$\underline{H}_2$), 1.68–1.53 (br m, 6H, C$\underline{H}_2$), 1.50–1.21 (br m, 68H, remaining C$\underline{H}_2$), 0.58 (dd, 3H, $^3J_{HP(trans)}$ = 7.0 Hz, $^3J_{HP(cis)}$ = 4.0 Hz, $^2J_{HPt}$ = 50 Hz,[48] PtC$\underline{H}_3$); ^{13}C $\{^1$H$\}$ (126 MHz) 30.9 (virtual t,[49] J_{CP} = 10.5 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 30.6 (s, $\underline{C}$H$_2$), 30.5 (s, $\underline{C}$H$_2$), 30.4 (s, $\underline{C}$H$_2$), 30.2 (s, $\underline{C}$H$_2$), 28.5 (s, $\underline{C}$H$_2$), 28.3 (s, $\underline{C}$H$_2$), 27.7 (s, $\underline{C}$H$_2$), 27.4 (s, $\underline{C}$H$_2$), 27.29 (s, $\underline{C}$H$_2$), 27.26 (s, $\underline{C}$H$_2$), 27.1 (s, $\underline{C}$H$_2$), 27.0 (s, $\underline{C}$H$_2$), 26.94 (s, $\underline{C}$H$_2$), 26.90 (s, $\underline{C}$H$_2$), 26.88 (s, $\underline{C}$H$_2$), 26.8 (s, $\underline{C}$H$_2$), 26.33 (s, $\underline{C}$H$_2$), 26.26 (s, $\underline{C}$H$_2$), 26.2 (s, $\underline{C}$H$_2$), 25.0 (s, $\underline{C}$H$_2$), 24.96 (s, $\underline{C}$H$_2$), 24.93 (s, $\underline{C}$H$_2$), 23.9 (s, $\underline{C}$H$_2$), 23.6 (s, $\underline{C}$H$_2$), 23.5 (s, $\underline{C}$H$_2$), 22.8 (virtual t,[49] J_{CP} = 7.3 Hz, P$\underline{C}$H$_2$), 4.5 (dd, $^2J_{CP(trans)}$ = 93.1 Hz, $^2J_{CP(cis)}$ = 8.0 Hz, Pt$\underline{C}$H$_3$); ^{31}P$\{^1$H$\}$ (202 MHz) 11.6 (d, $^2J_{PP}$ = 12.1 Hz, $^1J_{PPt}$ = 1765 Hz,[48] _trans_ to CH$_3$), 5.0 (d, $^2J_{PP}$ = 12.1 Hz, $^1J_{PPt}$ = 4278 Hz,[48] _cis_ to CH$_3$).

trans-Pt(Cl)(Me)(P((CH$_2$)$_{14}$)$_3$P) (_trans_-5c). A. Under air, a round bottom flask was charged with _cis_-4c (0.0245 g,

0.0273 mmol), silica gel (0.2577 g), and CH$_2$Cl$_2$ (2.5 mL). The mixture was stirred (rt). After 12 h, the sample was filtered and the silica gel further washed with CH$_2$Cl$_2$ (25 mL). The solvent was removed from the filtrate by rotary evaporation to yield a colorless oil, which solidified after 4 h to give _trans_-5c (0.0174 g, 0.0192 mmol, 70%) as a white solid, mp (open capillary) 123–127 °C. Anal. Calcd for C$_{43}$H$_{87}$ClP$_2$Pt (896.63): C, 57.60; H, 9.78. Found: C, 57.85; H, 10.05. B. Under air, a vial was charged with _cis_-5c (0.0255 g, 0.0284 mmol), silica gel (0.9528 g) and CH$_2$Cl$_2$ (10.0 mL). The mixture was stirred (rt). After 12 h, the sample was filtered and the silica gel further washed with CH$_2$Cl$_2$ (50 mL). The solvent was removed from the filtrate by rotary evaporation to yield a colorless oil, which solidified after 1 d to give _trans_-5c (0.0227 g, 0.0253 mmol, 89%) as a white solid. C. As described in the Crystallography section below, _trans_-5c was also obtained upon attempted crystallization of _cis_-5c.

NMR (CDCl$_3$, δ/ppm):[47] ^{1}H (500 MHz) 1.85–1.73 (br m, 12H, PC$\underline{H}_2$), 1.65–1.55 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.48–1.38 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.38–1.23 (br m, 48H, remaining C$\underline{H}_2$), 0.31 (t, 3H, $^3J_{HP}$ = 6.2 Hz, $^2J_{HPt}$ = 83 Hz,[48] PtC$\underline{H}_3$); ^{13}C$\{^1$H$\}$ (126 MHz) 30.2 (virtual t,[49] J_{CP} = 6.7 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 28.3 (s, $\underline{C}$H$_2$), 27.4 (s, $\underline{C}$H$_2$), 27.3 (s, $\underline{C}$H$_2$), 27.0 (s, $\underline{C}$H$_2$), 23.5 (br s, PCH$_2$$\underline{C}H_2$), 22.0 (virtual t,[49] J_{CP} = 15.7 Hz, P$\underline{C}$H$_2$), −23.6 (t, J_{CP} = 6.4 Hz, Pt$\underline{C}$H$_3$); ^{31}P$\{^1$H$\}$ (202 MHz) 10.8 (s, $^1J_{PPt}$ = 2824 Hz).[48]

cis-Pt(Cl)(Me)(P((CH$_2$)$_{18}$)$_3$P) (_cis_-5e) and _trans_-5e. A. Under air, a round bottom flask was charged with _cis_-4e (0.0838 g, 0.0802 mmol), CH$_2$Cl$_2$ (8 mL), and methanol (0.4 mL). Then HCl (2.0 M in Et$_2$O, 0.040 mL, 0.080 mmol) was added with stirring. After 0.5 h, the solvent was removed by rotary evaporation. The white solid was chromatographed on neutral alumina (first 3 : 1 : 0.02 v/v/v hexanes/CH$_2$Cl$_2$/Et$_3$N, then 25 : 1 : 0.2 v/v/v hexanes/EtOAc/Et$_3$N). The solvent was removed from the product containing fractions (TLC monitoring) by rotary evaporation. This gave _trans_-5e (0.0389 g, 0.0365 mmol, 46%), with subsequent fractions affording _trans_-5e/_cis_-5e mixtures. B. A vial was charged with a _trans_-5e/_cis_-5e mixture (0.0274 g, 0.0257 mmol; obtained from a different run of procedure A, _ca._ 1 : 2 by ^{31}P NMR), silica gel (1.2375 g) and CH$_2$Cl$_2$ (10 mL). The mixture was stirred (rt). After 12 h, the sample was filtered and the silica gel further washed with CH$_2$Cl$_2$ (40 mL). The solvent was removed from the filtrate to give _trans_-5e (0.0165 g, 0.0155 mmol, 60%) as a beige oil.

Data for cis-5e: NMR (CDCl$_3$, δ/ppm): ^{31}P$\{^1$H$\}$ (202 MHz) 10.3 (d, $^2J_{PP}$ = 12.3 Hz, $^1J_{PPt}$ = 1750 Hz, _trans_ to CH$_3$), 3.56 (d, $^2J_{PP}$ = 12.1 Hz, $^1J_{PPt}$ = 4362 Hz, _cis_ to CH$_3$).

Data for trans-5e: NMR (CDCl$_3$, δ/ppm):[47] ^{1}H (500 MHz) 1.88–1.75 (br m, 12H, PC$\underline{H}_2$), 1.65–1.50 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.46–1.38 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.38–1.23 (br m, 72H, remaining C$\underline{H}_2$), 0.31 (t, 3H, $^3J_{HP}$ = 6.2 Hz, $^2J_{HPt}$ = 83 Hz,[48] PtC$\underline{H}_3$); ^{13}C$\{^1$H$\}$ (126 MHz) 30.8 (virtual t,[49] J_{CP} = 6.4 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 28.6 (s, $\underline{C}$H$_2$), 28.48 (s, $\underline{C}$H$_2$), 28.47 (s, $\underline{C}$H$_2$), 28.4 (s, $\underline{C}$H$_2$), 28.0 (s, $\underline{C}$H$_2$), 27.8 (s, $\underline{C}$H$_2$), 23.9 (s, PCH$_2$$\underline{C}H_2$), 21.5 (virtual t,[49] J_{CP} = 15.9 Hz, P$\underline{C}$H$_2$), −23.4 (t, J_{CP} = 6.5 Hz, Pt$\underline{C}$H$_3$); ^{31}P$\{^1$H$\}$ (202 MHz) 8.8 (s, $^1J_{PPt}$ = 2824 Hz).[48]

cis-Pt(Cl)(Me)(P((CH$_2$)$_{22}$)$_3$P) (_cis_-5g). A. Under air, a round bottom flask was charged with _cis_-4g (0.0664 g, 0.0547 mmol),

CH_2Cl_2 (5 mL). Then HCl (2.0 M in Et_2O, 0.0274 mL, 0.0548 mmol) was added with stirring. After 0.5 h, the solvent was removed by rotary evaporation to give a beige oil containing a *cis*-**2g**/**4g**/**5g** mixture in an approximate 2 : 3 : 5 ratio by ^{31}P NMR, along with other unidentified species. Attempted chromatographic purifications were unsuccessful. B. A CH_2Cl_2 solution of crude *cis*-**4g** (0.2852 g, *ca.* 0.2332 mmol) was chromatographed on neutral alumina (100 : 5 : 1 v/v/v hexanes/EtOAc/Et$_3$N). The solvent was removed from the product containing fractions (TLC monitoring) by rotary evaporation to give a 18 : 1 mixture of *cis*/*trans*-**5g** that was *ca.* 80% pure by ^{31}P {^{1}H} NMR.

Data for cis-5e: NMR (CDCl$_3$, δ/ppm): [1]H (500 MHz) 1.91–1.68 (br m, 12H, PC$\underline{H}_2$), 1.54–1.43 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.43–1.34 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.34–1.23 (br m, 96H, remaining C$\underline{H}_2$), 0.59 (dd, 3H, $^3J_{HP(trans)}$ = 7.0 Hz, $^3J_{HP(cis)}$ = 4.0 Hz, $^2J_{HPt}$ = 49 Hz,[48] C$\underline{H}_3$); [31]P{[1]H} (202 MHz) 10.1 (d, $^2J_{PP}$ = 12.7 Hz, $^1J_{PPt}$ = 1739 Hz, *trans* to CH$_3$), 3.4 (d, $^2J_{PP}$ = 12.7 Hz, $^1J_{PPt}$ = 4260 Hz, *cis* to CH$_3$).

trans-Pt(Cl)(Me)(P((CH$_2$)$_{22}$)$_3$P) (trans-5g). A. Under air, a vial was charged with *cis*-**4g** (0.0146 g, 0.0120 mmol), silica gel (0.2572 g), and CH_2Cl_2 (2.5 mL). The mixture was stirred (rt). After 12 h, the sample was filtered and the silica gel further washed with CH_2Cl_2 (25 mL). The solvent was removed from the filtrate by rotary evaporation to give *trans*-**5g** (0.0118 g, 0.0096 mmol, 80%) as a colorless oil. B. A vial was charged with a *ca.* 18 : 1 *cis*/*trans*-**5g** mixture (0.0350 g, 0.0284 mmol; see preceding paragraph), silica gel (0.9325 g), and CH_2Cl_2 (10 mL). The mixture was stirred (rt). After 12 h, the sample was filtered and the silica gel further washed with CH_2Cl_2 (40 mL). The solvent was removed from the filtrate to give *trans*-**5g** (0.0224 g, 0.0182 mmol, 64%) as a beige oil. Anal. Calcd for C$_{67}$H$_{135}$ClP$_2$Pt (1233.26): C, 65.25; H, 11.03. Found: C, 65.53; H, 11.13.

NMR (CDCl$_3$, δ/ppm):[47] [1]H (500 MHz) 1.89–1.74 (br m, 12H, PC$\underline{H}_2$),[47] 1.62–1.47 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.45–1.35 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.35–1.18 (br m, 96H, remaining C$\underline{H}_2$), 0.31 (t, 3H, $^3J_{HP}$ = 6.2 Hz, $^2J_{HPt}$ = 84 Hz,[48] PtC$\underline{H}_3$); [13]C{[1]H} (126 MHz) 31.3 (virtual t,[49] J_{CP} = 6.4 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 29.4 (s, $\underline{C}$H$_2$), 29.24 (s, $\underline{C}$H$_2$), 29.18 (s, $\underline{C}$H$_2$), 29.1 (s, $\underline{C}$H$_2$), 28.9 (s, $\underline{C}$H$_2$), 28.6 (s, $\underline{C}$H$_2$), 28.5 (s, $\underline{C}$H$_2$), 28.3 (s, $\underline{C}$H$_2$), 24.1 (s, PCH$_2$$\underline{C}H_2$), 21.5 (virtual t,[49] J_{CP} = 15.8 Hz, P$\underline{C}$H$_2$), −23.1 (t, J_{CP} = 6.6 Hz, Pt$\underline{C}$H$_3$); [31]P{[1]H} (202 MHz) 8.3 (s, $^1J_{PPt}$ = 2796 Hz).[48]

trans-Pt(Br)(Me)(P((CH$_2$)$_{14}$)$_3$P) (trans-9c). A Schlenk flask was charged with *trans*-**5c** (0.0981 g, 0.1094 mmol), LiBr (0.0488 g, 0.562 mmol) and THF (10 mL). The mixture was stirred (rt). After 12 h, the sample was concentrated and chromatographed on silica gel (3 : 2 v/v hexanes/CH_2Cl_2). The solvent was removed from the product containing fractions (TLC monitoring) to give *trans*-**9c** as a colorless oil, which solidified after 1 h (0.0903 g, 0.0960 mmol, 88%), mp (open capillary) 110–119 °C. Anal. Calcd for C$_{43}$H$_{87}$BrP$_2$Pt (941.08): C, 54.88; H, 9.32. Found: C, 54.99; H, 9.42.

NMR (CDCl$_3$, δ/ppm):[47] [1]H (500 MHz) 1.95–1.73 (br m, 12H, PC$\underline{H}_2$), 1.66–1.52 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.48–1.37 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.37–1.20 (br m, 48H, remaining C$\underline{H}_2$), 0.39 (t,

3H, $^3J_{HP}$ = 6.1 Hz, $^2J_{HPt}$ = 82 Hz,[48] C$\underline{H}_3$); [13]C{[1]H} (126 MHz) 30.1 (virtual t,[49] J_{CP} = 6.8 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 28.3 (s, $\underline{C}$H$_2$), 27.4 (s, $\underline{C}$H$_2$), 27.3 (s, $\underline{C}$H$_2$), 26.9 (s, $\underline{C}$H$_2$), 23.5 (s, PCH$_2$$\underline{C}H_2$), 22.5 (virtual t,[49] J_{CP} = 16.0 Hz, P$\underline{C}$H$_2$), −20.2 (t, J_{CP} = 6.4 Hz, Pt$\underline{C}$H$_3$); [31]P{[1]H} (202 MHz) 8.5 (s, $^1J_{PPt}$ = 2804 Hz).[48]

trans-Pt(I)(Me)(P((CH$_2$)$_{14}$)$_3$P) (trans-10c). Under air, a vial was charged with *trans*-**5c** (0.0599 g, 0.0668 mmol), NaI (0.0557 g, 0.372 mmol), THF (4 mL) and acetone (4 mL). The mixture was stirred (rt). After 2 d, the sample was concentrated and chromatographed on silica gel (hexanes, then CH_2Cl_2). The solvent was removed from two sets of product fractions (TLC monitoring) to give *trans*-Pt(I)$_2$(P((CH$_2$)$_{14}$)$_3$P) (0.0077 g, 0.007 mmol, 10%)[4a] and *trans*-**10c** (0.0577 g, 0.0584 mmol, 87%) as yellow waxy oils that solidified after 2–4 h, mp (open capillary, *trans*-**10c**) 114–118 °C. Anal. Calcd for C$_{43}$H$_{87}$IP$_2$Pt (988.08): C, 52.27; H, 8.88. Found: C, 51.99; H, 8.91.

NMR (CDCl$_3$, δ/ppm):[47] [1]H (500 MHz) 2.01–1.88 (br m, 12H, PC$\underline{H}_2$), 1.61–1.50 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.47–1.38 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.37–1.19 (br m, 48H, remaining C$\underline{H}_2$), 0.48 (t, 3H, $^3J_{HP}$ = 6.2 Hz, $^2J_{HPt}$ = 81.5 Hz,[48] C$\underline{H}_3$); [13]C{[1]H} (126 MHz) 30.1 (virtual t,[49] J_{CP} = 6.6 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 28.2 (s, $\underline{C}$H$_2$), 27.4 (s, $\underline{C}$H$_2$), 27.3 (s, $\underline{C}$H$_2$), 26.9 (s, $\underline{C}$H$_2$), 23.9 (br m, PCH$_2$$\underline{C}H_2$), 23.5 (s, P$\underline{C}H_2$), −14.8 (t, J_{CP} = 6.2 Hz, Pt$\underline{C}$H$_3$); [31]P{[1]H} (202 MHz) 5.4 (s, $^1J_{PPt}$ = 2767 Hz).[48]

cis-Pt(Et)$_2$(P((CH$_2$)$_{14}$)$_3$P) (cis-6c). A Schlenk flask was charged with *trans*-**2c** (0.3018 g, 0.3291 mmol) and Et_2O (15 mL). Then a benzene solution of EtLi (0.5 M, 0.200 mL, 0.100 mmol) was added with stirring (rt). After 12 h, the mixture was exposed to air. After 1 h, the sample was filtered through celite, which was washed with Et_2O (10–20 mL). The solvent was removed from the filtrate by rotary evaporation. The residue was chromatographed on neutral alumina (1 : 0.005 v/v hexanes/Et$_3$N). The solvent was removed from the product containing fractions (TLC monitoring) by rotary evaporation. The sample was kept at 4 °C for 2 d but did not solidify, affording *cis*-**6c** as a colorless oil (0.2524 g, 0.2791 mmol, 85%). Anal. Calcd for C$_{44}$H$_{89}$P$_2$Pt (988.08): C, 61.10; H, 10.48. Found: C, 60.97; H, 10.70.

NMR (CDCl$_3$, δ/ppm):[47] [1]H (500 MHz) 1.84–1.75 (br m, 4H, PC$\underline{H}_2$), 1.72–1.50 (br m, 12H), 1.50–1.21 (br m, 68H, remaining C$\underline{H}_2$), 1.11–0.81 (br m, 10H, PtC$\underline{H}_2$C$\underline{H}_3$); [13]C{[1]H} (126 MHz) 31.1 (virtual t,[49] J_{CP} = 4.2 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 30.5 (virtual t,[49] J_{CP} = 6.7 Hz, $\underline{C}$H$_2$), 28.3 (s, $\underline{C}$H$_2$), 27.5 (s, $\underline{C}$H$_2$), 27.4 (s, $\underline{C}$H$_2$), 26.9 (s, $\underline{C}$H$_2$), 26.8 (s, $\underline{C}$H$_2$), 26.7 (s, $\underline{C}$H$_2$), 26.3 (s, $\underline{C}$H$_2$), 26.1 (s, $\underline{C}$H$_2$), 25.2 (virtual t,[49] J_{CP} = 2.1 Hz, PCH$_2$$\underline{C}H_2$), 23.2 (s, P$\underline{C}H_2$), 23.0 (s, P$\underline{C}H_2$), 16.4 (apparent t, J_{CP} = 2.1 Hz, PtCH$_2$$\underline{C}H_3$), 14.8 (dd, $^2J_{CP(trans)}$ = 99.8 Hz, $^2J_{CP(cis)}$ = 9.1 Hz, Pt$\underline{C}$H$_2$CH$_3$); [31]P{[1]H} (202 MHz) 6.6 (s, $^1J_{PPt}$ = 1746 Hz).[48]

trans-Pt(Cl)(Et)(P((CH$_2$)$_{14}$)$_3$P) (trans-7c). Under air, a round-bottom flask was charged with *cis*-**6c** (0.3781 g, 0.4181 mmol), CH_2Cl_2 (15 mL), and methanol (1.0 mL). Then CH_3COCl (0.0298 mL, 0.4214 mmol) was added with stirring. After 2 h, the solvent was removed by rotary evaporation. The residue was chromatographed on neutral alumina (5 : 1 : 0.02 v/v/v hexanes/Cl$_2$Cl$_2$/Et$_3$N). The solvent was removed from the product containing fractions (TLC monitoring) by rotary evap-

oration. This gave *trans*-**7c** as a white solid (0.1727 g, 0.1896 mmol, 45%), mp (open capillary) 119–131 °C. Anal. Calcd for $C_{44}H_{89}ClP_2Pt$ (910.65): C, 58.03; H, 9.85. Found: C, 58.30; H, 10.02.

NMR (CDCl$_3$, δ/ppm):[47] [1]H (500 MHz) 1.89–1.78 (br m, 12H, PC$\underline{H}_2$), 1.67–1.57 (br m, 12H, PCH$_2$C$\underline{H}_2$), 1.48–1.39 (br m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.37–1.24 (br m, 48H, remaining C$\underline{H}_2$), 1.18–0.98 (br m, 5H, PtC$\underline{H}_2$C$\underline{H}_3$); [13]C{[1]H} (126 MHz) 30.1 (virtual t,[49] J_{CP} = 6.7 Hz, PCH$_2$CH$_2$$\underline{C}H_2$), 28.3 (s, $\underline{C}$H$_2$), 27.4 (s, $\underline{C}$H$_2$), 27.3 (s, $\underline{C}$H$_2$), 26.9 (s, $\underline{C}$H$_2$), 23.5 (s, PCH$_2$$\underline{C}H_2$), 21.8 (virtual t,[49] J_{CP} = 15.2 Hz, P$\underline{C}$H$_2$), 18.3 (s, PtCH$_2$$\underline{C}H_3$), −9.6 (t, J_{CP} = 5.4 Hz, Pt$\underline{C}$H$_2$); [31]P{[1]H} (202 MHz) 10.5 (s, [1]J_{PPt} = 3002 Hz).[48]

***cis*-Pt(Cl)(Ph)(P((CH$_2$)$_{14}$)$_3$P)** (*cis*-**8c**) and *trans*-**8c**. Under air, a round bottom flask was charged with *cis*-Pt (Ph)$_2$(P((CH$_2$)$_{14}$)$_3$P) (*cis*-**3c**;[8] 0.0598 g, 0.0598 mmol) and CH$_2$Cl$_2$ (6 mL). Then HCl (2.0 M in Et$_2$O, 0.030 mL, 0.060 mmol) was added with stirring (rt). After 1 h (based upon TLC monitoring), another charge of HCl was added (0.012 mL, 0.024 mmol). After 0.5 h, the solvent was removed by rotary evaporation to give a white solid, which was chromatographed on neutral alumina (first 5 : 1 v/v hexanes/CH$_2$Cl$_2$, then 20 : 1 v/v hexanes/EtOAc). Two sets of fractions were collected (TLC monitoring). The solvents were removed by rotary evaporation, benzene was added, and the two samples were freeze dried. The first gave *trans*-**8c** (0.0167 g, 0.0174 mmol, 29%)[4b] as a white powder; the second gave *cis*-**8c** (0.0253 g, 0.0264 mmol, 44%) as a white powder, mp (open capillary) 50–55 °C. Anal. Calcd for $C_{48}H_{89}ClP_2Pt$ (958.70): C, 60.14; H, 9.36. Found: C, 60.35; H, 9.48. Data for *trans*-**8c** agreed with those published earlier.[4b]

*Data for cis-**8c***: NMR (CDCl$_3$, δ/ppm):[47,50] [1]H (500 MHz) 7.39 (m, *o*-Ph, 2H), 7.05 (apparent dt, J_{HH} = 7.3, 1.3 Hz, 2H, *m*-Ph), 6.89 (t, [1]J_{HH} = 7.3 Hz, 1H, *p*-Ph), 2.54–2.42 (m, 2H, PC$\underline{H}_2$), 2.03–1.91 (m, 2H, C$\underline{H}_2$), 1.90–1.73 (m, 4H, C$\underline{H}_2$), 1.72–1.11 (m, 76H, remaining C$\underline{H}_2$); [13]C{[1]H} (126 MHz) 136.1 (s, *o*-Ph), 127.93 (s, *m*-Ph), 127.88 (s, i-Ph), 112.8 (s, *p*-Ph), 30.93 (s, $\underline{C}$H$_2$), 30.86 (s, $\underline{C}$H$_2$), 30.8 (s, $\underline{C}$H$_2$), 30.7 (s, $\underline{C}$H$_2$), 30.6 (s, $\underline{C}$H$_2$), 30.4 (s, $\underline{C}$H$_2$), 30.3 (s, $\underline{C}$H$_2$), 27.6 (s, $\underline{C}$H$_2$), 27.43 (s, $\underline{C}$H$_2$), 27.37 (s, $\underline{C}$H$_2$), 27.3 (s, $\underline{C}$H$_2$), 27.14 (s, $\underline{C}$H$_2$), 27.11 (s, $\underline{C}$H$_2$), 27.0 (s, $\underline{C}$H$_2$), 26.94 (s, $\underline{C}$H$_2$), 26.93 (s, $\underline{C}$H$_2$), 26.5 (s, $\underline{C}$H$_2$), 26.4 (s, $\underline{C}$H$_2$), 26.3 (s, $\underline{C}$H$_2$), 26.24 (s, $\underline{C}$H$_2$), 25.21 (s, $\underline{C}$H$_2$), 25.19 (s, $\underline{C}$H$_2$), 24.8 (s, $\underline{C}$H$_2$), 23.7 (s, $\underline{C}$H$_2$), 23.4 (s, $\underline{C}$H$_2$), 23.2 (s, $\underline{C}$H$_2$), 23.0 (s, $\underline{C}$H$_2$); [31]P{[1]H} (202 MHz) 5.8 (d, [2]J_{PP} = 14.0 Hz, [1]J_{PPt} = 1671 Hz,[48] *trans* to Ph), 0.2 (d, [2]J_{PP} = 14.0 Hz, [1]J_{PPt} = 4228 Hz,[48] *cis* to Ph).

***cis*-Pt(Ph)$_2$(P((CH$_2$)$_{14}$)$_3$P) (*cis*-3c)** and *trans*-**3c**. *A*. A Schlenk flask was charged with *trans*-**2c** (0.1915 g, 0.2088 mmol)[4a] and Et$_2$O (20.0 mL). Then PhLi (1.8 M in Bu$_2$O, 0.235 mL, 0.423 mmol) was added dropwise with stirring (rt). After 12 h, the mixture was exposed to air. After 1 h, the sample was filtered through celite, which was washed with diethyl ether (20 mL). The solvent was removed from the filtrate by rotary evaporation. The residue was chromatographed on silica gel (first 8 : 1 v/v hexanes/CH$_2$Cl$_2$, then 2 : 1 v/v hexanes/CH$_2$Cl$_2$). The solvent was removed from two sets of product containing fractions (TLC monitoring) by rotary evaporation to give *trans*-

3c (0.1036 g, 0.1036 mmol, 50%) and *cis*-**3c** (0.0602 g, 0.0602 mmol, 29%) as white solids. The NMR data for each product agreed well with those published earlier.[4a,8] *B*. A Schlenk flask charged with *trans*-**2c** (0.2232 g, 0.2434 mmol)[4a] and Et$_2$O (20.0 mL). Then PhLi (1.8 M in Bu$_2$O, 0.300 mL, 0.540 mmol) was added dropwise with stirring (rt). After 12 h, the mixture was exposed to air. After 1 h, the sample was filtered through celite, which was washed with diethyl ether (20 mL). The solvent was removed from the filtrate by rotary evaporation. The residue was chromatographed on silica gel (8 : 1 v/v hexanes/CH$_2$Cl$_2$). The solvent was removed from product containing fraction (TLC monitoring) by rotary evaporation to give *trans*-**3c** (0.2077 g, 0.2076 mmol, 85%).

Thermolyses (Table 3 and Scheme 9)

NMR tubes were charged with the following materials and kept at the indicated temperature except for brief intervals when spectra (δ/ppm) were recorded.

Entry 1. *cis*-**2c** (0.0086 g, 0.0094 mmol or 0.0096 g, 0.0104 mmol), silica gel (0.0925 g), toluene-d_8 or CDCl$_3$ (0.6 mL), 25 °C, 24 h. ^{31}P{^{1}H} NMR 4.5 or 4.8 (s, [1]J_{PPt} = 3498 or 3548 Hz,[48] *cis*-**2c**, >99%).

Entry 2. *cis*-**3c** (0.0070 g, 0.0070 mmol), toluene-d_8 (0.7 mL), 80 °C, 10 h. ^{31}P{^{1}H} NMR 4.9 (s, [1]J_{PPt} = 1762 Hz,[48] *cis*-**3c**, >99%).

Entry 3. *cis*-**3c** (0.0090 g, 0.0090 mmol), mesitylene (0.6 mL), 140 °C, 30 h. ^{31}P{^{1}H} NMR 7.4 (s, unknown, 84%), 4.3 (s, unknown, 16%).[20] Spectra taken after 1.5–12 h showed additional minor signals.

Entry 4. *cis*-**3c** (0.0059 g, 0.0059 mmol), silica gel (0.0927 g), toluene-d_8 (0.6 mL), 25 °C, 5 h and then 80 °C, 24 h. ^{31}P{^{1}H} NMR 0.5 (s, [1]J_{PPt} = 1760 Hz,[48] *cis*-**3c**, >99%).

Entry 5. *cis*-**4c** (0.0062 g, 0.0068 mmol), toluene-d_8 (0.7 mL), 80 °C, 10 h. ^{31}P{^{1}H} NMR 7.3 (s, [1]J_{PPt} = 1868 Hz,[48] *cis*-**4c**, >99%).

Entry 6. *cis*-**4c** (0.0081 g, 0.0092 mmol), mesitylene (0.6 mL), 140 °C, 30 h. ^{31}P{^{1}H} NMR 13.6 (s, unknown, 8%), 10.8 (unknown, 2%), 9.3 (s, unknown, 6%), 7.3 (s, [1]J_{PPt} = 1865 Hz,[48] *cis*-**4c**, 84%).

Entry 7. *cis*-**4c** (0.0071 g, 0.0081 mmol), silica gel (0.1096 g), toluene-d_8 (0.6 mL), 25 °C, 24 h. ^{31}P{^{1}H} NMR 7.3 (s, [1]J_{PPt} = 1870 Hz,[48] *cis*-**4c**, >99%).

Entry 8. *cis*-**4c** (0.0072 g, 0.0082 mmol), silica gel (0.0927 g), toluene-d_8 (0.6 mL), 25 °C, 5 h (little conversion) and then 80 °C, 24 h. ^{31}P{^{1}H} NMR 11.4 (s, unknown, 76%), 6.2 (s, unknown, 24%).[20]

Entry 9. *cis*-**5c** (0.0061 g, 0.0068 mmol), toluene-d_8 (0.7 mL), 80 °C, 10 h. ^{31}P{^{1}H} NMR 11.3 and 5.0 (2 d, [2]J_{PP} = 11.5 Hz/[1]J_{PPt} = 1736 Hz [48] and [2]J_{PP} = 11.5 Hz/[1]J_{PPt} = 4167 Hz,[48] *cis*-**5c**, 86%), 11.1 (s, *trans*-**5c**, 14%). The 72 h experiment was similarly carried out in toluene-d_0.

Entry 10. *cis*-**5c** (0.0143 g, 0.0159 mmol), *o*-C$_6$H$_4$Cl$_2$ (0.6 mL), 100 °C, 3 h. ^{31}P{^{1}H} NMR 10.8 (s, [1]J_{PPt} = 2834 Hz,[48] *trans*-**5c**, >99%).

Entry 11. cis-**5c** (0.0064 g, 0.0071 mmol), o-$C_6H_4Cl_2$ (0.7 mL), 140 °C, 0.5 h. $^{31}P\{^1H\}$ NMR 10.8 (s, $^1J_{PPt}$ = 2834 Hz,[48] trans-**5c**, >99%).

Entry 12. cis-**5c** (0.0091 g, 0.0100 mmol), C_6D_5Br (0.6 mL), 110 °C, 7 h. $^{31}P\{^1H\}$ NMR 11.1 (s, $^1J_{PPt}$ = 2828 Hz,[48] trans-**5c**, >99%). ^1H NMR 2.00–1.84 (m, 12H, PC$\underline{H}_2$), 1.84–1.69 (m, 12H, PCH$_2$C$\underline{H}_2$), 1.61–1.49 (m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.49–1.32 (m, 48H, remaining C$\underline{H}_2$), 0.54 (t, 3H, $^3J_{HP}$ = 5.5 Hz, $^2J_{HPt}$ = 80 Hz,[48] PtC$\underline{H}_3$).

Entry 13. cis-**5c** (0.0059 g, 0.0066 mmol), mesitylene (0.6 mL), 140 °C, 0.5 h. $^{31}P\{^1H\}$ NMR 10.4 (s, $^1J_{PPt}$ = 2841 Hz,[48] trans-**5c**, >99%).

Entry 14. trans-**5c** (0.0072 g, 0.0080 mmol), mesitylene (0.6 mL), 140 °C, 30 h. $^{31}P\{^1H\}$ NMR 10.8 (s, $^1J_{PPt}$ = 2844 Hz,[48] trans-**5c**, 87%), 7.3 (s, unknown, 13%).

Entry 15. trans-**7c** (0.0089 g, 0.0098 mmol), mesitylene (0.6 mL), 140 °C, 30 h. $^{31}P\{^1H\}$ NMR 7.4 (s, $^1J_{PPt}$ = 2447 Hz,[48] unknown, >99%).[20] Spectra taken after 1.5–18 h showed one main intermediate: $^{31}P\{^1H\}$ NMR 18.3 (s, $^1J_{PPt}$ = 2756 Hz[48]); ^{31}P NMR (undecoupled): 18.3 (br s, $w_{1/2}$ = 27 Hz, $^1J_{PPt}$ = 2754 Hz[48]); ^1H NMR −16.78 (t, $^2J_{HP}$ = 13.8 Hz, $^1J_{HPt}$ = 1254 Hz,[48] referenced to $C_6\underline{H}_3(CH_3)_3$ at δ 6.78 ppm).

Entry 16. cis-**8c** (0.0075 g, 0.0078 mmol), o-$C_6H_4Cl_2$ (0.6 mL), 100 °C, 6 h. $^{31}P\{^1H\}$ NMR 7.7 (s, $^1J_{PPt}$ = 2806 Hz,[48] trans-**8c**, >99%).

Entry 17. cis-**8c** (0.0053 g, 0.0055 mmol), o-$C_6H_4Cl_2$ (0.6 mL), 140 °C, 0.5 h. $^{31}P\{^1H\}$ NMR 7.7 (s, $^1J_{PPt}$ = 2806 Hz,[48] trans-**8c**, >99%).

Entry 18. trans-**8c** (0.0098 g, 0.0100 mmol), mesitylene (0.6 mL), 140 °C, 30 h. $^{31}P\{^1H\}$ NMR 7.7 (s, $^1J_{PPt}$ = 2806 Hz,[48] trans-**8c**, >99%).

Scheme 9 (right). cis-**4c** (0.0134 g, 0.0153 mmol), C_6D_5Br (0.6 mL), 110 °C, 7 h and then 140 °C, 6 h. $^{31}P\{^1H\}$ NMR 8.9 (s, $^1J_{PPt}$ = 2806 Hz, trans-**9c**, >99%). ^1H NMR 2.28 (s, 1H, $C_6D_5C\underline{H}_3$),[51] 2.03–1.92 (m, 12H, PC$\underline{H}_2$), 1.79–1.68 (m, 12H, PCH$_2$C$\underline{H}_2$), 1.59–1.49 (m, 12H, PCH$_2$CH$_2$C$\underline{H}_2$), 1.49–1.37 (m, 48H, remaining C$\underline{H}_2$), 0.61 (t, 3H, $^3J_{HP}$ = 6.0 Hz, $^2J_{HPt}$ = 80 Hz,[48] PtC$\underline{H}_3$).

Scheme 9 (left). cis-**4c** (0.0062 g, 0.0071 mmol), o-$C_6H_4Cl_2$ (0.6 mL), 140 °C, 12 h. $^{31}P\{^1H\}$ NMR 10.8 (s, $^1J_{PPt}$ = 2834 Hz,[48] trans-**5c**, >99%). A spectrum taken after 1 h showed an additional minor signal at 8.9 (s, unknown).

Crystallography

A. Methanol was slowly added dropwise to an Et_2O solution of cis-**4c**. After each drop, the mixture was shaken to redissolve the white precipitate formed. When the precipitate persisted, Et_2O was added to regenerate a homogeneous solution, which was kept at 4 °C. After 3 d, colorless crystals were obtained, and data were collected as outlined in Table 1. Cell parameters were obtained from 45 frames using a 1° scan and refined with 102 005 reflections. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[52] Lorentz and polarization corrections were applied. Data were scaled, and absorption correction were applied using the program SADABS.[53] The space group was

determined from systematic reflection conditions and statistical tests. The structure was solved using XT/XS in APEX3.[52,54] The structure was refined (weighted least squares refinement on F^2) to convergence.[54,55] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions using a riding model. The atoms C29 through C42 and C23 to C24 exhibited elongated thermal ellipsoids and/or nearby residual electron density peaks. These were successfully modeled by disorder between two positions, with occupancy ratios of 0.64 : 0.36, and 0.81 : 0.19 respectively. Appropriate restraints and/or constraints were applied to keep the bond distances, angles, and thermal ellipsoids meaningful. The absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).[56] B. Colorless crystals of trans-**5c** were obtained in a procedure analogous to that for cis-**4c**, but starting from the isomer cis-**5c**. Either methanol or ethanol could be used. Data were collected on a crystal from each solvent system and both gave the same structure, which was solved as in A. Two pairs of atoms, Cl1/C1 and C39/ C40 exhibited abnormal thermal ellipsoids. These were successfully modeled by disorder between two positions, with occupancy ratios of 0.89 : 0.11 and 0.88 : 0.12 respectively. C. An Et_2O solution of trans-**10c** was layered with methanol. After 7 d, data were collected on the yellow blocks as outlined in Table 1. The structure was solved and refined in a manner parallel to that in A. The iodide and methyl ligands (I1, C1) were disordered, but this could be modeled and refined to a 86 : 14 occupancy ratio (I1 and I1a as well as C1 and C1a were constrained to have the same thermal ellipsoids). D. Colorless crystals of trans-**7c** were obtained in a procedure analogous to that for cis-**4c**. Data were collected and the structure was solved in a manner parallel to that in A. Three independent molecules were found in the asymmetric unit. For one, the carbon atoms of the methylene chains exhibited elongated thermal ellipsoids (C91–C132), suggesting disorder. This could be modeled between two positions with an occupancy ratio of 0.33 : 0.67. Appropriate restraints were used to keep bond distances, angles, and thermal ellipsoids meaningful. However, some thermal ellipsoids associated with the modeled positions remained elongated, suggesting further disorder.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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