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Review

Gyroscopes and the chemical literature: 1852–2002[☆]

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Contents

Abstract

A brief history of mechanical gyroscopes and their applications is followed by a summary of properties that are desirable in molecular gyroscopes. Molecules to which the descriptor gyroscope has been applied are then reviewed through early 2002. Syntheses as well as structural and dynamic properties of the macrocyclic platinum complexes *trans*-$(Cl)(C_6F_5)\overline{Pt(PPh_2(CH_2)_{2n+2}P}Ph_2)$ ($n = 4, 5, 6, 8, 9$), in which a single methylene chain spans the *trans* phosphorus atoms, are subsequently analyzed. No part of the Cl-Pt-C_6F_5 moiety can rotate through the macrocycle when it consists of 13 atoms; however, the chloride ligand can pass through macrocycles of ≥15 atoms, and the pentafluorophenyl ligand through macrocycles of ≥21 atoms. Analogous complexes in which two methylene chains span the *trans* phosphorus atoms are also discussed.

Keywords: Gyroscope; Alkene metathesis; Porphyrins; Cucurbituril; Phosphines; Turnstiles; Crystallography; Dynamic NMR

1. Introduction

The first device that closely resembled a modern mechanical gyroscope was described in 1817 by Johann von Bohnenberger, a Professor of mathematics and astronomy at the University of Tübingen in Germany [1,2]. However, credit for the discovery of the gyroscope is most widely attributed to the French scientist Jean Foucault in 1852 [1]. He sought to develop an instrument that would help visualize the rotation and precession of the Earth about its axis. Foucault coined the name for his invention from two Greek words—“gyros”, meaning circle or rotation, and “skopein”, meaning to view. A replica is depicted in Fig. 1 (left).

Since that time, gyroscopes have come to play very important roles in society and technology [1]. Most individuals are probably first introduced to gyroscopes as toys (Fig. 1, middle). However, there are many practical applications, such as anti-roll stabilizers in ships and high-speed trains, gyrocompasses and airplane autopilots, space station orientation and navigational systems, virtual reality headsets, and wireless computer pointing devices [4]. Gyroscopes – both macroscopic and molecular

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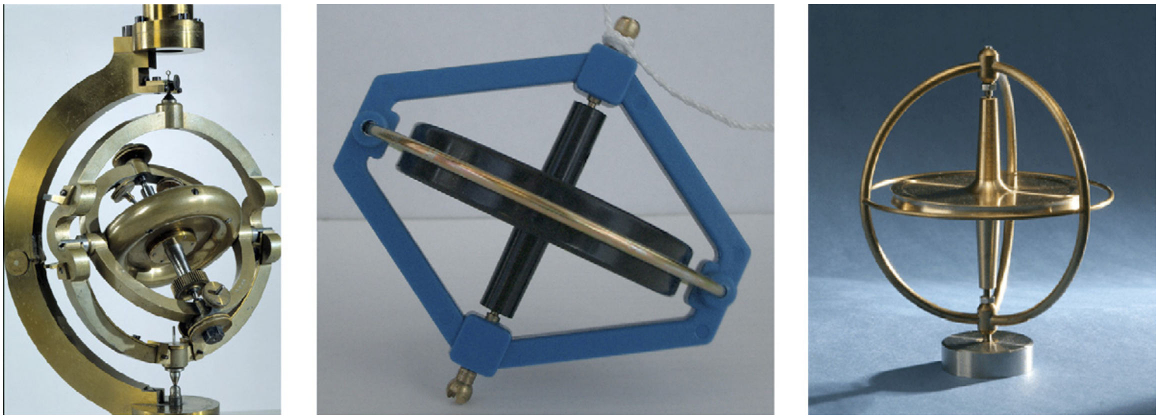


Fig. 1. Foucault gyroscope (left) and present-day toy versions or models (middle, right).

– can nearly always be dissected into two components, a rotator and a stator [3]. The latter is considered to be static, and the former spinning. However, motion is always a function of the reference frame of the observer. For this reason, the component with the greater moment of inertia is taken as the stator.

The purpose of this introductory review is not to present a detailed account of the complicated physics of a gyroscope. Rather, we seek to orient the reader intuitively with respect to common toy gyroscopes. Target properties for molecular models for gyroscopes are first proposed. We then review all cases where some type of molecule/gyroscope connection has been claimed in the literature, up to the beginning of our own efforts in 2002 [5,6]. These reports are evaluated with respect to the proposed target properties. This coverage corresponds to the sesquicentennial of Foucault's disclosure. However, it stops short of the important work of Garcia-Garibay [7,8], who has synthesized and characterized a variety of excellent models for molecular gyroscopes, a few of which are described in passing below.

2. Target properties, molecular gyroscopes

We have proposed that molecular gyroscopes should have the following properties: [5a]

1. There should be a *functional* axis of rotation, which allows an interior domain of the molecule (the rotator) to rotate independently of an exterior domain (the stator).
2. The exterior domain should sterically shield and optimally encase the rotator with "spokes", analogously to a common toy gyroscope. Although the physics of a gyroscope is not dependent upon an external assembly (simple toy spinning tops can also be regarded as gyroscopes), to our knowledge all gyroscopes used in real-world applications are enclosed in protective housings, for the logical purpose of insulating them from their environments.
3. They should closely model the connectivity and symmetry of a toy gyroscope. For those in Fig. 1, the point groups are $D_{2\mathrm{h}}$ (middle) and $D_{3\mathrm{h}}$ (right).

Systems with the above features would still have one shortcoming vis-à-vis real world gyroscopes. Namely, the rotators would not rotate unidirectionally. Rather, rotation would be Brownian—random, in both clockwise and counterclockwise directions. Although rotations of $\geq 360^\circ$ would be statistically possible, they would not be as frequent as simple back/forth movements. The obvious question remains: what can be done on a molecular level that is analogous to "pulling the string" on a toy gyroscope?

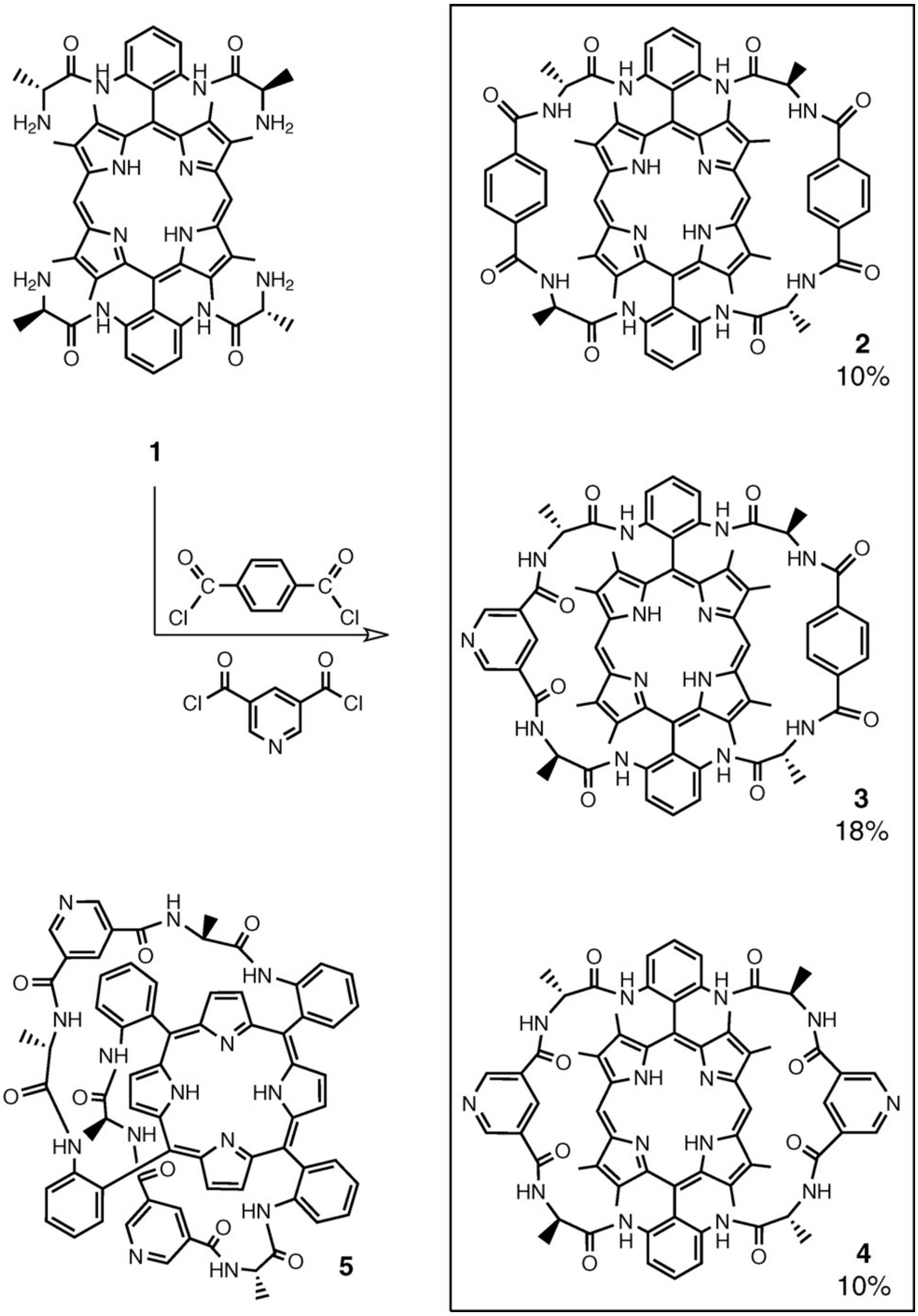
One answer is to introduce a dipole moment on the rotator. Dipole moments interact with electric fields. The rotator could then be oriented by a static electric field. Garcia-Garibay has termed such systems molecular compasses [7,8]. A rotating electric field could then be used to drive unidirectional rotation, the molecular-level physics for which has been well worked out [3]. However, the introduction of a dipole moment necessitates a desymmetrization. The point group D_{nh} would no longer be possible.

Perhaps other means of achieving unidirectional rotation in molecules with features (1)–(3) will be realized in the future. However, in view of this problem, we commonly refer to such systems as "gyroscope-like". We also extend this terminology to assemblies with (a) dipolar rotators, but where the groups on the rotator are roughly isosteric, such that the shape is nearly of D_{nh} symmetry, and (b) stators of one symmetry (e.g., three identical "spokes" defining equal angles) and rotators of another (e.g., an axis with two identical ligands at a 180° angle).

These codicils are a logical reflection of a rapidly developing field. As noted by a reviewer, functional characteristics may ultimately be more important than restrictive symmetry requirements. Hence, some evolution in the preceding target properties can be anticipated.

3. Porphyrin systems of Rose [9]

Starting with the picket fence series of Collman, designer porphyrins have often been given rather colorful names. The first molecules we are aware of to which the descriptor "gyroscope" was applied were reported by Rose in 1985 [9]. The "double picket fence" porphyrin **1** shown in Scheme 1 was initially synthesized. Then bridges were introduced below and/or above the plane of the porphyrin ring system, giving **2–4**. The properties of these gyroscope porphyrins were contrasted with those of the



1

2 10%

3 18%

4 10%

5

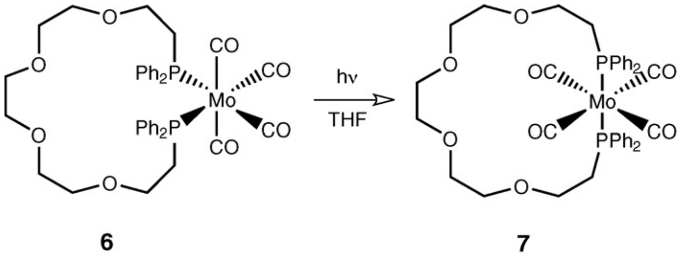
Scheme 1. Syntheses of “gyroscope” porphyrins (**2**–**4**) and a typical “*anses de panier*” or “basket handle” porphyrin (**5**).

type **5**, which were termed “*anses de panier*” or “basket handle” porphyrins. However, no exact definition of a gyroscope porphyrin or molecule was proposed.

The porphyrins of Rose have connectivities similar to two-spoke toy gyroscopes (Fig. 1, middle). The porphyrin cores can be viewed as potential rotators, with phenyl moieties capping the axes. However, the outer periphery of each porphyrin hemisphere consists of eleven atoms, whereas the spokes consist of only fifteen atoms. When the steric effects of the eight porphyrin methyl groups are considered, rotation is clearly impossible, as easily confirmed with molecular models. Hence, **2**–**4** cannot be regarded as functional models for molecular gyroscopes. Nonetheless, they represent intriguing building blocks for future studies. For example, the number of atoms in the spokes could be increased, and the *o*,*o*′-disubstituted phenyl rings that cap the axes might be further distanced with *p*-phenylene (p-C_6H_4) spacers. With appropriate molecular engineering, 360° rotation should be realizable.

4. Singly *trans*-spanning diphosphine complex of Gray [10]

To our knowledge, the second type of molecule coupled with the descriptor “gyroscope” was reported by Gray in 1994 [10].



Scheme 2. Synthesis of a molybdenum complex of a singly *trans*-spanning diphosphine.

In the context of a program involving metalla crown ethers, he prepared the molybdenum tetracarbonyl complex **6** (Scheme 2). This features a *cis*-diphosphine chelate ligand with a 14-atom backbone, resulting in a 17-membered macrocycle. Complex **6** underwent slow isomerization in the dark (15% conversion after 24 days at 5 °C) or rapid isomerization upon photolysis. The product, the singly *trans*-spanning diphosphine complex **7**, could be isolated in 45% yield after workup [11].

ORTEP and space-filling representations of the crystal structure of **7** are shown in Fig. 2. The macrocycle is rather symmetric about the $Mo(CO)_4$ plane, and roughly bisects one OC-Mo-CO angle. If rotation of the $Mo(CO)_4$ moiety were slow on the NMR time scale, two CO ^{13}C NMR signals would be expected. However, NMR spectra recorded at −80 °C showed only one broadened signal. This indicates a rather low barrier for the rotation of a carbonyl ligand through the macrocycle, as most would likely guess from Fig. 2.

The distances from molybdenum to the oxygen atoms of the carbonyl ligands in **7** are 3.159–3.175 Å. When the van der Waals radius of oxygen (1.52 Å) [12] is added to the latter (greater) value, the radius of the rotator – 4.69 Å – is obtained. We compute distances of 6.043–6.545 Å from molybdenum to the carbon and oxygen atoms of the macrocycle that are closest to the plane of the rotator. When the van der Waals radii of carbon (1.70 Å) or oxygen are subtracted, the "clearance" or "bridge height" offered by the macrocycle – 4.52–4.84 Å – is obtained. Hence, rotation of the $Mo(CO)_4$ moiety would be expected from metrical parameters as well.

Unlike the porphyrins **2**–**4**, the molybdenum tetracarbonyl complex **7** unambiguously qualifies as a molecular rotor [3]. However, like Rose, Gray did not attempt to define a molecular gyroscope. Complex **7** fulfills only the first of the three criteria proposed above. However, the stator does provide some steric shielding for the rotator (criterion two) by means of a single spoke connecting the termini of the axis (connectivity criterion three). Similar situations can be found with [*n*]paracyclophanes (facile C_6H_4 rotation for $n \geq 12$) [13] and many other quite common molecules.

5. Doubly *trans*-spanning bis(pyridine) complex of Lambert [14]

Although a brief communication by Lambert in 1999 did not mention the word gyroscope, it reported an important antecedent for our own work and is therefore summarized here. The paper described the two-fold ring-closing metathesis of the palladium complex **8** (Scheme 3) with Grubbs' catalyst to give the doubly *trans*-spanning bis(pyridine) complex **9**. This represents the first application of alkene metathesis in the synthesis of a *trans*-spanning chelate ligand. Since, the *o*,*o*′ alkene-containing substituents of **8** are likely directed above and below the palladium square plane, it should be pre-organized for efficient cyclization.

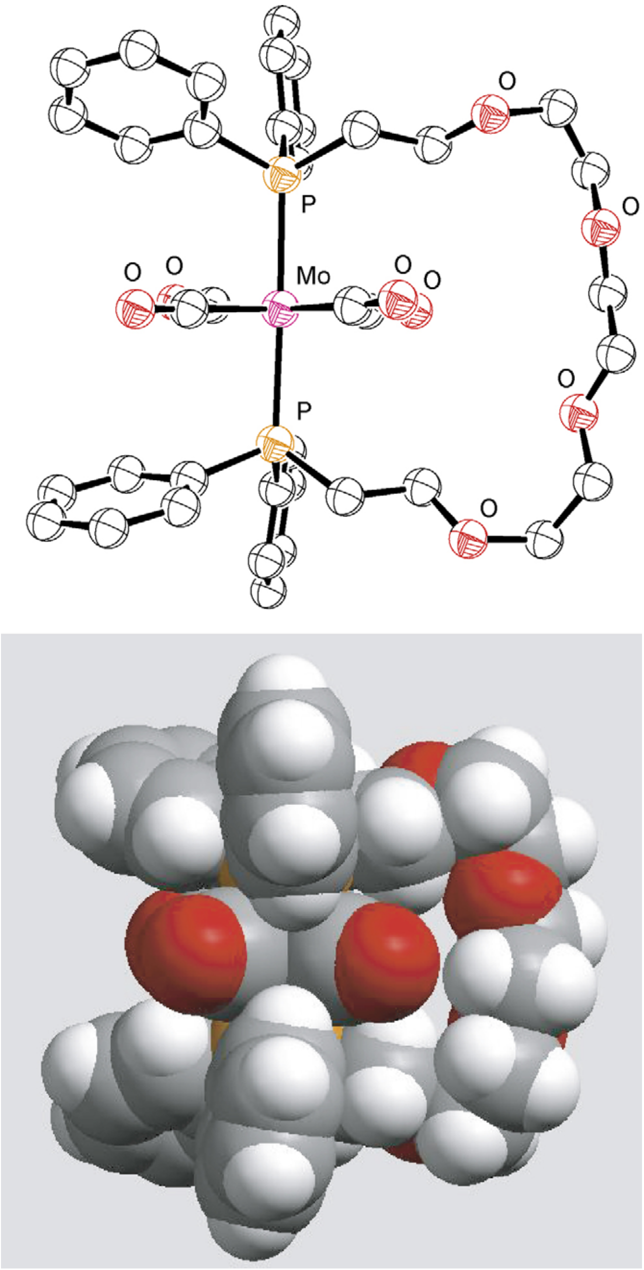
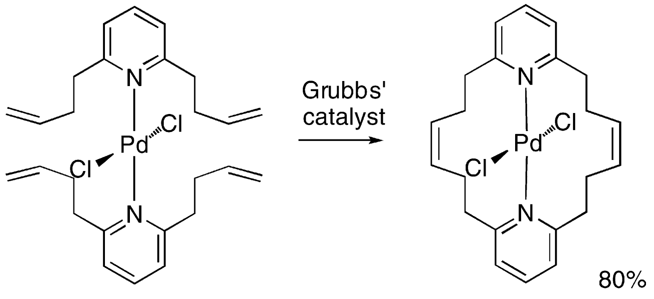


Fig. 2. ORTEP (top) and space filling (bottom) representations of the crystal structure of **7**.

The $PdCl_2$ moiety in **9** is a potential rotator. The spokes in **9** consist of eight atoms, and together with the axis of the rotator define 11-membered rings. As will be shown for our molecules below, it is sterically impossible for MCl_2 moieties to rotate within *trans*-spanning macrocycles consisting of thirteen atoms or fewer. Although **9**, like the porphyrins of Rose, cannot be



8 **9**

Scheme 3. Synthesis of a palladium complex of a doubly *trans*-spanning bis(pyridine).

viewed as a functional model of a gyroscope, higher homologs should fulfill criteria (1)–(3) above.

6. Cucurbituril-based gyroscanes of Day and Blanch [15,16]

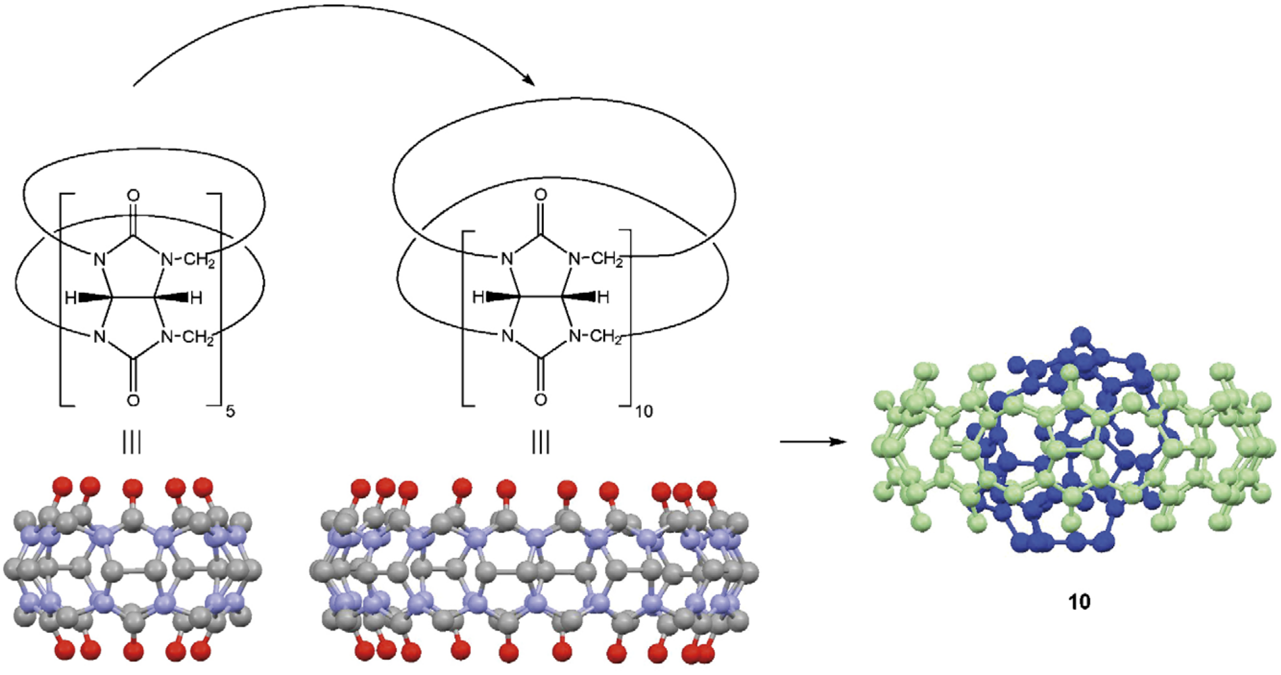
The next publication to intimately connect various molecules to gyroscopes carried the provocative title "Of Molecular Gyroscopes, Matroshka Dolls, and Other 'Nano'-Toys". [15] This highlight article offered fresh perspectives on several novel types of molecular rotors described earlier. The most relevant was the cucurbit[10]uril/cucurbit[5]uril host/guest complex **10** shown in Scheme 4, which was reported by Day and Blanch in January of 2002. [16] They unexpectedly encountered **10** while investigating the controlled synthesis of cucurbit[*n*]urils.

This assembly is formally derived by encasing cyclopentamer **10a** within cyclodecamer **10b**. Crystals grown from concentrated HCl feature a chloride ion in the center of the cyclopentamer, and capping H_2O or H_3O^+ moieties. The concentric cyclopentamer/cyclodecamer moieties are inclined at a 64° angle. Several experiments indicate that the mechanism of formation of **10** is *not* as simple as implied by Scheme 4. For example, **10b** has never been isolated or detected free of **10a**. Efforts to template the synthesis of **10b** with **10a** have also been unsuccessful to date.

Regardless, Day and Blanch could establish the independent rotation of the cyclopentamer and cyclodecamer in solution by NMR. Models suggest that both rings can rotate relative to one another, even when confined to the same plane. Although there is no covalent bond, fixed rotational axis, or fixed rotational orientation between the inner and outer rings, there is an obvious conceptual relationship to a gimbaled gyroscope. These feature several concentric rings that allow the spinning axis of a gyroscope to be oriented in any direction, similar to the Foucault instrument in Fig. 1 (left). Hence, Day and Blanch termed these substances "Gyroscanes". In our opinion, this name is well justified. However, given that there is no physical axis, we would not classify them as molecular gyroscopes.

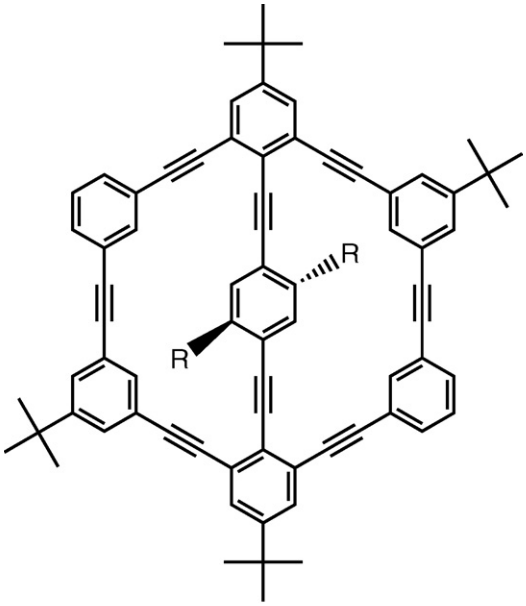
7. Molecular turnstiles of Moore [17]

Also mentioned in the highlight article, [15] and in our own papers, [5a] are the fascinating molecules **11** (Fig. 3), which were reported by Moore in 1995. [17] These feature a central *p*-phenylene moiety encased in a C≡C-expanded cyclohexa-*m*-phenylene, and were descriptively termed "molecular turnstiles". They were accessed in 35–50% yields by two-fold intramolecular Sonogashira couplings. When the substituents on the *p*-phenylene moiety are small, such as the



10a **10b** **10**

Scheme 4. Formal synthesis of cucurbit[10]uril/cucurbit[5]uril host/guest complex **10**.



11

R = **a**, H
b, CH$_2$OCH$_3$
c, CH$_2$O(3,5-C$_6$H$_3$(*t*-Bu)$_2$)

Fig. 3. Molecular turnstiles.

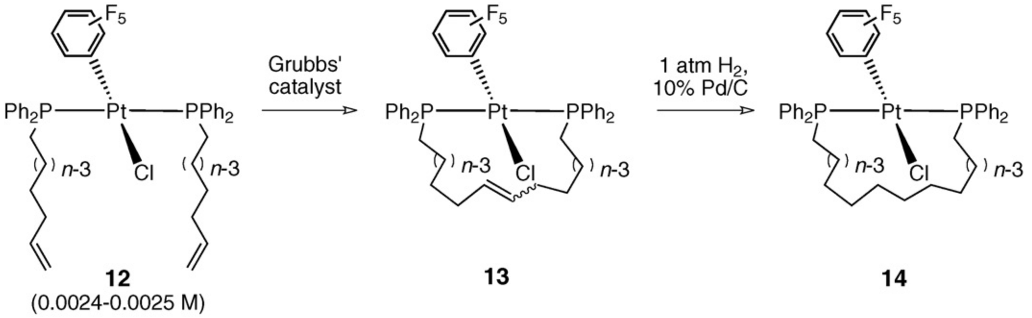
hydrogen atoms or CH$_2$OCH$_3$ groups in **11a**,**b**, rotation is fast on the NMR time scale. When the substituents are larger, such as in **11c**, rotation is blocked.

Compounds **11a**,**b** fulfill, at least in spirit, the criteria proposed above for molecular gyroscopes: (1) there is a functional axis of rotation; (2) the stator encases and sterically protects the rotator; (3) the symmetry comes very close to D_{2h}, that of a two-spoked toy gyroscope. In the case of **11a**, rigorous D_{2h} symmetry could be achieved by introducing two additional *t*-butyl groups, such that the stator achieves a horizontal mirror plane. In the case of **11b**, additional CH$_2$OCH$_3$ groups would also be needed on the rotator. However, as noted in Section 2, there are potential advantages associated with unsymmetrically substituted rotators. In any event, many interesting structural extensions of this class of molecules are readily envisioned.

8. Singly *trans*-spanning diphosphine complexes from the Gladysz group

In this section, we describe our early work with molecular rotors belonging to the same family as Gray. These systems were initially communicated in 2000, [6a] and additional examples appeared in subsequent full papers [6c,18]. We sought to access *trans*-spanning diphosphine complexes using alkene metathesis, similarly to Lambert's bis(pyridine) system **9**. First, KPPh$_2$ and the α,ω-bromoalkenes Br(CH$_2$)$_n$CH=CH$_2$ (n = **a**, 4; **b**, 5; **c**, 6; **d**, 8; **e**, 9) were reacted to give the alkene-containing phosphines PPh$_2$(CH$_2$)$_n$CH=CH$_2$ in 95–41% yields. These were treated with the platinum tetrahydrothiophene complex [Pt(μ-Cl)(C$_6$F$_5$)(tht)]$_2$ to give the bis(phosphine) complexes **12a**–**e** depicted in Scheme 5 in 80–54% yields.

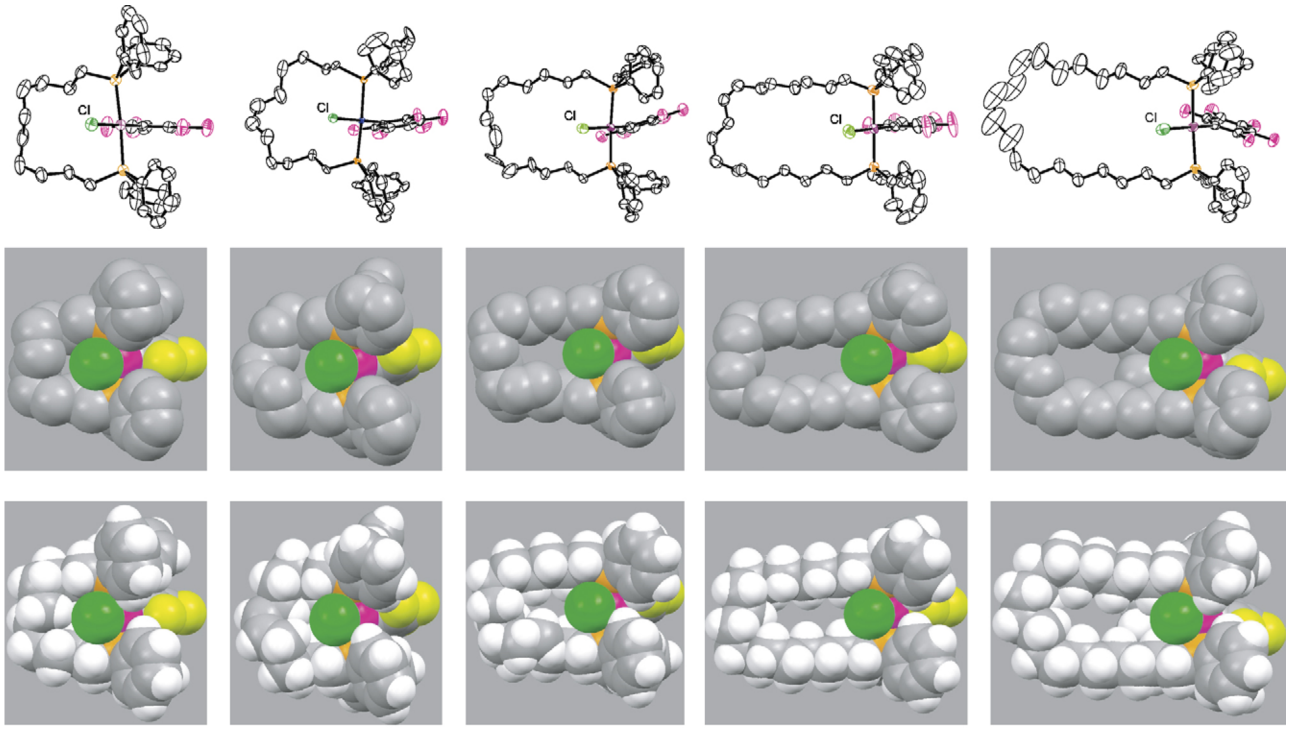
Alkene metatheses with Grubbs' catalyst gave **13a**–**e**, which feature 13- to 23-membered macrocycles, in 95–84% crude yields (Scheme 5). We were somewhat surprised by the success of these reactions; there is no obvious feature that would direct both CH=CH$_2$ moieties of **12a**–**e** on the same side of the platinum coordination plane, although such a conformation was observed in the crystal structure of **12b**. [18] ^{31}P NMR spectra generally showed *more* than the two signals that would be expected for *cis*/*trans* C=C isomers, suggesting the presence of oligomers or polymers (diplatinum byproducts, which can be detected by mass spectrometry [6d], were absent). Therefore, the first set of yields in Scheme 5 overstates the true



n	Yield, metathesis (%)^a	Yield, hydrogenation (%)^b	Overall yield (%)
a, 4	95	70	67
b, 5	84	98	82
c, 6	96	72	69
d, 8	90	59	53
e, 9	85	50	43

^{a} Includes minor amounts of polymeric or oligomeric byproducts. ^{b} After chromatography that removes polymeric or oligomeric byproducts.

Scheme 5. Syntheses of platinum complexes of singly *trans*-spanning diphosphines.



14a (*Z*)-**13b** **14c** **14d** **14e**

Fig. 4. ORTEP (top) and space filling (middle: without hydrogen atoms; bottom: with hydrogen atoms) representations of the crystal structures of **14a**, (*Z*)-**13b**, and **14c**–**e**.

yields of monoplatinum products. Subsequent hydrogenations gave the target complexes **14a**–**e** in 82–43% overall yields from **12a**–**e**.

A complex of each macrocycle size – the saturated systems **14a**,**c**–**e** and the alkene (*Z*)-**13b** – could be crystallographically characterized. ORTEP and space-filling representations are depicted in Fig. 4, the latter both with and without hydrogen atoms. Two questions can be formulated with respect to rotation of the Cl-Pt-C_6F_5 moieties about the P-Pt-P axes: (a) Is there sufficient room for the chloride ligand to pass through the macrocycle? (b) Is there sufficient room for the pentafluorophenyl ligand to pass through the macrocycle? Although the combined effect of the hydrogen atoms on the macrocycle cavity size can make a strong visual impression, experience has established that this can usually be neglected. Educated guesses can then be derived from the crystal structures as follows.

As summarized in Table 1, the platinum-chlorine distances range from 2.352 to 2.372 Å. When the van der Waals radius of chlorine is added (1.75 Å) [12], the radius of this portion of the rotator is obtained (4.10–4.12 Å). The distances from platinum to the *para* fluorine atom of the pentafluorophenyl ligand range from 6.161 to 6.184 Å. When the van der Waals radius of fluorine is added (1.47 Å) [12], the radius of this portion of the rotator is obtained (7.63–7.65 Å). Next, distances are calculated from the platinum to the remote carbon atoms of the macrocycle that are closest to the plane of the rotator – i.e., the two that are in the middle of the methylene chain (Table 1). When the van der Waals radius of carbon (1.70 Å) is subtracted from the smaller value, the “bridge height” defined by the *trans*-spanning diphosphine is obtained.

As can be seen from Table 1, the Pt-Cl radius or “height” (average value 4.11 Å) exceeds the “bridge height” in **14a**

Table 1
Key distances involving rotator and stator atoms for the platinum complexes in Fig. 4

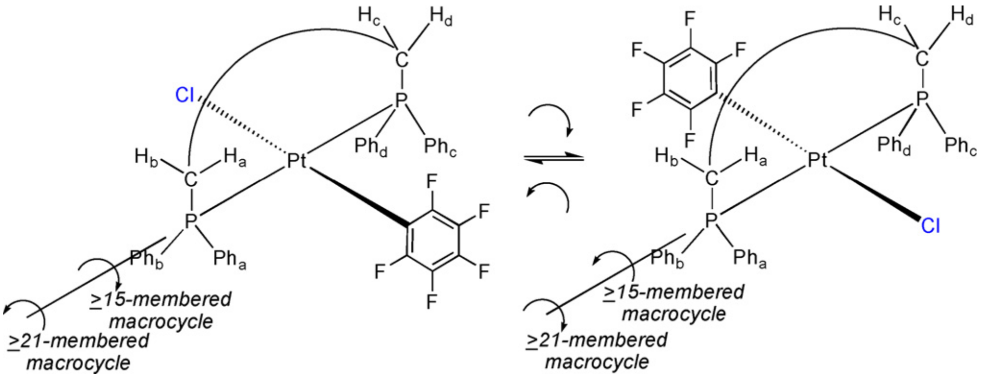
Complex	Macrocycle size	Distance, Pt-Cl (Å)	Plus van der Waals radius of chlorine (Å)[a]	Distance, Pt to *p*-fluorine (Å)	Plus van der Waals radius of fluorine (Å)[a]	Distance, Pt to distal carbons (Å)[b]	Minus van der Waals radius of carbon (Å)[a,d]
14a	13	2.3668 (10)[c]	4.12	6.183[c]	7.65	5.271,[c] 4.894[c]	3.19
(*Z*)-**13b**	15	2.3641 (18)	4.11	6.183	7.65	6.212, 6.175	4.47
14c	17	2.359 (2)	4.11	6.167	7.64	7.569, 7.263	5.56
14d	21	2.3524 (12)	4.10	6.161	7.63	10.156, 9.446	7.75
14e	23	2.3719 (16)	4.12	6.184	7.65	11.445, 11.363	9.66

[a] With respect to previous table entry.

[b] The remote carbon atoms of the macrocycle that are closest to the plane of the rotator—i.e., the two carbon atoms in the middle of the methylene chain.

[c] Average of two independent molecules in the unit cell.

[d] The shorter platinum-carbon distance is used.



Scheme 6. Analysis of Cl-Pt-C_6F_5 rotation in platinum complexes of singly *trans*-spanning diphosphines (**14**).

(3.19 Å). It is somewhat less than the "bridge height" in (*Z*)-**13b** (4.47 Å), and much less than that in **14c** (5.56 Å). Hence, the chlorine atom should only be able to pass through macrocycles of 15 atoms and larger, as illustrated in Scheme 6. Similarly, the Pt-C_6F_5 radius or "height" (average value 7.64 Å) exceeds the "bridge height" in **14c** (5.56 Å), but is less than that in **14d** (7.75 Å). Hence, the pentafluorophenyl ligand should be able to pass through macrocycles of 21 atoms and larger. Said differently, a 360° rotation of the rotator should be possible in **14d** and higher homologs. Only partial, back-and-forth rotation involving passage of the smaller chlorine ligand through the macrocycle should be possible with **14b**,**c**, and no rotation apart from low-amplitude oscillations should be possible with **14a**.

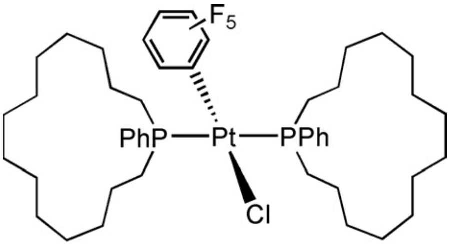
These predictions can be compared to the results of variable temperature NMR experiments. When the rotation of the Cl-Pt-C_6F_5 moieties in **14a–e** is slow on the NMR time scale, separate signals should be observed for the diastereotopic phenyl groups highlighted in Scheme 6. Other diastereotopic groups are present, and in theory should also give separate signals. Indeed, **14a** exhibits two ^{13}C signals for the *ipso* phenyl carbons at room temperature. No coalescence occurs in toluene at 95 °C. Together with other data, a lower limit for the barrier to rotation of the chloride ligand through the macrocycle can be calculated: $\Delta G^\ddagger$ (95 °C) $\geq$ 17.4 kcal/mol.

In contrast, **14b** exhibits only a single set of ^{13}C NMR signals at room temperature. A ca. 180° rotation of the Cl-Pt-C_6F_5 moiety, presumably involving passage of the smaller chloride ligand through the macrocycle, is required to exchange the diastereotopic groups. At low temperatures in $CDFCl_2$, separate signals decoalesce for the diastereotopic *ortho*, *meta*, and *para* phenyl carbon atoms (the *ipso* signals are obscured). Line shape analysis gives a very low barrier, with $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of 6.0 ± 0.4 kcal/mol and -13.9 ± 2.6 eu. Not surprisingly, no decoalescence is observed with the higher homolog **14c**.

Importantly, ML_n rotation in the preceding molecules would be expected to be coupled to conformational changes in the stators. In other words, given the snug "floor to ceiling" clearance evident in Fig. 4, rotation should be correlated to macrocycle-based conformational processes that will increase the activation barrier. Accordingly, slightly negative activation entropies are always observed [5a]. These interactions will attenuate as spacing is increased between the rotator and the termini of the axis.

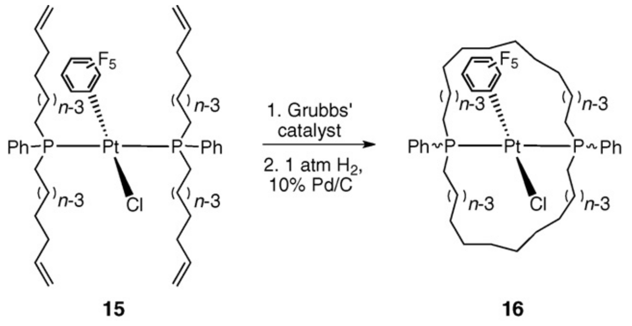
9. Doubly *trans*-spanning diphosphine complexes from the Gladysz group

We sought to extend the chemistry in the preceding section to substrates with *trans* phosphine ligands bearing two $(CH_2)_nCH{=}CH_2$ chains. Thus, complexes **15a–d** in Scheme 7 were synthesized by analogous methods. The first results with **15c** were communicated in 2000; [6a] those with **15a**,**b**,**d** were subsequently detailed. [6d] Such complexes can undergo either *inter*ligand or *intra*ligand metathesis. The former process would give products in which two chains span the *trans* phosphorus atoms. These would be distinctly more gyroscope-like than singly-bridged **14a–e**. In order to better assay for the latter process, an authentic sample of **17c** (below) was prepared. This compound contains two 15-membered macrocyclic *mono*phosphines.



17c

As shown in Scheme 7, interligand metatheses and hydrogenations could be effected to give the target complexes **16a–d**. Two stereoisomers are possible, differing in the relative orientations of the phenyl groups with respect to the planes of the macrocycles (syn or anti). In the case of **16c**, which features 17-membered macrocycles, both were isolated (31% syn, 7% anti). The structures were confirmed crystallographically, as shown in Fig. 5. However, they can also be distinguished by NMR. The syn isomer possesses idealized C_{2v} symmetry, and exhibits a single ^{31}P NMR signal and one set of methylene ^{13}C NMR signals. The anti isomer possesses C_1 symmetry, and exhibits two



n	Concentration (M)	Isolated yield (%)[a]
a, 4	0.0067	20 or 55[b]
b, 5	0.0019	5
c, 6	0.0034	38[c]
d, 8	0.0033	14

[a] Isomer with phenyl groups syn, unless noted. [b] Yield using Grubbs' second generation catalyst. [c] 31% syn, 7% anti; spectroscopic yield (syn), 52%.

Scheme 7. Syntheses of platinum complexes of doubly *trans*-spanning diphosphines.

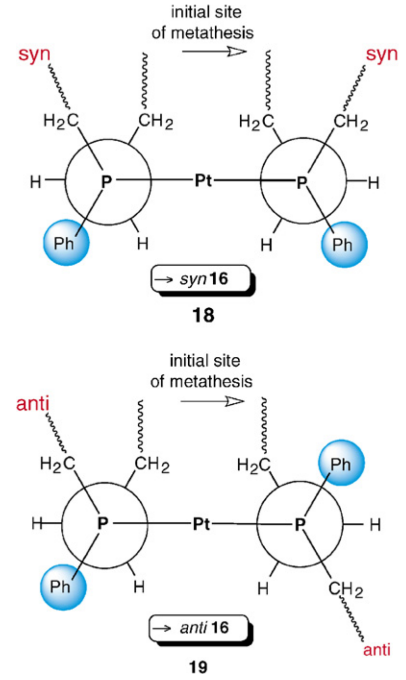


Fig. 6. Limiting conformations for interligand metatheses of **15**.

mutually coupled ^{31}P NMR signals, and two sets of methylene ^{13}C NMR signals.

In contrast, with **16a**,**b**,**d** only syn isomers were isolated. As illustrated in Fig. 6, the syn/anti stereochemistry is set in the first alkene metathesis step. In the assembly **18**, which leads to syn isomers, the alkenyl chains for the second metathesis step are directed on the same side of the platinum coordination plane. However, in **19**, which leads to anti isomers, they are on opposite sides. Hence, oligomerization processes can likely better compete with the formation of anti isomers.

When the crude reaction mixture containing **16c** was examined by NMR, none of the intraligand metathesis product **17c** was detected. An upper limit of 2% could be placed on the yield. The yield and isomer distribution were similar when Grubbs' second-generation catalyst was employed. No intraligand metathesis products were detected with the other substrates, and we presently have no rationale for this selectivity. Interestingly, the yield of **16a**, which contains 13-membered macrocycles, greatly improved with Grubbs' second-generation catalyst (55% versus 20%). We have observed similar trends with other 13-membered macrocycles.

Disappointingly, the yields of **16b** and **16d**, which feature 15- and 21-membered macrocycles, remained low with both generations of Grubbs' catalyst. Thus, these two-fold interligand metatheses lack the efficiency of the single-macrocycle-forming reactions in Scheme 5. Not surprisingly, similar sequences involving analogous complexes in which the *trans* phosphine ligands bear *three* $(CH_2)_nCH{=}CH_2$ chains did not give the target complexes. These would possess three spokes, and be even more gyroscope-like. This problem was later solved by

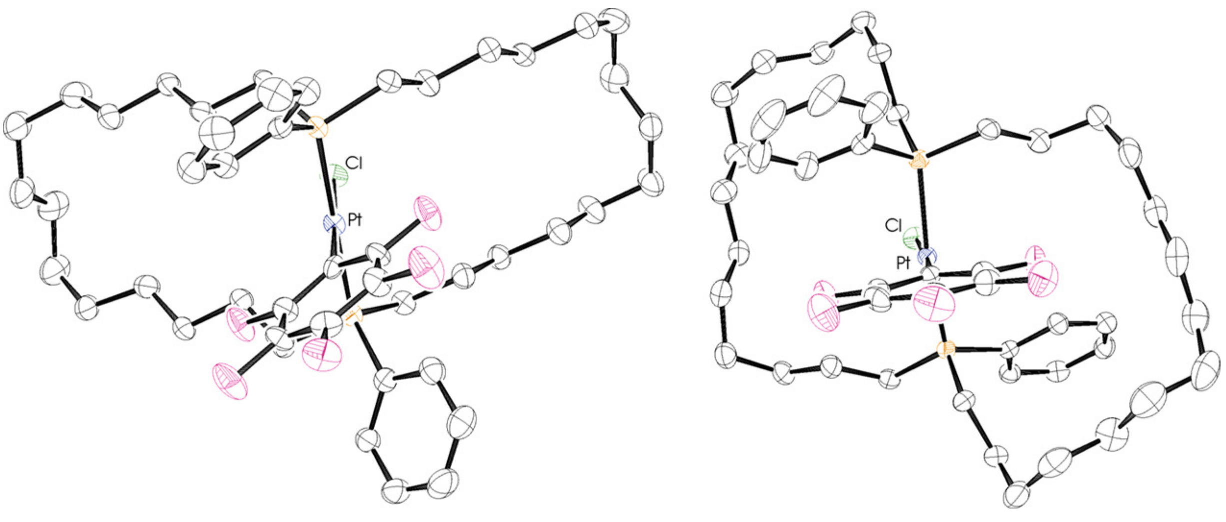


Fig. 5. ORTEP representations of the crystal structures of syn-**16c** (left) and anti-**16c** (right).

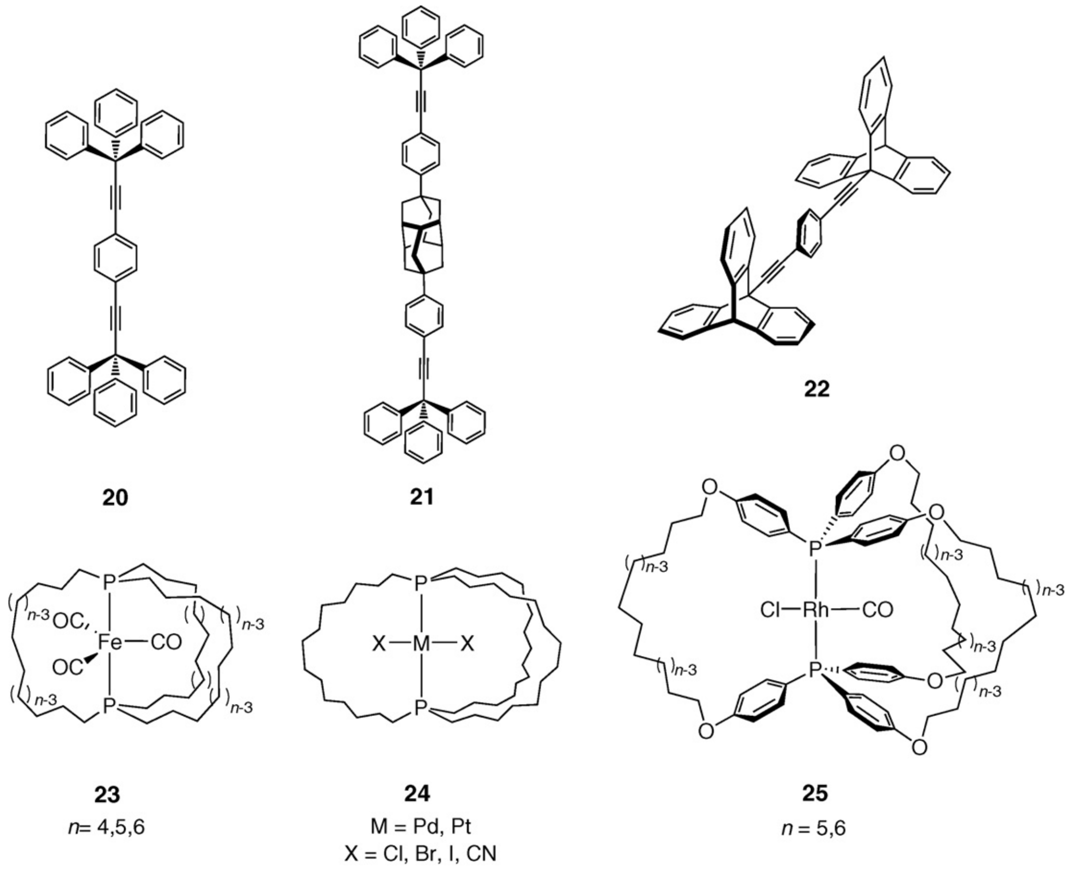


Fig. 7. Newer gyroscope-like molecules synthesized by the Garcia-Garibay (**20**–**22**) and Gladysz (**23**–**25**) groups.

reducing the sizes of the non-phosphine ligands on platinum [5b].

Variable temperature NMR spectra of **16a–d** did not reveal any dynamic behavior. Importantly, a ca. 180° rotation of the Cl-Pt-C_6F_5 moiety about the P-Pt-P axis in anti-**16c** would render the two phosphorus atoms equivalent. However, this would require both ligands to pass through a 17-membered macrocycle. Consistent with the structural analysis in the previous section (Table 1) and the visual impression from Fig. 5, the pentafluorophenyl ligand is too large, and separate ^{31}P NMR signals are observed at 95 °C. In contrast, if anti-**16d** could be obtained (21-membered macrocycles), coalescence to a single ^{31}P NMR signal at a moderate temperature would be predicted. The isolated isomer syn-**16d** also likely qualifies as a functional rotor, but unfortunately lacks a convenient probe for this behavior.

10. Advanced systems, 2002–present

Due to space limitations, it is not possible to describe the many developments involving gyroscope-like molecules during the period 2002–2007. These efforts, led by Garcia-Garibay and our group, have involved more sophisticated models as exemplified by **20**–**25** (Fig. 7) [5,7,8]. The Garcia-Garibay systems **20**–**22** are distinguished by axes with bulky termini, diminishing the need for spokes to sterically protect the rotator. In several cases, rotational barriers have been measured in the solid state. The syntheses of the triply-spoked organometallic systems **23**–**25**, as well as the estimation and quantification of rotational barriers from crystallographic and NMR data, build directly on the principles covered above.

These models will be treated in depth in future reviews. Importantly, molecular gyroscopes are also receiving attention within the physics community [19,20]. Assemblies that may model the precessional properties of macroscopic gyroscopes have been proposed [21], and increasing contributions from other scientific disciplines can be anticipated.

11. Conclusion

This review has attempted to analyze all uses of the descriptor gyroscope in the chemical literature through the sesquicentennial of Foucault's disclosure of the mechanical gyroscope. Some systems previously regarded as molecular gyroscopes feature functional rotators, whereas others do not. Thus, updated criteria for molecular gyroscopes have been proposed. These and other analyses set the stage for the further evolution of this fascinating and fast-moving subject.

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