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Gyroscope-like Molecules Consisting of PdX_2/PtX_2 Rotators Encased in Three-Spoke Stators: Synthesis via Alkene Metathesis, and Facile Substitution and Demetalation

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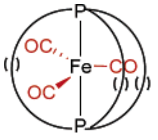
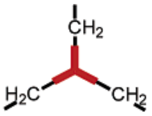
Rotating objects are ubiquitous components of macroscopic machines, and most are encased in protective housings. These serve various functions, such as human safety or protection against other moving parts. Similarly, many types of molecular devices involve a rotating component,[1,2] and the design of suprastructures that can shield them is receiving increasing attention.[3−5] Two such cases would be molecular compasses and gyroscopes,[3,4] which are composed of "rotators" and "stators".[1] The ultimate goal would be stators that enclose the rotators in frictionless environments, both in solution and in the crystalline lattice.

We recently reported that trigonal-bipyramidal iron tricarbonyl bis(phosphine) complexes *trans*-$Fe(CO)_3(P((CH_2)_nCH{=}CH_2)_3)_2$ undergo three-fold intramolecular alkene metathesis and hydrogenation to give cage molecules **I**.[6] These contain trans-spanning diphosphine ligands[7] and duplicate the connectivity and symmetry (D_{nh}) of commercial toy gyroscopes. The three $(CH_2)_{2n+2}$ "spokes" provide a high degree of insulation with respect to solvent and/or neighboring molecules, and when n is sufficiently large, the $Fe(CO)_3$ moieties can rotate.[8] However, the transition state for rotation involves a three-fold eclipsing interaction between the carbonyl ligands and spokes (**II**). To minimize this intramolecular "friction", we sought similar complexes with rotators of the formula ML_2. The corresponding transition states would feature only a single eclipsing interaction (**III**).



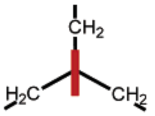
I

( ) = $(CH_2)_{2n+2}$



II

= $Fe(CO)_3$



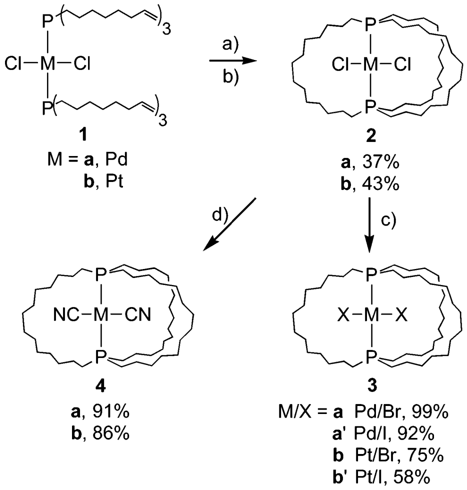
III

= PdX_2, PtX_2

In earlier efforts, we were unable to similarly encase a pentafluorophenyl-substituted $Pt(C_6F_5)Cl$ rotator.[9] We therefore sought substrates with smaller ligands and prepared the palladium and platinum dichloride complexes *trans*-$MCl_2(P((CH_2)_6CH{=}CH_2)_3)_2$ (M = Pd, **1a**; Pt, **1b**) by routine procedures detailed in the Supporting Information. As shown in Scheme 1, 0.0035 M CH_2Cl_2 solutions of **1a**,**b** were treated with Grubbs' catalyst. The crude products were hydrogenated to give the target molecules **2a**,**b** in 37−43% yields. These and all new compounds described below were characterized by microanalysis, NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy, and mass spectrometry (Supporting Information).

The crystal structure of **2a** was determined, and two views are shown in Figure 1. The palladium−chlorine distance (2.308(6) Å) can be compared with that from palladium to the distal carbon atom of the macrocycle (7.255 Å). When the van der Waals radius of chlorine[10] is added to the former, and that of carbon is subtracted from the latter, considerable "horizontal clearance" remains (4.058 vs 5.555 Å).[11] Accordingly, ^{13}C NMR spectra of **2a**,**b** at room temperature showed only seven methylene signals, or one type of $P(CH_2)_{14}P$ bridge. When MCl_2 rotation is slow on the NMR time scale, decoalescence to two sets of ^{13}C signals (2:1) should occur. However, low-temperature ^{13}C NMR spectra gave only severely broadened signals (e.g., $CDFCl_2$, −120 °C).

Scheme 1. Syntheses of Gyroscope-like Complexes[a]



[a] Reagents and conditions: (a) 3.0−14 mol % Grubbs' catalyst, CH_2Cl_2, reflux. (b) $RhCl(PPh_3)_3$, 5 bar H_2, CH_2Cl_2, 45−55 °C. (c) LiBr/THF or NaI/THF/acetone. (d) KCN, CH_2Cl_2/MeOH.

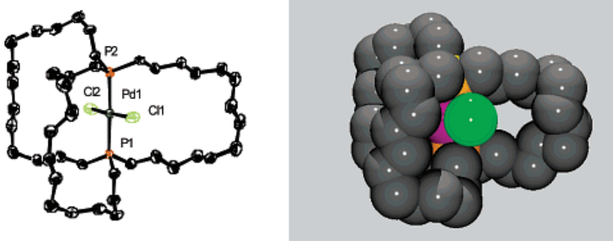


Figure 1. ORTEP and space-filling representations of **2a**. Four methylene groups are disordered ((82−80):(20−22)); the dominant form is depicted.

Thus, larger ligands were sought. One important fundamental question regarding such cage compounds is whether substitution at the metal is possible. As shown in Scheme 1, reactions of **2a**,**b** with LiBr and NaI gave the corresponding dibromide and diiodide complexes **3a**,**b** and **3a′**,**b′** in 58−99% yields. NMR monitoring showed the palladium reactions to be complete within 10 min, but the platinum reactions required hours. The dicyanide complexes **4a**,**b** were similarly synthesized using KCN. Metathesis/hydrogenation sequences with the $PdBr_2$ analogue of **1a** gave mixtures of **3a**, **2a**, and a PdBrCl complex (19%). The byproducts presumably arise from the chloride ligand in Grubbs' catalyst.

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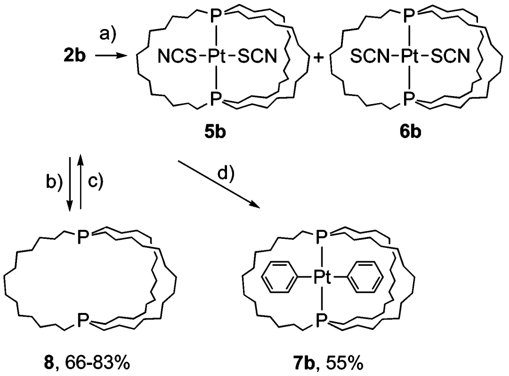
Scheme 2. Additional Reactions of Platinum Complex **2b**^{a}



^{a} Reagents and conditions: (a) KSCN, THF/acetone. (b) NaC≡CH, xylene/THF or excess KCN, CH_2Cl_2/MeOH. (c) $PtCl_2$, C_6D_6. (d) Ph_2Zn, THF.

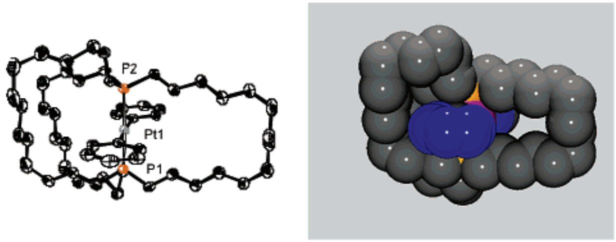


Figure 2. ORTEP and space-filling representations of the crystal structure of **7b**·(n-C_5H_{12}) with solvent molecule omitted.

Interestingly, low-temperature ^{13}C NMR spectra of **3** and **4** also showed only broadened methylene signals. Decoalescence could not be achieved. The CN ^{13}C NMR signals of **4a**,**b** are coupled to phosphorus, ruling out dissociative mechanisms that might render the $P(CH_2)_{14}P$ bridges equivalent. Many complexes of the type $MX_2(PR_3)_2$ (M = Pd, Pt) have been crystallographically characterized, and typical M−Br, M−I, and M−CN distances are 2.43, 2.61, and 3.13 Å. When the van der Waals radii of the terminal atoms[10] are added, the radii of the rotators are obtained (4.28, 4.59, 4.68 Å). These remain significantly less than the horizontal clearance estimated above (5.555 Å). However, as can be extrapolated from the space filling structure in Figure 1, vertical or "floor to ceiling" clearance becomes an issue with increasing size of the halide ligands. In particular, MI_2 rotation[8] must be strongly correlated to conformational changes in the $P(CH_2)_{14}P$ bridges.

Still larger ligands were sought, and reactions of **2b** with KSCN and Ph_2Zn were investigated. As shown in Scheme 2, the former afforded two chromatographically separable products, one the symmetrically substituted bis(thiocyanate) complex **5b** and the other the linkage isomer **6b**. Complex **5b** exhibited a single IR ν_{SCN} band, but **6b** two. The latter reaction afforded the diphenyl complex **7b** (55%). Room-temperature ^{13}C NMR spectra of **5b**−**7b** showed two sets of methylene signals, with one set more intense. Thus, with sufficiently large ligands, MX_2 rotation can be braked.

The crystal structure of a solvate of **7b** was determined. As is easily seen from the representations in Figure 2, $PtPh_2$ rotation would be sterically prohibitive. The distance from platinum to the para hydrogen of the phenyl ring is 7.087 Å, inclusive of the van der Waals radius. The corresponding value for **5b** and **6b** can be estimated as 6.26 Å. Interestingly, the ^1H and ^{13}C NMR spectra of **7b** exhibited five phenyl CH signals (o, o', m, m', p). This further requires restricted rotation about the Pt−C_{ipso} axis. No coalescence was observed when spectra were recorded at 80 °C in $CDCl_3$.

An unanswered question regarding such gyroscope-like complexes is whether the metal can be extruded from the diphosphine. This was inadvertently addressed while investigating the reaction of **2b** and NaC≡CH. Substitution did not go to completion with 2−4 equiv. Hence, a large excess was employed. As shown in Scheme 2, workup gave **8** (66%). When the reaction of **4b** and KCN was repeated with a greater excess of KCN, **8** was also isolated (83%). These reactions provide novel "Houdini-style" entries into bimacrocyclic dibridgehead diphosphines.[12] The ^{31}P NMR spectra showed one signal (≥98%), indicating the phosphorus lone pairs to be either both "*in*" (double retention) or "*out*" (double inversion). Although this point could not be directly established, reaction with $PtCl_2$ regenerated **2b**, suggesting an *in*/*in* isomer. Efforts to identify the platinum coproducts are in progress.[13]

In summary, we have demonstrated that it is possible to enclose rotators of the formula $PdCl_2$ and $PtCl_2$ in trans-spanning diphosphine ligands using three-fold alkene metathesis, elaborate the caged rotators via substitution reactions, and extrude the rotator from the diphosphine. All of these steps pose fascinating mechanistic questions, which are under investigation. Consistent with the design elements noted above (i.e., **III** vs **II**), the MCl_2, MBr_2, MI_2, and $M(CN)_2$ complexes appear to have considerably lower rotational barriers[8] than their $Fe(CO)_3$ and $[Fe(CO)_2(NO)]^+$ analogues ($\Delta H^\ddagger$ 9.5 kcal/mol, $\Delta S^\ddagger$ −6.5 eu for the cation).[6] Attempts to quantify these remain in progress. Current efforts are directed at the synthesis of unsymmetrically substituted MXX′ analogues, the dipole moments of which should be responsive to external electric fields. This represents a means of orienting the rotators or driving unidirectional rotation, as in compasses and gyroscopes.

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Supporting Information Available: Experimental procedures, characterization of new compounds, and crystallographic data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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