Gyroscope-like molecules consisting of three-spoke stators that enclose "switchable" neutral dipolar rhodium rotators; reversible cycling between faster and slower rotating Rh(CO)I and Rh(CO)$_2$I species†

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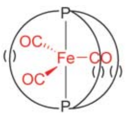
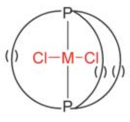
***trans*-$\overline{\mathrm{Rh(CO)(Cl)(P((CH_2)_{14})_3P}}$) is prepared from *trans*-Rh(CO)(Cl)(P((CH$_2$)$_6$CH=CH$_2$)$_3$)$_2$ by a metathesis/hydrogenation sequence, and converted by substitution or addition reactions to Rh(CO)(I), Rh(CO)$_2$(I), Rh(CO)(NCS), and Rh(CO)(Cl)(Br)(CCl$_3$) species; the Rh(CO)(Cl) and Rh(CO)(I) moieties rapidly rotate within the cage-like diphosphine, but the other rhodium moieties do not.**

Rotating components feature prominently in many molecular devices.[1,2] Such assemblies can in turn be dissected into "rotators" and "stators".[1,3] However, little attention has been directed at the development of simple, easily reversible "switches" for modulating rotary motion. We recently reported convenient routes to molecules that mimic the connectivity and symmetry of simple toy gyroscopes.[4–6] These possess structures of the types **I** and **II**, with Fe(CO)$_3$ or MCl$_2$ rotators encased in *trans*-spanning diphosphine stators.[4] The diphosphines consist of three (CH$_2$)$_n$ "spokes" that are generated by alkene metathesis/hydrogenation sequences. Although ML$_m$ rotation – which is Brownian – can be rapid on the NMR timescale (*e.g.*, $n \geqslant 14$ at room temperature), in most cases only one type of limiting behavior is observable (*i.e.*, fast exchange/"on" or slow exchange/"off").



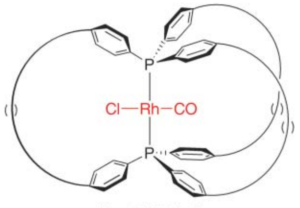
( ) = (CH$_2$)$_n$
n = 10, 12, 14

I



( ) = (CH$_2$)$_n$
n = 14
M = Pd, Pt

II



( ) = O(CH$_2$)$_n$O
n = 12, 14

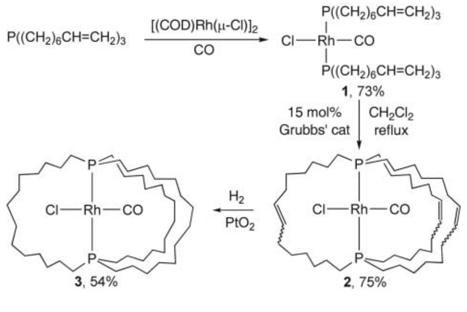
III

We wondered whether it might be possible to reversibly bind additional ligands to systems of the types **I** and **II**, such that rotation would be slowed or braked, but restored to the original rate upon ligand release. For this purpose, we were attracted to square-planar sixteen-valence electron rhodium(I) complexes. Such species add suitable Lewis bases to give five-coordinate trigonal bipyramidal complexes, and undergo oxidative additions to give six-coordinate octahedral complexes. We recently showed that "giant" gyroscope-like rhodium complexes **III** could be accessed, and were able to restrict X–Rh–CO rotation by replacing the chloride by a lengthy C≡CC$_6$H$_4$-*p*-CH$_3$ ligand.[5] However, this constitutes an irreversible transformation.

Thus, in a standard procedure,[7] the rhodium chloride [(COD)Rh(μ-Cl)]$_2$, the alkene containing phosphine P((CH$_2$)$_6$-CH=CH$_2$)$_3$, and CO were combined. As shown in Scheme 1, workup gave the bis(phosphine) carbonyl complex (**1**) in 73% yield. Complex **1** was characterized by microanalysis, and IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, as described in the supporting information. The NMR spectra showed the usual ^{103}Rh and virtual couplings associated with such compounds.

Next, 0.0018 M CH$_2$Cl$_2$ solutions of **1** were treated with Grubbs' catalyst (15 mol%). Chromatography gave the crude triene **2** (Scheme 1), consisting of three seventeen-membered macrocycles, in 75% yield. NMR spectra showed mixtures of *E*/*Z* isomers, and additional minor signals that were tentatively ascribed to dimers or oligomers. Hydrogenation (4 atm, PtO$_2$) gave the target molecule **3** in 54% yield (40% from **1**). The IR ν_{CO} value was similar to that of **1** (1949 *vs.* 1953 cm^{-1}), indicating a negligible cage effect. A room temperature ^{13}C NMR spectrum showed seven CH$_2$ signals, or one type of P(CH$_2$)$_{14}$P bridge. When Cl–Rh–CO rotation becomes slow on the NMR timescale, decoalescence to two or more sets of signals should occur. However, spectra recorded in CDFCl$_2$ at −120 °C exhibited only severely broadened signals, similar to the MCl$_2$ species **II**.[4b]

Thus, larger ligands were sought. As shown in Scheme 2, reactions of **3** with NaI and KSCN gave the iodide and isothiocyanate complexes **4** and **5** in high spectroscopic yields, or 45% and 73% after workup. The formulation of **5** as an isothiocyanate or RhNCS complex was made by analogy to reactions of other *trans*-Rh(CO)(Cl)(PR$_3$)$_2$ species and KSCN, and the close correspondence of the IR ν_{NCS} values (2084 *vs.* 2089–2100 cm^{-1}).[8] Low temperature ^{13}C NMR spectra of **4** (CDFCl$_2$,



Scheme 1 Syntheses of gyroscope-like rhodium chloride complexes.

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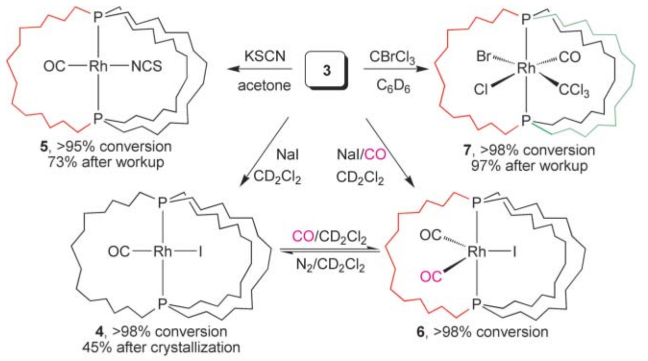
† Electronic supplementary information (ESI) available: Synthesis and characterization of **1–7**. See DOI: 10.1039/b606728j



Scheme 2 Substitution and addition reactions of chloride complex **3**.

−120 °C) gave only severely broadened signals, indicative of rapid I–Rh–CO rotation on the NMR timescale. However, **5** exhibited two sets of CH$_2$ ^{13}C signals at room temperature, with one set more intense (*ca.* 2 : 1).

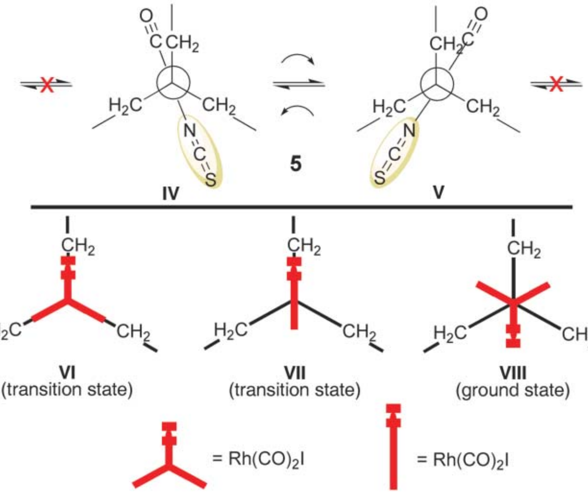
To help interpret these phenomena, the crystal structure of **4** was determined (supporting information).‡ The I–Rh–CO rotator was disordered, with two orientations differing by *ca.* 180°. These refined to an 89 : 11 occupancy ratio, and the dominant rotamer is shown in Fig. 1. The Rh–I and **Rh**–**CO** distances (2.68 Å, 2.95 Å) can be compared to those from rhodium to the distal carbon atoms of the macrocycles (6.97–7.75 Å). When the van der Waals radius of iodide or oxygen[9] is added to the former, and that of carbon is subtracted from the latter, ample "horizontal clearance" remains (4.66–4.47 Å *vs.* 5.27–6.05 Å).[10] Based upon the structure of a related rhodium isothiocyanate complex,[8c] the **Rh**–NCS distance in **5** can be estimated as 4.82 Å. When the van der Waals radius of sulfur is added, the effective length of the rotator (6.62 Å) becomes much greater than the clearance allowed by the macrocycles. Thus, the NCS ligand should be confined within a 120° arc defined by two bridges. However, as illustrated in Scheme 3 (top), the CO ligand remains (as in **3** and **4**) small enough to pass through a macrocycle. This exchanges two of the P(CH$_2$)$_{14}$P bridges, in accord with the 2 : 1 ratio of NMR signals.

Next, the reaction of **3** and NaI was repeated in the presence of CO. Under similar conditions, several trigonal bipyramidal dicarbonyl iodide complexes *trans*-Rh(CO)$_2$(I)(PR$_3$)$_2$ have been generated.[11] These are usually quite labile, reverting to the corresponding monocarbonyl iodide complexes under N$_2$. This presents an attractive possible means of reversibly modulating the properties of the rotator. One would expect the activation barrier for Rh(CO)$_2$(I) rotation to be intrinsically higher than that for I–Rh–CO rotation, as the former transition state involves a three-fold eclipsing interaction, but the latter only a single eclipsing interaction (**VI** *vs.* **VII**, Scheme 3).

As shown in Scheme 2, the dicarbonyl iodide complex **6** was quantitatively generated. The IR spectrum exhibited two ν_{CO} bands, as opposed to the single absorption for **4** (1988 (m) and 1930 (s) *vs.* 1940 (s) cm^{-1}). The ^{31}P NMR chemical shift was somewhat downfield of that of **4** (26.2 *vs.* 15.8 ppm, $^{1}J_{\mathrm{PRh}}$ 85 *vs.* 113 Hz). Crystals could be grown from CH$_2$Cl$_2$–methanol, but sufficed only for a preliminary structure solution that showed the expected staggered Rh–P conformation **VIII** (Scheme 3). When **6** was purged under a N$_2$ stream, **4** was quantitatively regenerated.

Low temperature ^{13}C NMR spectra of **6** were recorded under CO (1 atm), and showed two sets of CH$_2$ signals, with one set more intense (*ca.* 2 : 1). Hence, the second CO ligand allows the slow exchange regime to be accessed. Upon warming, the sets coalesced, as shown for the PCH$_2$***C***H$_2$ signals in Fig. 2; cooling regenerated the original spectra. However, as sketched in Scheme 4, two limiting mechanisms for equivalencing the bridges can be formulated. One would involve a simple Rh(CO)$_2$(I) rotation. The other would entail CO dissociation to give **4**, followed by Rh(CO)(I) rotation, and recoordination of the CO ligand.

Current evidence suggests the latter mechanism has the lower energy barrier. First, low temperature ^{13}C NMR spectra of **6** show a doublet of triplets ($^{1}J_{\mathrm{CRh}}$, $^{2}J_{\mathrm{CP}}$) for the CO signal. As the coalescence temperature is approached, the couplings become less well resolved. Only a broad singlet is observed at the coalescence temperature or above. Second, line shape analyses allowed k_{obs}



Scheme 3 Rotational equilibrium in **5** (**IV**, **V**) and selected rotator conformations in **4** (**VII**) and **6** (**VI**, **VIII**).

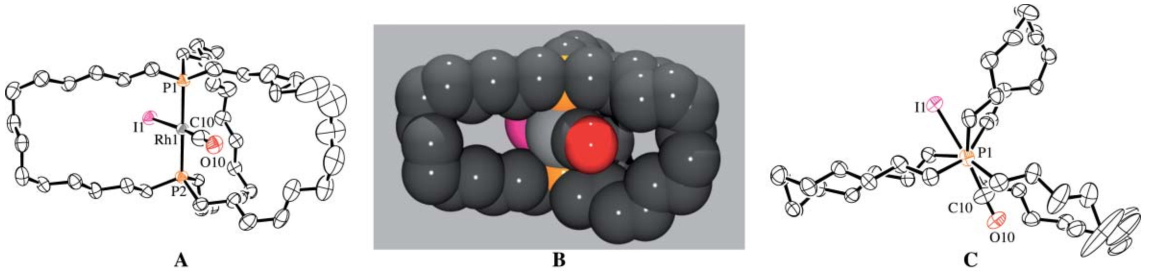


Fig. 1 ORTEP (**A**, **C**) and space-filling (**B**) representations of the dominant I–Rh–CO rotamer in the crystal structure of **4**.

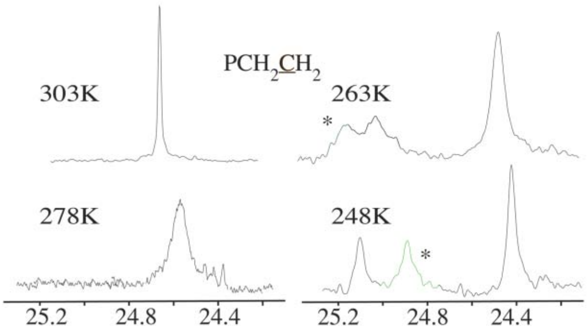
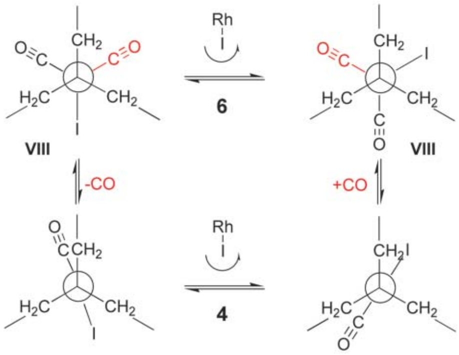


Fig. 2 Variable temperature ^{13}C NMR spectra of **6** in CD_2Cl_2 under CO (1 atm; the peak * is from another CH_2 group).



Scheme 4 Dissociative and non-dissociative mechanisms for exchange of $P(CH_2)_{14}P$ bridges in **6**.

values to be estimated at seven temperatures from 248 to 303 K. An Eyring plot gave $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 18.6(4) kcal mol^{-1} and 20.3(1.6) eu. The markedly positive $\Delta S^{\ddagger}$ value best fits an initial dissociative step. In contrast, the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for $Fe(CO)_2(NO)^+$ rotation within the same stator are 9.5(2) kcal mol^{-1} and −6.5(8) eu.[4a] In this case, dissociative equilibria can be excluded. Analogous rotation of the roughly isosteric $Rh(CO)_2I$ moiety in **6** would be expected; however, the activation energy must be higher than that for CO dissociation.

As a final approach to modulating rotation in this series of compounds, the reaction of **3** and $CBrCl_3$ was studied. As shown in Scheme 2, the octahedral adduct **7** was isolated in 97% yield. The stereochemistry was tentatively assigned by analogy to that of a crystallographically characterized analog.[12] The chlorine atoms of the large CCl_3 ligand define a cone with a van der Waals diameter of 6.84 Å, greatly exceeding the vertical clearance of the stator and the P–Rh–P distance (4.65 Å). Accordingly, the ^{13}C NMR spectrum (room temperature) exhibited 21 CH_2 signals, indicative of three distinct $P(CH_2)_{14}P$ bridges and consistent with the lower symmetry of **7** as compared to the preceding complexes. Hence, oxidative addition can also be exploited to restrict rotation.

In summary, it is possible to generate a variety of gyroscope-like molecular rotors that feature rhodium-based rotators encased within a three-spoke stator. These can be reversibly converted between faster and slower rotating square planar and trigonal bipyramidal forms, or braked by substitution or oxidative addition reactions that introduce sterically more demanding ligands. Future efforts will exploit the dipolar nature of the rotators. The dipole moments can be used to orient the rotators, or drive unidirectional rotation, as in macroscopic compasses and gyroscopes.[1,6]

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Notes and references

‡ *Crystal data, **4***: formula $C_{43}H_{84}IOP_2Rh$, monoclinic, *a* = 23.4154(4), *b* = 12.3194(3), *c* = 34.0731(8) Å, *β* = 109.066(1)°, *V* = 9289.7(4) Å^3, *T* = 173(2) K, space group *C*2/*c*, *Z* = 8, *μ*(Mo-Kα) = 1.130 mm^{-1}, 18326 reflections measured, 10641 unique (R_{int} = 0.0562), which were used in calculations. Final *R* values: *R*1 [$I > 2\sigma(I)$] = 0.0494; *wR*2 (all data) = 0.1433. Several methylene carbon atoms were disordered, as described together with additional data in the ESI. CCDC 602258. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606728j

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