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# Octahedral Gyroscope-Like Molecules with $M(CO)_3(X)$ Rotators Encased in Three-Spoked Diphosphine Stators: Syntheses by Alkene Metathesis/Hydrogenation Sequences, Structures, Dynamic Properties, and Reactivities

Gisela D. Hess,† Frank Hampel,† and John A. Gladysz*,†,‡

*Institut für Organische Chemie and Interdisciplinary Center for Molecular Materials,*
*Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany, and*
*Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012*

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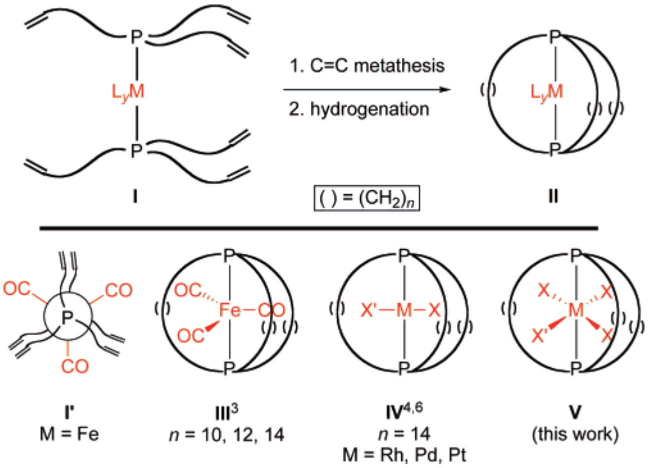
*Summary: Threefold ring-closing metatheses of mer,trans-*$Re(CO)_3(X)(P((CH_2)_6CH{=}CH_2)_3)_2$ *(X = Cl, Br), followed by hydrogenations, yield the gyroscope-like species* $Re(CO)_3(X)(P((CH_2)_{14})_3P)$*, which react with NaI or* $Ph_2Zn$ *to give substitution products; crystal structures have been determined, and low-temperature NMR data indicate rapid rotation of the* $Re(CO)_3(X)$ *moieties.*

There is rapidly increasing interest in syntheses and applications of molecular devices that incorporate rotating components.[1−3] Such “rotors” can in turn be dissected into “rotators” and “stators”, the latter being assigned to the moiety with the greater moment of inertia.[1] We have had an ongoing interest in metal-based rotors that approximate the connectivities and symmetries of toy gyroscopes.[4−8] As sketched in Scheme 1, these have been accessed from precursors with *trans*-phosphine ligands (**I**) via alkene metathesis/hydrogenation sequences. The overall yields of the cagelike diphosphine adducts **II** can be remarkably high, reflecting the extraordinary effectiveness of modern alkene metathesis catalysts. Conceptually related nonmetallic systems have been studied in detail by Garcia-Garibay.[2]

Our first successes involved trigonal-bipyramidal iron tricarbonyl species (**III**; Scheme 1).[4] Since both the $Fe(CO)_3$ fragment and phosphine ligands in precursor **I** possess local $C_3$ axes, the energetically favorable doubly staggered conformation **I′** is possible. This preorganizes the vinyl groups for *intra*molecular, *inter*ligand metathesis. We then found that analogous sequences could be carried out with square-planar species, provided that the non-phosphine ligands were small (Cl, CO).[5,7] However, consistent with the “mismatched” metal fragment and phosphine symmetries ($C_2$ vs $C_3$ axes), the products **IV** were obtained in lower yields, or were not detected at all for certain ring sizes. The question remained as to whether this methodology might be extended to other coordination geometries with mismatched symmetries. In this communication, we report the surprisingly successful application of such sequences to octahedral systems that feature *four* non-phosphine ligands, as well as key structural, dynamic, and chemical properties of the resulting complexes **V**.

**Scheme 1. Previous Syntheses of Gyroscope-Like Complexes in Which *trans*-Phosphorus Atoms Are Linked by Three Aliphatic Bridges**



In standard procedures that have been applied to related complexes,[9] the rhenium pentacarbonyl halides $(CO)_5Re(X)$ (X = Cl, Br) and 2.0−2.1 equiv of the alkene-containing phosphine $P((CH_2)_6CH{=}CH_2)_3$ were reacted in chlorobenzene at 140 °C. Workups gave the substitution products *mer*,*trans*-$Re(CO)_3(X)(P((CH_2)_6CH{=}CH_2)_3)_2$ (X = Cl (**1**), Br (**2**)), shown in Scheme 2, in 70−73% yields. A reaction of **1** and NaI (THF/acetone, reflux) afforded the corresponding iodide complex **3**. These and all other new complexes below were characterized by microanalysis and by IR and NMR ($^1H$, $^{13}C$, $^{31}P$) spectroscopy, as summarized in the Supporting Information. The *mer* relation-

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* To whom correspondence should be addressed at Texas A&M University. E-mail: gladysz@mail.chem.tamu.edu.

† Universität Erlangen-Nürnberg.

‡ Texas A&M University.

[1] Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281.

[2] (a) Khuong, T.-A. V.; Nuñez, J. E.; Godinez, C. E.; Garcia-Garibay, M. A. *Acc. Chem. Res.* **2006**, *39*, 413 and earlier work from this group cited therein. (b) Khuong, T.-A. V.; Dang, H.; Jarowski, P. D.; Maverick, E. F.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 839. (c) Jarowski, P. D.; Houk, K. N.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 3110.

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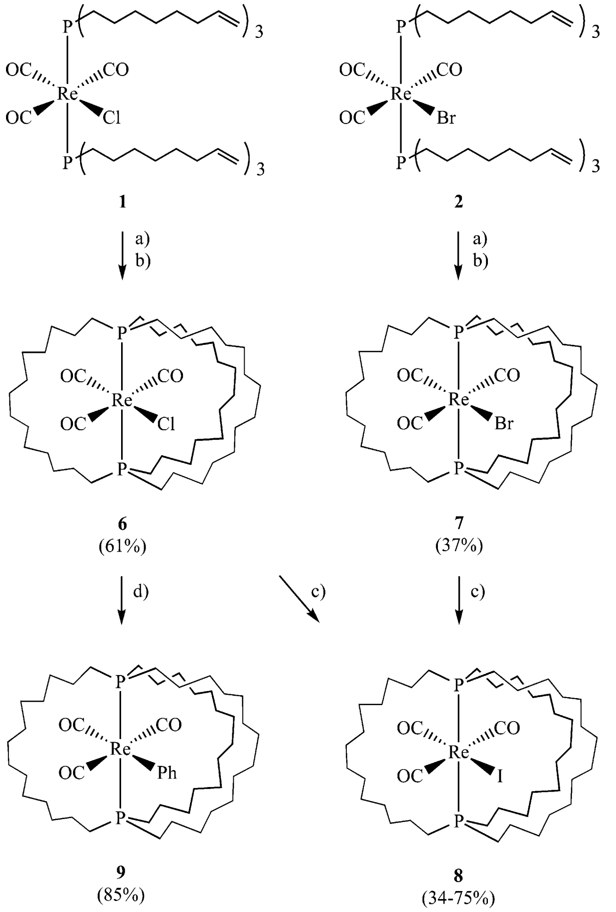
**Scheme 2. Syntheses of Title Complexes**[a]



[a] Legend: (a) 5 mol % Grubbs' catalyst, chlorobenzene, $N_2$ stream; (b) 10 mol % $PtO_2$, 5 bar of $H_2$, THF; (c) NaI, THF, acetone, reflux; (d) $Ph_2Zn$, THF, reflux.

ship of the carbonyl ligands was reflected by the IR $\nu_{CO}$ pattern, and the *trans* relationship of the phosphine ligands was indicated by the single $^{31}P$ NMR signal.

Chlorobenzene solutions of **1** and **2** (0.0011−0.0012 M) were treated with Grubbs' catalyst (5−6 mol %) and aspirated with $N_2$ to aid removal of the byproduct ethene. After 2 days, alumina filtrations gave the crude metathesis products (**4** and **5**) in 76−90% yields. Mass spectra showed the expected parent ions. Hydrogenations (5 bar, $PtO_2$) afforded the target gyroscope-like molecules **6** and **7** (Scheme 2) in 81−41% yields (overall: **6**, 61%; **7**, 37%). The two most intense IR $\nu_{CO}$ bands were only slightly shifted versus those of **1** and **2** (0−8 $cm^{-1}$), indicating a small ligand cage effect. Ambient-temperature $^{13}C$ NMR spectra exhibited (1) two CO signals (2:1 area ratio) that were phosphorus-coupled and (2) seven $CH_2$ signals, or one type of $P(CH_2)_{14}P$ bridge. If $Re(CO)_3(X)$ rotation were slow on the NMR time scale, two sets of $CH_2$ signals (2:1) should be observed.

Substitution reactions were attempted. As shown in Scheme 2, **6** and **7** were combined with NaI in refluxing acetone. After 1−8 days, workups gave the corresponding iodide complex **8** in 34−75% yields. Similarly, **6** and $Ph_2Zn$ were combined in refluxing THF. After 2 days, workup gave the phenyl complex **9** in 85% yield. The $^{13}C$ NMR spectrum of **8** also exhibited seven $CH_2$ signals. However, that of **9** exhibited 12 (theory: 14), indicating that the phenyl ligand brakes the rotation of the $Re(CO)_3(X)$ moiety. Low-temperature $^{13}C$ NMR spectra of **7** and **8** were recorded. The $CH_2$ signals broadened at −40 and −75 °C, respectively (toluene-$d_8$). However, no decoalescence was observed upon further cooling to −100 °C.

We sought to assay for any ligand cage effects on substitution rates. Thus, in side-by-side experiments, the reactions of the chloride complexes **1** and **6** with NaI in refluxing acetone/THF were monitored by NMR. Surprisingly, the acyclic and gyroscope-like iodide complexes **3** and **8** formed with virtually identical rates (conversions: 4.25 h, 23−26%; 6.50 h, 32−34%; 11.75 h, 58−59%). Although further study is required, we view this as inconsistent with a rate-determining step that involves iodide association. Similar substitutions have been effected with other nucleophiles (e.g., thiolates), and these will be detailed in our full paper.

Structural data were sought. Crystals of **6**, **7**, and **9** (or solvates thereof) could be grown. The X-ray structures were solved as described in the Supporting Information, and thermal ellipsoid diagrams are collected in Figure 1. The bromide ligand in **7** was disordered into the two *cis* positions (70:15:15), but only the dominant conformation is depicted and analyzed below. The unit cell of **9** exhibited four independent molecules with similar conformations, all of which are included in the average values given below.

The P−Re−P angles in the three structures range from 169.4 to 174.5° (average 171.3°), indicating slightly more distorted octahedral coordination geometries as compared to analogues without *trans*-spanning diphosphine ligands (177−180°);[10] angles between the other *trans* ligands average 176.4°. The *trans* $P(CH_2)_3$ moieties are approximately eclipsed, as can be seen in Figure 1 (upper right) and quantified by the corresponding $CH_2$−P−P−$CH_2$ torsion angles (15.6−35.3° for the *syn* segments; average 24.2°). In each structure, the non-carbonyl ligand approximately bisects two macrocycles. For the halide complexes **6** and **7**, this translates into two X−P−P−$CH_2$ torsion angles of 48.3−48.9° and two of 70.3−71.5° (sum ca. 120°). As a result, two of the OC−P−P−$CH_2$ torsion angles for the carbonyl ligand *trans* to the halide ligand are close to 0° (11.0−14.0°).

The halide complexes **6** and **7** crystallize in identical space groups ($P2_1/n$) and with very similar lattice constants ($Z = 4$, $V = 4739.02(19)$ and 4765.79(15) Å$^3$) and macrocycle conformations (Figure 1, upper and lower left). There are two sets of molecules with parallel P−Re−P axes, but with a nonparallel relationship to each other. Depending upon the exact measure employed, the axes define angles of 31−34°. The phenyl complex **9** crystallizes in a more complicated lattice, with four sets of molecules that will be more fully analyzed in our full paper. Interestingly, the DSC trace of **6** showed a significant endotherm, not corresponding to melting, at 41 °C.

The structural data provide a framework for analyzing the barriers to $Re(CO)_3(X)$ rotation. The rhenium−oxygen (*Re*C*O*) distances in **6** and **7** range from 2.96 to 3.08 Å. When the van der Waals radius of oxygen is added (1.52 Å),[11] a maximum value of 4.60 Å is obtained. The rhenium−chloride and −bromide distances are somewhat shorter (2.53 and 2.66 Å), and when the van der Waals radii of the halides are added (1.75 and 1.85 Å), slightly lower values are obtained (4.28 and 4.51 Å). Hence, the effective radius of the rotator in **6** and **7** can be taken as 4.60 Å.

Distances can also be calculated from rhenium to the remote carbon atoms of the macrocycle that are closest to the plane of

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(10) Structurally characterized complexes of the formula *mer,trans*-$Re(CO)_3(Cl)(PR_3)_2$: (a) Bucknor, S.; Cotton, F. A.; Falvello, L. R.; Reid, A. H.; Schmulbach, C. D., Jr. *Inorg. Chem.* **1986**, *25*, 1021 (R = Et). (b) Florke, U.; Haupt, H.-J. *Z. Kristallogr.* **1993**, *204*, 316 (R = Ph).

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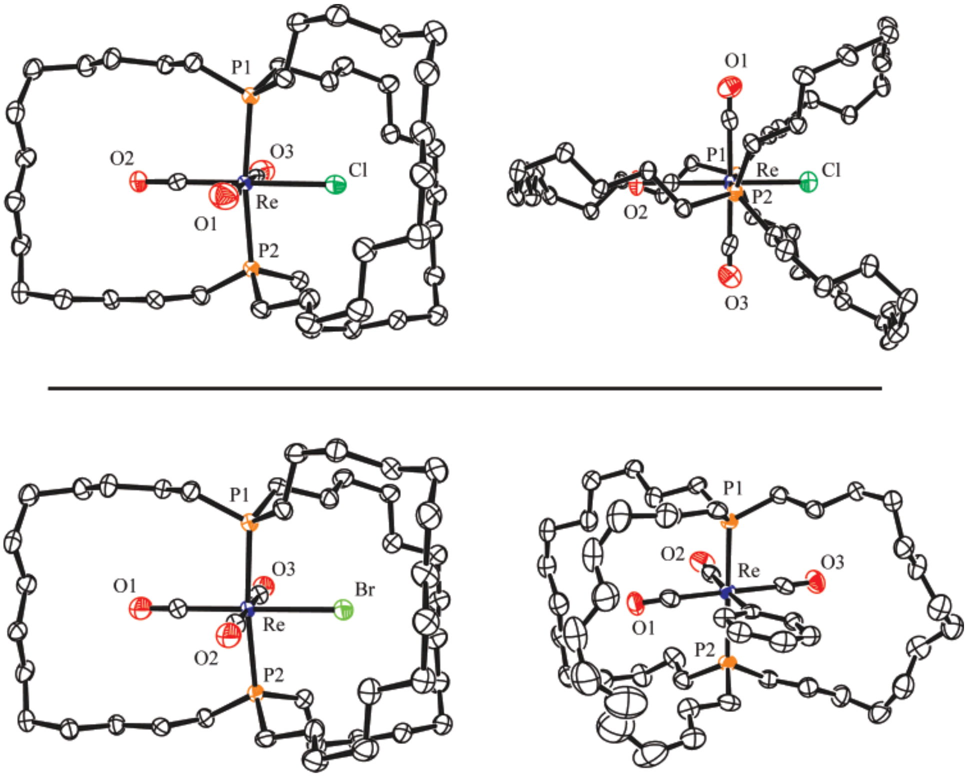
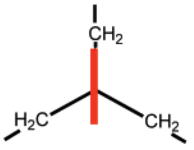


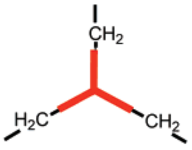
**Figure 1.** Molecular structures of **6** (top left and right), **7** (bottom left; dominant $Re(CO)_3(Br)$ rotamer), and **9**·4THF (bottom right; one of four similar independent molecules in the unit cell).

the rotator—i.e., the two carbon atoms in the middle of the methylene chain (6.54−7.25 Å). When the van der Waals radius of $sp^3$ carbon (1.70 Å)[11] is subtracted from the shorter distance, a minimum clearance is obtained (4.84 Å). Thus, there is sufficient horizontal clearance for rotation in the halide complexes. However, with the phenyl complex **8**, analogous calculations indicate an effective rotator radius of 7.24 Å (average of four molecules in the unit cell, including the van der Waals radius of hydrogen). Hence, there is insufficient clearance for rotation, in accord with the $^{13}C$ NMR data.[12]

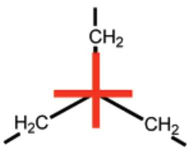
Other considerations are relevant to the apparently facile $Re(CO)_3(X)$ rotation in **6** and **7**. We showed earlier that the barrier to Rh(CO)(I) rotation in complexes of the type **IV** (Scheme 1) is much lower than that for $Rh(CO)_2(I)$ rotation in the trigonal-bipyramidal analogue.[7] Accordingly, the transition state for the latter requires a threefold eclipsing interaction (**VII**), but the former requires only a single eclipsing interaction (**VI**). Said differently, there is a larger energy difference between the staggered ground state and the triply eclipsed transition state for the latter and a smaller energy difference between ground and transition states in the former. Both **6** and **7** would also have singly eclipsed transition states (**VIII**). However, as reflected in the torsion angle analyses above, nearly eclipsed groups cannot be avoided in the ground state, due to the higher coordination number. These destabilizing interactions should further diminish the energy barriers.



**VI**
(transition state
for rotation, **IV**)



**VII**
(transition state
for rotation, **III**)



**VIII**
(transition state
for rotation, **V**)

In summary, gyroscope-like complexes that feature tetrasubstituted $Re(CO)_3(X)$ rotators encased within three-spoked $P((CH_2)_{14})_3P$ stators are easily prepared in remarkably good yields by alkene metathesis/hydrogenation sequences. Such octahedral systems have heretofore been available only by protonations of the $Fe(CO)_3$ centers in **III**[4] or by oxidative additions to Rh(CO)(I) centers in **IV**.[7] When X is chloride or bromide, rotation about the P−Re−P axis is facile, and substitution reactions can be effected. Future reports will detail (1) similar syntheses of analogous $M(CO)_4$ species,[13] (2) extensions of Scheme 2 to other types of stators, and (3) exploitation of the dipole moments of the rotators to effect directed rotation.[1]

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**Supporting Information Available:** Text giving experimental procedures and characterization for all complexes, tables giving crystallographic data, and figures giving crystallographic, IR, and rate data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] A related issue is vertical clearance. The van der Waals *diameters* of the chloride and bromide atoms (3.50 and 3.70 Å)[11] are less than the $P$−Re−$P$ distances (4.84−4.85 Å) and the eclipsed $CH_2$−P−Re−P−$CH_2$ distances (6.19−6.69 Å). However, when twice the van der Waals radius of carbon (3.40 Å) is subtracted from the last range, the clearance is insufficient. Presumably, rotation is correlated to conformational changes in the $P(CH_2)_{14}P$ linkages.

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