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Three-Fold Intramolecular Ring-Closing Metatheses Involving Square-Planar Platinum Complexes with *cis*-Phosphorus Donor Ligands: Syntheses, Structures, and Properties of Parachute-like Complexes

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Reactions of the phosphite and phosphine complexes *cis*-$PtCl_2((PX(CH_2)_mCH{=}CH_2)_3)_2$ (X/m = O/3, O/4, O/5, -/5, -/6) with Grubbs' catalyst, followed by hydrogenations, yield *cis*-$PtCl_2(P(X(CH_2)_{2m+2}X)_3P)$ (6–40%). Crystal structures establish parachute-like motifs in which one $X(CH_2)_{2m+2}X$ bridge lies roughly in the platinum coordination plane, and the others lie above and below.

Over the past decade, there has been an explosion of interest in alkene metatheses in metal coordination spheres.[1] These efforts are often directed at what might be termed "designer" inorganic or organometallic molecules with specific target properties.[2–11] Sauvage and co-workers pioneered this field with many elegant syntheses of catenanes and related topologically novel molecules.[2] We have focused much attention on assemblies that resemble insulated molecular wires[4] and gyroscopes.[6–11] The latter have been prepared by three-fold intramolecular ring-closing metatheses of trans adducts of phosphorus donor ligands, or **I** → **II** in Scheme 1. Such macrocyclizations are particularly efficient for trigonal-bipyramidal $Fe(CO)_3$ adducts (**III**)[6,11] but also can be applied to square-planar[7–9] and octahedral[10] targets (**IV** and **V**), provided that the ancillary ligands are small.

During the course of these efforts, it became of interest to gauge the conformational flexibility of the diphosphorus ligands in **II**−**V**, which in certain cases can be detached from the metal,[7] and more deeply probe certain dynamic properties. For example, rotation about the P−M−P axis in **II** can obviously exchange the ancillary ligands L_y. However, might geometric (e.g., trans/cis) isomerism also provide an exchange mechanism? Can the diphosphorus ligands otherwise contort, for example, in motifs that would allow both lone pairs to simultaneously bind to a surface? With the hope of probing such issues, we set out to examine alkene metatheses of related complexes in which the phosphorus donor ligands were cis, such as **VI** → **VII** in Scheme 1.

As shown in Scheme 2, reactions of $PtCl_2$ and the alkene-containing trialkylphosphites $P(O(CH_2)_mCH{=}CH_2)_3$ (**1**; m = 3 (**a**), 4 (**b**), 5 (**c**))[11] afforded the adducts *cis*-$PtCl_2(P(O(CH_2)_mCH{=}CH_2)_3)_2$ (*cis*-**2a**−**2c**) in 60–95% yields as light-yellow or colorless oils after chromatographic workups. Complexes *cis*-**2a**−**2c**, and all new compounds below, were characterized by NMR (^{1}H, ^{13}C, and ^{31}P) and mass spectrometry, as summarized in the Supporting Information. The $^1J_{PPt}$ values (5696–5698 Hz) implied cis isomers, in accordance with other syntheses of dihaloplatinum bis(phosphite) complexes.[12–15] This likely reflects the cis/trans thermodynamic stabilities,[12a] and possible contributing electronic factors have been analyzed.[12b]

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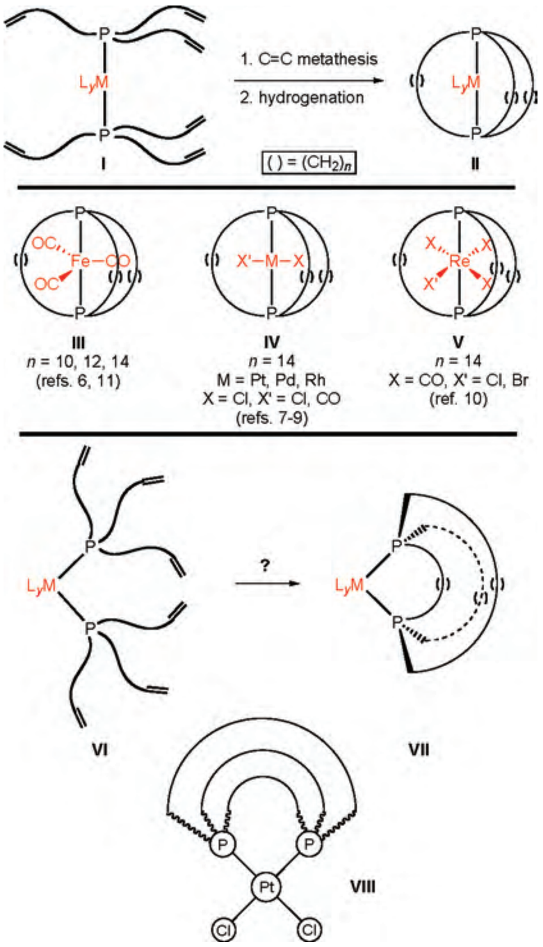
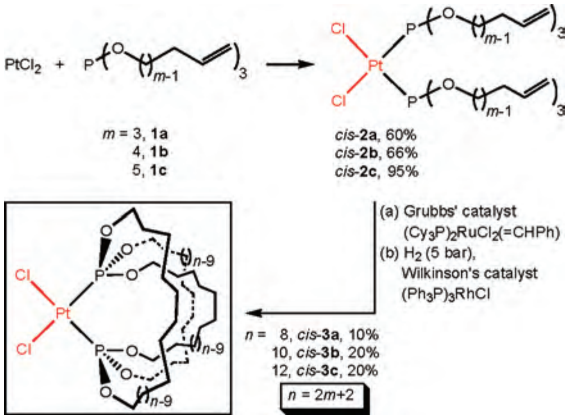
Scheme 1. Syntheses of Gyroscope-like Complexes in Which *trans*-Phosphorus Atoms are linked by Three Bridges (Top, Middle) and Possible Extensions to Parachute-like Cis Analogues (Bottom)



Scheme 2. Syntheses of Phosphite Complexes



Next, CH_2Cl_2 solutions of *cis*-**2a**−**2c** (0.79–0.99 mM) and Grubbs' catalyst (10–20 mol %) were refluxed. After 12–36 h, the metathesis products were chromatographed and treated with H_2 (5 bar) and Wilkinson's catalyst (15–20 mol %). As shown in Scheme 2, workups gave the target complexes *cis*-$PtCl_2(P(O(CH_2)_nO)_3P)$ (*cis*-**3a**−**3c**; $n = 2m + 2$) in 10–20% overall yields. These feature 13-membered (*cis*-**3a**) to 17-membered (*cis*-**3c**) macrocycles in which the phosphorus donor atoms are tethered by three bridges of 10−14 atoms. Certain NMR properties were inconsistent with trans isomers. For example, two sets of OCH_2 ^{13}C NMR signals (2:1) and up to three sets of OCH_2 ^1H NMR signals (1:1:1 or 2:1) were observed. With gyroscope-like **IV**, X−M−X′ rotation is rapid on the NMR time scale (room temperature to −80 °C), resulting in a single set of signals.[7]

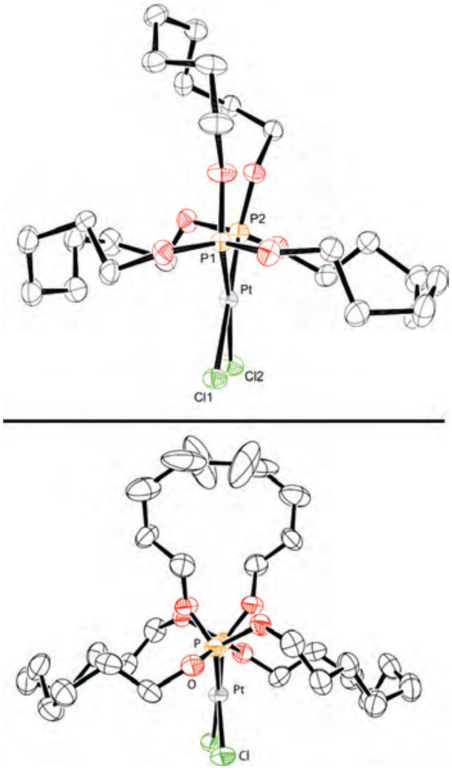


Figure 1. Thermal ellipsoid diagrams (50% probability level) for *cis*-**3a** (top; one of two independent molecules in the unit cell) and *cis*-**3b** (bottom).

To verify these assignments, the crystal structures of *cis*-**3a** and -**3b** were determined (Supporting Information). The former featured two independent molecules in the unit cell and the latter a C_2 symmetry axis. Thermal ellipsoid diagrams are depicted in Figure 1. In each complex, there is a "middle" bridge connecting the two phosphorus atoms that lie nearest to the platinum coordination plane. The outer bridges lie above and below the coordination plane, partially shielding the axial sites. As illustrated by **VIII** (Scheme 1), this generates a parachute-like motif, in which the P_2PtCl_2 moiety resembles the arms, body, and legs of the parachutist. The bond lengths and angles about the platinum, phosphorus, and

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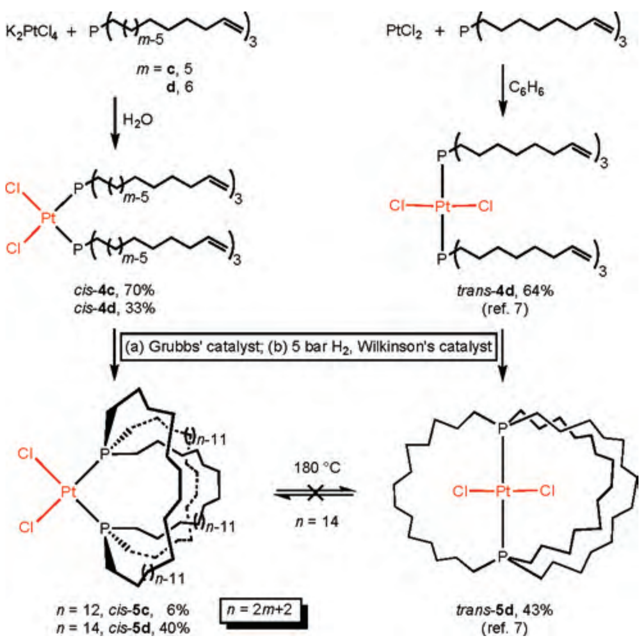
(15) (a) It has been shown that *cis*-dihaloplatinum bis(phosphine) complexes exhibit greater $^1J_{PPt}$ values than trans isomers: Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133. (b) The $^1J_{PPt}$ values of two *trans*-dihaloplatinum bis(phosphite) complexes have been reported (4680–4405 Hz)[12a,15c] and are less than those of *cis*-**2a**−**2c** and -**3a**−**3c**. (c) van der Vlugt, J. I.; Ackerstaff, J.; Dijkstra, T. W.; Mills, A. M.; Kooijman, H.; Spek, A. L.; Meetsma, A.; Abbenhuis, H. C. L.; Vogt, D. *Adv. Synth. Catal.* **2004**, *346*, 399.

Scheme 3. Syntheses of Phosphine Complexes



oxygen atoms are similar to those of other dichloroplatinum bis(phosphite) complexes (Supporting Information).[13,14]

We next turned our attention to metatheses of analogous *cis*-phosphine complexes. These have the potential of affording isomers of previously reported gyroscope-like complexes *trans*-$\mathrm{PtCl_2(P((CH_2)_n)_3P)}$ (*trans*-**5**).[7] As shown in Scheme 3 (left), $\mathrm{K_2PtCl_4}$ and $\mathrm{P((CH_2)_mCH{=}CH_2)_3}$ (m = 5 (**c**), 6 (**d**)[6] were combined in the polar solvent water. Chromatographic workups produced two bands, the first providing the known isomers *trans*-$\mathrm{PtCl_2(P(CH_2)_mCH{=}CH_2)_3)_2}$ (*trans*-**4c** and -**4d**)[7] and the second the new species *cis*-**4c** and -**4d** in 70% and 33% yields, respectively. The $^1J_{\mathrm{PPt}}$ values confirmed the stereochemistry (3511–3510 Hz vs 2381 Hz for *trans*-**4d**).[15a] For reference, the synthesis of *trans*-**4d**, which is conducted in a nonpolar solvent, is also depicted in Scheme 3.

Complexes *cis*-**4c** and -**4d** were subjected to metathesis/hydrogenation sequences analogous to those in Scheme 2. Products arising from three-fold intramolecular metatheses, *cis*-**5c** and -**5d**, could be isolated in 6% and 40% yields, respectively. Complex *cis*-**5c** features 15-membered macrocycles, as opposed to the 17-membered macrocycles in the phosphite complex with the same number of methylene groups, *cis*-**4c**. Complex *cis*-**5d** features 17-membered macrocycles. As shown in Scheme 3 (right), when an analogous sequence is conducted with *trans*-**4d**, *trans*-**5d** is obtained in a yield comparable to that of *cis*-**5d**.[7]

The structures of *cis*-**5c** and -**5d** were supported by the $^1J_{\mathrm{PPt}}$ values (3568–3543 Hz vs 2398 Hz for *trans*-**5d**)[15a] and the observation of two $\mathrm{PCH_2}$ ^{13}C NMR signals (2:1). The mass spectra showed intense molecular ions and the successive loss of chloride ligands; unlike the precursors *cis*-**4c** and -**4d**, no ions corresponding to free phosphines were detected. However, samples suitable for crystallography have not yet been obtained. Nonetheless, *cis*-**5c** and -**5d** and *cis*-**3a**−**3c** establish that the macrocyclic dibridgehead diphosphines or diphosphites are extremely flexible. As shown in Figure 2, they readily adopt conformations **XI** in which the lone-pair vectors are twisted by 270° with respect to the reference structure **IX**. Hence, adducts of ligands with less twisted conformations, such as **X**, should also be possible.

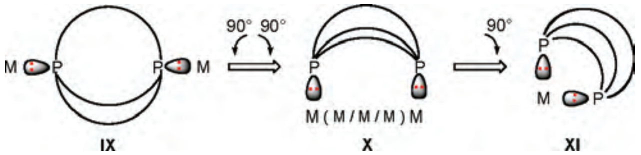


Figure 2. Selected limiting structures for complexes of dibridgehead phosphites and phosphines.

Importantly, the availability of both *cis*-**5d** and *trans*-**5d** allows the energy barriers and thermodynamics associated with cis/trans isomerization to be probed. Thermogravimetric analysis measurements with *cis*-**5d** showed an onset of mass loss at 204 °C, and differential scanning calorimetry experiments indicated a melting endotherm at 200 °C. Analogous measurements with *trans*-**5d** showed an onset of mass loss at 284 °C, a melting endotherm at 115 °C, and no other transitions prior to mass loss.[7] These data do not suggest any isomerization, which would be evidenced by an exotherm with the less stable species. As a check, thermolyses were conducted. In one series of experiments, NMR tubes were charged with 1,2-dichlorobenzene solutions of *cis*-**5d** and *trans*-**5d** and kept at 180 °C for 14 h. In a second, solid samples were similarly heated, and then $\mathrm{CDCl_3}$ was added. The samples were analyzed by ^{31}P NMR. The experiments with *cis*-**5d** showed 10% conversion to a second species with a signal coincident with that of *trans*-**5d**. Those with *trans*-**5d** showed either no conversion (solid state) or 8% conversion (1,2-dichlorobenzene) to an unidentified species. Hence, there is no low-energy cis/trans isomerization pathway, excluding the involvement of such equilibria in ligand exchange or other dynamic processes.

In summary, platinum complexes that contain *cis*-phosphite or -phosphine ligands with suitable alkene substituents undergo three-fold intramolecular alkene metatheses to give architecturally unusual adducts with parachute-like geometries. Some of these constitute isomers of previously reported gyroscope-like complexes. The ligands partially screen the axial sites associated with the platinum square plane, an attribute that can enhance the stabilities of certain types of derivatives,[16] and might lead in other d^8 metal complexes to catalysts with unusual selectivities or activities. Efforts in these directions, and extensions to other types of cis coordination geometries, are in progress and will be reported in due course.

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

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