

Square-Planar Palladium Complexes with Trans Di- and Tribenzylphosphine Ligands Bearing O(CH₂)₄CH=CH₂ Substituents; Two- and Three-Fold Intramolecular Ring-Closing Metatheses

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Summary: When trans-PdCl₂{PPh_n[CH₂C₆H₄O(CH₂)₄CH= CH₂]_{3-n}}₂, with ortho or meta C₆H₄ linkages and n = 0, 1(tribenzyl- or dibenzylphenylphosphine cores), are treated with Grubbs' catalyst and then H₂/PtO₂, the macrocycles trans-

 $PdCl_{2}\{P[CH_{2}-o-C_{6}H_{4}O(CH_{2})_{10}O-o-C_{6}H_{4}CH_{2}][CH_{2}-o-C_{6}H_{4}-O(CH_{2})_{10}O-o-C_{6}H_{4}CH_{2}]P[CH_{2}-o-C_{6}H_{4}O(CH_{2})_{10}O-o-C_{6}H_{4}C-H_{2}]\}, trans-PdCl_{2}\{PPh[CH_{2}C_{6}H_{4}O(CH_{2})_{10}OC_{6}H_{4}CH_{2}]\}_{2} (o- or m-C_{6}H_{4}), and trans-PdCl_{2}\{PPh[CH_{2}-m-C_{6}H_{4}O(CH_{2})_{10}-O(CH_{2})_{10}OC_{6}H_{4}CH_{2}]\}_{2} (o-m-C_{6}H_{4}CH_{2})_{2}PhP\} are isolated in high yields.$

It is now well established that alkene metatheses can be effected in a variety of metal coordination spheres, enabling

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We wondered whether such macrocyclizations could be extended to group 10 metals and tribenzylphosphine- and dibenzylphenylphosphine-based ligands that feature O(CH₂)₄-CH=CH₂ substituents ortho or meta to the benzylic carbon atoms. These would possess additional conformational degrees of freedom, which could possibly lead to different selectivities and/or higher fractions of oligomeric products. Also, tribenzylphosphine is sterically and electronically intermediate between PPh₃ and PCy₃.⁶ In this communication, we describe intramolecular alkene metatheses of complexes of the formula trans-PdCl₂{PPh_n[CH₂C₆H₄O(CH₂)₄CH=CH₂]_{3-n} $\}_2$, in which the CC_6H_4O linkages can be ortho or meta and *n* can be 0 or 1. Interestingly, these systems exhibit a distinct preference for macrocyclizations involving *intra*ligand metathesis and give little or no di- or polypalladium byproducts. They furthermore generate novel ditertiary diphosphines that would be otherwise very difficult to prepare and for which the possibility of facile decomplexation has been demonstrated.⁵

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Scheme 1. Possible Intramolecular Ring-Closing Metathesis Products (II, III) derived from *trans*-Bis(phosphine) Complexes with Vinyl-Terminating Phosphorus Substituents (I) and Some Previously Synthesized Complexes (IV, V)



In a Williamson ether recipe, 2-hydroxybenzaldehyde, 6-bromohex-1-ene, and the base K_2CO_3 (1:1:1) were combined in DMF at 55 °C. Workup gave the corresponding ether O=CH-o-C₆H₄O(CH₂)₄CH=CH₂ (1a) in ~98% yield. As shown in Scheme 2, subsequent reduction with NaBH₄ and treatment with SOCl₂ afforded the benzyl chloride ClCH₂-o-C₆H₄O(CH₂)₄CH=CH₂ (2a; 79%). The corresponding Grignard reagent was treated with PCl₃ (3.1:1.0 mol ratio) to give the phosphine P(CH₂-o-C₆H₄O(CH₂)₄CH=CH₂)₃ (3a; 63%). The new compounds 1a-3a and all others below were characterized by NMR (¹H, ¹³C, and ³¹P) and microanalyses, as summarized in the Supporting Information.

The reaction of 3a and Pd(COD)Cl₂ afforded the palladium bis(phosphine) complex trans-PdCl₂{P[CH₂-o-C₆H₄- $O(CH_2)_4CH=CH_2]_3\}_2$ (4; 60%) (Scheme 2). Next, 4 (ca. 0.001 M in CH₂Cl₂) and Grubbs' catalyst (first generation; ~half of 15 mol %) were combined with stirring at room temperature under a nitrogen atmosphere. The remaining catalyst was added after 24 h, and the solution was then refluxed for 24 h. Following chromatography, the crude mixture of C=C isomers was hydrogenated (1 atm H_2 , 15 mol % of PtO_2) to give 5 as a yellow solid in 86% overall yield. The ³¹P NMR spectrum exhibited a singlet at 10.8 ppm. However, the ¹³C NMR spectrum showed two sets of PCH_2 -o-C₆H₄O- signals in a ca. 2:1 ratio, with the PCH₂ peaks being phosphorus-coupled virtual triplets.⁷ This would be inconsistent with a product with the symmetry of II (Scheme 1). Accordingly, the structure shown in Scheme 2, corresponding to macrocyclization mode III, was tentatively assigned.

As shown in Figure 1, a crystal structure confirmed the composition of **5**. In this structure and all others below, the bond lengths and angles about palladium were routine.





Figure 1. Molecular structure of 5 with thermal ellipsoids at the 50% probability level.

The substituents on the trans phosphorus atoms were essentially eclipsed, as reflected by $CH_2-P-P-CH_2$ torsion angles of ca. 0° (0.9–11.6°) and 120° (105.9–134.6°). The trans spanning linkage involved a $CH_2-P-P-CH_2$ moiety with a ca. 120° torsion angle (see Figure s1, Supporting Information).

Alkene metatheses of the dibenzylphenylphosphine adducts trans-PdCl₂{PPh[CH₂C₆H₄O(CH₂)₄CH=CH₂]₂; (**7a,b**, *o*-/*m*-C₆H₄) were investigated next. These were accessed by first generating Grignard reagents derived from **2a** (Scheme 2) or the meta isomer **2b** (analogously prepared per the Supporting Information) and condensing them with PhPCl₂. As shown in Schemes 3 and 4, the resulting crude phosphines PPh(CH₂-C₆H₄O(CH₂)₄CH=CH₂)₂ (**6a,b**, *o*-/*m*-C₆H₄) were directly combined with (PhCN)₂PdCl₂ to give **7a,b** (12–17%).

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Scheme 4. Alkene Metathesis/Hydrogenation of 7b



In the case of 7a, a metathesis/hydrogenation sequence followed by chromatography afforded 9a, derived from *intra*ligand metathesis, in 80% yield (Scheme 3). This structure, as opposed to one derived from *inter*ligand metathesis, was assigned on the basis of a crystal structure of the bis(alkene) intermediate **8a**. Although ³¹P NMR spectra of all crude metatheses products showed three or more signals, consistent



Figure 2. Molecular structure of (E,E)-8a with thermal ellipsoids at the 50% probability level.



Figure 3. Molecular structure of 9c with thermal ellipsoids at the 50% probability level.

with mixtures of E/Z C=C linkages, only (*E*,*E*)-**8a** crystallized. As is evident in Figure 2, the C-P-P-C units were nearly staggered (torsion angles 52.8–63.6 and 180°), with the phenyl groups anti. The 180° value results from an inversion center at platinum, a feature also found in the other structure below.

On the other hand, a similar sequence with **7b** (Scheme 4) afforded a mixture of two products, **9b**,**c**, which could be crystallized from CH₂Cl₂/hexane and then carefully separated according to habit with tweezers (45% and 46%, respectively). It was thought that one was likely derived from *intra*ligand metathesis and the other from *inter*ligand metathesis. However, there was no obvious NMR criterion for assigning the structure. Fortunately, the crystal structure of **9c** could be determined, the results of which are shown in Figure 3. This established that **9c** was an *inter*ligand metathesis product, as rendered in Scheme 4. In principle, two stereoisomers differing in the relative orientation of the PPh moieties are possible. Figure 3 shows that these are anti with respect to the "plane" of the largest macrocycle. In this context, the C–P–P–C units are staggered, with torsion angles of 56.3–59.1 and 180°.

Results from several other studies are relevant to the preceding data. First, ring-closing metatheses of aliphatic analogues of the dibenzylphenyl systems **7a**,**b**, *trans*-PtCl(C₆F₅)(PPh((CH₂)_nCH=CH₂)₂)₂, have been carried out (n = 4-6, 8).^{4c} In every case, the only monoplatinum products detected were derived from *inter*ligand metatheses

(analogous to **9c**). Second, Garcia-Garibay has reported the metathesis of a *p*-diethynylbenzene capped with meta-substituted trityl groups, $(H_2C=CH(CH_2)_4O-m-C_6H_4)_3CC=C-p-C_6H_4C=CC(m-C_6H_4O(CH_2)_4CH=CH_2)_3$.⁸ Interestingly, the sole monomeric product after hydrogenation corresponded to macrocyclization mode III (Scheme 1). Finally, we have generated additional complexes of the type III via metatheses of octahedral species with two trans aliphatic phosphines P((CH_2)_nCH=CH_2)_3, but almost always as minor byproducts accompanying II.⁹

In summary, we have demonstrated that palladium complexes of the formula *trans*-PdCl₂{PPh_n[CH₂C₆H₄O(CH₂)₄-CH=CH₂]_{3-n}}₂ (*o*- or *m*-C₆H₄; n = 0, 1) undergo ready twoand 3-fold intramolecular alkene metatheses in high yields. There is generally a distinct preference for *intra*ligand metathesis, as opposed to the essentially exclusive formation of *inter*ligand metathesis products from square-planar complexes with related trans-disposed trialkylphosphine or para-substituted triphenylphosphine ligands. Perhaps the benzylic and ortho or meta linkages in Schemes 2–4 facilitate the adoption of conformations more favorable for *intra*ligand metathesis, and studies to probe such possibilities are in progress. These, and extensions of this chemistry to other substituted tribenzylphosphine complexes, will be detailed in future reports.

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Supporting Information Available: Text, figures, tables, and CIF files giving experimental procedures and characterization data for all new compounds and crystallographic data for 5, 8a, and 9c. This material is available free of charge via the Internet at http://pubs.acs.org.

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