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Olefin metatheses in metal coordination spheres: novel *trans*-spanning bidentate and facially-spanning tridentate macrocyclic phosphine complexes

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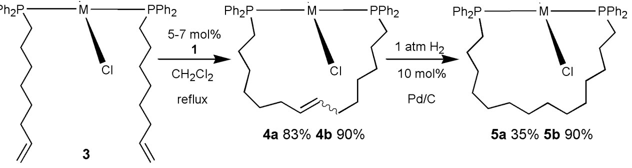
The title reaction is applied to square-planar rhodium and platinum complexes with *trans* $PPh_2(CH_2)_6CH{=}CH_2$ ligands, and square-planar platinum or octahedral tungsten complexes with *trans* or facial $PPh[(CH_2)_6CH{=}CH_2]_2$ ligands. Ring-closing (poly)macrocyclizations occur.

New applications of olefin metathesis are rapidly appearing in nearly every area of organic synthesis.[1] However, there have been few reports of olefin metatheses in metal coordination spheres.[2–7] Some early observations of Rudler and coworkers[2] were followed by elegant applications in catenane syntheses[3,4] and ferrocenophane polymerizations.[5] We recently showed that Grubbs' catalyst, $Cl_2(Cy_3P)_2Ru({=}CHPh)$ **1**, can be applied to a variety of coordinatively saturated and unsaturated, neutral and charged, alkene-containing phosphine or thioether complexes—unequivocally demonstrating general applicability.[6] From this beginning, we sought to develop directed syntheses of more sophisticated organometallic targets. Here, we present three innovative and progressively more topologically challenging extensions: (1) monomacrocyclizations involving *trans* phosphine ligands, each with one terminal alkene moiety, (2) dimacrocyclizations involving *trans* phosphine ligands, each with two terminal alkene moieties, and (3) trimacrocyclizations involving facial phosphine ligands, each with two terminal alkene moieties.

The phosphine-monoalkene $PPh_2(CH_2)_6CH{=}CH_2$ **2**,[6] bridging chloride complex $[Rh(\mu\text{-}Cl)(cod)]_2$, and CO were combined under conditions previously used to prepare rhodium bisphosphine complexes *trans*-$Rh(Cl)(CO)(L)_2$.[8] Workup gave *trans*-$Rh(Cl)(CO)[PPh_2(CH_2)_6CH{=}CH_2]_2$ **3a** as a yellow powder in 83% yield. The reaction of **2** and the tetrahydrothiophene (SR_2) complex $[Pt(\mu\text{-}Cl)(C_6F_5)(SR_2)]_2$[9] similarly led to the platinum bis-phosphine complex *trans*-$Pt(Cl)(C_6F_5)[PPh_2(CH_2)_6CH{=}CH_2]_2$ **3b**, (90%). As shown in Scheme 1, CH_2Cl_2 solutions of **3a** or **3b** (0.0027–0.0025 M) and **1** (5.0–7.0 mol%) were refluxed. Workups gave macrocycles **4** (M/X = Rh/CO **a**, Pt/C_6F_5 **b**) in 83–90% yields and as 90–83 : 10–17 mixtures of *E*/*Z* C=C isomers, as assayed by standard ^{13}C or ^1H NMR criteria.[3b,6] Hydrogenations over 10% Pd/C (1 atm) gave the corresponding saturated macrocycles **5a** (yellow oil, 35%) and **5b** (white powder, 90%). The structures of all the preceding compounds followed readily from their spectroscopic properties.[10] Fig. 1 shows the crystal structure of **5b**,† highlighting the basket-handle-like *trans*-spanning ligand.



Scheme 1 Monomacrocyclizations catalyzed by $Cl_2(Cy_3P)_2Ru({=}CHPh)$ **1**. M/X = **a**, Rh/CO; **b**, Pt/C_6F_5.

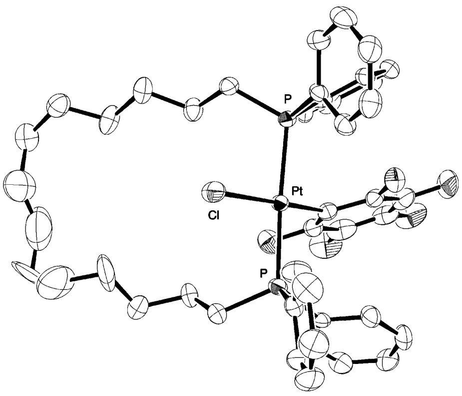
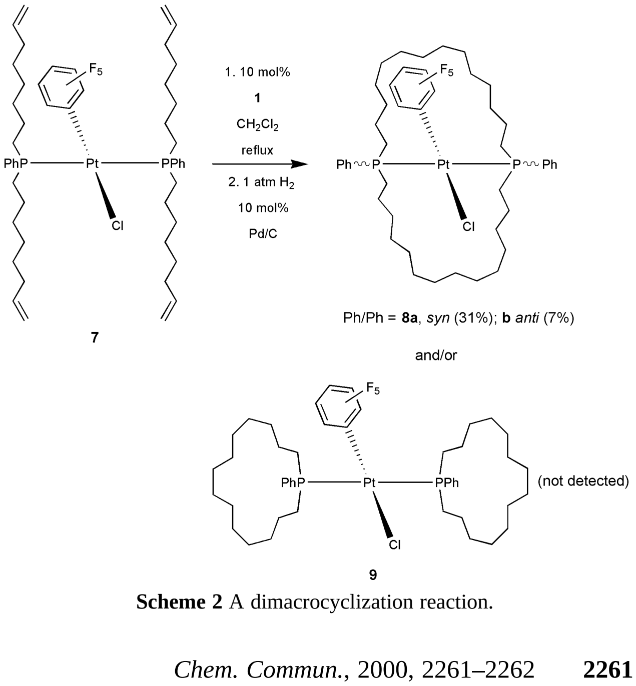


Fig. 1 Crystal structure of **5b**.

Next, the phosphine-dialkene $PPh[(CH_2)_6CH{=}CH_2]_2$ **6** was prepared in 78% yield from H_2PPh, Bu^nLi (2.1 equiv), and $Br(CH_2)_6CH{=}CH_2$ (2.0 equiv.). Reaction with $[Pt(\mu\text{-}Cl)(C_6F_5)(SR_2)]_2$ gave *trans*-$Pt(Cl)(C_6F_5)\{PPh[(CH_2)_6CH{=}CH_2]_2\}_2$ **7** (91%), which could give two types of metathesis/hydrogenation products, **8** and **9**, as shown in Scheme 2. The latter features two macrocyclic monophosphines, an efficient cyclization mode for 1 : 1 metal complexes of **6**.[11] The former features one macrocyclic diphosphine, with two diastereomers differing in the orientations of the phenyl groups (**8a**,**b**). Under conditions similar to those in



Scheme 2 A dimacrocyclization reaction.

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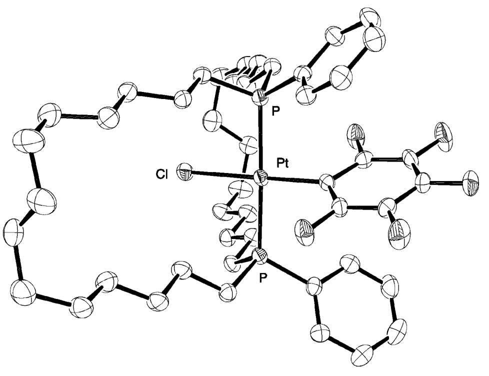
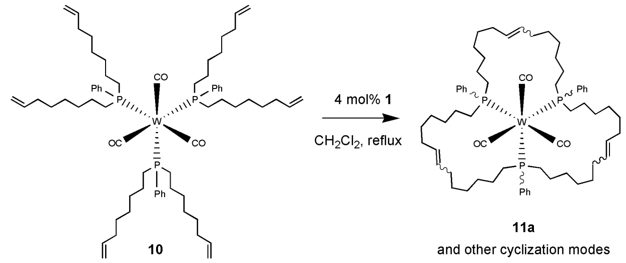


Fig. 2 Crystal structure of **8a**.



Scheme 3 A trimacrocyclization reaction

Scheme 1, reactions of **7** and **1** gave 84–65% yields of metathesized products, which were hydrogenated and chromatographed on alumina. The two least polar products were isolated in 31 and 7% yields, and shown by X-ray crystallography to be **8a** and **8b**, respectively.† The structure of the former is given in Fig. 2. Some diplatinum products form, and the conditions for this sequence are still being optimized. However, no traces of **9** have been detected to date—a surprising and highly exploitable selectivity.

We sought to attempt even more speculative types of macrocyclizations. Many tungsten triphosphine complexes *fac*-$W(CO)_3(L)_3$ are known, and **10** (Scheme 3) was prepared by a standard method.[12] This could give three different types of metathesis products, each with a plethora of C=C and/or PPh isomers (**a**: one triphosphine, 16 isomers; **b**: one diphosphine and one monophosphine, 18 isomers; **c**: three monophosphines, 4 isomers). Reaction with **1** as above and chromatography gave a sample of empirical formula $W(CO)_3\{PPh[(CH_2)_6CH{=}]_2\}_3$ **11** (83%), as assayed by NMR and mass spectrometry. HPLC showed three overlapping regions of many partially resolved peaks. Hydrogenation could be effected (94%), but under no conditions was a preparatively meaningful purification achieved. Nonetheless, two macrocyclic triphosphine complexes (**11a′**, **11a″**) could be crystallized from the mixture before hydrogenation, and X-ray structures of both were determined.† That of **11a′**, which is representative, is shown in Fig. 3. All PPh groups are *anti* to the $W(CO)_3$ moiety in **11a′**, whereas one is *syn* in **11a″**. Each has three *E*-C=C linkages.

The preceding syntheses have many noteworthy features. First, a variety of complexes with *trans*-spanning diphosphines are known.[13] However, our route is the first to link two existing monophosphines with a hydrocarbon tether. Second, doubly *trans*-spanning diphosphines such as in **8** are to our knowledge unknown. However, a conceptually similar two-fold ring-closing metathesis involving *trans* 2,6-disubstituted pyridine ligands has recently been reported.[7a] Here, the pyridine geometry favors the formation of *trans*-spanning bridges, whereas **7** lacks a structure-based driving force. Third, in contrast to the surprisingly selective conversion of **7** to **8**, **10** appears to give virtually every possible product. Such behavior, disparaged in the past, is now praised as an efficient route to a combinatorial library. Importantly, other strategies have been used to effect high-yield template syntheses of 10–15 membered facially-spanning triphosphine complexes from trismonophosphine complexes.[14] In conclusion, we have demonstrated the utility of Grubbs' catalyst **1** for the construction of topologically novel organometallic (poly)macrocycles from easily accessed precursors in a single step.

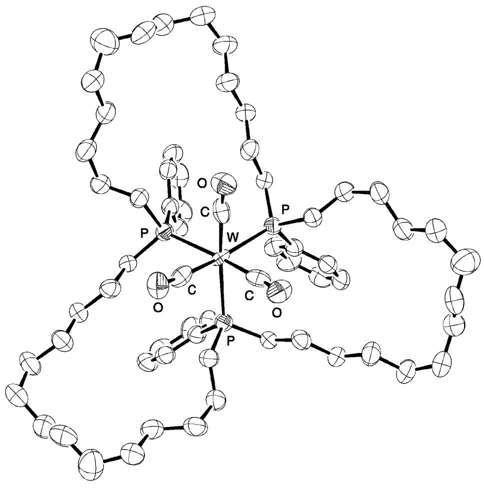


Fig. 3 Crystal structure of **11a′**.

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Notes and references

† *Crystal data*; **5b/8a/11a′**: $C_{44}H_{48}ClF_5P_2Pt/C_{46}H_{66}ClF_5P_2Pt/C_{63}H_{93}O_3P_3W$, M = 964.30/1006.47/1175.13, monoclinic/monoclinic/hexagonal, a = 31.7963(7)/24.8121(3)/18.900(8), b = 10.7342(3)/10.5438(2)/18.900(8), c = 24.9213(6)/18.0730(4)/9.842(3) Å, V = 8311.2(4)/4575.32(14)/3045(2) Å^3, T = 173(2)/173(2)/95(2) K, space groups $C2/c$, $P2_1/c$, $P3$, Z = 8/4/2, μ(Mo-Kα) = 3.570/3.246/2.017 mm^{-1}, 15944/17699/14105 reflections measured, 9273/10322/3555 unique (R_{int} = 0.0683/0.0549/0.0796), which were used in calculations. Final R values: $R1$ [$I > 2\sigma(I)$] = 0.0435/0.0404/0.1018; $wR2$ (all data) = 0.1278/0.0796/0.1647. Two CH_2 groups in **5b** were disordered and could not be fully resolved. Refined partial occupancy (C10/C10′, C11/C11′): 55:45. CCDC 182/1815. See http://www.rsc.org/suppdata/cc/b0/b007405p/ for crystallographic files in .cif format.

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