Olefin Metatheses in Metal Coordination Spheres: A New Strategy for Cyclic and Macrocyclic Organometallic Compounds

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Summary: The cationic and neutral rhenium and platinum complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_2CH{=}CH_2)_2)]^+TfO^-$, $fac\text{-}(OC)_3Re(Br)\{PPh_2(CH_2)_6CH{=}CH_2\}_2$, *and* $cis\text{-}Pt(Cl)_2\{PPh_2(CH_2)_6CH{=}CH_2\}_2$, *which contain sulfide or phosphine ligands with* $(CH_2)_nCH{=}CH_2$ *substituents, undergo efficient intramolecular metatheses with* $(Cl)_2(PCy_3)_2Ru(=CHPh)$ *to give new sulfide and chelating diphosphine complexes with 5- and 17-membered rings.*

Over the past decade, the olefin metathesis reaction has been applied in virtually every arena of chemical synthesis.[1,2] This has been in large part prompted by the commercial availability of catalysts and significant air, moisture, and functional group tolerance.[2] The recent development of enantioselective catalysts should further accelerate activity.[3] However, applications in organometallic synthesis remain scant.[4−6] We were curious whether olefin metathesis might be a viable approach to complex target molecules currently under pursuit in our group. Thus, we set out to investigate a selection of model reactions. In this communication, we report that it is possible to utilize the popular Grubbs catalyst $(Cl)_2(PCy_3)_2Ru(=CHPh)$ (**1**)[7] for a variety of ring-closing olefin metatheses in metal coordination spheres.

In principle, olefin metathesis can be applied *within* or *between* ligands. As a test of the former, CH_2Cl_2 solutions of the previously reported cationic rhenium diallyl sulfide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_2CH{=}CH_2)_2)]^+TfO^-$ (**2**; 0.0026 M)[8] and **1** (2 mol %, 0.0015 M) were combined (Scheme 1). After 3 h at reflux, NMR spectra of the homogeneous mixture showed the essentially quantitative formation of a product. Workup gave the crystalline dihydrothiophene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_2CH{=}CHCH_2)]^+TfO^-$ (**3**) in 75% yield. The structure of **3** followed from its spectroscopic properties,[9] which were similar to those of many related diallyl sulfide complexes characterized earlier.[8] Interestingly, ring-closing metatheses of free diallyl sulfide with catalysts similar to **1** fail, presumably due to catalyst deactivation.[10] In this regard, it should be noted that sulfide ligands are easily detached from the rhenium Lewis acid in **2** and **3**.[8]

We next sought to attempt macrocyclizations involving alkenes on different ligands. Reaction of $(OC)_5Re(Br)$ and the phosphine $PPh_2(CH_2)_6CH{=}CH_2$ (**4**)[11] in refluxing $CHCl_3$ (Scheme 1) gave the neutral rhenium

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(5) Ferrocene-based examples: (a) Gamble, A. S.; Patton, J. T.; Boncella, J. M. *Makromol. Chem., Rapid Commun.* **1993**, *13*, 109. (b) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507.

(6) There are, of course, many examples of $L_nM{=}C + C{=}C$ metatheses in metal coordination spheres, but catalyzed $C{=}C + C{=}C$ metatheses are very rare.[4]

(7) Compound **1** has been designated as the 1998 "Reagent of the Year" by Fluka, one of several commercial vendors. The Schrock molybdenum catalyst is also now commercially available.

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(9) All new complexes were characterized by microanalysis and IR, NMR ($^1H/^{13}C/^{31}P$), and mass spectrometry, as detailed in the Supporting Information. *Representative procedure*: A Schlenk flask was charged with **5** (0.286 g, 0.303 mmol) and CH_2Cl_2 (110 mL). Another Schlenk flask was charged with **1** (0.005 g, 0.006 mmol) and CH_2Cl_2 (10 mL). The purple solution was added by cannula to the colorless solution of **5**. The mixture was refluxed (3 h). Solvent was removed by rotary evaporation. The residue was chromatographed on a silica column (CH_2Cl_2). The solvent was removed by rotary evaporation to give **6** as a white powder (0.221 g, 0.242 mmol, 80%), mp 184−185 °C. NMR ($CDCl_3$, major trans C=C isomer): ^1H (δ) 7.62−7.23 (m, $4C_6H_5$), 5.39 (m, $CH{=}CH$), 2.77 (m, $2PPh_2CHH•$), 2.07 (m, $2PPh_2CHH• + CH_2CH{=}CH$), 1.56−1.18 (m, $8CH_2$); $^{13}C\{^1H\}$ (ppm) 190.0, 189.3 (2 t, 1:2, J_{CP} = 28.7, *C*O), 131.1 (s, *C*H=*C*H), 134−133 (complex *i*-Ph), 133.2, 132.8 (2 virtual t, J_{CP} = 4.5, *o*-Ph), 130.1, 130.1 (2 s, *p*-Ph), 128.7, 128.3 (2 virtual t, J_{CP} = 4.1, *m*-Ph), 32.3 (s, *C*H_2CH=CH), 30.5 (virtual t, J_{CP} = 5.6), 29.2 (s), 28.7 (s), 25.5 (virtual t, J_{CP} = 12.1), 24.4 (br s); $^{31}P\{^1H\}$ −8.2 (s) ppm.

(10) Armstrong, S. K.; Christie, B. A. *Tetrahedron Lett.* **1996**, *37*, 9373.

(11) The new phosphine **4** was isolated in 88% yield from the reaction of $LiPPh_2$ and commercial $Br(CH_2)_6CH{=}CH_2$. The lower homologue $PPh_2(CH_2)_4CH{=}CH_2$ has been characterized previously: Jackson, W. R.; Perlmutter, P.; Suh, G.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 724.

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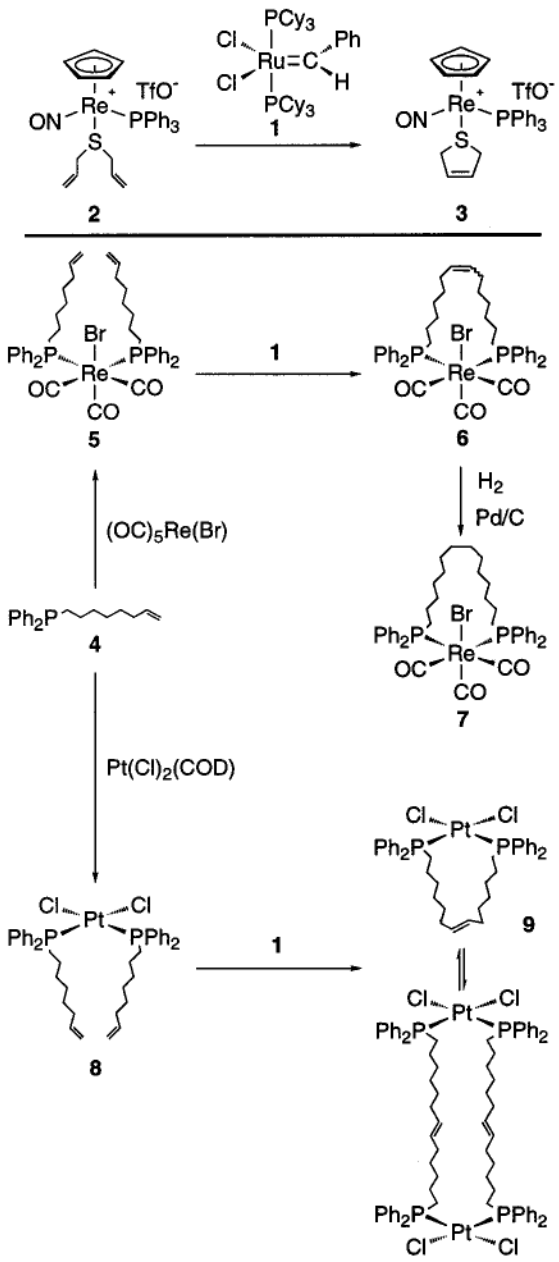
Scheme 1. Ring-Closing Olefin Metathesis in Metal Coordination Spheres



bis(phosphine) complex *fac*-(OC)$_3$Re(Br){PPh$_2$(CH$_2$)$_6$CH=CH$_2$}$_2$ (**5**) in 72% yield.[9] Then CH_2Cl_2 solutions of **5** (0.0028 M) and **1** (2 mol %; 0.0012 M) were combined and refluxed (3 h). Workup gave the macrocycle *fac*-(OC)$_3$Re(Br){PPh$_2$(CH$_2$)$_6$CH=CH(CH$_2$)$_6$PPh$_2$} (**6**) in 80% yield as an (83−80):(17−20) mixture of geometric isomers, as evidenced by two CH=CH ^{1}H NMR signals (δ, acetone-d_6, decoupling: 5.42, 5.37). The =CH*C*H$_2$ ^{13}C NMR chemical shifts (32.3, 29.5 ppm) showed the major species to be a trans isomer.[12] Hydrogenation (1 atm, Pd/carbon, toluene/ethanol) gave the saturated macrocycle *fac*-(OC)$_3$Re(Br){PPh$_2$(CH$_2$)$_{14}$PPh$_2$} (**7**) in 98% yield.

The crystal structures of **6** and **7** were determined as described in the Supporting Information, and selected results are given in Figure 1. The data confirm the macrocyclic nature of **6** and **7**, which exhibit remarkably similar Ph$_2$P(CH$_2$)$_6$CH$_n$CH$_n$(CH$_2$)$_6$PPh$_2$ conformations (despite some disorder in **7**), identical space groups ($P2_1/c$, $Z = 4$), and nearly equal unit cell dimensions. The metrical parameters are routine, but van der Waals representations show some void space within the macrocycles. NMR spectra of crystalline **6** show both C=C isomers. Interestingly, either trans or cis isomers can dominate in macrocyclizations catalyzed by **1**.[12]

We next sought to attempt macrocyclizations involving different metals. Accordingly, a reaction of Pt(Cl)$_2$(COD) and **4** in CH_2Cl_2 (Scheme 1) gave the neutral platinum bis(phosphine) complex *cis*-Pt(Cl)$_2${PPh$_2$(CH$_2$)$_6$CH=CH$_2$}$_2$ (**8**) in 70% yield.[9] This test substrate is also, in contrast to those above, coordinatively unsaturated. Solutions of **8** (0.0027 M) and **1** (2 mol %; 0.0012 M) in CH_2Cl_2 were combined and refluxed (3 h). Workup gave an analytically pure complex of empirical formula *cis*-Pt(Cl)$_2${PPh$_2$(CH$_2$)$_6$CH=CH(CH$_2$)$_6$PPh$_2$} (**9**) in 71% yield. The =CH*C*H$_2$ ^{13}C NMR chemical shift (32.2 ppm) indicated a trans isomer.[12] Careful analysis showed a minor second component (^{31}P NMR: 91:9 in $CDCl_3$ (7.7, 7.9 ppm) or acetone). On the basis of precedent with other Pt(Cl)$_2$ adducts of chelating phosphines,[13] we suspected that one component was a dimer formed by bridging two phosphines between two platinums, as shown in Scheme 1.

Indeed, FAB mass spectra showed strong ions with masses corresponding to (**9** − Cl)$^+$ and (**9** + **9** − Cl)$^+$ (63% and 46%). However, an osmotic molecular weight determination established that the major species in solution was the monomer (calcd, 830.8; found ($CHCl_3$), 844). As depicted in Figure 1, a crystal structure showed only the monomer **9**. The unit cell dimensions of six additional crystals were determined, and all were identical. Nonetheless, crystals were dissolved in acetone that had been cooled to −80 °C, and a ^{31}P NMR spectrum was immediately recorded. Interestingly, both isomers were present (91:9).

There are two highly significant previous reports of related chemistry.[4] Sauvage and Grubbs have found that cationic alkene-substituted copper 1,10-phenanthroline complexes and **1** can react to give macrocycles that are easily elaborated to novel catenanes or molecular knots. In conclusion, the preceding data show that **1** is able to catalyze olefin metatheses in the coordination spheres of both cationic and neutral, and coordinatively saturated and unsaturated, metal complexes. Given our success with phosphine and sulfur donor ligands, we extrapolate that a wide variety of alkene-bearing ligands can be utilized. The conversion of **2** to **3** further demonstrates that transition metals can be employed as protecting groups for functionality that would otherwise deactivate the catalyst. These findings open up an exciting range of new architectural possibilities for directed organometallic synthesis. Applications to complex targets will be reported soon.

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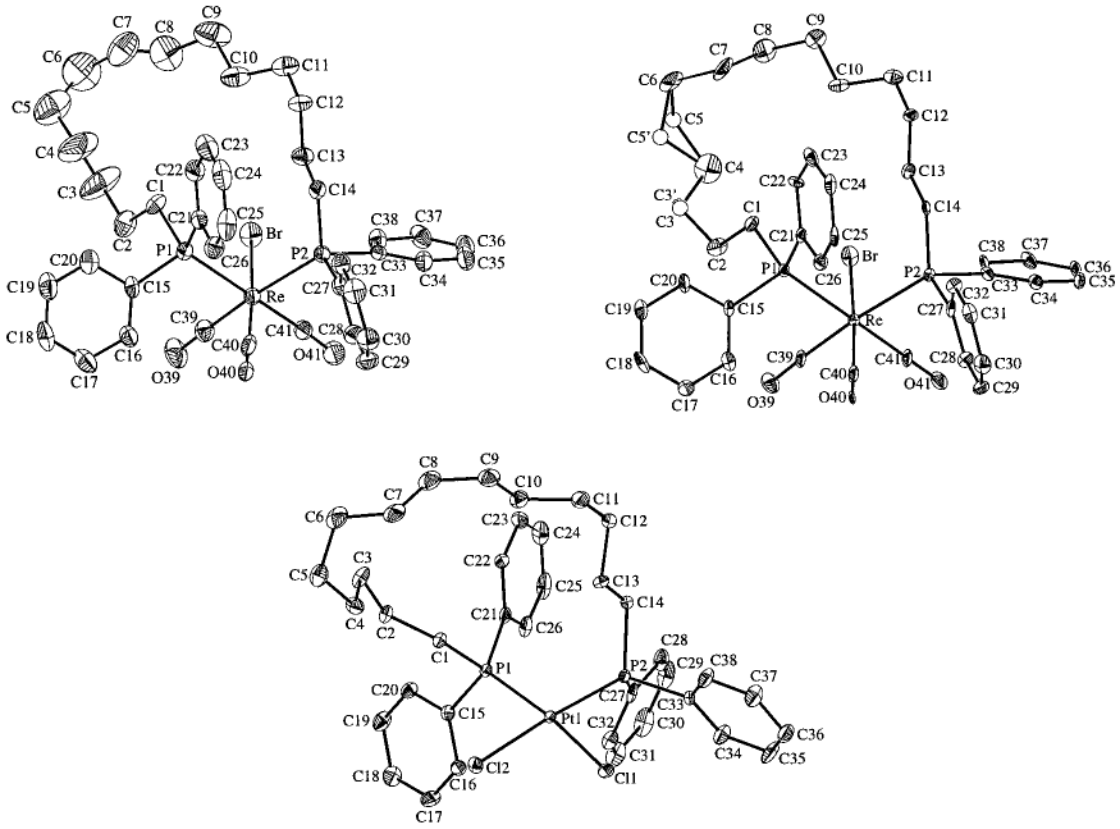

Figure 1. Molecular structures of **6** (top left), **7** (top right), and **9** (bottom). Key bond lengths (Å) and angles (deg) are as follows. **6**/**7**: Re−Br, 2.6614(14)/2.6540(12); Re−C39, 1.899(10)/1.949(11); Re−C40, 1.912(11)/2.054(13); Re−C41, 1.901(8)/1.936(10); Re−P1, 2.499(2)/2.487(3); Re−P2, 2.534(2)/2.520(3); P1−C1, 1.830(8)/1.819(10); C1−C2, 1.507(13)/1.526(14); C2−C3, 1.520(18)/1.53(3); C3−C4, 1.30(3)/1.53(3); C4−C5, 1.45(2)/1.58(2); C5−C6, 1.43(3)/1.48(2); C6−C7, 1.48(3)/1.53(2); C7−C8, 1.23(2)/1.50(2); C8−C9, 1.59(2)/1.52(2); C9−C10, 1.525(16)/1.502(14); C10−C11, 1.518(16)/1.52(2); C11−C12, 1.512(13)/1.511(13); C12−C13, 1.530(12)/1.521(14); C13−C14, 1.506(12)/1.529(13); P2−C14, 1.840(8)/1.826(9); P1−Re−P2, 97.48(7)/97.97(8); C1−P1−Re, 114.9(3)/115.5(4); C2−C1−P1, 114.6(7)/114.4(7); C1−C2−C3, 111.5(11)/113(10); C4−C3−C2, 123.5(19)/112(3); C3−C4−C5, 127(3)/111(10); C6−C5−C4, 116(2)/116.6(11); C5−C6−C7, 120.1(19)/114.6(12); C8−C7−C6, 126(2)/116.8(12); C7−C8−C9, 129(2)/115.3(11); C10−C9−C8, 109.7(13)/112.4(10); C11−C10−C9, 114.9(11)/114.5(9); C12−C11−C10, 112.4(9)/115.3(9); C11−C12−C13, 115.7(9)/114.1(9); C14−C13−C12, 111.5(7)/111.9(8); C13−C14−P2, 113.5(6)/114.1(7); C14−P2−Re, 121.2(3)/122.3(3). **9**: Pt−P1, 2.261(2); Pt−P2, 2.2492(13); Pt−Cl1, 2.337(2); Pt−Cl2, 2.3586(13); P1−C1, 1.818(4); C1−C2, 1.546(6); C2−C3, 1.544(7); C3−C4, 1.532(7); C4−C5, 1.527(7); C5−C6, 1.524(8); C6−C7, 1.445(9); C7−C8, 1.353(9); C8−C9, 1.472(8); C9−C10, 1.522(8); C10−C11, 1.509(7); C11−C12, 1.519(8); C12−C13, 1.528(6); C13−C14, 1.527(7); P2−C14, 1.829(5); P1−Pt−Cl2, 84.86(5); P2−Pt−Cl1, 89.85(5); Cl1−Pt−Cl2, 87.10(5); P2−Pt−P1, 98.22(5); C1−P1−Pt, 107.7(2); C2−C1−P1, 119.6(3); C1−C2−C3, 111.3(4); C4−C3−C2, 112.7(4); C5−C4−C3, 114.1(5); C4−C5−C6, 115.3(5); C7−C6−C5, 113.7(5); C8−C7−C6, 124.1(6); C7−C8−C9, 127.0(6); C8−C9−C10, 111.3(5); C11−C10−C9, 115.4(5); C10−C11−C12, 113.9(5); C13−C12−C11, 112.5(5); C14−C13−C12, 112.8(4); C13−C14−P2, 113.5(3); C14−P2−Pt, 116.1(2).

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Supporting Information Available: Experimental procedures and tables of crystallographic data for **6**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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