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Tungsten-Catalyzed Alkyne Metatheses in Transition-Metal Coordination Spheres: Versatile New Syntheses of Metallamacrocycles

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Summary: The title reaction (10−15 mol % of $(t\text{-BuO})_3W(\equiv C\text{-}t\text{-Bu})$*, chlorobenzene, 80 °C) is applied to octahedral and square-planar 18- and 16-valence-electron rhenium, ruthenium, and platinum complexes with cis- or trans-* $Ph_2P(CH_2)_6C\equiv CCH_3$ *ligands. NMR analyses show ca. 90−70% educt conversions, and 17-membered diphosphine chelates have been isolated in 59−47% yields and crystallographically characterized.*

Over the past few years, alkene metathesis has been applied with increasing frequency in inorganic and organometallic synthesis—in other words, *within* metal coordination spheres.[1−3] Despite the many conceivable types of side reactions, it has proved possible to apply Grubbs' catalyst, $Ru(=CHPh)(PCy_3)_2(Cl)_2$, to coordinatively unsaturated complexes, charged complexes, and species containing $C\equiv C$ linkages or other functionalities known to react with alkylidene ligands. However, one disadvantage of alkene metathesis is that mixtures of (*E*)- and (*Z*)-C=C isomers are typically obtained.[4] For this and other reasons, increasing attention is being focused on the sister reaction, alkyne metathesis.[5−8] Here the resulting $C\equiv C$ linkage can be stereoselectively reduced to either the (*E*)- or the (*Z*)-C=C isomer or transformed to another functionality.

However, most presently available alkyne metathesis catalysts require higher reaction temperatures, often 80−150 °C.[5,6,8] Furthermore, intermediate metal alkylidyne species, $L_nM\equiv CR$, are involved. Alkylidyne ligands react with a broad spectrum of organic functional groups and might be expected to be compatible with a rather limited range of inorganic and organometallic systems under high-temperature conditions. Indeed, the only prior examples of alkyne metatheses in metal coordination spheres of which we are aware involve group VIII metallocenes[9]—one of the most robust platforms for organometallic chemistry. Accordingly, we selected a standard catalyst, $(t\text{-BuO})_3W(\equiv C\text{-}t\text{-Bu})$ (**1**),[10] and set out to investigate its reactions with alkyne-containing organometallic compounds featuring various coordination geometries and electronic configurations.[11]

For initial studies, an alkyne-containing phosphine ligand was sought. Thus, the α,ω-dibromide $Br(CH_2)_6Br$ and $NaC\equiv CH$ were first reacted to give the known terminal alkyne $Br(CH_2)_6C\equiv CH$ (**2**)[12a] in 66% yield after workup. Terminal alkynes are normally poor substrates for metathesis, but methylated alkynes that can eliminate volatile 2-butyne are usually excellent choices.[5,13] Hence, **2** was treated with *n*-BuLi (−45 °C) and then CH_3I (0 °C) to give the known 2-alkyne $Br(CH_2)_6C\equiv CCH_3$ (**3**; 71%).[12b] Subsequent reactions with the diphenylphosphido nucleophiles $MPPh_2$ (M = Li, K) gave the target ligand $Ph_2P(CH_2)_6C\equiv CCH_3$ (**4**) in 81−55% yields.[14]

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(14) All new compounds have been characterized by microanalysis, NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy, and mass spectrometry, as described in the Supporting Information.

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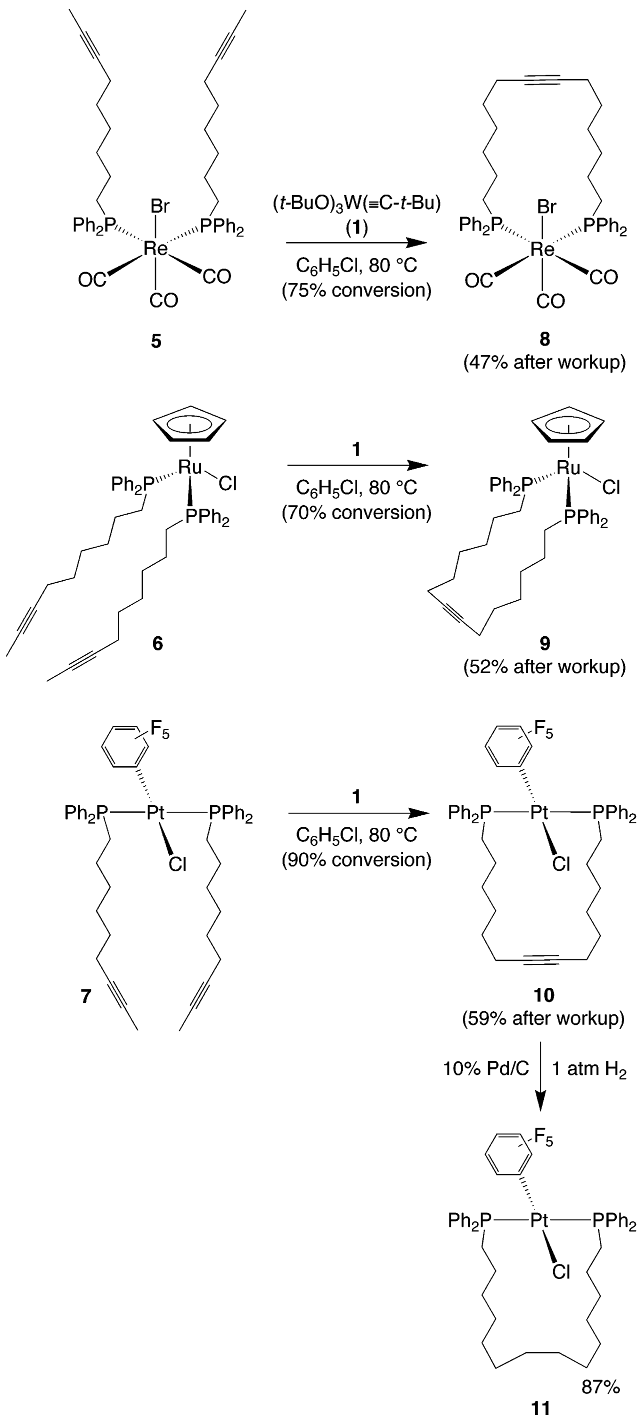
Scheme 1. Tungsten-Catalyzed Metatheses of Transition-Metal-Containing Alkynes



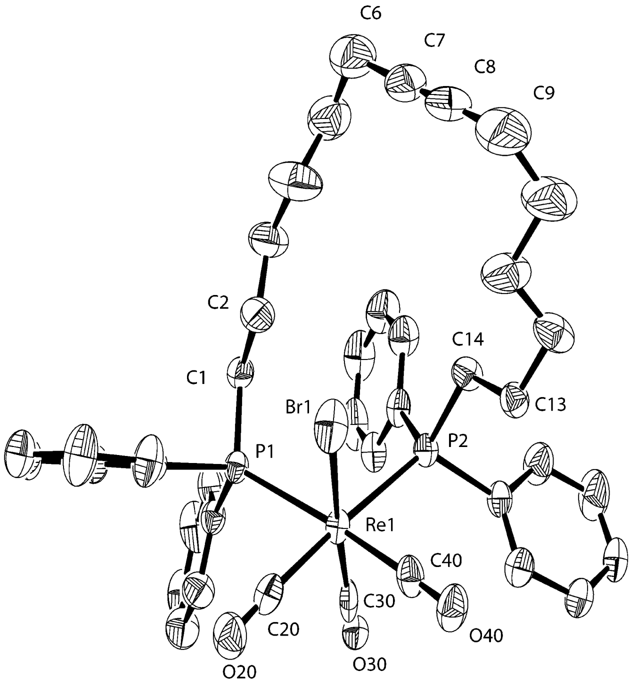


Figure 1. Molecular structure of **8**. Key bond lengths (Å), bond angles (deg), and torsion angles (deg): Re1−C40, 1.936(5); Re1−C20, 1.961(5); Re1−C30, 2.032(7); Re1−P2, 2.4987(10); Re1−P1, 2.5203(10); Re1−Br1, 2.6387(5); C6−C7, 1.454(10); C7−C8, 1.171(9); C8−C9, 1.505(11); C40−Re1−C20, 87.41(18); C40−Re1−C30, 91.97(19); C20−Re1−C30, 90.00(19); C40−Re1−P2, 90.36(13); C20-Re1−P2, 176.85(13); C30−Re1−P2, 87.85(13); C40−Re1−P1, 171.21(12); C20−Re1−P1, 85.41(13); C30−Re1−P1, 93.09(12); P2−Re1−P1, 97.00(3); C40−Re1−Br1, 83.93(14); C20−Re1−Br1, 90.69(14); C30−Re1−Br1, 175.80(12); P2−Re1−Br1, 91.29(3); P1−Re1−Br1, 91.09(3); C8−C7−C6, 177.7(7); C7−C8−C9, 177.7(8); Re1−P1−C1−C2, −56.1(4); Re1−P2−C14−C13, 65.3(4).

Although many monophosphine complexes of **4** could have been prepared and evaluated in *inter*molecular metatheses, we were attracted more by bis(phosphine) complexes with the potential for *intra*molecular macrocyclizations. The rhenium, ruthenium, and platinum species $(CO)_5Re(Br)$, $(\eta^5\text{-}C_5H_5)Ru(Cl)(PPh_3)_2$, and $[Pt(\mu\text{-}Cl)(C_6F_5)(SR_2)]_2$ (SR_2 = tetrahydrothiophene) are established precursors to bis(phosphine) complexes[1a,15,16] and were reacted with **4** under standard conditions. Workups gave the 18-valence-electron rhenium and ruthenium *cis*-bis(phosphine) complexes **5** and **6**, depicted in Scheme 1, and the square-planar 16-valence-electron platinum *trans*-bis(phosphine) complex **7**.[14] All were obtained in analytically pure form, but no efforts were made to optimize yields (54−30% after chromatography). The spectroscopic properties matched those of closely related complexes prepared earlier.[1a,15,16]

As shown in Scheme 1, a ca. 0.022 M chlorobenzene solution of the rhenium complex **5** was treated with 15 mol % of **1** at 80 °C. In accord with common practice,[5] nitrogen was bubbled through the solution to help volatilize the 2-butyne. After 2 h, solvent was removed, and a ^{31}P NMR spectrum of the crude mixture established a conversion of ca. 75%. Chromatography and crystallization gave the new compound **8** in 47% yield. The mass spectrum exhibited molecular and other ions consistent with a macrocycle derived from *intra*molecular alkyne metathesis. The ^1H and ^{13}C NMR spectra showed the absence of $\equiv CCH_3$ signals, and the ^{13}C NMR spectrum gave a single $\equiv C$ signal (δ 80.5, as compared to δ 79.1 and 75.4 in **5**). To unambiguously eliminate a dimeric or oligomeric macrocycle derived from *inter*molecular metathesis, a crystal structure was executed. The result, shown in Figure 1, confirmed the presence of a 17-membered macrocyclic ring.

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The ruthenium complex **6** was similarly treated with 10 mol % of **1**. NMR analysis of the crude reaction mixture indicated 70% conversion. Chromatography gave the new complex **9** in 52% yield. The NMR and mass spectral data were very similar to those of **8**, and as shown in Scheme 1, an analogous structure was assigned. Hence, intramolecular macrocyclization appears to be general for such *cis*-bis(phosphine) complexes, even at concentrations that are not particularly dilute. One factor favoring intramolecular reaction may be the PPh_2 linkages. These would be expected, by analogy to the "geminal dialkyl effect" in carbocycle synthesis,[17] to decrease the fraction of metal/C_β anti conformers about the $MPPh_2-CH_2C_\beta$ linkages. Cyclizations of all-anti assemblies are of course impossible, and gauche $RePPh_2-CH_2C_\beta$ conformations are evident in Figure 1 (torsion angles −56.1(4)/65.3(4)°).

Macrocyclizations involving antiperiplanar- or trans-directed groups as in platinum complex **7** are intrinsically more difficult. Since the coordinative unsaturation of **7** could have presented additional complications, we were not optimistic of success. Nonetheless, analysis of a reaction with **1** (15 mol %) by NMR showed 90% conversion. Chromatography gave the new compound **10** (Scheme 1), containing an unusual trans-spanning diphosphine chelate,[18] in 59% yield. Replicate experiments showed this metathesis to be more efficient than the others above. However, no special feature that would direct both alkynes to the same side of the platinum square plane, thereby favoring intramolecular over intermolecular cyclization, is obvious. The $\equiv C$ ^{13}C NMR chemical shift was in a normal region (δ 80.7), indicating the absence of interactions with platinum.

To broaden the synthetic utility of the above reactions, we sought to effect a $C\equiv C$ hydrogenation. Accordingly, **10** was treated with H_2 (1 atm) in the presence of 10% Pd/C catalyst, as shown in Scheme 1. Workup gave **11**, with a saturated carbon bridge between the phosphorus atoms, in 87% yield. This compound was previously prepared by an alkene metathesis/hydrogenation sequence and crystallographically characterized.[1a] Hence, it constitutes additional evidence for the structure of **10**. Macrocycles **8**−**11** exhibit good thermal stabilities (e.g., chlorobenzene/80 °C; mp ≥162 °C) and have never been observed to dimerize or oligomerize. When $[Pt(\mu\text{-}Cl)(C_6F_5)(SR_2)]_2$ and the diphosphine $Ph_2P(CH_2)_{14}PPh_2$[3a] were combined in an NMR tube in CD_2Cl_2 (1:1 Pt/diphosphine ratio, ca. 0.018 M), a multitude of products formed, as assayed by NMR and TLC. The ^{31}P NMR spectrum allowed an upper limit of 15% to be placed upon the yield of **11**. Thus, metathesis provides a singularly successful route to such macrocycles.

In summary, this study has demonstrated that tungsten-catalyzed alkyne metathesis can be effected in a variety of types of metal coordination spheres in much the same manner as alkene metathesis. Macrocycles can be readily generated, with no appreciable quantities of byproducts in the cases examined. It can be anticipated that these reactions can be extended to more complicated and/or topologically novel systems, and additional applications in organometallic and/or inorganic synthesis will be described in future reports.

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Supporting Information Available: Text and tables giving experimental procedures and characterization data[12] for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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