Alkyne Metatheses in Transition Metal Coordination Spheres: Convenient Tungsten- and Molybdenum-Catalyzed Syntheses of Novel Metallamacrocycles

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Received: January 28, 2004; Accepted: May 14, 2004

Dedicated with affection to a fellow Editor, Dr. Joe P. Richmond, on the occasion of his 60th birthday.

Abstract: Reactions of $(CO)_5Re(Br)$, $(\eta^5\text{-}C_5H_5)Ru(Cl)(PPh_3)_2$, and $[Pt(\mu\text{-}Cl)(C_6F_5)(S(CH_2CH_2\text{-})_2)]_2$ with the alkyne-containing phosphine $Ph_2P(CH_2)_6C{\equiv}CCH_3$ give the bis(phosphine) complexes *fac*-$(CO)_3Re(Br)(Ph_2P(CH_2)_6C{\equiv}CCH_3)_2$ (**5**), $(\eta^5\text{-}C_5H_5)Ru(Cl)(Ph_2P(CH_2)_6C{\equiv}CCH_3)_2$ (**6**), and *trans*-$(Cl)(C_6F_5)Pt(Ph_2P(CH_2)_6C{\equiv}CCH_3)_2$ (**7**). Alkyne metatheses with the catalyst $(t\text{-}BuO)_3W({\equiv}C\text{-}t\text{-}Bu)$ (10–15 mol %, chlorobenzene, 80 °C) give the seventeen-membered metallamacrocycles

fac-$(CO)_3Re(Br)(Ph_2P(CH_2)_6C{\equiv}C(CH_2)_6PPh_2)$ (**8**),

$(\eta^5\text{-}C_5H_5)Ru(Cl)(Ph_2P(CH_2)_6C{\equiv}C(CH_2)_6PPh_2)$ (**9**),

and *trans*-$(Cl)(C_6F_5)Pt(PPh_2(CH_2)_6C{\equiv}C(CH_2)_6PPh_2)$(**10**).

^{31}P NMR analyses show 90–75% conversions to **8**–**10** (59–47% isolated after chromatography). The identity of **8** was confirmed by a crystal structure, and **10** was hydrogenated over Pd/C to

fac-$(CO)_3Re(Br)(Ph_2P(CH_2)_6C{\equiv}C(CH_2)_6PPh_2)$ (**12**, 87%),

which was crystallographically characterized earlier. A catalyst derived from $Mo(CO)_6$/4-chlorophenol effects a slower conversion of **7** to **10** at 140 °C. In the case of **5**, a *mer, trans* isomer of **8** is isolated (**11**, 44%), as established by NMR and IR data. In **10**–**12**, the diphosphines span *trans* positions. These results, together with previous examples involving group VIII metallocenes, establish the wide viability of the title reaction.

Keywords: alkylidyne complexes; alkynes; macrocycles; metathesis; molybdenum; rhenium; tungsten

Introduction

Alkene metathesis is being increasingly employed in syntheses of inorganic and organometallic molecules.[1] Recent applications have included many topologically novel metallo- and metallamacrocycles.[2–6] Most studies have utilized Grubbs' catalyst, $Ru(=CHPh)(PCy_3)_2(Cl)_2$, or newer generation derivatives. There have been surprisingly few reports of side-reactions involving ancillary ligands or the "spectator" metal center.

However, alkene metatheses commonly give mixtures of *E*/*Z* C=C isomers. Thus, increasing attention is being directed at the less commonly utilized sister reaction, alkyne metathesis.[7] The new C≡C linkage can be stereoselectively reduced to either *E* or *Z* C=C isomers, or transformed to other functionality. Hence, we sought to probe the feasibility of analogous alkyne metatheses in a variety of types of metal coordination spheres. As detailed in the discussion section, three other groups have also made important contributions.[8–10] However, all involve group VIII metallocenes, which are among the most robust platforms for organometallic chemistry.

Several types of alkyne metathesis catalysts are known. One of the most extensively applied is Schrock's catalyst $(t\text{-}BuO)_3W({\equiv}C\text{-}t\text{-}Bu)$ (**1**),[11,12] which is commonly used at 80 °C. Another family was first reported by Mortreux and Blanchard,[13] and has been subsequently refined[14] or investigated[7a,15] by others. These groups have shown that active but undefined catalysts can be generated from commercially available $Mo(CO)_6$ and various phenols in decalin, chlorobenzene, and related high-boiling solvents at 130–160 °C. Although the metathesis conditions are harsh, it is not

DOI: 10.1002/adsc.200404026

necessary to exclude oxygen or moisture, and the three-step synthesis of **1** can be avoided.

More recently, catalysts derived from Mo(N(*t*-Bu)Ar)$_3$,[16] Mo(O-1-adamantyl)$_3$, and Mo[O-(*o*-XC_6H_4)]$_3$[17,18] fragments that can be applied at room temperature have been reported. However, the syntheses are more demanding than that of **1**. For all catalyst types, methylacetylenes $RC{\equiv}CMe$ are preferred to terminal acetylenes $RC{\equiv}CH$ as substrates. With the latter, several deactivation pathways have been documented.[19] Also, methylacetylenes afford volatile 2-butyne, which is often aspirated from the reaction mixture to help displace the equilibrium.

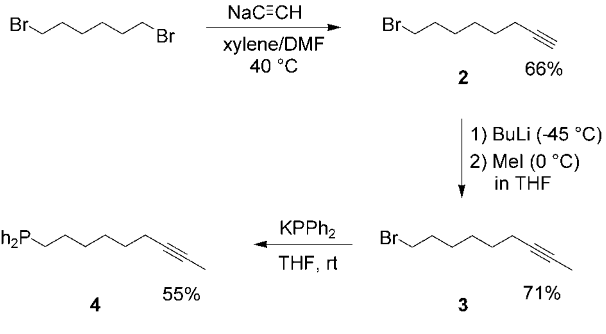
In our exploratory studies of alkene metatheses in metal coordination spheres, we made extensive use of alkene-containing phosphine ligands.[3–5] Accordingly, as described in this paper, we set out to synthesize and study representative complexes with similar alkyne-containing phosphine ligands. As detailed below, both **1** and Mo(CO)$_6$-derived catalysts can be used to effect alkyne metatheses with various octahedral and square-planar, eighteen- and sixteen-valence-electron rhenium, ruthenium, and platinum complexes. A portion of this work has been communicated.[20]

Results

Starting Ligands and Complexes

As shown in Scheme 1, the α,ω-dibromide $Br(CH_2)_6Br$ and $NaC{\equiv}CH$ were reacted at 40 °C. Distillation gave the known terminal alkyne $Br(CH_2)_6C{\equiv}CH$ (**2**)[21a] in 66% yield. A subsequent deprotonation with n-BuLi (–45 °C), followed by the addition of CH_3I (0 °C), afforded the known 2-alkyne $Br(CH_2)_6C{\equiv}CCH_3$ (**3**) in 71% yield.[21b] The reaction of **3** and commercial $KPPh_2$ gave the target phosphine $PPh_2(CH_2)_6C{\equiv}CCH_3$ (**4**) as a colorless oil in 81–55% yields after distillation.

Importantly, some disubstitution occurred during the reaction of $Br(CH_2)_6Br$ and $NaC{\equiv}CH$. Since the boiling points of this byproduct, $Br(CH_2)_6Br$, and **2** (as well as **3**) are quite close, complete separations were difficult. Thus, some starting material and disubstituted product were carried through the syntheses of **2**, **3**, and **4**. However, these were completely removed when the much heavier **4** was distilled. Phosphine **4** was stable in air on the time scale of hours, and was completely characterized by IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, mass spectrometry, and microanalysis.



Scheme 1. Synthesis of the alkyne-containing phosphine **4**.

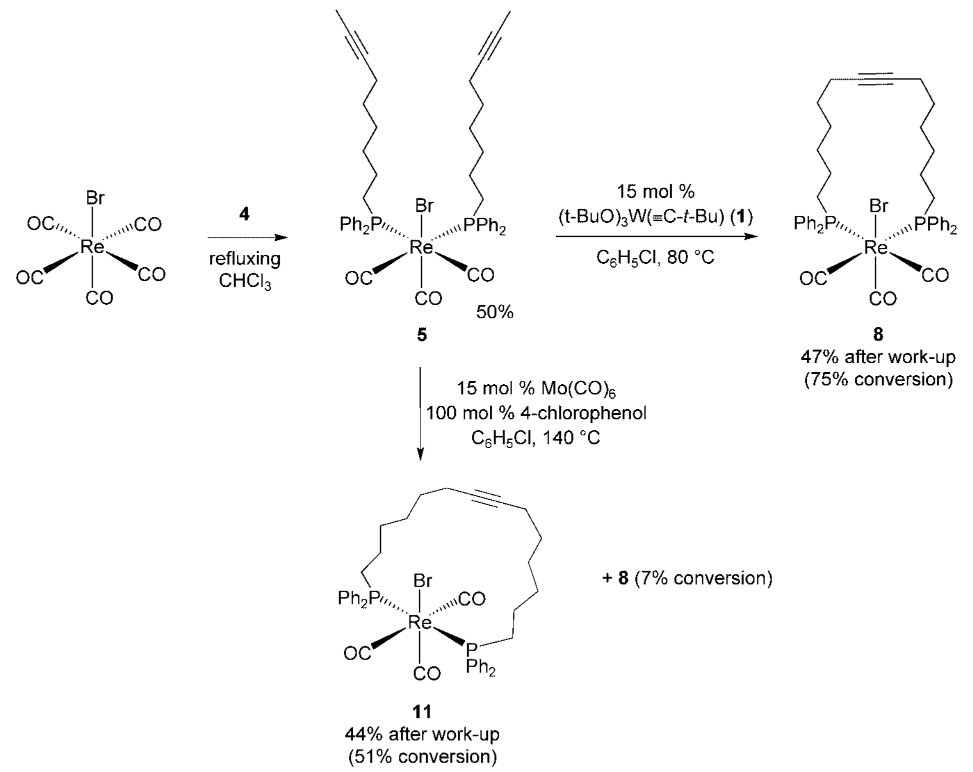
One possibility would have been to prepare monophosphine complexes from **4**, and then investigate intermolecular metatheses. However, we were more attracted to bis(phosphine) complexes with the potential for intramolecular macrocyclizations. The octahedral eighteen-valence-electron rhenium carbonyl bromide (CO)$_5$Re(Br)[22] is an established precursor to rhenium bis(phosphine) complexes.[3a,23,24] As shown in Scheme 2, a reaction with **4** in refluxing $CHCl_3$ gave the facially-substituted tricarbonyl *fac*-(CO)$_3$Re(Br)($Ph_2P(CH_2)_6C{\equiv}CCH_3$)$_2$ (**5**) in 50% yield. The course of this reaction, and the product stereochemistry, is conveniently assayed by IR spectroscopy.[24,25]

The easily-prepared half-sandwich eighteen-valence-electron ruthenium bis(phosphine) complex (η^5-C_5H_5)Ru(Cl)(PPh_3)$_2$[26] undergoes thermal phosphine exchange.[27] As shown in Scheme 3, a reaction with **4** in refluxing toluene gave the expected product (η^5-C_5H_5)Ru(Cl)($Ph_2P(CH_2)_6C{\equiv}CCH_3$)$_2$ (**6**) as orange oil in 30–38% yields after chromatography. The chlorine-bridged diplatinum complex [Pt(μ-Cl)(C_6F_5)-($S(CH_2CH_2–)_2$)]$_2$[28] is an established precursor to square-planar sixteen-valence-electron *trans* bis(phosphine) complexes.[3] As shown in Scheme 4, a reaction with **4** at room temperature afforded the anticipated adduct *trans*-(Cl)(C_6F_5)Pt($Ph_2P(CH_2)_6C{\equiv}CCH_3$)$_2$ (**7**) in 54% yield after chromatography.

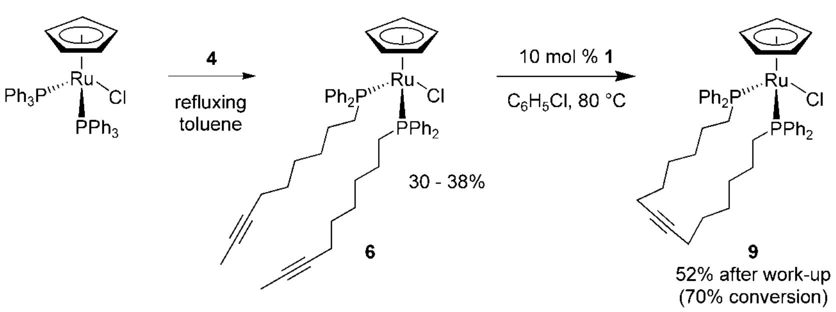
Complexes **5**, **6**, and **7** were characterized analogously to **4**, as detailed in the experimental section. However, no efforts were made to optimize yields. The spectroscopic properties matched those of closely related complexes prepared earlier.[3]

Alkyne Metatheses with 1

As shown in Scheme 2, a chlorobenzene solution of the rhenium complex **5** (*ca.* 0.022 M) and the catalyst **1** (*ca.* 7.5 mol %) were combined. The sample was heated to 80 °C, and after 1 h, a second catalyst charge (*ca.* 7.5 mol %) was added. Nitrogen was aspirated through the solution to help volatilize the 2-butyne. The solvent was removed, and a ^{31}P NMR spectrum of the crude mixture showed a 75:20:5 ratio of the product (**8**), educt **5**, and an unidentified byproduct (Experimental Section). Chromatography and crystallization gave **8** in 47% yield, which was characterized analogously to the other new complexes above.



Scheme 2. Synthesis and metathesis of alkyne-containing rhenium complexes.

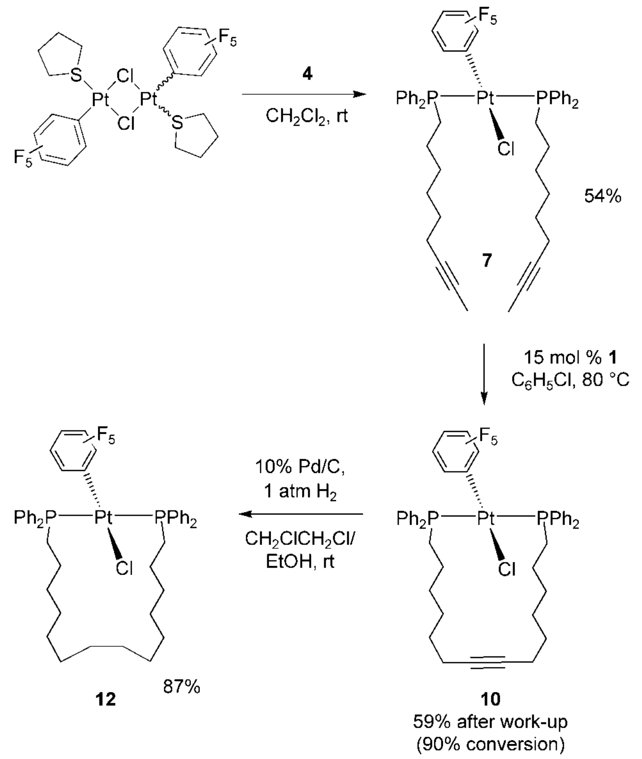


Scheme 3. Synthesis and metathesis of alkyne-containing ruthenium complexes.

The mass spectrum of **8** exhibited a molecular ion and fragments consistent with a seventeen-membered macrocycle derived from intramolecular metathesis. The ^{1}H and ^{13}C NMR spectra showed the absence of $\equiv CCH_3$ resonances, and the ^{13}C NMR spectrum gave a single $\equiv C$ signal at 80.5 ppm, as compared to 79.1 and 75.4 ppm in **5**. In order to unambiguously eliminate a dimeric or oligomeric macrocycle derived from *inter*molecular metathesis, a crystal structure was executed (below). This confirmed the formulation in Scheme 2. Note that the P*Ph* groups are diastereotopic. Consequently, two sets of *i/o/m/p* ^{13}C NMR signals are observed.

As shown in Scheme 3, chlorobenzene solutions of the ruthenium complex **6** (*ca.* 0.022 M) and **1** (15 mol %) were similarly kept at 80 °C. After two hours, a ^{31}P NMR spectrum of the crude mixture showed a 70:25:5 ratio of the product (**9**), overlapping educt and byproduct signals, and a second byproduct. Chromatography gave **9** in 52% yield. The NMR and mass spectral properties were very similar to those of **8**. Accordingly, an analogous structure was assigned, as illustrated in Scheme 3.

Intramolecular macrocyclizations involving *trans*-directed groups as in platinum complex **7** are conformationally more challenging than those involving *cis* groups as in **5** and **6**. As shown in Scheme 4, **7** and **1** were reacted in chlorobenzene as for **5** and **6**. A ^{31}P NMR spectrum of the crude mixture showed a 90:10 ratio of the product (**10**) and educt **7**. Replicate experiments showed this metathesis to be more efficient than the others. Chromatography gave **10** in 59% yield. Based upon the mass spectrum and further transformations below, **10** could be unambiguously assigned as a monoplatinum complex with an unusual *trans*-spanning



Scheme 4. Synthesis, metathesis, and hydrogenation of alkyne-containing platinum complexes.

chelating diphosphine ligand.[29] The C≡C ^{13}C NMR chemical shift was in a normal region (80.7 ppm), indicating the absence of interactions with platinum.

Alkyne Metatheses with $Mo(CO)_6$-Derived Catalysts

Since the $Mo(CO)_6$-derived alkyne metathesis catalysts require higher temperatures, the thermal stabilities of some of the preceding compounds were probed. Although the rhenium complex **5** was commonly an oil, DSC and TGA measurements were conducted with **7–10**. In all cases, only one DSC endotherm was observed, corresponding to the melting point (Experimental Section). As would be intuitively expected, the platinum macrocycle **10** melted higher than the precursor **7** (255 *vs.* 102 °C). Temperatures of 239–300 °C were required to initiate mass loss – well above the most extreme conditions used for metathesis.

A screening reaction was modeled after a standard protocol.[15a] Thus, chlorobenzene solutions of platinum complex **7** were treated with $Mo(CO)_6$ (15–22 mol %) and 4-chlorophenol (*ca.* 100 mol %). The mixtures were heated to 140 °C and nitrogen was aspirated through the solutions. After 6–18 h, the solvents were removed, and the crude mixtures analyzed by NMR. The ^{31}P NMR spectra showed **10**, **7**, and two byproducts in 53–59:39–33:5–4:3–4 ratios. The ^{1}H and ^{13}C NMR spectra confirmed the identity of **10**. However, rather than optimize these conditions further, another substrate was tested.

Thus, the rhenium complex **5** was similarly treated with $Mo(CO)_6$ and 4-chlorophenol as shown in Scheme 2. After 12 h, a ^{31}P NMR spectrum indicated the presence of a *new* complex **11**, the previously characterized macrocycle **8**, the educt **5**, and three byproducts in a 51:8:7:20:10:4 ratio. Chromatography afforded **11** as a white powder in 44% yield. Interestingly, **11** gave a mass spectrum similar to that of **8**, and the NMR properties were consistent with a comparable macrocyclic structure. However, the ^{13}C NMR spectrum showed only a single set of P*Ph* signals, as opposed to the two found with **8**. Hence, the P*Ph* groups are no longer diastereotopic.

Complexes of the formula *fac*-$(CO)_3Re(X)(PX_3)_2$ are known to thermally isomerize to meridional (*mer*) isomers.[23,24] Thus, the IR spectra of **8** and **11** were carefully compared. The former exhibited a pattern of ν_{CO} bands characteristic of a *fac*-$(CO)_3Re$ fragment (2023, 1949, 1926, 1876 cm^{-1}, s/sh/s/s).[25] However, **11** exhibited a pattern consistent with a *mer*-$(CO)_3Re$ fragment (1943, 1893 cm^{-1}, s/s).[25,30] Since **11** gave only one ^{31}P NMR signal, a *mer* isomer with two *cis* phosphorus atoms could be excluded (one would be *trans* to a bromide ligand, and the other *trans* to a carbonyl group). Hence, **11** was assigned the *mer, trans* structure shown in Scheme 2.

In view of these data, a sample of **8** was melted at 175–195 °C (*ca.* 10 min). An IR spectrum of the cooled sample showed > 90% conversion to **11**. In the DSC measurement, the exotherm that would be expected for isomerization is apparently masked by the melting endotherm. Also, a $C_6D_5NO_2$ solution of **5** was kept at 120 °C and monitored by ^{31}P NMR. Over the course of 21 h, **5** (– 8.7 ppm) disappeared. One new signal dominated (– 0.8 ppm, 50%), with a chemical shift close to that of **11**. The mass spectrum of the mixture was similar to that of **5**, consistent with the formation of a *mer* isomer. Although **11** is structurally somewhat unusual, there is ample precedent for *trans*-spanning diphosphine ligands in octahedral coordination environments.[29] Efforts to date to grow crystals have been unsuccessful.

Additional Data

The crystal structure of **8** was determined as summarized in Table 1 and the Experimental Section. Key metrical parameters are listed in Table 2, and the molecular structure is shown in Figure 1. Several features are analyzed below.

To broaden the utility of this chemistry, we sought to demonstrate that the C≡C linkages in the metathesis products can be hydrogenated. In order to simultaneously effect a structure proof, **10** was selected. As shown in Scheme 4, a reaction with H_2 (1 atm) was conducted in the presence of 10% Pd/C catalyst. Chromatography gave **12**, with a saturated $(CH_2)_{14}$ bridge between the phosphorus atoms, in 87% yield. Complex **12** has been independently prepared by an alkene metathesis/hydrogenation sequence, and crystallographically characterized.[3a, b]

Table 1. General crystallographic data for **8**.

Empirical formula	$C_{41}H_{44}BrO_3P_2Re$
Formula weight	912.81
Diffractometer	Nonius KappaCCD
Temperature [K]	173(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a, [Å]	17.9002(2)
b, [Å]	10.54090(10)
c, [Å]	22.1519(4)
α, [°]	90
β, [°]	111.074(6)
γ, [°]	90
V, [Å^3]	3900.16(9)
Z	4
ρ_{calc}, [Mg/m^3]	1.555
Absorpt. coeff. [mm^{-1}]	4.258
F(000)	1816
Crystal size, [mm^3]	$0.30 \times 0.30 \times 0.20$
θ limit, [°]	1.91 to 27.47°
Index ranges (h, k, l)	−22 to 22; −13 to 11; −28 to 28
Reflections collected	15263
Independent reflections	8887 [R(int) = 0.0247]
Reflections [$I > 2\sigma(I)$]	7175
Data/restraints/parameters	8887/0/433
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0358, wR2 = 0.0898
R indices (all data)	R1 = 0.0499, wR2 = 0.0963
Largest diff. peak and hole Δp (max), e/[Å^3]	1.277 and −1.919

Discussion

As mentioned in the introduction, alkyne metatheses of several ferrocene and ruthenocene derivatives have also been reported. As summarized in Scheme 5, all are intermolecular. Together with our results in Schemes 2–4,

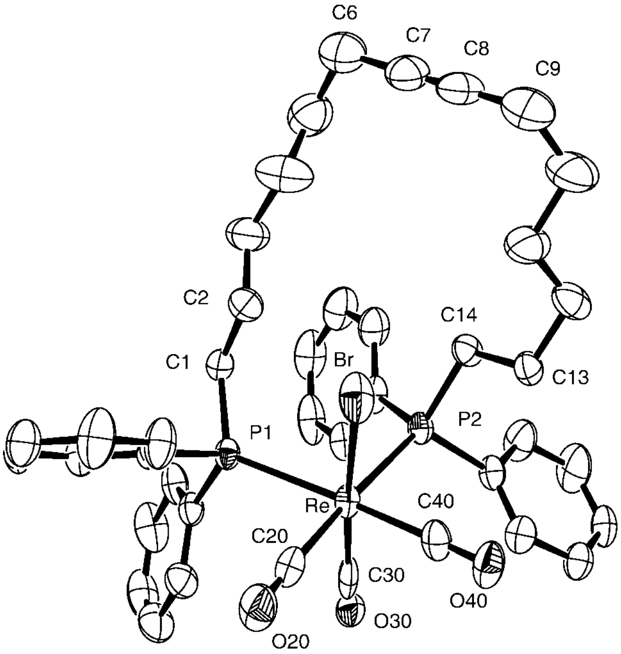
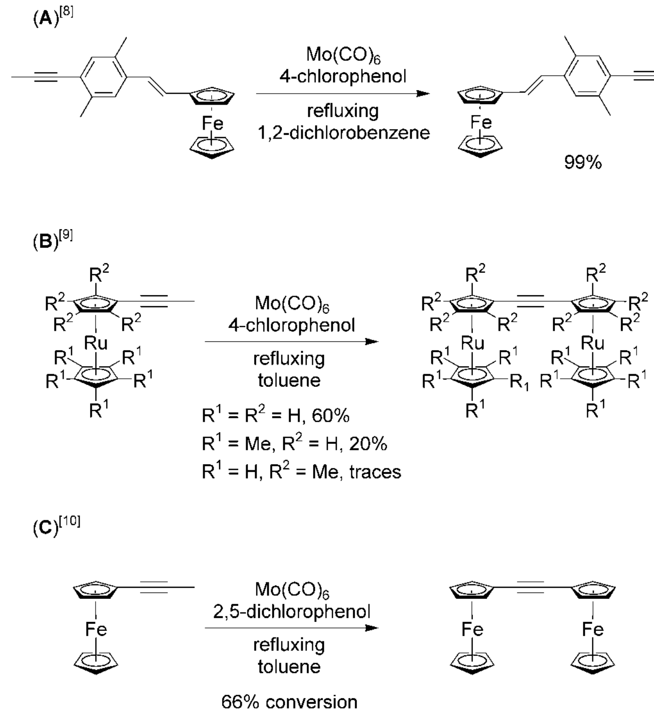


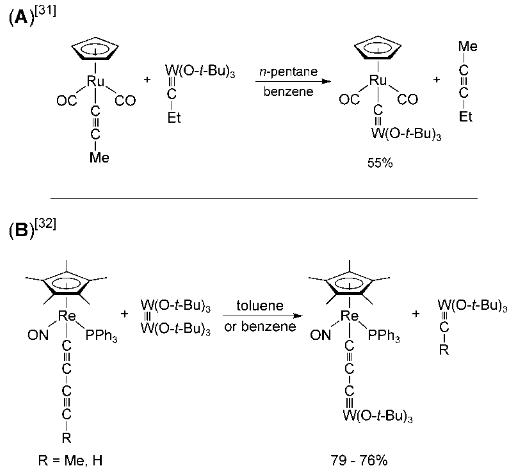
Figure 1. Molecular structure of **8**.

Table 2. Key bond lengths, bond angles, and torsion angles for **8**.

Bond lengths [Å]		Bond angles [°]		Torsion angles [°]	
Re-P(1)	2.5203(10)	C(40)-Re(1)-C(20)	87.41(18)	P(2)-Re-P(1)-C(1)	28.43(17)
Re-P(2)	2.4987(10)	C(40)-Re(1)-C(30)	91.97(19)	P(1)-Re-P(2)-C(14)	103.21(16)
Re-Br	2.6387(5)	C(20)-Re(1)-C(30)	90.00(19)	Re-P(1)-C(1)-C(2)	−56.1(4)
Re-C(20)	1.961(5)	C(40)-Re(1)-P(2)	90.36(13)	P(1)-C(1)-C(2)-C(3)	173.5(4)
Re-C(30)	2.032(7)	C(20)-Re(1)-P(2)	176.85(13)	C(1)-C(2)-C(3)-C(4)	−173.3(5)
Re-C(40)	1.936(5)	C(30)-Re-P(2)	87.85(13)	C(2)-C(3)-C(4)-C(5)	159.4(6)
C(1)-C(2)	1.546(6)	C(40)-Re-P(1)	171.21(12)	C(3)-C(4)-C(5)-C(6)	176.7(6)
C(2)-C(3)	1.492(7)	C(20)-Re-P(1)	85.41(13)	C(4)-C(5)-C(6)-C(7)	61.6(9)
C(3)-C(4)	1.596(8)	C(30)-Re-P(1)	93.09(12)	C(5)-C(6)-C(7)-C(8)	−143(18)
C(4)-C(5)	1.439(8)	P(2)-Re-P(1)	97.00(3)	C(6)-C(7)-C(8)-C(9)	38(30)
C(5)-C(6)	1.547(9)	C(40)-Re-Br(1)	83.93(14)	C(7)-C(8)-C(9)-C(10)	132(17)
C(6)-C(7)	1.454(10)	C(20)-Re-Br(1)	90.69(14)	C(8)-C(9)-C(10)-C(11)	−57.2(11)
C(7)-C(8)	1.171(9)	C(30)-Re-Br(1)	175.80(12)	C(9)-C(10)-C(11)-C(12)	171.8(7)
C(8)-C(9)	1.505(11)	P(2)-Re-Br(1)	91.29(3)	C(10)-C(11)-C(12)-C(13)	−173.6(5)
C(9)-C(10)	1.434(11)	P(1)-Re-Br(1)	91.09(3)	C(11)-C(12)-C(13)-C(14)	63.1(6)
C(10)-C(11)	1.521(8)	C(6)-C(7)-C(8)	177.7(7)	C(12)-C(13)-C(14)-P(2)	177.5(4)
C(11)-C(12)	1.482(9)	C(7)-C(8)-C(9)	177.7(8)	Re-P(2)-C(14)-C(13)	65.3(4)
C(12)-C(13)	1.511(6)				
C(13)-C(14)	1.533(6)				



Scheme 5. Alkyne metatheses involving group VIII metallocenes.



Scheme 6. Stoichiometric alkyne metatheses in metal coordination spheres.

which are all intramolecular, it is clear that metatheses can be effected with a variety of alkyne-containing metal complexes with different electronic configurations, coordination environments, and spectator ligands. This indicates that the active W≡CR and Mo≡CR catalyst species have a broad "functional group tolerance". Examples of stoichiometric alkyne metatheses in metal coordination spheres have also been reported, two of which are illustrated in Scheme 6.[31,32] These hint at an even broader degree of applicability.

Some advantages and disadvantages of the two catalyst systems investigated, **1** and $Mo(CO)_6$/4-chlorophenol, were noted in the introduction. Our results with **7** confirm that the former is much more active. With thermally robust substrates such as the metallocenes in Scheme 5, this presents no problem. However, Scheme 2 provides a nice example of a tractable side reaction that results from the harsher conditions. Our data do not establish whether it is the educt, product, or possibly a catalyst adduct that isomerizes from a *fac* to a *mer* isomer. Such isomerizations can also be effected by chemical or electrochemical oxidation/reductions cycles.[24] Hence, redox catalysis under the reaction conditions is also conceivable.

Schemes 2–4 clearly demonstrate that alkyne metathesis can be used to generate unusual metallamacrocycles, including two types of *trans*-spanning diphosphine chelates. No products derived from intermolecular metathesis are detected. The educt concentrations employed (*ca.* 0.022 M) are close to those used for related metatheses of terminal alkenes.[3] However, somewhat more effort is required to drive the alkyne metatheses to completion. Also, the examples in Scheme 5B show that steric effects can hinder catalysis.

In earlier papers, we have argued that similar alkene metatheses are often aided by some analogue of the "geminal dialkyl effect".[33] It is well known that when geminal dialkyl groups are introduced on a methylene chain (e.g., a $CH_2CR_2CH_2CH_2$ moiety), intramolecular α,ω cyclizations are promoted. The alkyl groups render the energies of *anti* and *gauche* conformations much closer; when only *anti* linkages are present, the termini cannot approach each other. A PPh_2, MPPh, or similar group might play a role analogous to a CR_2 group in making *gauche* conformations of four-atom segments energetically more competitive. Shaw has furthermore studied reactions of diphosphines $R_2P(CH_2)_nPR_2$ and square planar complexes that lead to *trans* substitution products.[34] He finds that the ratio of monometallic to di- and polymetallic products dramatically increases with the size of the phosphorus substituent.

Accordingly, the Re-PPh_2-C(14)-C(13) and Re-PPh_2-C(1)-C(2) linkages in crystalline **8** (Figure 1) exhibit *gauche* conformations, with torsion angles of 65.3(4)° and −56.1(4)°. The neighboring P(1)-C(1)-C(2)-C(3) and C(12)-C(13)-C(14)-P(2) segments adopt *anti* conformations. Of the eleven four-carbon segments, four exhibit *gauche* conformations, including the two that terminate with the $C\equiv C$ linkage. The bond lengths and angles about rhenium are unexceptional, and comparable to those found earlier in analogous complexes in which *cis*-C=C and CH_2CH_2 moieties have replaced the alkyne.[3a] These were prepared by alkene metatheses and subsequent hydrogenation. The four Re-PPh_2-C-C segments in these complexes also adopt *gauche* conformations.

Conclusion

In summary, this study has demonstrated that tungsten- and molybdenum-catalyzed alkyne metatheses can be effected with octahedral and square-planar, eighteen- and sixteen-valence-electron rhenium, ruthenium, and platinum complexes. Metallamacrocycles such as **8–11** can be readily generated under only moderately dilute conditions, with no appreciable quantities of byproducts. In accord with past observations, the Schrock catalyst **1** has superior performance characteristics. This methodology provides a valuable complement to related alkene metatheses developed earlier. Taken together, these efforts are significantly advancing the applicability of metal-catalyzed metathesis reactions to the synthesis of architecturally unusual inorganic and organometallic assemblies.

Experimental Section

General

Most experimental and instrumental procedures were analogous to those in previous full papers.[3] Solvents and reagents were used as follows: THF, Et_2O, benzene, hexane, toluene, and xylene, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2 (reactions) or simple distillation (chromatography); DMF (99%, Fluka), distilled from CaH_2; $CHCl_3$ and chlorobenzene, distilled from P_2O_5; ethanol and hexanes, simple distillation; $ClCH_2CH_2Cl$ (99%, Fluka), $NaC\equiv CH$ (Acros, 18% in xylene/light oil, 95%), CH_3I (99%, Riedel-de Haën), $HPPh_2$ (Aldrich), Pd/C (Fluka), $KPPh_2$ (Aldrich, 0.5 M in THF), $Mo(CO)_6$ (98%, ABCR), and 4-chlorophenol (99%, Lancaster) used as received; $Br(CH_2)_6Br$ (96%, EGA-Chemie) vacuum distilled; n-BuLi (Aldrich, 2.1 M in hexane), standardized.[35]

$Br(CH_2)_6C\equiv CH$ (2)[21a]

A three-necked flask was charged with $NaC\equiv CH$ (18% in xylene/ light oil, 95% purity; 9.152 g, 32.59 mmol) and DMF/xylene (100 mL, 37.5 : 62.5 v/v), and fitted with a dropping funnel and a condenser. The mixture was heated to 40 °C, and $Br(CH_2)_6Br$ (5.01 mL, 7.946 g, 33 mmol) was added over a period of 20 min. After 12 h, the mixture was filtered. The filtrate was fractionally distilled to give **2** (bp *ca.* 70 °C/1.3×10^{-3} mbar) as a colorless liquid; yield: 4.040 g (21.4 mmol, 66%).[36] ^1H NMR ($CDCl_3$): $\delta = 3.41$ (t, $^3J_{HH} = 6.6$ Hz, $BrCH_2$), 2.22–2.17 (td, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 2.7$ Hz, $CH_2C\equiv$), 1.95 (t, $^4J_{HH} = 2.7$ Hz, $\equiv CH$), 1.92–1.82 (m, CH_2), 1.60–1.40 (m, $3CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 84.6$ (s, $CH_2C\equiv$), 68.5 (s, $\equiv CH$), 34.0 (s, $BrCH_2$), 32.8 (s, $BrCH_2CH_2$), 28.4, 28.0, 27.5 (3 s, $CH_2CH_2CH_2CH_2C\equiv$), 18.5 (s, $CH_2C\equiv$); IR ν = (CH_2Cl_2): 3306 (w, $\nu_{0\equiv CH}$), 2116 cm^{-1} (s, $\nu_{C\equiv C}$).

$Br(CH_2)_6C\equiv CCH_3$ (3)[21b]

A Schlenk flask was charged with **2** (0.943 g, 4.99 mmol) and THF (20 mL), and cooled to −45 °C (CO_2/2-propanol). Then *n*-BuLi (2.1 M in hexane; 2.5 mL, 5.3 mmol) was added with stirring. After 10 min, the −45 °C bath was replaced by a 0 °C bath. After another 10 min, CH_3I (3.0 mL, 48 mmol) was added, and the 0 °C bath was removed. After 3 h, the solution was passed through a silica gel plug (2 × 3 cm). The solvent was removed from the filtrate by oil pump vacuum. Vacuum distillation gave **3** (bp *ca.* 95 °C/1.3×10^{-3} mbar) as a colorless liquid; yield: 0.721 g (3.55 mmol, 71%). ^1H NMR ($CDCl_3$): $\delta = 3.43$ (t, $^3J_{HH} = 8.3$ Hz, $BrCH_2$), 2.16–2.11 (m, $CH_2C\equiv C$), 1.89–1.87 (m, CH_2), 1.78 (t, $^5J_{HH} = 2.9$ Hz, CH_3), 1.59–1.39 (m, $3CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 79.0$ (s, $CH_2C\equiv C$), 75.5 (s, $C\equiv CCH_3$), 33.8 (s, $BrCH_2$), 32.7 (s, $BrCH_2CH_2$), 28.8, 27.9, 27.7 (3 s, $CH_2CH_2CH_2CH_2C\equiv$), 18.6 (s, $CH_2C\equiv$), 3.4 (s, $\equiv CCH_3$).

$PPh_2(CH_2)_6C\equiv CCH_3$ (4)

A Schlenk flask was charged with **3** (1.328 g, 6.54 mmol) and THF (22 mL), and cooled to 0 °C. Then $KPPh_2$ (0.5 M in THF; 13 mL, 6.5 mmol) was added dropwise with stirring over 15 min. A precipitate formed, and near the end of the addition the mixture turned red. After 30 min, the cold bath was removed. After 30 min, the solvent was removed by oil pump vacuum, giving a white solid suspended in an oil. The residue was extracted with hexanes (3 × 15 mL). The extract was filtered, and the solvent removed by rotary evaporation. The residue was vacuum distilled (150 °C/10^{-2} mbar) to give **4** as a viscous colorless liquid; yield: 1.111 g (3.60 mmol, 55%). Anal. calcd. for $C_{21}H_{25}P$: C 81.79, H 8.17; found: C 81.41, H, 8.21. ^1H NMR ($CDCl_3$): $\delta = 7.47–7.32$ (m, 2Ph), 2.14–2.02 (m, PCH_2 and $CH_2C\equiv C$), 1.78 (t, $^5J_{HH} = 3.2$ Hz, CH_3), 1.52–1.36 (m, $4CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$):[37] $\delta = 139.2$ (d, $^1J_{CP} =$

12.6 Hz, *i*-Ph), 132.9 (d, $^2J_{CP}$=18.1 Hz, *o*-Ph), 128.6 (d, $^3J_{CP}$=9.1 Hz, *m*-Ph), 128.6 (s, *p*-Ph), 79.5 (s, CH$_2$*C*≡), 75.6 (s, ≡*C*CH$_3$), 31.0 (d, $^3J_{CP}$=12.6 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.1, 28.7 (2 s, *C*H$_2$*C*H$_2$CH$_2$C≡), 28.2 (d, $^1J_{CP}$=11.1 Hz, P*C*H$_2$), 26.1 (d, $^2J_{CP}$=16.1 Hz, PCH$_2$*C*H$_2$), 18.9 (s, *C*H$_2$C≡), 3.7 (s, *C*H$_3$); ^{31}P {^{1}H} NMR (CDCl$_3$): δ=−15.6 (s). IR (liquid film): ν=3073 (w), 3053 (w), 2930 (m), 2856 (m), 1482 (s), 1432 (s), 1096 (m), 1027 (m), 737 (s), 695 cm^{-1} (s). MS:[38] *m/z*=309 (**4**$^+$, 100%).

fac-(CO)$_3$Re(Br)(PPh$_2$(CH$_2$)$_6$C≡CCH$_3$)$_2$ (5)

A Schlenk flask was charged with (CO)$_5$Re(Br) (0.289 g, 0.713 mmol),[22] **4** (0.440 g, 1.427 mmol), and CHCl$_3$ (12 mL), and fitted with a condenser with a nitrogen inlet/bubbler on top. The mixture was refluxed (46 h) under a nitrogen flow.[39] The solvent was removed by oil pump vacuum. The residue was chromatographed (12 × 2.5 cm column; neutral Al$_2$O$_3$, 1:1 v/v CH$_2$Cl$_2$/hexanes). The solvent was removed from the product fraction by oil pump vacuum to give **5** as a colorless oil which solidified after several days; yield: 0.344 g (0.356 mmol, 50%). Anal. calcd. for C$_{45}$H$_{50}$BrO$_3$P$_2$Re: C 55.90, H 5.21; found: C 55.20, H 5.18. ^{1}H NMR (CDCl$_3$): δ=7.43–7.28 (m, 4Ph), 2.63–2.58 (m, 2PC*H*H′), 2.08–2.04 (m, 2C*H$_2$*C≡), 1.92 (m, 2PCH*H′*), 1.78–1.77 (t, $^5J_{HH}$=5.0 Hz, 2C*H$_3$*), 1.36–1.30 (m, 2C*H$_2$*), 1.20 (m, 4C*H$_2$*), 1.00–0.99 (m, 2C*H$_2$*); ^{13}C{^{1}H} NMR (CDCl$_3$):[40] δ=189.8 (br s, *C*O), 189.2 (br s, 2*C*O), 133.5–131.8 (complex, *i*-Ph), 133.1 (virtual t,[41] J_{CP}=4.5 Hz, *o*-Ph), 132.8 (virtual t,[41] J_{CP}=4.7 Hz, *o*-Ph′), 130.0 (s, *p*-Ph), 128.2 (m, *m*-Ph), 79.1 (s, CH$_2$*C*≡), 75.4 (s, ≡*C*CH$_3$), 30.4 (virtual t,[41] J_{CP}=5.9 Hz, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.2 (s, *C*H$_2$), 26.3 (virtual t,[41] J_{CP}=13.4 Hz, *C*H$_2$), 23.8 (br s, *C*H$_2$), 18.6 (s, *C*H$_2$C≡), 3.5 (s, *C*H$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ=−8.5 (s). IR (powder film): ν=3057 (w), 2934 (m), 2856 (m), 2104 (m), 2026 (s, ν_{CO}), 1999 (sh), 1938 (s, ν_{CO}), 1895 (s, ν_{CO}), 1482 (m), 1436 (m), 1096 (m), 741 (s), 695 cm^{-1} (s); IR (CHCl$_3$, partial): ν=2033 (s, ν_{CO}), 1952 (s, ν_{CO}), 1906 cm^{-1} (s, ν_{CO}). MS:38 *m/z*=966 (**5**$^+$, <5%), 910 ([**5**–2CO]$^+$, 20%), 987 ([**5** – Br]$^+$, 30%), 600 ([**5**–PPh$_2$R–2CO]$^+$, 20%), 574 ([**5**–PPh$_2$R–3CO]$^+$, 40%), 549 ([**5**–PPh$_2$R–Br–CO]$^+$, 35%), 309 (PPh$_2$R$^+$, 100%).

(η^5-C$_5$H$_5$)Ru(Cl)(PPh$_2$(CH$_2$)$_6$C≡CCH$_3$)$_2$ (6)

A Schlenk flask was charged with (η^5-C$_5$H$_5$)Ru(Cl)(PPh$_3$)$_2$ (0.235 g, 0.324 mmol),[26a] **4** (0.250 g, 0.811 mmol), and toluene (2.5 mL), and fitted with a condenser with a nitrogen inlet/bubbler on top. The orange suspension was refluxed (18 h) under a nitrogen flow. The solvent was removed by oil pump vacuum. The residue was chromatographed using a Chromatotron® (2 cm silica gel plate, 1:1 v/v Et$_2$O/hexanes). The solvent was removed from the product fraction by oil pump vacuum to afford **6** as an orange oil; yield: 0.080 g (0.098 mmol, 30%). Anal. calcd. for C$_{47}$H$_{55}$ClP$_2$Ru: C 68.98, H 6.77; found: C 69.07, H 6.85. ^{1}H NMR (CDCl$_3$): δ=7.40–7.18 (m, 4Ph), 4.19 (s, C$_5$H$_5$), 2.54–2.48 (m, 2PC*H*H′), 2.07–2.03 (m, 2C*H$_2$*C≡), 1.77 (t, $^5J_{HH}$=5.0 Hz, 2C*H$_3$*), 1.49–1.47 (m, 2PCH*H′*), 1.36–1.30 (m, 2C*H$_2$*); 1.18–1.05 (m, 6C*H$_2$*); ^{13}C{^{1}H} NMR (CDCl$_3$):[40] δ=138.8–138.4 (complex, *i*-Ph), 132.8 (virtual t,[41] J_{CP}=4.8 Hz, *o*-Ph), 132.1 (virtual t,[41] J_{CP}=4.2, *o*-Ph′), 128.8 (s, *p*-Ph), 128.6 (s, *p*-Ph′), 127.9 (virtual t,[41] J_{CP}=4.0 Hz, *m*-Ph), 127.5 (virtual t,[41] J_{CP}=4.4 Hz, *m*-Ph′), 79.9 (s, *C*$_5$H$_5$), 79.3 (s, CH$_2$*C*≡), 75.3 (s, ≡*C*CH$_3$), 30.7 (virtual t,[41] J_{CP}=5.7 Hz, *C*H$_2$), 28.9 (s, *C*H$_2$), 28.4 (s, *C*H$_2$), 26.5 (m, *C*H$_2$), 24.5 (br s, *C*H$_2$), 18.6 (s, *C*H$_2$C≡), 3.5 (s, *C*H$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ=37.5 (s). IR (powder film): ν=3049 (w), 2922 (m), 2856 (m), 1432 (m), 1092 cm^{-1} (m). MS:[38] *m/z*=818 (**6**$^+$, 100%), 783 ([**6**–Cl]$^+$, 45%), 510 ([**6**–PPh$_2$R]$^+$, 75%), 473 ([**6**–PPh$_2$R–Cl]$^+$, 85%), 309 (PPh$_2$R$^+$, 95%).

trans-(Cl)(C$_6$F$_5$)Pt(PPh$_2$(CH$_2$)$_6$C≡CCH$_3$)$_2$ (7)

A Schlenk flask was charged with [Pt(μ-Cl)(C$_6$F$_5$)(S(CH$_2$CH$_2$-)$_2$)]$_2$ (0.394 g, 0.405 mmol),[28] **4** (0.500 g, 1.621 mmol), and CH$_2$Cl$_2$ (23 mL). The mixture was stirred (16 h) and the solvent was removed by oil pump vacuum. The residue was chromatographed (10 × 2.5 cm column; neutral Al$_2$O$_3$, 1:1 v/v CH$_2$Cl$_2$/hexanes). The solvent was removed from the product fraction by oil pump vacuum to give **7** as a colorless oil which solidified after several days; yield: 0.444 g (0.438 mmol, 54%); mp 102 °C (DSC; T$_i$/T$_e$/T$_p$/T$_c$/T$_f$ 81.2/101.5/105.1/108.8/116.8 °C).[42] TGA: onset of mass loss, 239.4 °C (T$_e$). Anal. calcd. for C$_{48}$H$_{50}$ClF$_5$PPt: C 56.84, H 4.97; found: C 56.96, H 5.10. ^{1}H NMR (CDCl$_3$): δ=7.45–7.41 (m, 8H of 4Ph), 7.28–7.18 (m, 12H of 4Ph), 2.53–2.52 (m, 2PC*H$_2$*), 2.06–2.05 (m, 2C*H$_2$*C≡), 1.85 (m, 2PCH$_2$C*H$_2$*), 1.72 (t, $^5J_{HH}$=5.0 Hz, 2C*H$_3$*), 1.44–1.30 (m, 6C*H$_2$*); ^{13}C{^{1}H} NMR (CDCl$_3$):[40,43,44] δ=133.0 (virtual t,[41] J_{CP}=5.8 Hz, *o*-Ph), 130.8 (virtual t,[41] J_{CP}=27.0 Hz, *i*-Ph), 130.2 (s, *p*-Ph), 128.0 (virtual t,[41] J_{CP}=5.0 Hz, *m*-Ph), 79.2 (s, CH$_2$*C*≡), 75.5 (s, ≡*C*CH$_3$), 30.9 (virtual t,[41] J_{CP}=7.3 Hz, PCH$_2$CH$_2$*C*H$_2$), 28.8 (s, *C*H$_2$), 28.5 (s, *C*H$_2$), 25.9 (virtual t,[41] J_{CP}=16.8 Hz, P*C*H$_2$), 25.5 (s, PCH$_2$*C*H$_2$), 18.7 (s, *C*H$_2$C≡), 3.5 (s, *C*H$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ=16.4 (s, $^1J_{PPt}$=2660 Hz).[45] IR (powder film): ν=3057 (w), 2934 (m), 2856 (m), 1502 (s), 1459 (s), 1436 (s), 1100 (m), 1058 (s), 953 (s), 807 (m), 737 (s), 691 (cm^{-1} s). MS:[38] *m/z*=1013 (**7**$^+$, 15%), 978 ([**7**–Cl]$^+$, 80%), 810 ([**7**–Cl–C$_6$F$_5$]$^+$, 20%), 501 ([**7**–Cl–C$_6$F$_5$–PPh$_2$R]$^+$, 100%).

fac-(CO)$_3$Re(Br)(Ph$_2$P(CH$_2$)$_6$C≡C(CH$_2$)$_6$PPh$_2$) (8)

A Schlenk flask was charged with **5** (0.052 g, 0.054 mmol), chlorobenzene (5.9 mL; the resulting solution is 0.022 M in **5**) and *ca.* half of the catalyst (*t*-BuO)$_3$W(≡C-*t*-Bu) (**1**; 0.004 g, 0.008 mmol, 15 mol%).[12] A nitrogen stream was bubbled through the solution, which was stirred at 80 °C. After 1 h, the remaining catalyst was added. After 1 h, the solvent was removed by oil pump vacuum and a ^{31}P{^{1}H} NMR spectrum recorded (δ, CDCl$_3$): −5.3 (s, 5%), −8.3 (s, 75%, **8**), −8.5 (s, 20%, **5**). The residue was extracted with CH$_2$Cl$_2$/hexanes (1:1 v/v). The extract was filtered through neutral Al$_2$O$_3$ (2.5 × 4 cm pad, 1:1 v/v CH$_2$Cl$_2$/hexanes). The solvent was removed by rotary evaporation and oil pump vacuum. The residue was dissolved in a minimum of CH$_2$Cl$_2$, layered with ethanol, and stored at −18 °C. After 4 days, the white crystals were collected by filtration and dried by oil pump vacuum (with loss of crystallinity) to give **8** as a white powder; yield: 0.023 g (0.025 mmol, 47%), mp 174 °C (capillary), 170 °C (DSC: T$_i$/T$_e$/T$_p$/T$_c$/T$_f$ 137.3/169.7/182.1/184.6/185.4 °C).[42] TGA: onset of mass loss, 293 °C (T$_e$). Anal. calcd. for C$_{41}$H$_{44}$BrO$_3$P$_2$Re: C

53.95, H 4.86; found: C 54.14, H 5.06. ^{1}H NMR ($CDCl_3$): δ = 7.80–7.70 (m, 4H of 4Ph), 7.37–7.28 (m, 16H of 4Ph), 2.86–2.82 (m, 2PC*H*H′), 2.25–2.17 (m, 2PCH*H′* and 2C*H*$_2$C≡), 1.56–1.25 (m, 8C*H*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$):[40] δ = 189.7 (br s, *C*O), 189.4 (br s, 2*C*O), 134.4–132.5 (complex, *i*-Ph), 133.0 (virtual t,[41] J_{CP} = 4.5 Hz, *o*-Ph), 132.6 (virtual t,[41] J_{CP} = 4.6 Hz, *o*-Ph′), 129.91 (s, *p*-Ph), 129.86 (s, *p*-Ph′), 128.5 (virtual t,[41] J_{CP} = 4.5 Hz, *m*-Ph), 128.1 (virtual t, J_{CP} = 4.7 Hz, *m*-Ph′), 80.5 (s, *C*≡), 30.2 (virtual t, J_{CP} = 6.0 Hz, *C*H$_2$), 28.7 (s, *C*H$_2$), 27.7 (s, *C*H$_2$), 25.6 (virtual t,[41] J_{CP} = 12.1 Hz, *C*H$_2$), 24.2 (br s, *C*H$_2$), 18.6 (s, CH$_2$C≡); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −8.3 (s). IR (powder film): ν = 3053 (w), 2926 (m), 2856 (m), 2023 (s, ν_{CO}), 1949 (sh), 1926 (s, ν_{CO}), 1876 (s, ν_{CO}), 1482 (m), 1436 (m), 1096 (m), 741(s), 695 cm^{-1} (s). MS:[38] *m/z* = 912 (**8**$^+$, 40%), 856 ([**8**–2CO]$^+$, 65%), 833 ([**8**–Br]$^+$, 100%).

***mer,trans*-$(CO)_3Re(Br)(Ph_2P(CH_2)_6C\equiv C(CH_2)_6PPh_2)$ (11)**

A Schlenk flask was charged with **5** (0.100 g, 0.0493 mmol), chlorobenzene (20 mL; the resulting solution is *ca.* 0.005 M in **5**), $Mo(CO)_6$ (*ca.* 0.002 g, *ca.* 0.0076 mmol, *ca.* 15 mol %), and 4-chlorophenol (0.006 g, 0.05 mmol). A nitrogen stream was bubbled through the solution, which was stirred at 140 °C. After 1.5 h, the reaction mixture had turned tan. After 12 h, the solvent was removed by oil pump vacuum and a ^{31}P{^{1}H} NMR spectrum recorded (δ, $CDCl_3$): 1.0 (**11**, 51%), 0.3 (10%), 0.1 (4%), 0.5 (20%), −8.3 (**8**, 8%), −8.5 (**5**, 7%). The sample was chromatographed (10 × 2.5 cm column; neutral Al_2O_3; 1:1 v/v CH_2Cl_2/hexanes) to give **11** as a white powder; yield: 0.042 g (0.046 mmol, 44%), mp 190–192 °C (capillary), 171 °C (DSC: 146.0/170.9/181.6/189.3/195.0 °C).[42] TGA: onset of mass loss, 299 °C (T_e). Anal. calcd. for $C_{41}H_{44}BrO_3P_2Re$: C 53.95, H 4.86; found: C 54.07, H 4.94. ^{1}H NMR ($CDCl_3$): δ = 7.65–7.63 (m, 8H of 4Ph), 7.44–7.28 (m, 12H of 4Ph), 2.78–2.76 (m, 2PC*H*$_2$), 2.13–2.06 (m, 2C*H*$_2$C≡), 1.62–1.33 (m, 8C*H*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$):[40,43] δ = 136.4 (virtual t,[41] J_{CP} = 23.0 Hz, *i*-Ph), 132.4 (virtual t,[41] J_{CP} = 5.1 Hz, *o*-Ph), 129.9 (s, *p*-Ph), 128.4 (virtual t,[41] J_{CP} = 4.6 Hz, *m*-Ph), 80.6 (s, *C*≡), 30.2 (virtual t,[41] J_{CP} = 8.1 Hz, *C*H$_2$), 30.0 (virtual t,[41] J_{CP} = 15.4, *C*H$_2$), 28.6 (s, *C*H$_2$), 28.4 (s, *C*H$_2$), 23.9 (br s, *C*H$_2$), 18.7 (s, *C*H$_2$C≡); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 1.0 (s). IR (powder film): ν = 2927 (m), 2852 (m), 1943 (s, ν_{CO}), 1893 (s, ν_{CO}), 1434 (m), 1094 (m), 737 (s), 692 cm^{-1} (s). MS:[38] *m/z* = 912 (**11**$^+$, 40%), 856 ([**11**–2CO]$^+$, 100%), 833 ([**11**–Br]$^+$, 70%), 826 ([**11**–3CO]$^+$, 80%).

$(\eta^5\text{-}C_5H_5)Ru(Cl)(Ph_2P(CH_2)_6C\equiv C(CH_2)_6PPh_2)$ (9)

A Schlenk flask was charged with **6** (0.227 g, 0.277 mmol), chlorobenzene (12.5 mL; the resulting solution is 0.022 M in **6**), and *ca.* half of the catalyst **1** (0.013 g, 0.028 mmol, 10 mol %).[12] A nitrogen stream was bubbled through the solution, which was stirred at 80 °C. After 1 h, the remaining catalyst was added. After 1 h, the solvent was removed by oil pump vacuum and a ^{31}P{^{1}H} NMR spectrum recorded (δ, $CDCl_3$): 40.4 (s, 70%, **9**), 38.0 (s, 5%), 37.5/37.4 (overlapping s, 25%, **6**). The residue was extracted with Et_2O/hexanes (1:1 v/v). The extract was chromatographed (10 × 2.5 cm column; neutral Al_2O_3, 1:1 v/v Et_2O/hexanes). The product fractions were concentrated to *ca.* 10 mL and stored at −18 °C (16 h). The precipitate was collected by filtration and dried by oil pump vacuum to give **9** as an orange powder; yield: 0.111 g (0.145 mmol, 52%), mp 178 °C (capillary), 203 °C (DSC; $T_i/T_e/T_p/T_c/T_f$ 194.1/203.3/208.8/211.0/216.3 °C).[42] TGA: onset of mass loss, 300.2 °C (T_e). Anal. calcd. for $C_{43}H_{49}ClP_2Ru$: C 67.57, H 6.46; found: C 66.74, H 6.62 (NMR spectra show baseline purity). ^{1}H NMR ($CDCl_3$): δ = 7.76–7.74 (m, 4H of 4Ph), 7.34–7.32 (m, 6H of 4Ph), 7.31–7.28 (m, 2H of 4Ph), 7.13–7.10 (m, 4H of 4Ph), 6.92 (m, 4H of 4Ph), 4.07 (s, C$_5$*H*$_5$), 2.95–2.88 (m, 2PC*H*H′), 2.20 (m, 2C*H*$_2$C≡), 1.97 (m, 2PCH*H′*), 1.64–1.18 (m, 8C*H*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$):[40] δ = 139.8–139.4 (complex, *i*-Ph), 137.1–136.7 (complex, *i*-Ph′), 133.0 (virtual t,[41] J_{CP} = 5.0 Hz, *o*-Ph), 131.3 (virtual t,[41] J_{CP} = 4.6 Hz, *o*-Ph′), 128.7 (s, *p*-Ph), 128.2 (s, *p*-Ph′), 128.0 (virtual t,[41] J_{CP} = 4.2 Hz, *m*-Ph), 127.4 (virtual t,[41] J_{CP} = 4.7 Hz, *m*-Ph′), 81.0 (s, *C*$_5$H$_5$), 80.3 (s, *C*≡), 30.5 (virtual t,[41] J_{CP} = 5.2 Hz, *C*H$_2$), 29.1 (s, *C*H$_2$), 27.5 (s, *C*H$_2$), 25.4 (m, *C*H$_2$), 25.0 (virtual t,[41] J_{CP} = 9.9 Hz, *C*H$_2$), 18.3 (s, *C*H$_2$C≡); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 40.4 (s). IR (powder film): ν = 3053 (w), 2930 (m), 2856 (m), 1482 (m), 1432 (m), 1092 cm^{-1} (m). MS:[38] *m/z* = 764 (**9**$^+$, 100%), 729 ([**9**–Cl]$^+$, 60%).

***trans*-$(Cl)(C_6F_5)Pt(PPh_2(CH_2)_6C\equiv C(CH_2)_6PPh_2)$ (10)**

Method A: A Schlenk flask was charged with **7** (0.210 g, 0.207 mmol), chlorobenzene (10.0 mL; the resulting solution is 0.021 M in **7**), and *ca.* half of the catalyst **1** (0.016 g, 0.031 mmol, 15 mol%).[12] A nitrogen stream was bubbled through the solution, which was stirred at 80 °C. After 1 h, the remaining catalyst was added. After 1 h, the solvent was removed by oil pump vacuum and a ^{31}P{^{1}H} NMR spectrum recorded (δ, $CDCl_3$): 17.3 (s, $^1J_{PPt}$ = 2681 Hz,[45] 90%, **10**), 16.4 (s, $^1J_{PPt}$ = 2657 Hz,[45] 10%, **7**). The tan powder was extracted with CH_2Cl_2. The extract was chromatographed (12 × 2.5 cm column; neutral Al_2O_3, 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed by rotary evaporation and oil pump vacuum to give **10** as a white powder; yield: 0.117 g (0.122 mmol, 59%), mp 244 °C (capillary), 255 °C (DSC; $T_i/T_e/T_p/T_c/T_f$ 241.5/254.6/256.7/258.3/266.3 °C).[42] TGA: onset of mass loss, 291.3 °C (T_e). Anal. calcd. for $C_{44}H_{44}ClF_5P_2Pt$: C 55.03, H 4.62; found: C 54.76, H 4.82. ^{1}H NMR ($CDCl_3$): δ = 7.49–7.44 (m, 8H of 4Ph), 7.32–7.21 (m, 12H of 4Ph), 2.70–2.66 (m, 2PC*H*$_2$), 2.34–2.33 (t, $^3J_{HH}$ = 11 Hz, 2C*H*$_2$C≡), 2.23 (m, 2PCH$_2$C*H*$_2$), 1.77–1.70 (m, 2PCH$_2$CH$_2$C*H*$_2$), 1.68–1.25 (m, 4C*H*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$):[40,44] δ = 145.0 (dm, $^1J_{CF}$ = 210 Hz, *o*-C$_6$F$_5$), 136.0 (dm, $^1J_{CF}$ = 237 Hz, *m/p*-C$_6$F$_5$), 132.7 (virtual t,[41] J_{CP} = 5.8 Hz, *o*-Ph), 131.8 (virtual t,[41] J_{CP} = 27.5 Hz, *i*-Ph), 130.1 (s, *p*-Ph), 128.0 (virtual t,[41] J_{CP} = 5.5 Hz, *m*-Ph), 80.7 (s, *C*≡), 31.7 (virtual t,[41] J_{CP} = 8.5 Hz, PCH$_2$CH$_2$*C*H$_2$), 28.9 (s, *C*H$_2$), 28.6 (s, *C*H$_2$), 27.4 (s, *C*H$_2$), 26.9 (virtual t,[41] J_{CP} = 17.4 Hz, P*C*H$_2$), 18.7 (s, *C*H$_2$C≡); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 17.3 (s, $^1J_{PPt}$ = 2683 Hz).[45] IR (powder film): ν = 3057 (w), 2934 (m), 2856 (m), 1502 (s), 1459 (s), 1436 (s), 1100 (m), 1058 (s), 1023 (m), 953 (s), 803 (m), 737 (s), 691 cm^{-1} (s). MS:[38] *m/z* = 960 (**10**$^+$, < 1%), 924 ([**10**–Cl]$^+$, 100%), 755 ([**10**–Cl–C$_6$F$_5$]$^+$, 95%).

Method B: A Schlenk flask was charged with **7** (0.050 g, 0.0493 mmol), chlorobenzene (10.0 mL; the resulting solution is *ca.* 0.005 M in **7**), $Mo(CO)_6$ (*ca.* 0.002 g, *ca.* 0.0076 mmol, *ca.* 15 mol %), and 4-chlorophenol (0.006 g, 0.05 mmol). A nitrogen stream was bubbled through the solution, which was stirred at 140 °C. After 1.5 h, the reaction mixture had become tan. After 6 h, the solvent was removed by oil pump vacuum and NMR spectra were recorded (δ, $CDCl_3$): ^1H (partial) 0.91 (t, $^5J_{HH} = 5.1$ Hz, 0.8H, CH_3); $^{13}C\{^1H\}$ (partial) 80.7 (s, $C\equiv$); $^{31}P\{^1H\}$ 17.3 (s, $^1J_{PPt} = 2681$ Hz,[45] 53%, **10**), 16.8 (s, 5%), 16.5 (s, $^1J_{PPt} = 2657$ Hz,[45] 39%, **7**), 15.8 (s, 3%). A second similar experiment [0.036 g of **7**, *ca.* 22 mol % of $Mo(CO)_6$, 19 h] gave a 59:4:33:4 ratio.

***trans*-$(Cl)(C_6F_5)\overline{Pt(PPh_2(CH_2)_{14}P}Ph_2)$ (12)[3a,b]**

A Schlenk flask was charged with **10** (0.045 g, 0.056 mmol), 10% Pd/C (0.006 g, 0.006 mmol Pd), $ClCH_2CH_2Cl$ (3 mL), and ethanol (3 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 45 h. The solvent was removed by rotary evaporation, and the residue chromatographed (6 × 2.5 cm column; silica gel, 1:2 v/v CH_2Cl_2/hexanes). The solvent was removed from the product fraction by oil pump vacuum to give **12** as a white powder; yield: 0.047 g (0.049 mmol, 87%). The IR, NMR (^1H, ^{13}C, ^{31}P), and mass spectra were identical with those reported previously.[3a, b]

Crystallography

A CH_2Cl_2 solution of **8** was layered with ethanol and stored at − 20 °C. After one month, a colorless prism was taken directly to a Nonius KappaCCD area detector for data collection as outlined in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with 8156 reflections. Lorentz, polarization, and absorption corrections[46] were applied. The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on F^2 using SHELXL-97.[47] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from literature.[48]

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG, GL 300/1–3) and Johnson Matthey PMC (platinum and ruthenium loans) for support, Dr. Takanori Shima and Ms. Agnieszka Nawara for some reactivity data, and Dr. Slawomir Szafert for preliminary experiments.

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