# A New Route to Heterobimetallic $C_3$ Complexes via C≡C Metatheses of 1,3-Diynyl Ligands: Synthesis and Structure of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C\equiv CC\equiv)W(O\text{-}t\text{-}Bu)_3$

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*Summary: Reactions of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C\equiv CC\equiv CR)$ (R = Me, H) and $(t\text{-}BuO)_3W\equiv W(O\text{-}t\text{-}Bu)_3$ give $(t\text{-}BuO)_3W\equiv CR$ and the title complex (79−76%), which crystallizes from toluene as a solvated tert-butoxy-bridged dimer. The NMR, IR, and crystallographic properties establish dominant $Re{-}C\equiv C{-}C\equiv W$ as opposed to $^+Re{=}C{=}C{=}C{=}W^-$ character.*

Compounds in which wire-like unsaturated elemental carbon chains span two metals, $L_nMC_xM'L'_{n'}$ (**I**-$C_x$), are attracting attention from numerous fundamental and applied viewpoints.[2−6] To date, $C_1$, $C_2$, $C_3$, $C_4$, $C_5$, $C_6$, $C_8$, $C_{10}$, $C_{12}$, $C_{16}$, and $C_{20}$ adducts have been isolated. However, odd carbon chains, which possess unique electronic characteristics,[3d] remain conspicuously underrepresented. We have described a family of cumulated $C_3$ complexes of the formula $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)({=}C{=}C{=}C{=})M(CO)_a(\eta^5\text{-}C_5H_cCl_{5-c})_b]^+\ BF_4^-$ (M/*a*/*b*/*c* = Mn/2/1/5, Mn/2/1/4, Mn/2/1/0/, Fe/4/0/−) and one labile $C_5$ homolog.[3d] Templeton has reported labile group 6 cumulated systems, such as $2K^+[Tp'(CO)_2Mo({=}C{=}C{=}C{=})W(CO)_2Tp']^{2-}$, which can be oxidized to isolable alkynyl/carbyne species, such as $[Tp'(O)_2Mo(C\equiv CC\equiv)W(CO)_2Tp']$.[5] All other examples feature $C_1$ bridges.[4]

One factor contributing to this *gerade/ungerade* imbalance is that chains assembled solely by coupling readily available C≡C building blocks must contain even numbers of carbons.[3d] Odd carbon chains require more sophisticated synthetic strategies. As illustrated in Scheme 1 (reaction a), the above $C_3$ complexes were prepared from various two-carbon and one-carbon precursors. However, we wondered about the feasibility of degrading ligands with even numbers of sp carbons (reaction b). For example, routes to longer polyynyl complexes, $L_nM(C\equiv C)_mR$ ($m$ = 2−6), are constantly improving.[3e,7] At the same time, methodologies for C≡C bond metathesis[8] are rapidly advancing.[9] In a conceptually pioneering experiment (Scheme 1, reaction c), Selegue demonstrated that RuC≡CMe and RC≡W species could condense to give the ruthenium/tungsten $C_1$ complex **1**.[4b] Chisholm reported related reactions of platinum alkynyl complexes believed to proceed via PtC≡W intermediates.[10] Accordingly, we set out to probe extensions to longer carbon chains.

As shown in Scheme 2, the chiral rhenium 1,3-pentadiynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C\equiv CC\equiv CMe)$ (**2a**)[3a] and ditungsten *tert*-butoxy complex $(t\text{-}BuO)_3W\equiv W(O\text{-}t\text{-}Bu)_3$ were combined in toluene (1:1 mol ratio). The latter compound is known to participate in a variety of stoichiometric and catalytic C≡C metatheses.[8−10] After 0.5 h, workup gave a brown-orange air-sensitive powder, which showed properties (below) consistent with the target rhenium/tungsten $C_3$ complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C\equiv CC\equiv)W(O\text{-}t\text{-}Bu)_3$ (**3**), in 79% yield. The butadiynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C\equiv CC\equiv CH)$ (**2b**),[3a] which contains a potentially reactive end group but is available in fewer steps than **2a**, was similarly reacted. Workup gave **3** in 76% yield.

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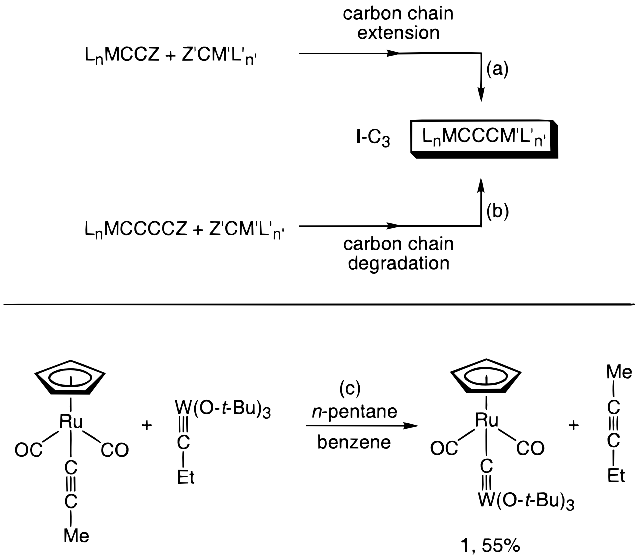
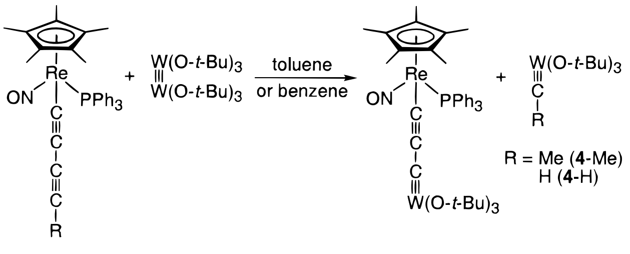
**Scheme 1. (Top) Some Synthetic Approaches to $C_3$ Complexes; (Bottom) C≡C Metathesis Approach to $C_1$ Complexes**



**1**, 55%

**Scheme 2. Syntheses of a Rhenium/Tungsten $C_3$ Complex**



R = Me (**2a**)
H (**2b**)

**3**, 79-76%

Reactions were monitored by $^1$H, $^{13}$C, and $^{31}$P NMR in $C_6D_6$. No intermediates or byproducts were detected, and the $^{13}$C NMR signals of the tungsten coproduct (*t*-BuO)$_3$W≡CMe (**4**-Me) closely matched literature values.[8b]

The $^1$H and $^{13}$C NMR spectra supported the structural assignment **3**. First, the $C_5Me_5$ and *t*-Bu $^1$H signals gave the correct relative integration (15:27). Second, the ReC $^{13}$C signal showed a chemical shift (94 ppm) and $J_{CP}$ value (17.8 Hz) characteristic of an alkynyl ligand.[3e,7] Distinctive changes occur with even slight $^+$Re=C character.[3] Third, the CW $^{13}$C signal exhibited a chemical shift (236 ppm, s) characteristic of a carbyne ligand, similar to those of **4**-Me and Templeton's MC≡CC≡M′ systems (254−246 ppm).[5] The central carbon gave an intermediate chemical shift (146 ppm, s). The IR $\nu_{NO}$ value, which is also a function of $^+$Re=C character, was essentially identical to those of **2a**,**b** (1643−1647 vs 1644−1651 cm$^{-1}$).[3a,e] A strong $\nu_{C\equiv C}$ band was also observed (1960−1973 cm$^{-1}$). However, efforts to obtain a correct microanalysis or a mass spectral parent ion were unsuccessful. NMR spectra showed no solvate molecules or impurities.

Deep red prisms were grown by slow evaporation of toluene solutions of **3**. A crystal structure was determined as described in the Supporting Information. As shown in Figure 1, a solvate of the *tert*-butoxy-bridged dimer **3·3** was obtained. The rhenium atoms are of opposite configurations and related by an inversion center (meso isomer). 3D graphics show that the ditungsten core occupies about the same volume as each rhenium end group (32 non-hydrogen atoms each), with no van der Waals contacts. Other complexes with (*t*-BuO)$_3$W≡C moieties have been structurally characterized. Some crystallize as dimers (**4**-Me, **4**-NMe$_2$),[11] whereas others do not (**1**, **4**-Ph).[4b,12] The tungsten atoms in the dimers adopt distorted trigonal bipyramidal geometries, with axial bridging tungsten−oxygen bonds that are much longer than the three equatorial bridging and nonbridging tungsten−oxygen bonds (2.492(5) vs 1.927(5), 1.881(5), 1.880(5) Å in **3·3**). Simple nitrogen donor ligands and **4**-R give similar trigonal bipyramidal adducts.[8,13]

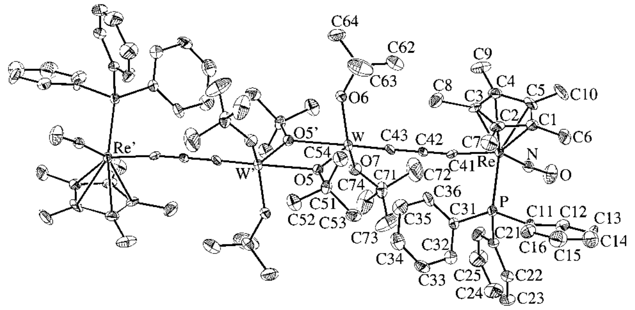


**Figure 1.** Structure of the dimeric portion of **3·3**·(toluene)$_4$. Selected interatomic distances and angles: Re−P, 2.369(2); Re−N, 1.753(6); Re−C41, 2.039(8); C41−C42, 1.227(10); C42−C43, 1.398(11); C43−W, 1.769(8); Re−W, 6.422(3); W−O5, 1.927(5); W−O5′, 2.492(5); W−O6, 1.881(5); W−O7, 1.880(5). Key angles: N−Re−P, 88.5(2); P−Re−C41, 90.2(2); N−Re−C41, 101.9(3); Re−N−O, 173.0(6); Re−C41−C42, 173.8(6); C41−C42−C43, 179.0(8); W−C43−C42, 178.2(6); C43−W−O5, 102.0(3); C43−W−O5′, 177.3(2); C43−W−O6, 102.4(3); C43−W−O7, 101.9(3); W−O5−W′, 104.6(2); O5−W−O5′, 75.4(2); O5−W−O6, 112.5(2); O5−W−O7, 113.7(2); O5′−W−O6, 78.4(2); O5′−W−O7, 79.8(2); O6−W−O7, 121.0(2).

In accord with the solution NMR and IR data, **3·3** exhibits ReC≡, C≡C, and ≡CC≡ bond lengths (2.039(8), 1.227(10), 1.398(11) Å) close to those in several ($\eta^5$-$C_5Me_5$)Re(NO)(PPh$_3$)(C≡CC≡CX) species (1.998(12)−2.037(5), 1.202(7)−1.28(2), 1.35(2)−1.389(5) Å).[3b,7] The C≡W bond length (1.769(8) Å) is similar to those in **1**, **4**-Me, **4**-NMe$_2$, and **4**-Ph (1.75(2)−1.77(2) Å) and related amine adducts.[13] The ReC≡C angle is slightly bent (173.8(6)°), but the C≡CC and CC≡W angles are nearly linear (179.0(8)°, 178.2(6)°). Hence, the Re−W distance (6.422(3) Å) is very close to the sum of the bond lengths (6.432 Å). Only one other $C_3$ complex has been structurally characterized to date.[3d] It exhibits a $^+$Re=C=C=C=Mn linkage and much different NMR and IR properties.

As a powder, **3** melted with decomposition at 121−123 °C. In contrast to $^+$Re=C=C=C=Mn systems, UV-visible spectra showed only featureless tails arising from shoulders at 290/266 nm (benzene/CH$_2$Cl$_2$, $\epsilon$ 18 000/17 000 M$^{-1}$cm$^{-1}$). The absence of special metal−metal

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interactions, and the ReC≡CC≡W bonding model, is further supported by density functional calculations.[14] Finally, the silylalkyne EtC≡CSiMe$_3$ and ($t$-BuO)$_3$W≡W(O-$t$-Bu)$_3$ are known to undergo metathesis.[8] However, the silylbutadiynyl complex ($\eta^5$-C$_5$Me$_5$)Re(NO)(PPh$_3$)-(C≡CC≡CSiMe$_3$)[3a] gave no reaction over the course of 24 h in benzene at 60 °C, even with the reactive neopentylidyne complex **4**-*t*-Bu.[8]

In conclusion, we have demonstrated the viability of strategy b in Scheme 1 for accessing complexes of the type **I** with >C$_1$ odd-carbon chains. Furthermore, our approach gives species with C≡W linkages that should be metathesis active. These have possibilities as precursors to monometallic complexes with longer chains, as progenitors of other types of bimetallic adducts, and as polymerization catalysts. Efforts toward these ends will be reported in due course.

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

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