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The synthesis of *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$, *cis,cis*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$, and related metal-capped ene-ynes, and evaluation of them as catalysts for preparing polydiacetylenes *

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Abstract

Reaction of 0.5 equiv. of *trans*-5-decene-3,7-diyne with $W(CEt)(OCMe_3)_3$ yields *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$ (**2**) via the intermediate *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt$ (**1**), while reaction of 1 equiv. of *cis*-5-decene-3,7-diyne with $W(CEt)(OCMe_3)_3$ yields *cis,cis*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$ (**4**) via *cis*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt$ (**3**). Reaction of additional *cis*- or *trans*-5-decene-3,7-diyne with either **2** and/or **4** results in decomposition. Bipyridyl adducts of related metal-capped oligomers have been prepared and are more stable, but they are too insoluble to serve as intermediates in polymerization reactions. Reaction of 0.5 equiv. of 1,4-dibutynylbenzene with $W(CEt)(OCMe_3)_3$ yields $(Me_3CO)_3W{\equiv}C(1,4\text{-}C_6H_4)C{\equiv}W(OCMe_3)$, while reaction of 1 equiv. of 1,2-dipentynylbenzene with $W(CEt)(OCMe_3)_3$ yields $(Me_3CO)_3W{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}W(OCMe_3)_3$. Addition of 4 or more equiv. of 1,4-dibutynyl- or 1,2-dipentynyl-benzene to $W(CEt)(OCMe_3)_3$ results in formation of a yellow intractable product in less than 50% yield. It appears that either instability or insolubility of the growing polymers in this general class will limit their utility as catalysts.

Introduction

Diacetylenes can be polymerized in the solid state to give polymers having a polyenyne (polydiacetylene) backbone (*trans* double bonds; eq. 1) [1]. A variety of R groups is possible, e.g. urethanes, alkyls, and functionalized alkyls [2]. Polydi-

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* This paper is dedicated to Professor Dr. E.O. Fischer on the occasion of his 70th birthday.

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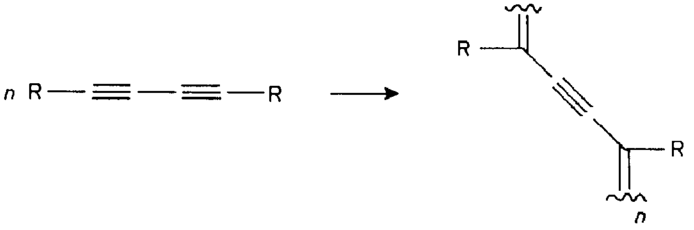
acetylenes have received much attention because of the unusual nature of the fully conjugated backbone, the potential for non-linear optical applications [3], and unusual chromotropic [4] and dichroic [5] effects in solution.



(1)

There are no reported procedures for synthesizing the parent polyenyne (R = H) or the phenyl substituted polymer ($R = C_6H_5$) from the diacetylenes, or for preparing analogous polymers having *cis* double bonds. Wudl [6] has reported the synthesis of t-Bu$(C{\equiv}CCH{=}CH)_nC{\equiv}C$-t-Bu oligomers by coupling the appropriate alkynylzinc reagent with *trans*-diiodoethylene, and has fully characterized the series where $n = 1,2,3,5$ and 7. This method requires the appropriate alkynylzinc reagent, and ultimately will be limited by the large number of synthetic steps required to prepared long polyenynes ($n > 8$). A method in which a mixture of polyenynes could be prepared by a controlled polymerization reaction would be highly desirable. The reaction of this type shown in eq. 2 would utilize the known rapid disproportionation of acetylenes in the presence of $W(CR)(OCMe_3)_3$ complexes [7]. The reaction should be driven to completion by removal of 3-hexyne. An analogous reaction that would yield a class of polymers containing a *cis*-enyne backbone is shown in eq. 3. In this paper we report attempts to carry out these and related reactions that give conjugated polymers containing triple bonds.

$$n\ trans\text{-}EtC{\equiv}CCH{=}CHC{\equiv}CEt \xrightarrow{\text{catalyst}} trans\text{-}EtC[CCH{=}CHC]_nCEt + (n-1)\text{3-hexyne} \quad (2)$$

$$n\ cis\text{-}EtC{\equiv}CCH{=}CHC{\equiv}CEt \xrightarrow{\text{catalyst}} cis\text{-}EtC[CCH{=}CHC]_nCEt + (n-1)\text{3-hexyne} \quad (3)$$

Results

Addition of 0.5 equiv. of *trans*-5-decene-3,7-diyne [8] to $W(CEt)(OCMe_3)_3$ in pentane yields yellow crystalline *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$ (**2**) in 83% yield. Removal of 3-hexyne from the system is not necessary for the reaction to go virtually to completion, although the method of isolation (removing solvent and 3-hexyne in vacuo) ensures that the reaction is complete. The ^1H and ^{13}C NMR spectra of **2** are straightforward; the alkylidyne α carbon atom resonance is found at 255.5 ppm and the olefinic carbon atom resonance at 141.8 ppm (J(CH) 151 Hz). (^1H and ^{13}C NMR spectra of related compounds to be discussed here also are not unusual, and so will not be discussed in any detail). Resonances consistent with the expected intermediate, *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt$ (**1**), can be observed during the reaction before the solvent and 3-hexyne are removed in vacuo (see

Experimental). Therefore the reaction is believed to take place via the sequence shown in eq. 4 and 5.

$$\mathrm{W(CEt)(OCMe_3)_3} + \textit{trans}\text{-}\mathrm{EtC{\equiv}CCH{=}CHC{\equiv}CEt} \rightarrow$$

$$\text{3-hexyne} + \textit{trans}\text{-}\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt} \qquad (4)$$

(1)

$$\mathbf{1} + \mathrm{W(CEt)(OCMe_3)_3} \xrightarrow{-\text{3-hexyne}} \textit{trans}\text{-}\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$$

(2)

(5)

Addition of 1 equiv. of *cis*-5-decene-3,7-diyne to $\mathrm{W(CEt)(OCMe_3)_3}$ does not yield *cis*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$, which would be formed in a reaction analogous to that shown in eq. 5. Instead *cis*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt}$ **(3)** is observed in solution (eq. 6), along with about 5% of the species **4** that is isolated upon removal of 3-hexyne and the solvent from the reaction mixture in vacuo (eq. 7). A weak singlet resonance at 7.51 ppm observed in reaction mixtures has been ascribed to the olefinic protons in *cis*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$, the required intermediate between **3** and **4**. Attempts to isolate *cis*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$ by addition of 0.5 equiv. of *cis*-5-decene-3,7-diyne to $\mathrm{W(CEt)(OCMe_3)_3}$ always led to considerable decomposition and isolation of **4** in low yield. We speculate that steric interaction between the $\mathrm{W(OCMe_3)_3}$ groups in *cis*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$ is the primary reason why the latter is not formed in significant quantities in solution relative to other species. Note that *trans*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$ is not similarly crowded, and therefore is energetically similar to other tungsten complexes in solution.

$$\mathrm{W(CEt)(OCMe_3)_3} + \textit{cis}\text{-5-decene-3,7-diyne} \rightarrow$$

$$\text{3-hexyne} + \textit{cis}\text{-}\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt} \qquad (6)$$

(3)

$$\mathrm{W(CEt)(OCMe_3)_3} + \mathbf{3} + \textit{cis}\text{-5-decene-3,7-diyne} \rightarrow$$

$$2\ \text{3-hexyne} + \textit{cis,cis}\text{-}\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3} \qquad (7)$$

(4)

When one equivalent of *trans*-5-decene-3,7-diyne was added to a dilute solution of $\mathrm{W(CEt)(OCMe_3)_3}$ (1.1×10^{-2} m*M*) in $\mathrm{C_6D_6}$ the solution immediately turned brown-yellow. After 2 h the solution had become red. The ^{1}H NMR spectrum showed resonances from *trans*-5-decene-3,7-diyne and *trans*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt}$, and two sets of doublets centered at 8.12 and 5.73 ppm that we assign to the second insertion product *trans,trans*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$. The instability of the second insertion product at room temperature and moderate concentrations prevented our obtaining a ^{13}C NMR spectrum. Attempts to isolate *trans,trans*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$ by concentrating solutions in vacuo yielded a red oil that had no ^{1}H NMR signals.

Addition of either *trans*- or *cis*-5-decene-3,7-diyne to either **2** or **4** did not give oligomers higher than *trans,trans*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$ or **4**. Although dilute solutions were stable at room temperature for 10 to 12 h, concentration of these solutions (and removal of 3-hexyne in vacuo) led to an increase in the rate of decomposition and formation of a red oil that showed no ^{1}H NMR signals. Golden-yellow precipitates were obtained upon addition of excess pentane to the dilute solutions, but they decomposed within minutes after being isolated by filtration. These precipitates are likely to be higher oligomers, but they are obviously unstable, even in the solid state.

Since alkylidyne complexes containing several different types of alkoxide ligands are available [7], we could determined how the stabilities of some of the types of complexes described above vary with the nature of the alkoxide. Reaction of 0.5 equiv. of *trans*-5-decene-3,7-diyne with $\mathrm{W(CEt)[OCMe_2(CF_3)]_3}$ in ether gives *trans*-$\mathrm{[(CF_3)Me_2CO]_3(ether)W{\equiv}CCH{=}CHC{\equiv}W[OCMe_2(CF_3)]_3(ether)}$ (**5**) in 44% yield. No analogous solvent-free product could be isolated. The significant reduction in the yield of **5**, and our failure to synthesize *cis,cis*-$\mathrm{[(CF_3)Me_2CO]_3(ether)W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W[OCMe_2(CF_3)]_3(ether)}$ (analogous to **4**) by the reaction of *cis*-5-decene-3,7-diyne with $\mathrm{W(CEt)[OCMe_2(CF_3)]_3}$ suggest that the presence of electron-withdrawing alkoxide ligands that make the metal significantly more electrophilic than it is in the t-butoxide analogs does not stabilize longer oligomers, and may actually promote decomposition.

We thought it might be possible to stabilize bis metal-capped oligomeric enynes by making adducts. $\mathrm{W(CEt)[OCMe_2(CF_3)]_3(bipy)}$ can be made straightforwardly from $\mathrm{W(CEt)[OCMe_2(CF_3]_3}$ and bipyridyl. Addition of 1 equiv. of *cis*-decene-3,7-diyne to $\mathrm{W(CEt)[OCMe_2(CF_3)]_3(bipy)}$ yields *cis*-$\mathrm{W(CCH{=}CHC{\equiv}CEt)[OCMe_2(CF_3)]_3(bipy)}$ (**6**) (eq. 8). Addition of 0.5 equiv. of *trans*-5-decene-3,7-diyne to $\mathrm{W(CEt)[OCMe_2(CF_3)]_3(bipy)}$ yields an insoluble golden precipitate. All attempts at ^{1}H NMR spectroscopic examination in a variety of solvents failed because of the low solubility of this product, but we assume that it is **7** as shown in eq. 9. We speculate that an increase in steric interaction around the tungsten as a result of coordination of the bipy ligand now virtually prevents reaction between $\mathrm{W(CEt)[OCMe_2(CF_3)]_3(bipy)}$ and **6**. As noted above even *cis*-$\mathrm{(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3}$ is a relatively high energy molecule compared to **3** and **4**. All attempts to

$$\mathrm{W(CEt)[OCMe_2(CF_3)]_3(bipy)} + \mathit{cis}\text{-5-decene-3,7-diyne} \rightarrow$$

$$\mathit{cis}\text{-}\mathrm{W(CCH{=}CHC{\equiv}CEt)[OCMe_2(CF_3)]_3(bipy)} \quad (8)$$

(6)

$$\mathrm{W(CEt)[OCMe_2(CF_3)]_3(bipy)} + 0.5\ \mathit{trans}\text{-5-decene-3,7-diyne} \rightarrow$$

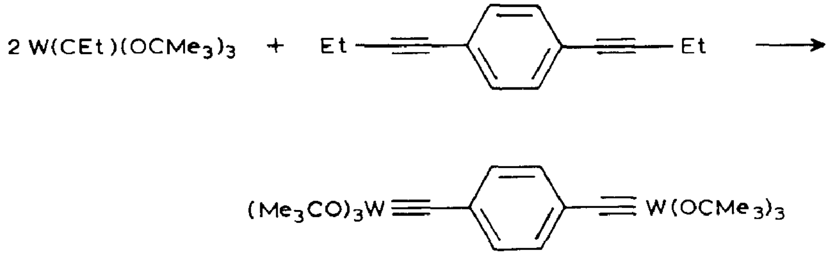
$$\mathit{trans}\text{-}\mathrm{[(CF_3)Me_2CO]_3(bipy)W{\equiv}CCH{=}CHC{\equiv}W[OCMe_2(CF_3)]_3(bipy)} \quad (9)$$

(7)

prepare *cis,cis*-$\mathrm{[(CF_3)Me_2CO]_3(bipy)W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W[OCMe_2(CF_3)]_3(bipy)}$ (e.g., by heating **6**) produced an insoluble golden precipitate that may be the desired product, but it could not be identified because of its insolubility. These results suggest that the bipy ligands do indeed slow down intermolecular decomposition, but they also make the bis-metal capped enynes essentially insoluble. It is somewhat surprising that bipy adducts react so readily with acetylenic carbon–carbon bonds, something one would not expect if both ends of the bipy coordinate strongly to yield a pseudo-octahedral species. NMR studies suggest that free bipy does not exchange with coordinated bipy on the ^{1}H NMR time scale in **7**, so the rate at which bipy dissociates cannot be greater than approximately 10 s^{-1}.

Steric crowding about the metal is the simplest and most likely cause of bipy lability.

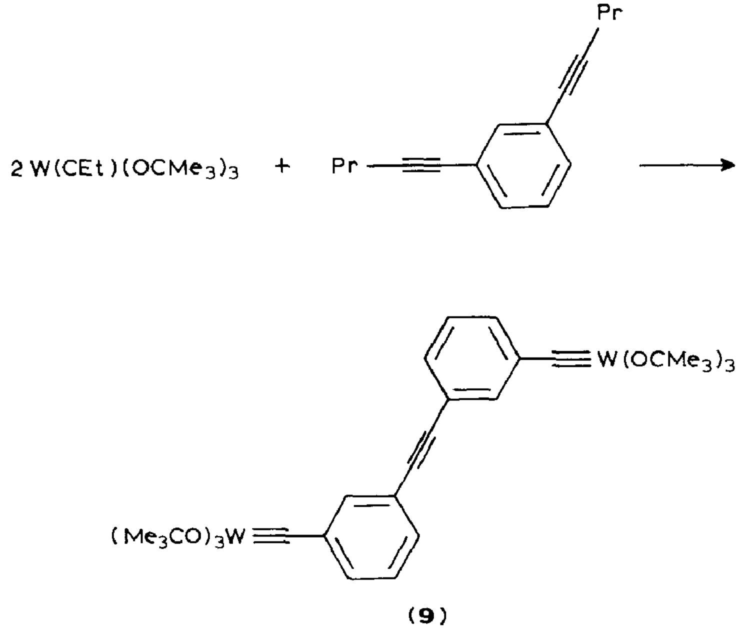
It seemed likely that polymers analogous to those shown in eq. 1 and 2 but having phenyl rings in the place of the olefinic bonds might become more stable towards decomposition as the length of the chain in the metal-capped oligomers is increased. Reaction of 0.5 equiv. of 1,4-dibutynylbenzene with W(CEt)(OCMe$_3$)$_3$ followed by removal of solvents in vacuo and recrystallization of the residue from a mixture of toluene and pentane gave **8** (eq. 10) in good yield. When 4 equiv. of 1,4-dibutynylbenzene were added to W(CEt)(OCMe$_3$)$_3$ in refluxing toluene a yellow insoluble precipitate was formed in 50% yield. All attempts to dissolve this precipitate in a variety of solvents (*o*-dichlorobenzene, toluene, THF, CH_2Cl_2) failed. We speculate that the yellow insoluble precipitate contains at least the next higher analog of **8**.



(10)

(**8**)

Reaction of 1,2-dipentynyl benzene with W(CEt)(OCMe$_3$)$_3$ results in the isolation of the sparingly soluble **9** (eq. 11) in 63% yield. Monitoring of the reaction by ^{1}H NMR spectroscopy suggested that it proceeds via the intermediate (Me$_3$CO)$_3$W$\equiv$C(1,2-C_6H_4)C$\equiv$CPr. As in the case of *cis*-(Me$_3$CO)$_3$W$\equiv$CCH=CHC$\equiv$CEt, removal



(11)

(**9**)

of solvents in vacuo leads to isolation of $(Me_3CO)_3W{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}C(1,2\text{-}C_6H_4)\text{-}C{\equiv}W(OCMe_3)_3$. Again, reaction of $n \geq 2$ equiv. of 1,2-dialkynyl- or 1,4-dialkynylbenzene derivatives with $W(CEt)(OCMe_3)_3$ gives insoluble precipitates (in yields typically < 50% based on dialkynylbenzene added) that we assume to be intractable higher oligomers.

Discussion

One of the findings that will continue to be important when considering metathetical approaches to conjugated polymers is that alkylidyne complexes having a conjugated chain attached to the alkylidyne carbon atom appear to be of significantly lower energy relative to $W(CR)(OCMe_3)_3$ complexes where R is a saturated alkyl chain. This is not surprising in view of the fact that complexes such as $(Me_3CO)_3W{\equiv}C\text{–}C{\equiv}W(OCMe_3)_3$ and $(Me_3CO)_3W{\equiv}CCH{=}CH_2$ are especially readily formed, and appear to be of lower energy than $W(CR)(OCMe_3)_3$ alternatives [9]. One can rationalize that the polarization of the W≡C bond (negative on C), and subsequent delocalization of the negative charge on carbon along the conjugated chain is what stabilizes such species relative to $W(CR)(OCMe_3)_3$ complexes [9]. Therefore the growing polymer will always be capped at both ends by the $W(OCMe_3)_3$ unit, if that is sterically possible, i.e. conjugation of the tungsten–carbon triple bond with the double bond increases the thermodynamics stability of the metal-capped oligomers relative to $W(CEt)(OCMe_3)_3$ to the point that the chain carrier is virtually exclusively the unstable metal-capped oligomer. This circumstance is not necessarily a problem. However, it is a problem in the cases described here since longer oligomers are either unstable, or insoluble, thereby preventing the required chain growth. We conclude that it will be difficult if not impossible to form polydiacetylenes in a metathetical reaction of the type described here.

Experimental

General experimental procedures can be found elsewhere [9]. *trans*- and *cis*-5-decene-3,7-diyne were prepared by methods analogous to those reported by Vollhardt et al. [8] and alkynylbenzenes were prepared by a related method [10]. ^1H NMR data and ^{13}C NMR are reported in C_6D_6 at ~ 298 K relative to TMS unless otherwise noted.

Observation of trans-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt$ (1)

trans-5-Decene-3,7-diyne (0.055 mmol, 9μl) was added to a solution of $W(CEt)(OCMe_3)_3$ (0.11 mmol, 50 mg) in deuterated benzene (1 ml). The solution immediately became brown-yellow: ^1H NMR (C_6D_6, 250 MHz) δ 8.11 (d, 1, J(HH) 15.9 Hz, WCC*H*=CH), 5.50 (dt, 1, ^3J(HH) 15.8 Hz, ^5J(HH) 2.3 Hz, WCCH=C*H*), 2.27 (dq, 2, ^3J(HH) 7.5 Hz, ^5J(HH) 2.2 Hz, $WCCH{=}CHC{\equiv}CCH_2CH_3$), 1.36 (s, 27, $OCMe_3$), 0.97 (t, 3, J(HH) 7.4 Hz, $WCCH{=}CHC{\equiv}CCH_2CH_3$). If the volatile components are removed from such solutions in vacuo then *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$ is isolated (see below). If the solutions are left for ~ 1 hour at room temperature then ^1H NMR examination shows that they contain ~ 95% *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$.

Preparation of trans-[(Me$_3$CO)$_3$W≡CCH=CHC≡W(OCMe$_3$)$_3$] (2)

trans-5-Decene-3,7-diyne (0.563 mmol, 87 μl) was added to a pentane (10 ml) solution of W(CEt)(OCMe)$_3$ (1.13 mmol, 0.50 g). The solvent was removed in vacuo and the residue was recrystallized from pentane at −30 °C to give a yellow microcrystalline product (0.40 g, 83%): ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 7.54 (s, 1, WCC*H*), 1.48 (s, 27, OC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$, 67.9 MHz) δ 255.5 (s, WCCH), 141.8 (d, *J*(CH) 151 Hz, WC*C*H), 8.14 (s, OCMe$_3$), 32.6 (q, *J*(CH) 126 Hz, OC*Me*$_3$). Anal. Found: C, 39.32; H, 6.61. WC$_{14}$H$_{26}$O$_3$ calcd.: C, 39.45; H, 6.15%.

Observation of cis-(Me$_3$CO)$_3$W≡CCH=CHC≡CEt (3)

cis-5-Decene-3,7-diyne (0.28 mmol, 45 μl) was added to a solution of W(CEt)(OCMe$_3$)$_3$ (125 mg, 0.28 mmol) in deuterated benzene (1 ml). The solution immediately became brown-yellow and eventually red-brown during several hours. Removal of the solvent in vacuo gave *cis,cis*-[(Me$_3$CO)$_3$WCCH=CHC≡CCH-=CHCW(OCMe$_3$)$_3$] (see below): ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 7.60 (br d, 1, *J*(HH) 11 Hz, WCC*H*=CH), 4.65 (dt, 1, ^{3}*J*(HH) 11 Hz, ^{5}*J*(HH) 2.4 Hz, WCCH=C*H*), 2.31 (dq, 2, ^{3}*J*(HH) 7.4 Hz, ^{5}*J*(HH) 2.4 Hz, WCCH=CHC≡CC*H*$_2$CH$_3$), 1.49 (s, 27, OCMe$_3$), (WCCH=CHC≡CCH$_2$C*H*$_3$ is obscured); ^{13}C NMR (C$_6$D$_6$, 75.4 MHz) δ 257.5 (s, WCCH=CH), 141.2 (d, *J*(CH) 156 Hz, WC*C*H=CH), 113.0 (d, *J*(CH) 163 Hz, WCCH=*C*H), 96.9 (s, WCCH=CHC≡CCH$_2$CH$_3$), 81.0 (s, WCCH=CHC≡*C*CH$_2$CH$_3$), 80.8 (s, OCMe$_3$), 32.3 (q, *J*(CH) 126 Hz, OC*Me*$_3$), 14.1 (q, *J*(CH) 128 Hz, WCCH=CHC≡CCH$_2$*C*H$_3$), 13.7 (t, *J*(CH) 128 Hz, WCCH=CHC≡C*C*H$_2$CH$_3$).

cis,cis-[(Me$_3$CO)$_3$W≡CCH=CHC≡CCH=CHC≡W(OCMe$_3$)$_3$] (4)

cis-5-Decene-3,7-diyne (1.125 mmol, 1.18 μl) was added to a cooled pentane (15 ml, −30 °C) solution of W(CEt)(OCMe$_3$)$_3$ (2.25 mmol, 1.0 g). The solution immediately became yellow. The solvents were removed in vacuo and the residue was recrystallized from pentane at −30 °C to give a yellow microcrystalline product (263 mg, 52%): ^{1}H NMR (C$_6$D$_6$, 250 MHz), δ 7.69 (br d, 1, *J*(HH) 10 Hz, WCC*H*CHC), 4.92 (br d, 1, *J*(HH) 10 Hz, WCCHC*H*C), 1.50 (s, 27, OC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$, 67.9 MHz) δ 257.8 (s, WCCHCHC), 142.0 (d, *J*(CW) 27 Hz, *J*(CH) 156 Hz, WC*C*HCHC), 112.8 (d; *J*(CH) 164 Hz, WCCH*C*HC), 96.0 (s, WCCHCH*C*), 81.2 (s, O*C*Me$_3$), 32.3 (1, *J*(CH) 127 Hz, OC*Me*$_3$). Anal. Found: C, 42.49; H, 6.31. WC$_{16}$H$_{29}$O$_3$ calcd.: C, 42.40; H, 6.44%.

Preparation of trans-[(ether)[(CF$_3$)Me$_2$CO]$_3$W≡CCH=CHC≡W[OCMe$_2$(CF$_3$)]-(ether)] (5)

trans-5-Decene-3,7-diyne (0.424 mmol, 66 μl) was added to an ether (10 ml) solution of W(CMe)[OCMe$_2$(CF$_3$)]$_3$ (0.847 mmol, 500 mg). The solvents were removed in vacuo and the residue recrystallized from pentane at −30 °C to give yellow needles (250 mg, 44%): ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 7.42 (s, 1, WCC*H*), 3.59 (q, 4, *J*(HH) 7 Hz, OC*H*$_2$CH$_3$), 1.54 (s, 18, OC*Me*$_2$(CF$_3$)), 1.04 (t, 6, *J*(HH) 7 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$, 75.4 MHz) δ 260.3 (s, WCCH), 143.2 (d, *J*(CH) 156 Hz, WC*C*H), 127.6 (q, *J*(CF) 285 Hz, OCMe$_2$(*C*F$_3$)), 83.0 (q, ^{2}*J*(CF) 28 Hz, O*C*Me$_2$(CF$_3$)), 64.2 (t, *J*(CH) 143 Hz, O*C*H$_2$CH$_3$), 25.2 (q, *J*(CH) 128 Hz, OC*Me*$_2$(CF$_3$)), 14.2 (q, *J*(CH) 126 Hz, OCH$_2$*C*H$_3$). Anal. Found: C, 31.72; H, 4.19. WC$_{18}$H$_{29}$F$_9$O$_4$ calcd.: C, 32.55; H, 4.40%.

Preparation of cis-[(CF$_3$)Me$_2$CO]$_3$(bipy)W≡CCH=CHC≡CEt (6)

cis-5-Decene-3,7-diyne (0.395 mmol, 62 μl) was added to an ether (5 ml) solution of W(CEt)[OCMe$_2$(CF$_3$)]$_3$(bipy) (0.395 mmol, 300 mg). After 1 h the solvents were removed in vacuo and the residue recrystallized from toluene at −30 °C to give small red cubes (186 mg, 50%): ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 9.96, 9.20 (dd, 2, bipy), 8.36 (d, 1, *J*(HH) 11 Hz, WCC*H*=CH), 7.13, 7.03, 6.98, 6.85, 6.61 (m, 6, bipy), 4.30 (dt, 1, ^3J(HH) 11 Hz, ^5J(HH) 2.3 Hz, WCCH=C*H*), 2.42 (dq, 2, ^3J(HH) 7.6 Hz, ^5J(HH) 2 Hz, WCCH=CHC≡CCH_2CH$_3$), 1.88, 1.59, 1.51 (s, 18, OCMe_2(CF$_3$)), 1.04 (t, 3, *J*(HH) 7.6 Hz, WCCH=CHC≡CCH$_2$CH_3); ^{13}C NMR (C$_6$D$_6$, 75.4 MHz) δ 271.2 (s, W*C*CH=CH), 158.8 (d, *J*(CH) 188 Hz, bipy), 154.0, 151.5 (s, bipy), 147.7 (d, *J*(CH) 186 Hz, bipy), 140.7 (d, *J*(CH) 147 Hz, *J*(CW) 50 Hz, WC*C*H=CH), 138.7, 137.8 (d, *J*(CH) 186, 152 Hz, bipy), 129.3, 128.7 (q, *J*(CF) 285, 287 Hz, OCMe$_2$(CF$_3$)), 125.3, 124.6, 121.9, 121.3 (d, *J*(CH) 165, 166, 165, 164 Hz, bipy), 113.9 (d, *J*(CH) 163 Hz, WCCH=*C*H), 97.1 (s, WCCH=CH*C*≡C), 80.7 (q, ^2J(CF) 28 Hz, O*C*Me$_2$(CF$_3$)), 79.7 (s, WCCH=CHC≡*C*), 79.6 (q, ^2J(CF) 28 Hz, O*C*Me$_2$(CF$_3$)), 25.6, 24.7, 24.4 (q, *J*(CH) 128, 129, 128 Hz, OCMe_2(CF$_3$)), 14.5 (q, *J*(CH) 130 Hz, WCCH=CHC≡CCH$_2$*C*H$_3$), 13.6 (t, *J*(CH) 129 Hz, WCCH=CC≡C*C*H$_2$CH$_3$).

Preparation of $(Me_3CO)_3W{\equiv}C(1,4\text{-}C_6H_4)C{\equiv}W(OCMe_3)_3$ *(8)*

1,4-Dibutynylbenzene (1.16 mmol, 510 mg) in 5 ml of toluene was added to a toluene (10 ml) solution of W(CMe)(OCMe$_3$)$_3$ (2.32 mmol, 1.00 g). The solution was stirred at room temperature for 1 h. The solvents were removed in vacuo and the residue was recrystallized from a mixture of toluene and pentane (5/1) to give orange microcrystals (650 mg, 65%): ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 7.42 (s, WCCC*H*), 1.46 (s, OCMe_3); ^{13}C NMR (C$_6$D$_6$, 69.7 MHz) δ 257.82 (s, W*C*CCH), 146.21 (s, WC*C*CH), 131.24 (d, *J*(CH) 158 Hz, WCC*C*H), 81.12 (s, O*C*CMe$_3$), 32.70 (q, *J*(CH) 125 Hz, OCMe_3).

Preparation of $(Me_3CO)_3W{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}W(OCMe_3)_3$ *(9)*

1,2-Dipentynylbenzene (0.45 mmol, 95 μl) was added to a pentane (5 ml) solution of W(CEt)(OCMe$_3$)$_3$ (0.45 mmol, 200 mg). The solution was stirred at room temperature for 3 h. The yellow precipitate was removed by filtration. Recrystallization from THF at −30 °C gave yellow cubes (142 mg, 63%): ^{1}H NMR (THF-d_8, 250 MHz) δ 7.48 (d, 1, *J*(HH) 7.8 Hz, WCCC*H*CHCHCHC), 7.12 (m, 2, WCCCHC*H*CHC*H*C), 6.73 (m, 1, WCCCHCHC*H*CHC), 1.45 (s, 27, OCMe_3); ^{13}C NMR (THF-d_8, 67.9 MHz), δ 259.6 (s, W*C*(1,2-C$_6$H$_4$)), 149.9 (s, WC*C*CHCHCHCHC), 134.1 (d, *J*(CH) 160 Hz, WCC*C*HCHCHCHC), 132.6 (d, *J*(CH) 159 Hz, WCCCHCHCHCHC), 128.5 (s, WCCCHCHCHCH*C*), 127.1 (d, *J*(CH) 159 Hz, WCCCHC*H*CHCHC), 124.6 (d, *J*(CH) 158 Hz, WCCCHCHC*H*CHC), 97.3 (s, WCCCHCHCHCHC*C*≡C), 80.5 (s, OCMe$_3$), 32.9 (q, *J*(CH) 124 Hz, OCMe_3). Anal. Found: C, 47.82; H, 6.25. W$_2$C$_{40}$H$_{62}$O$_6$ calcd.: C, 47.73; H, 6.21%.

Observation of $(Me_3CO)_3W{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}CPr$

1,2-Dipentynylbenzene (0.45 mmol, 95 mg) was added to a toluene (5 ml) solution of W(CEt)(OCMe)$_3$ (0.45 mmol, 200 mg). After 20 minutes the volatiles were removed in vacuo. The yellow residue was 90–95% pure by ^{1}H NMR. Attempts to recrystallize the residue resulted in the isolation of the bimetallic species, (Me$_3$CO)$_3$WC(1,2-C$_6$H$_4$)C≡C(1,2-C$_6$H$_4$)CW(OCMe$_3$)$_3$: ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 7.54 (d, 1, *J*(HH) 8 Hz, CCC*H*CHCHCHC), 7.38 (d, 1, *J*(HH) 8 Hz,

$\mathrm{CCCHCHCHC}\mathit{H}\mathrm{C}$), 7.07 (t, 1, *J*(HH) 8 Hz, $\mathrm{CCCHC}\mathit{H}\mathrm{CHCHC}$), 6.65 (t, 1, *J*(HH) 8 Hz, $\mathrm{CCCHCHC}\mathit{H}\mathrm{CHC}$), 2.34 (t, 2, *J*(HH) 8 Hz, $\mathrm{C{\equiv}CC}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.54 (m, 2, $\mathrm{C{\equiv}CCH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.51 (s, 27, $\mathrm{OC}\mathit{Me}_3$), 0.96 (t, 3, *J*(HH) 7 Hz, $\mathrm{C{\equiv}CCH_2CH_2C}\mathit{H}_3$).

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