ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 6321–6328 6321
DOI: 10.1021/om100702x

$[W(CO)(dppe)_2]$ Cumulenylidene and Acetylide Complexes Accessed via Stannylated Acetylenes and Butadiynes

Sergey N. Semenov, Olivier Blacque, Thomas Fox, Koushik Venkatesan, and Heinz Berke*

Department of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Received July 16, 2010

The tungsten butatrienylidenes [*cis*-$W(CO)(dppe)_2\{C{=}C{=}C{=}C(R)(SnMe_3)\}$] (R = $SnMe_3$ (**2**) and $SiMe_3$ (**3**); dppe = 1,2-bis(diphenylphosphinoethane)) were prepared from the reactions of [*trans*-$W(CO)(N_2)(dppe)_2$] (**1**) and the respective butadiynes displaying a 1,4-shift of the respective $SnMe_3$ groups along the butadiyne chains. Stannyl deprotection of **2** with $NBu_4F\cdot 3H_2O$ led to the anionic butadiyne derivative [*trans*-$W(CO)(dppe)_2(C{\equiv}CC{\equiv}CH)$][$NBu_4$] (**10**). The reaction of **1** with stannylated acetylenes gave the vinylidene derivatives [*cis*-$W(CO)(dppe)_2\{C{=}C(SnMe_3)(R)\}$] (R = Ph (**5**) or $SnMe_3$ (**6**)), which lost a $SnMe_3$ group, yielding W(I) acetylides of the type [*trans*-$W(CO)(dppe)_2$-$(C{\equiv}CR)$] (R = Ph (**7**), $SnMe_3$ (**8**), and $SiMe_3$ (**9**)). They were studied by cyclic voltammetry and EPR spectroscopy.

Introduction

Metallacumulenes $[L_xM{=}C({=}C)_nRR']$ possess a high degree of unsaturation, which makes these compounds unique candidates for application as materials with special electronic and NLO (nonlinear optical) properties.[1,2] Related binuclear cumulene complexes revealed a high degree of delocalization of the unpaired electron in mixed valence species.[3,4] While compounds with vinylidenes $:C{=}CRR'$ and allenylidenes $:C{=}C{=}CRR'$ as cumulenic ligands are quite common,[1,5] reports on the existence of butatrienylidenes and pentatetraenylidenes of the type $[L_xM(C{=}C{=}C{=}CRR')]$ and $[L_xM({=}C{=}C{=}C{=}C{=}CRR')]$ are very rare. X-ray diffraction studies of the fairly stable species $[Cl(PiPr_3)_2Ir{=}C({=}C)_n(Ph)_2]$ (n = 3, 4),[6–8] $[Cl(dppe)_2Ru(C{=}C{=}C{=}C{=}CPh_2)]$ (dppe = 1,2-bis(diphenylphosphinoethane)),[9] $[W(CO)_5\{C{=}C{=}C{=}C{=}C(NMe_2)_2\}]$,[10] and $[(Cp)(dmpe)Mn\{C{=}C{=}C{=}C(SnPh_3)_2\}]$ (dmpe = 1,2-bis(dimethylphosphinoethane))[11,12] revealed bond length alternation along the cumulenylidene chain. The longest terminal cumulenic chain was found in the C_7 compound $[M(CO)_5\{C{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2\}]$ (M = Cr, W).[13] Other types of group 6 metal centers were also shown to stabilize long-chain cumulenylidenes.[14] Thus, recently C_4 tungsten complexes [*cis*-$W(CO)(dppe)_2\{C{=}C{=}C{=}C(R)(p\text{-}C_6H_4\text{-}t\text{Bu})\}$] (R = $SnMe_3$ or H) were reported.[15] The preparation of butatrienylidenes often starts from terminal diynes involving 1,4-H shifts; however 4-H-butatrienylidenes proved to be unstable. We found that topologically related 1,4-$SnMe_3$ shifts may be utilized to circumvent the often too reactive H-substituted cumulenylidenes.

Cationic ruthenium complexes containing a $[Ru(C{=}C{=}C{=}C{=}CRH)]^+$ fragment were prepared *in situ* (R = H) by Bruce[16] (R ≠ H), Dixneuf,[17] and Winter.[17] They found a variety of typical reactions based on nucleophilic attack at C_γ and subsequent cycloaddition. The [2 + 2] addition between the Ru cumulene and butadiyne derivatives led to binuclear

---

*To whom correspondence should be addressed. E-mail: hberke@aci.uzh.ch.

(1) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797.

(2) (a) Bruce, M. I. *Coord. Chem. Rev.* **2004**, *248*, 1603. (b) Cadierno, V.; Gimeno, J. *Chem. Rev.* **2009**, *109*, 3512.

(3) (a) Unseld, D.; Krivykh, V. V.; Heinze, K.; Wild, F.; Artus, G.; Schmalle, H.; Berke, H. *Organometallics* **1999**, *18*, 1525. (b) Venkatesan, K.; Fox, T.; Schmalle, H. W.; Berke, H. *Organometallics* **2005**, *24*, 2834. (c) Rigaut, S.; Massue, J.; Touchard, D.; Fillaut, J. L.; Golhen, S.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4513. (d) Rigaut, S.; Le Pichon, L.; Daran, J. C.; Touchard, D.; Dixneuf, P. H. *Chem. Commun.* **2001**, 1206. (e) Rigaut, S.; Olivier, C.; Costuas, K.; Choua, S.; Fadhel, O.; Massue, J.; Turek, P.; Saillard, J. Y.; Dixneuf, P. H.; Touchard, D. *J. Am. Chem. Soc.* **2006**, *128*, 5859.

(4) Venkatesan, K.; Fox, T.; Schmalle, H. W.; Berke, H. *Eur. J. Inorg. Chem.* **2005**, 901.

(5) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(6) Ilg, K.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1632.

(7) Ilg, K.; Werner, H. *Chem.—Eur. J.* **2002**, *8*, 2812.

(8) (a) Werner, H.; Ilg, K.; Lass, R.; Wolf, J. *J. Organomet. Chem.* **2002**, *661*, 137. (b) Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem.—Eur. J.* **1996**, *2*, 19.

(9) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157.

(10) (a) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 1139. (b) Roth, G.; Fischer, H.; Meyer-Friedrichsen, T.; Heck, J.; Houbrechts, S.; Persoons, A. *Organometallics* **1998**, *17*, 1511.

(11) Venkatesan, K.; Fernandez, F. J.; Blacque, O.; Fox, T.; Alfonso, M.; Schmalle, H. W.; Berke, H. *Chem. Commun.* **2003**, 2006.

(12) Venkatesan, K.; Blacque, O.; Fox, T.; Alfonso, M.; Schmalle, H. W.; Berke, H. *Organometallics* **2004**, *23*, 4661.

(13) Dede, M.; Drexler, M.; Fischer, H. *Organometallics* **2007**, *26*, 4294.

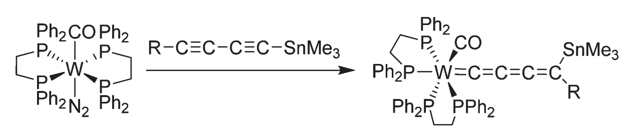
(14) Fischer, H.; Szesni, N. *Coord. Chem. Rev.* **2004**, *248*, 1659.

(15) Semenov, S. N.; Blacque, O.; Fox, T.; Venkatesan, K.; Berke, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5203.

(16) (a) Bruce, M. I.; Hinterding, P.; Ke, M. Z.; Low, P. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1997**, 715. (b) Bruce, M. I.; Hinterding, P.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 467. (c) Bruce, M. I.; Hinterding, P.; Low, P. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1996**, 1009.

(17) (a) Haquette, P.; Touchard, D.; Toupet, L.; Dixneuf, P. *J. Organomet. Chem.* **1998**, *565*, 63. (b) Winter, R. F.; Hornung, F. M. *Organometallics* **1999**, *18*, 4005. (c) Winter, R. F. *Eur. J. Inorg. Chem.* **1999**, 2121. (d) Winter, R. F.; Hornung, F. M. *Organometallics* **1997**, *16*, 4248.

Scheme 1



R = $SnMe_3$ (**2**) 72%, $SiMe_3$ (**3**) 62%, *p*-C_6H_4tBu (**4**) 73%

Table 1. IR, NMR, and UV−Vis Data of Complexes 2, 3, and 4

	IR [cm^{-1}]		NMR ^{13}C [ppm]				absorption [nm] (ε/1000 [M^{-1} cm^{-1}])		
	ν (C_4)	ν (CO)	C_α	C_β	C_γ	C_δ	λ_1	λ_2	λ_3
2	1925	1808	249.5	124.8	124.7	46.8	376 (29.6)	466 (4.9)	900 (4.4)
3	1940	1803	254.1	142.4	142.5	49.1	373 (37.4)	468 (5.2)	899 (2.2)
4^a	1935	1798	267.6	162.6	140.0	70.7	386 (163)	525 (82)	768 (0.7)

^{a} Data from ref 15.

complexes possessing a cyclobutene bridge.[18] The related dimerization of tungsten butatrienylidene is another rare example of relatively clean self-coupling.[15] In this work we approached the deprotection of $SnMe_3$-substituted derivatives generating the parent tungsten butadiyne complexes.

On the short chain side there would be tin-substituted vinylidenes, which could undergo chain extension by Stille-type coupling reactions. Up to now mainly tin-substituted manganese vinylidene derivatives were explored,[4,19] which is now extended to tin-substituted tungsten vinylidenes.

Results and Discussion

Synthesis and Structural Studies on Tungstenacumulenes. Butatrienylidene complexes were obtained via primary addition and π binding of 1,4-butadiyne tin derivatives to coordinatively unsaturated electron-rich metal centers. These systems subsequently rearrange to end-on butatrienylidene complexes. For the preparation of tungsten complexes [*trans*-W(CO)(N_2)(dppe)$_2$] (**1**) was chosen as the metal precursor, offering for ligand exchanges the labile N_2 ligand.[20,21] The four electron-donating dppe ligands were anticipated to create a pronounced preference for "end-on" cumulenylidene ligands via enhanced back-donation, stabilizing the binding of this highly unsaturated ligand.

1 reacts with $Me_3SnC{\equiv}CC{\equiv}CR$ derivatives[15] (Scheme 1) with heating, and repeated removal of N_2 *in vacuo* enabled the binding of the butadiyne ligand accompanied by a 1,4-$SnMe_3$-shift and formation of the butatrienylidene derivative.

The bis-stannylated product [*cis*-W(CO)(dppe)$_2${C=C=C=C($SnMe_3$)$_2$}] (**2**) was isolated as very air sensitive crystals in 72% yield. A *cis*-position of the diphosphines was indicated in the ^{31}P NMR spectra, showing two doublets of multiplets (J_{P-P} = 100 Hz) originating from coupling with the *trans* phosphorus atoms and two multiplets for the phosphorus atoms located *trans* to CO and *trans* to the C_4 chain. This assignment was confirmed by a COSY experiment. The ^{13}C NMR spectra of **2** showed four resonances for the C_4 cumulenic chain at 249.5 (C_α), 124.9 (C_β), 124.8 (C_γ), and 46.8 ppm (C_δ). All four signals are shifted to high field with respect to the related species [*cis*-W(CO)(dppe)$_2${C=C=C=C($SnMe_3$)(*p*-C_6H_4tBu)}] (**4**) (Table 1). The ^{119}Sn NMR spectrum of **2** shows Sn−P coupling for the unique signal at −22.5 ppm. A typical ν(C≡O) band is observed at 1786 cm^{-1}, as well as a ν(C_4) vibration at 1926 cm^{-1}. The position of these bands is similar to those of the previously reported [*cis*-W(CO)(dppe)$_2$(C=CHR)] and [Ir(Cl)(P*i*Pr$_3$)$_2$(C=C=C=CPh$_2$)].[6,7,22]

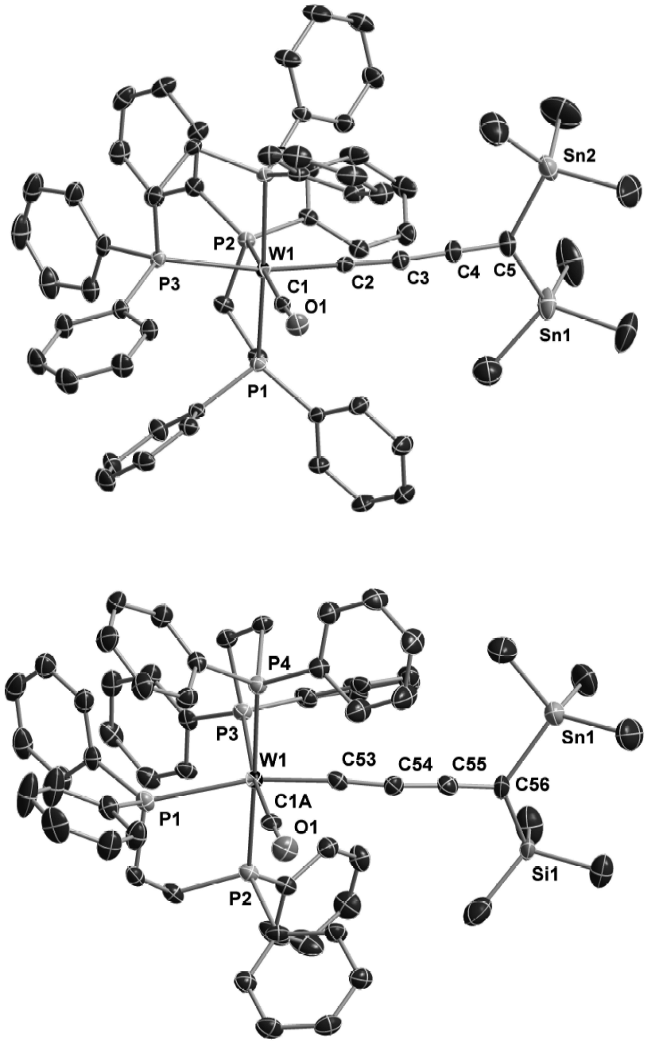


Figure 1. Thermal ellipsoid plots of the structures of **2** (top) and **3** (bottom) (30% probability level). Hydrogen atoms and solvent molecules are omitted for clarity.

The spectroscopically derived structure of **2** was finally confirmed by X-ray structural analysis (Figure 1). Details of the data collection and refinement are presented in Tables 1S and 2S, and selected bond lengths are reported in Table 2.

The unsaturated carbon chain slightly deviates from linearity at C2 with a C1−C2−C3 angle of 170.6°. The lengths of the C2−C3 and C4−C5 double bonds are longer (1.305(5) and 1.307(5) Å) than the internal C3−C4 bond (1.285(5) Å). This behavior is significantly different from the reported Ir−C_4 and Mn−C_4 cumulenic species, where the C_α−C_β and C_γ−C_δ lengths are short and the C_β−C_γ length is longer.[6,11] The W=C bond distance of **2** of 1.937(4) Å is slightly longer than that observed for **4** (1.923(3) Å), presumably indicating weaker

---

[18] Bruce, M. I.; Ellis, B. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2005**, *690*, 1772.

[19] Venkatesan, K.; Blacque, O.; Fox, T.; Alfonso, M.; Schmalle, H. W.; Kheradmandan, S.; Berke, H. *Organometallics* **2005**, *24*, 920.

[20] Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *J. Organomet. Chem.* **1991**, *409*, 355.

[21] Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *Chem. Lett.* **1988**, 441.

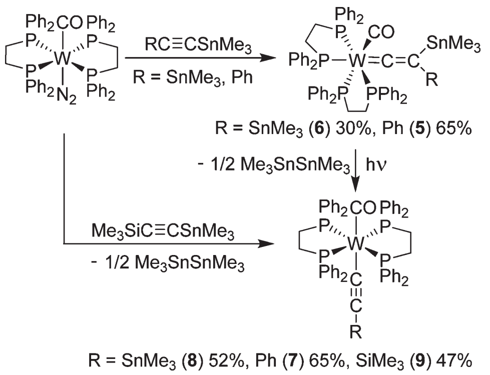
[22] Nakamura, G.; Harada, Y.; Mizobe, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3305.

Table 2. Selected Average Bond Lengths of Compounds 2−5, 7, and 9[a]

	W−P[b]	W−CO	W−C_α	C_α−C_β	C_β−C_γ	C_γ−C_δ
2	2.5054(6)	1.961(3)	1.937(3)	1.305(4)	1.285(4)	1.307(4)
3[c]	2.505(2)	1.98(1)	1.93(1)	1.31(1)	1.27(1)	1.32(1)
4[d]	2.5205(8)	1.937(3)	1.923(3)	1.306(4)	1.273(4)	1.325(4)
5	2.509(1)	1.940(5)	2.007(4)	1.298(6)		
7	2.4718(5)	2.041(3)	2.207(2)	1.158(3)		
9	2.4783(7)	2.019(4)	2.153(3)	1.204(3)		

[a] Assignment of the bond lengths in the C_4 and C_2 chains according to the following notation: $[W]C_\alpha C_\beta C_\gamma C_\delta$. [b] An average value of the four W−P bonds is presented. [c] An average value for two crystallographically independent molecules of **3** is presented. [d] Data from ref 15.

Scheme 2



π-acceptor properties of the C4 chain of **2** relative to the one with aromatic substituent.

The stannyl acetylene method was used to access asymmetrically substituted butatrienylidene complexes. Applying **1** in the reaction with $Me_3SnC{\equiv}CC{\equiv}CSiMe_3$, the compound [*cis*-W(CO)(dppe)$_2${C=C=C=C($SnMe_3$)($SiMe_3$)}] (**3**) was formed, which could be isolated in 62% yield. Like **2**, **3** revealed *cis*-diphosphines, established via ^{31}P NMR spectroscopy showing four resonances and the expected coupling patterns. The ^{13}C NMR spectra of **3** exhibited butatrienylidene resonances slightly shifted to low field with respect to the bis-trimethyltin-substituted derivative at 254.1 (C_α), 142.4 (C_β), 142.5 (C_γ), and 49.1 ppm (C_δ). In general, the ^{13}C NMR data of the tungsten C_4 cumulenes **2**−**4** turned out to be quite comparable to those of the MnC_4 series except for the C_δ signals, which are located at lower field.[11,12] The ^{119}Sn NMR spectrum of **3** showed a signal similar to **2** at −26.1 ppm. It was simulated using the following ^{119}Sn, ^{31}P coupling constancies: 27.6, 42.3, 44.1, and 59.3 Hz. The crystal structure of **3** was determined from crystals grown from a toluene/pentane mixture. The unit cell contains two independent molecules. The bond alternation of the C_4 chain in the independent molecules was found to be similar to **2**. In both **2** and **3** molecules the W−CO axis is orthogonal to plane of the terminal CSnSn or CSnSi fragment. This could be rationalized on the basis of the idea that the empty p orbital of C_α prefers to be perpendicular to W−CO since it is not concurrent with CO in back-bonding. The double-bond alternation will lead to the observed orientation of the W−CO axis relative to the terminal fragment.

Trimethyltin acetylenes were expected to react in a manner analogous to the diynes, producing via a shift of the stannyl group trimethyltin-substituted vinylidenes. The reaction of **1** with $Me_3SnC{\equiv}CPh$ was carried out under conditions similar to those for **2**, monitoring the progressing reaction by ^{31}P NMR spectroscopy (Scheme 2).

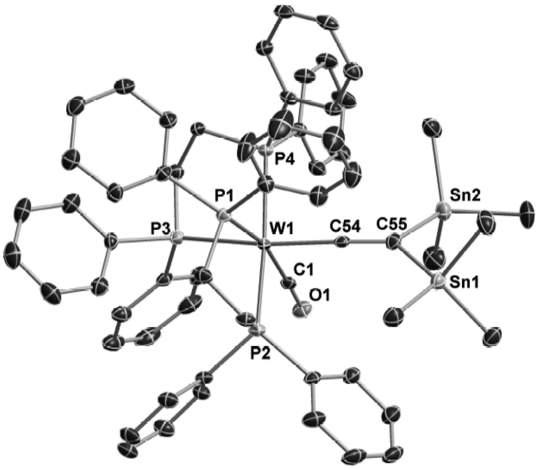


Figure 2. Thermal ellipsoid plot of the structure of **6** (30% probability level). Hydrogen atoms and solvent molecules are omitted for clarity.

The vinylidene complex [*cis*-W(CO)(dppe)$_2${C=C($SnMe_3$)(Ph)}] (**5**) could eventually be isolated by crystallization from benzene/pentane in the dark. The structure of **5** was fully established by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. The ^{31}P NMR spectrum revealed the tungsten environment to be analogous to **2** and **3** with *cis*-configured diphosphines, and in addition the ^{13}C NMR spectrum of **5** exhibited resonances for the vinylidene unit at 309 (C_α) and 111.6 ppm (C_β), which were comparable to the data of other tungsten vinylidenes.[22,23] The reaction of **1** applying $Me_3SnC{\equiv}CSnMe_3$ afforded the bis-trimethylstannyl-substituted vinylidene complex [*cis*-W(CO)(dppe)$_2${C=C($SnMe_3$)$_2$}] (**6**) in 30% yield. The structure of **6** was established by spectroscopic methods and confirmed by an X-ray diffraction study (Figure 2).

The [*cis*-W(CO)(dppe)$_2$] substructure of **6** is overall similar to that of **2** and **3**. The W=C bond distance of 2.007(4) Å is longer than that observed for related vinylidene species [cis-W(CO)(dppe)$_2$(C=CHCOOEt)] (1.88(1) Å)[22,24] and is slightly longer than the W=C bond distance in the butatrienylidene complex **2**. This is in line with the theoretical prediction of increasing π-acceptor properties with an increase in the number of cumulenic carbon atoms.[25] The formation of vinylidene derivatives directly from **1** and tin-substituted acetylenes is in contrast to the reactivity of terminal acetylenes, where the required acetylene/vinylidene rearrangement was not accessible; rather the alternative pathways of C−H oxidative additions prevailed.[22]

The reaction of **1** with $Me_3SnC{\equiv}CSiMe_3$ furnished also a vinylidene derivative, which could be detected by NMR in solution, but could not be isolated due to its too low stability. The main product of this reaction was [*trans*-W(CO)(dppe)$_2$(C≡C-$SiMe_3$)] (**9**). In a similar fashion loss of the tin group occurred for **6** and **5**, producing [*trans*-W(CO)(dppe)$_2$(C≡C-$SnMe_3$)] (**8**), phenylacetylide complex [*trans*-W(CO)(dppe)$_2$(C≡CPh)] (**7**), and $Me_3SnSnMe_3$. The yields of **5** and **6** according to Scheme 2 are low, because even in thermally induced reactions they are intermediates on the way to **7** and **8**. Full conversions of **5** and **6** to **7** and **8** could be accomplished by

---

(23) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789.

(24) Marrone, A.; Re, N. *Organometallics* **2002**, *21*, 3562.

(25) Re, N.; Sgamellotti, A.; Floriani, C. *Organometallics* **2000**, *19*, 1115.

short periods of UV irradiation. The photolytic activation of the tin-substituted vinylidenes is expected to operate on the same basis as the thermal processes breaking the C−Sn bond with subsequent recombination of the $SnMe_3$ radical to form $Me_3SnSnMe_3$. The remaining radical on the β-carbon atom delocalizes to the tungsten center with structures best described as W(I) acetylide complexes. All three compounds **7**−**9** are paramagnetic d^5 species and are related in the way of their formation to dinuclear tungsten acetylide complexes recently obtained in our group.[15] **7** and **9** were characterized by single-crystal X-ray diffraction analyses (Figure 3 and Supporting Information).

The coordinative environment of the tungsten center in **9** is pseudo-octahedral, composed of a square of phosphorus atoms (*trans* diphosphines) and *trans*-disposed CO and alkynyl ligands. Average W−P distances of 2.472(1) and 2.478(1) Å were found for **7** and **9**, respectively.

We then attempted the deprotection of **2** by treatment with a THF water solution in a similar way to that for **4**;[15] however a complex mixture was obtained that could not be fully unraveled into its components. To gain further insight into this transformation, a low-temperature study of the reaction between **2** and $NBu_4F \cdot 3H_2O$ was initiated and monitored by ^1H and ^{31}P NMR spectroscopy. We found no evidence for the formation of a H-substituted cumulenylidene complex, even at low temperature (−40 °C). Instead two overlapping singlets were detected in the ^{31}P NMR spectrum, remaining at room temperature, but changing in intensities during the course of the reaction. The reaction mixture was evaporated to dryness, and the solid residue was washed with toluene to give an orange powder of complex **10** (Scheme 3). This compound showed a singlet in the ^{31}P NMR spectrum with a chemical shift similar to other complexes with *trans*-disposed dppe ligands and identical to one of the singlets of the VT NMR.[26] The ^{13}C NMR spectrum shows four signals for the C4 carbon atoms at 149.2 (C_α), 98.9 (C_β), 76.8 (C_γ), and 48.7 ppm (C_δ). A DEPT experiment confirmed that C_δ is bonded to one proton. The ^1H NMR spectrum also clearly demonstrated the presence of the $[NBu_4]^+$ cation. On the basis of these data the pseudo-octahedral structure [*trans*-W(CO)(dppe)$_2$(C≡C-C≡CH)][NBu$_4$] (**10**) was proposed, which could be confirmed by an X-ray diffraction analysis (Figure 4). **10** is presumably formed via consecutive destannylation of **2** with [*trans*-W(CO)(dppe)$_2$(C≡CC≡CSnMe$_3$)][NBu$_4$] as an intermediate, which was attributed the second singlet appearing in the VT ^{31}P NMR spectra.

Spectroscopic and Electrochemical Properties. The butatrienylidene complexes **2**−**4** were characterized by UV−vis−NIR and CV (cyclic voltammetry) studies. The UV−vis−NIR data are presented in Figure 5.

All three complexes **2**−**4** exhibit three main absorptions. Their intensities decrease with increasing wavelengths (Table 1). The lowest energy transition could be attributed to the HOMO/LUMO transition. The *p*-*t*BuC$_6$H$_4$ substituent turns out to be a special case in this series of spectra, because this substituent strongly affects both the position and intensities of the absorptions (Figure 5), while the change of the $SnMe_3$ to a $SiMe_3$ substituent has only little influence on the spectra. As could be seen from the spectra, the band for **4** reveals a strong blue shift and decreases in intensity. This could imply an increase in the HOMO−LUMO gap, which would be consistent with the higher stability of the deprotected complex bearing an aromatic substituent.

CV studies of **2** and **4** revealed irreversible oxidation and reduction processes (see Supporting Information for details).

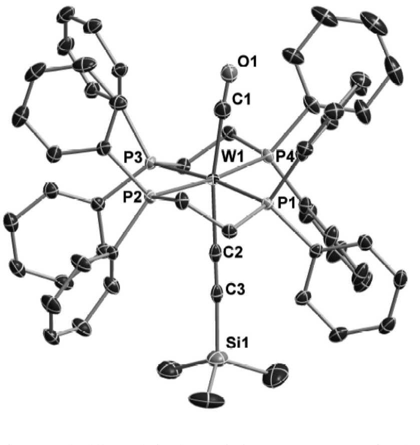


Figure 3. Thermal ellipsoid plot of the structure of **9** (30% probability level). Hydrogen atoms and solvent molecules are omitted for clarity.

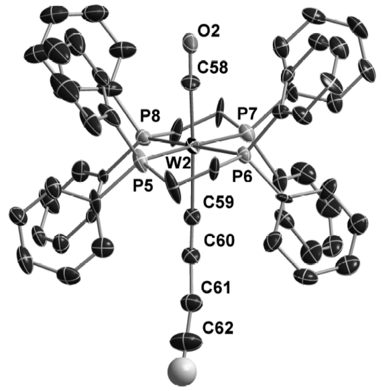
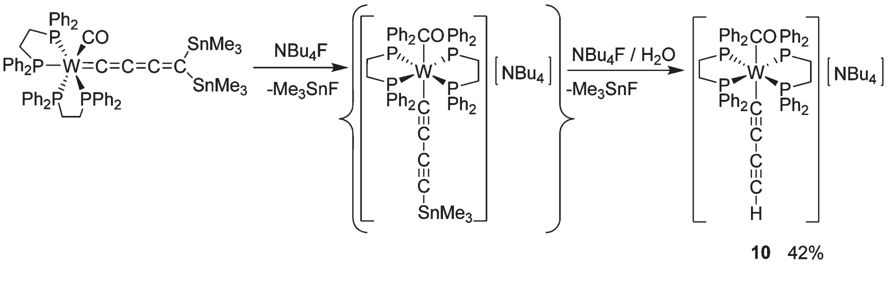


Figure 4. Thermal ellipsoid plot of the structure of the anionic part of **10** (30% probability level). The tetrabutylammonium cation and selected hydrogen atoms are omitted for clarity. Only one of the two crystallographically independent molecules is presented.

Scheme 3



10 42%

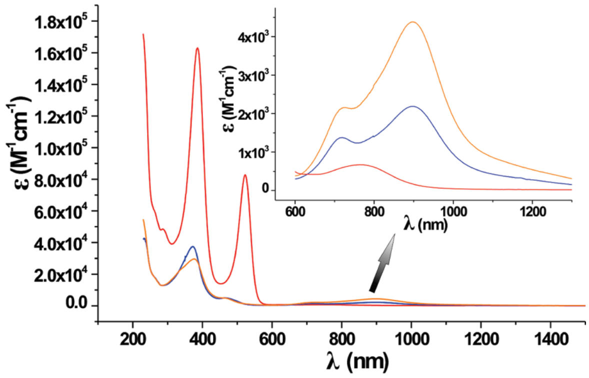


Figure 5. UV−vis−NIR spectra for **2** (orange), **3** (blue), and **4** (red).

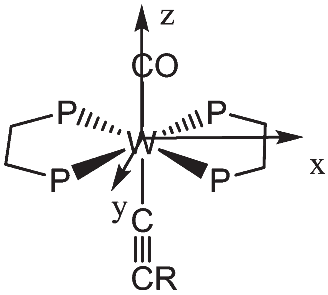


Figure 6. Coordinate system for the interpretation of the CV and EPR data. *x* and *y* are chosen arbitrarily.

Complexes **7**−**9** possess a d^5 configuration. The d_{xy} orbital (see Figure 6 for coordinate system) is expected to be the SOMO. As a result, facile oxidations and reductions were anticipated. The redox properties of **9** were also probed by CV measurements in CH_2Cl_2 and THF solutions (Figures 7 and Supporting Information). They show a fully reversible reduction wave ($E_{1/2} = -1.62$ V vs $Fc^{0/+}$, $i_c/i_a = 1$ in THF; $E_{1/2} = -1.62$ V vs $Fc^{0/+}$, $i_c/i_a = 1.03$ in CH_2Cl_2) and an irreversible oxidation process ($E_{p/2} = -0.869$ V in THF; $E_{p/2} = -0.882$ V in CH_2Cl_2) followed by a reversible oxidation ($E_{1/2} = 0.13$ V, $i_c/i_a = 0.94$ in THF; $E_{1/2} = 0.16$ V, $i_c/i_a = 1.01$ in CH_2Cl_2). The reduction wave probably belongs simply to one electron reduction of **9** to $\mathbf{9}^-$ anion. The irreversibility of the first oxidation wave is not yet understood. The full irreversibility retains up to 2 V/s, suggesting that fast transformation is coupled with oxidation process. This transformation probably does not involve exchange of ligand to solvent because of similarity of behaviors of this wave in THF and CH_2Cl_2.

9 was also investigated by EPR spectroscopy (Figure 8). No signal was observed at room temperature; however at temperatures below 50 K a signal was detected. It is strongly anisotropic with individual *g* factor components ranging from 2.6 to 1.6. The fitting of this spectrum could be carried out approximating the structure of **9** to rhombic symmetry with the *z*-axis in the direction of the acetylide ligand and the *x*- and *y*-axes in the direction of the C_2-axis between the phosphorus atoms (Figure 6).

The spectrum however was modeled with $g_x = 2.57$, $g_y = 2.24$, and $g_z = 1.61$ (Figure 8). The quality of the spectrum did not allow a reliable estimate of the hyperfine coupling of the P nuclei. The obtained values for components of the *g*-factor are in the expected range for d^5 low-spin systems,[27] where two main factors affect the anisotropy of *g*: (a) the splitting of the T_{2g} ground term due to the low symmetry of the coordination sphere and (b) the spin−orbital coupling leading to mixing of these split states. The crystal field in our case is strongly distorted from octahedral symmetry with the *π*-acceptor interaction as an important factor. Such asymmetry around a 5d metal atom could lead to significant separation of the d_{xy} from d_{xz} and d_{yz} orbitals to give an isotropic signal at g = 2. However, spin−orbital coupling, which can be strong for the heavy metal tungsten, has an opposite influence and would increase the *g* anisotropy. Particularly for d^5 low-spin complexes of group VI metals, such strong *g* anisotropy is not typical. The related $[trans\text{-}M(CO)_2(dppm)_2]^+$ (M = Cr, Mo; dppm = 1,2-bis(diphenylphosphinomethane)) have well-resolved EPR

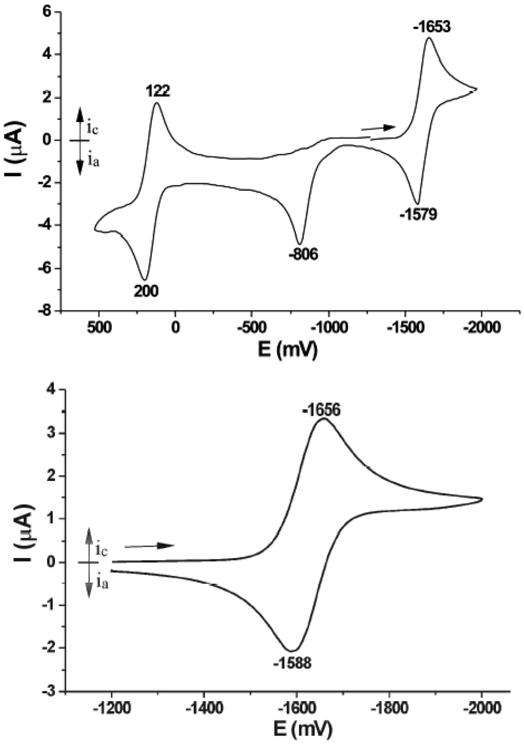


Figure 7. Cyclic voltammogram of **9** in CH_2Cl_2 (top) and in THF (bottom); 0.1 M $[nBu_4N][PF_6]$; Au electrode; *E* vs $Fc^{0/+}$; scan rate = 100 mV/s; 20 °C.

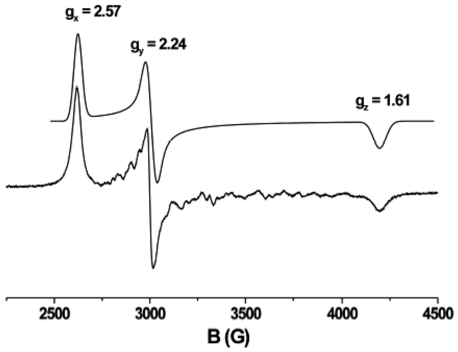


Figure 8. Experimental (bottom) and modeled (top) solid-state EPR spectra of powdered **9** at 30 K.

---

(26) Semenov, S. N.; Blacque, O.; Fox, T.; Venkatesan, K.; Berke, H. *J. Am. Chem. Soc.* **2010**, *132*, 3115.

(27) Rieger, P. H. *Coord. Chem. Rev.* **1994**, *135*, 203.

spectra, while for [*trans*-$W(CO)_2(dppm)_2]^+$ only unclearness of the spectrum was mentioned.[28] The *g* tensor obtained for **9** is less anisotropic than in Ru^{3+} or Os^{3+} tris-bipyridyl complexes, where strong spin−orbital coupling cannot be compensated by strong distortion, and it is then closer to the $[Fe(bipy)_3]^{3+}$ (bipy-2,2′-bipyridyl) values.[29] The EPR experiment indeed confirmed the mixing of d_{xy} with d_{xz} and d_{yz} orbital characters in the [*trans*-W(CO)(dppe)$_2$(C≡C)] fragment.[15] This would also provide an explanation for the significant antiferromagnetic coupling between such centers in related bridged W(d^5)(bridge)W(d^5) molecules. Electrons in a pure d_{xy} orbital (δ-symmetry) cannot interact with the orbitals of the acetylide ligand, since these are of π-symmetry; however upon mixing with the d_{xz} and d_{yz}, the orbital symmetry restriction is lifted, thereby providing an antiferromagnetic long-distance through-bridge exchange in the dinuclear case.[15]

Conclusion

In conclusion, we have shown that [*trans*-W(CO)(N_2)(dppe)$_2$] is a suitable starting material for the preparation of tungsten butatrienylidene complexes of the type [*cis*-W(CO)(dppe)$_2${C=C=C=C($SnMe_3$)(R)}]. We demonstrated that R has a strong influence on the deprotection process and also showed that the bistrimethyltin derivative could be readily destannylated by NBu_4F to give the corresponding butadiyne compound. The UV-vis data revealed that such a difference in stability can be attributed to electronic effects, particularly the higher HOMO/LUMO gap in the case of aryl substitution. The reaction of the N_2 complex with stannylated acetylenes and subsequent removal of the $SnMe_3$ moieties by UV or thermal activation constitutes a new synthetic access to unique [*trans*-W(CO)(dppe)$_2$(C≡CR)] acetylides. The electronic structures of these complexes were studied by CV and EPR measurements. The accessibility of the butadiyne derivatives and the W(I) acetylide complexes opens up new avenues for the development of binuclear complexes with longer conjugated bridges, i.e., for instance μ-C_8 compounds.

Experimental Section

General Procedures. All the manipulations were carried out under a nitrogen atmosphere using Schlenk techniques or a drybox. Reagent grade benzene, toluene, hexane, pentane, diethyl ether, and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl prior to use. Dichloromethane and acetonitrile were distilled from CaH_2. The literature procedures were used to prepare the following compounds: $Me_3SnC≡CC≡CSiMe_3$,[30] [*trans*-W(CO)(N_2)(dppe)$_2$],[20] and [*cis*-W(CO)(dppe)$_2${C=C=C=C($SnMe_3$)(*p*-C_6H_4*t*Bu)}].[15] $Me_3SnC≡CC≡CSnMe_3$ was prepared by a modified literature protocol (see Supporting Information).[31] All other chemicals were used as obtained from commercial suppliers. The IR spectra were obtained on a Bio-Rad FTS-45 instrument and a Bio-Rad Excalibur FTS-3500 instrument. NMR spectra were measured on a Varian Mercury spectrometer at 200 MHz for the ^1H nucleus and at 81 MHz for $^{31}P\{^1H\}$ spectra, on a Varian Gemini-2000 spectrometer at 300 MHz for ^1H spectra and at 75 MHz for $^{13}C\{^1H\}$ spectra, and on Bruker-DRX-500 and Bruker-AV2-500 spectrometers at 500 MHz for ^1H, 125.8 MHz for $^{13}C\{^1H\}$, and 202.5 MHz for $^{31}P\{^1H\}$. Chemical shifts for ^1H and ^{13}C are given in ppm relative to TMS, and those for ^{31}P relative to phosphoric acid. The UV−vis and near-IR spectra were recorded on Varian CARY 50 Scan UV−visible and on Varian CARY 500 Scan UV−visible/near-IR spectrometers. CHN elemental analyses were performed with a LECO CHN-932 microanalyzer. Cyclic voltammograms were obtained with a BAS 100 W voltammetric analyzer equipped with the low-volume cell. The cell was equipped with an Au working and a Pt counter electrode and a nonaqueous reference electrode. All sample solutions (THF or CH_2Cl_2) were approximately 2×10^{-3} M in substrate and 0.1 M in Bu_4NPF_6 and were prepared under nitrogen. Ferrocene was subsequently added, and the calibration of voltammograms recorded. The BAS 100W program was employed for data analysis. X-band EPR spectra were obtained using a Bruker EMX electron spin resonance system (resolution 2048; central field 3400 G; sweep width 3000 G; frequency 9.448 GHz; modulation frequency 100 kHz; modulation amplitude 10 G; time constant 20.48 ms, conversion time 40.96 ms; receiver gain 2.24×10^4). The spectrum was modeled using the SimFonia program (frequency 9.448 GHz; $g_x = 2.57$; $g_x = 2.24$; $g_x = 1.61$; line width *x*-direction 42 G; line width *y*-direction 48 G; line width *y*-direction 68 G).

X-ray Diffraction Studies on 2, 3, 6, 7, 9, and 10. Intensity data for all crystals were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector, and a single-wavelength Enhance X-ray source with Mo Kα radiation, $\lambda = 0.71073$ Å)[32] using the CrysAlisPro program.[32] The selected single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. The crystal structures were solved with SHELXS-97[33] using direct methods. The structure refinements were performed by full-matrix least-squares on F^2 with SHELXL-97.[33] The program PLATON[34] was used to check the results of the X-ray analyses. All programs used during the crystal structure determination process are included in the WINGX software.[34] CCDC 783485−783490 contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[*cis*-W(CO)(dppe)$_2${C=C=C=C($SnMe_3$)$_2$}] (2). [*trans*-W(CO)(N_2)(dppe)$_2$] (100 mg, 0.096 mmol) and $Me_3SnC≡CC≡CSnMe_3$ (43 mg, 0.116 mmol) were placed in a Young-Schlenk tube in 10 mL of benzene. Three freeze−pump−thaw cycles were carried out on the resulting solution to remove any dissolved nitrogen. The reaction mixture was heated under vacuum at 60 °C for 5 h. The resulting dark orange solution was concentrated to 1.5 mL *in vacuo* and layered with 10 mL of pentane. Complex **2** was obtained as brown-orange prisms in 10 h. Yield: 95 mg (0.069 mmol, 72%). Single crystals suitable for X-ray diffraction were grown by layering a benzene solution with pentane. Anal. Calcd for $C_{63}H_{66}OP_4Sn_2W$: C, 54.66; H, 4.81. Found: C, 54.92; H, 4.99. IR (cm^{-1}): $\nu =$ 1786 (CO), 1808 (CO), 1926 (C_4). ^1H NMR (500 MHz, C_6D_6): δ 8.59 (t, $J_{H-H} = 9$ Hz, 2H, C_6H_5), 8.54 (t, $J_{H-H} = 9$ Hz, 2H, C_6H_5), 7.45 (t, $J_{H-H} = 8$ Hz, 2H, C_6H_5), 7.35−7.25 (m, 5H, C_6H_5), 7.21−6.56 (m, 20H, C_6H_5), 6.38 (t, $J_{H-H} = 8$ Hz, 1H, C_6H_5), 6.17 (t, $J_{H-H} = 8$ Hz, 2H, C_6H_5), 3.15−2.88 (m, 2H, CH_2), 2.64 − 2.05 (m, 2H, CH_2), 1.85−1.72 (m, 4H, CH_2), 0.31 (s, 9H, $SnCH_3$ (d, satellite, $^2J_{H-Sn} = 52$ Hz)). ^{119}Sn NMR (184.6 MHz, C_6D_6): δ −22.5 (m, $SnMe_3$). ^{31}P NMR (81 MHz, C_6D_6): δ 48.8 (m, 1P), 44.9 (m, 1P), 30.0 (m, 1P), 26.8 (m, 1P). ^{13}C NMR (125 MHz, C_6D_6): 249.5 (q, $^2J_{C-P} = 11$ Hz, Cα), 222.8 (d, $^2J_{C-P} = 28$ Hz, CO), 144.1

---

(28) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 2526.

(29) DeSimone, R. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 2343.

(30) Zheng, Q. L.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, *23*, 5896.

(31) Brefort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, T.; Garnier, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500.

(32) *Xcalibur CCD System*; Oxford Diffraction Ltd: Abingdon, Oxfordshire, England, 2007.

(33) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(34) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(d, $^1J_{C-P}$ = 28 Hz, ipso-C_6H_5), 142.3 (d, $^1J_{C-P}$ = 29 Hz, ipso-C_6H_5), 140.7 (d, $^1J_{C-P}$ = 25 Hz, ipso-C_6H_5), 139.9 (d, $^1J_{C-P}$ = 46 Hz, ipso-C_6H_5), 139.4 (d, $^1J_{C-P}$ = 45 Hz, ipso-C_6H_5), 137.9 (d, $^1J_{C-P}$ = 25 Hz, ipso-C_6H_5), 136.4 (d, $^1J_{C-P}$ = 28 Hz, ipso-C_6H_5), 134.6 (d, J_{C-P} = 11 Hz, C_6H_5), 133.4 (d, J_{C-P} = 10 Hz, C_6H_5), 133.1 (m, C_6H_5), 132.6 (s, C_6H_5), 132.5 (s, C_6H_5), 132.4 (s, C_6H_5), 132.3 (s, C_6H_5), 131.7 (d, J_{C-P} = 11 Hz, C_6H_5), 131.3 (dd, J_{C-P} = 10 Hz, J_{C-P} = 3 Hz, C_6H_5), 129.1 (dd, J_{C-P} = 18 Hz, J_{C-P} = 2 Hz, C_6H_5), 128.5 (s, C_6H_5), 128.4 (s, C_6H_5), 128.3 (s, C_6H_5), 124.8 (s, Cβ), 124.7 (s, Cγ), 46.8 (s, (d, satellite, $^1J_{C-Sn}$ = 303 Hz) Cδ), 32.5 (m, CH_2), 30.2 (dd, $^1J_{C-P}$ = 23 Hz, $^2J_{C-P}$ = 13 Hz, CH_2), 28.5 (dd, $^1J_{C-P}$ = 23 Hz, $^2J_{C-P}$ = 15 Hz, CH_2), −7.0 (s, (d, satellite, $^1J_{C-Sn}$ = 324 Hz), CH_3).

[*cis*-W(CO)(dppe)$_2${C=C=C=C(SnMe$_3$)(SiMe$_3$)}] (3). An analogous procedure to **2** was followed applying [*trans*-W(CO)(N_2)(dppe)$_2$] (100 mg, 0.096 mmol) and $Me_3SnC{\equiv}CC{\equiv}CSiMe_3$ (33 mg, 0.116 mmol). Yield: 80 mg (0.062 mmol, 65%). Single crystals suitable for X-ray diffraction were grown by layering a toluene solution with pentane. Anal. Calcd for $C_{63}H_{66}OP_4SnSiW$: C, 58.49; H, 5.14. Found: C, 58.62; H, 5.09. IR (cm^{-1}): ν = 1798 (CO), 1935 (C_4). ^{1}H NMR (500 MHz, C_6D_6): δ 8.48 (t, J_{H-H} = 9 Hz, 2H, C_6H_5), 8.43 (t, J_{H-H} = 9 Hz, 2H, C_6H_5), 7.60 (t, J_{H-H} = 8 Hz, 2H, C_6H_5), 7.35 (t, J_{H-H} = 8 Hz, 2H, C_6H_5), 7.21 (q, J_{H-H} = 8 Hz, 2H, C_6H_5), 7.14−7.09 (m, 10H, C_6H_5), 7.03−6.68 (m, 12H, C_6H_5), 6.62 (t, J_{H-H} = 8 Hz, 4H, C_6H_5), 6.53 (t, J_{H-H} = 7 Hz, 2H, C_6H_5), 6.49 (t, J_{H-H} = 8 Hz, 2H, C_6H_5), 6.06 (t, J_{H-H} = 8 Hz, 2H, C_6H_5), 3.05−2.80 (m, 2H, CH_2), 2.56−2.25 (m, 2H, CH_2), 2.19−1.97 (m, 3H, CH_2), 1.73−1.62 (m, 1H, CH_2), 0.28 (s, 9H, $SiCH_3$), 0.25 (s, (d, satellite, $^2J_{H-Sn}$ = 52 Hz), 9H, $SnCH_3$). ^{119}Sn NMR (184.6 MHz, C_6D_6): δ −26.1 (m, $SnMe_3$). ^{31}P NMR (81 MHz, C_6D_6): δ 48.7 (m, 1P), 44.3 (m, 1P), 29.5 (m, 1P), 26.2 (m, 1P). ^{13}C (125 MHz, C_6D_6): 254.1 (q, $^2J_{C-P}$ = 12 Hz, Cα), 222.5 (d, $^2J_{C-P}$ = 32 Hz, CO), 143.9 (d, $^1J_{C-P}$ = 28 Hz, ipso-C_6H_5), 142.4 (s, Cβ), 142.5 (s, Cγ), 142.1 (d, $^1J_{C-P}$ = 30 Hz, ipso-C_6H_5), 140.4 (d, $^1J_{C-P}$ = 27 Hz, ipso-C_6H_5), 139.8 (d, $^1J_{C-P}$ = 46 Hz, ipso-C_6H_5), 139.2 (d, $^1J_{C-P}$ = 46 Hz, ipso-C_6H_5), 137.9 (dd, $^1J_{C-P}$ = 27 Hz, J_{C-P} = 6 Hz, ipso-C_6H_5), 137.2 (dd, $^1J_{C-P}$ = 27 Hz, J_{C-P} = 3 Hz, ipso-C_6H_5), 136.0 (dd, $^1J_{C-P}$ = 25 Hz, J_{C-P} = 3 Hz, ipso-C_6H_5), 134.7 (d, J_{C-P} = 11 Hz, C_6H_5), 133.4 (d, J_{C-P} = 10 Hz, C_6H_5), 132.5 (d, J_{C-P} = 9 Hz, C_6H_5), 132.5 (d, J_{C-P} = 11 Hz, C_6H_5), 132.4 (d, J_{C-P} = 12 Hz, C_6H_5), 131.8 (d, J_{C-P} = 11 Hz, C_6H_5), 131.4 (dd, J_{C-P} = 10 Hz, J_{C-P} = 4 Hz, C_6H_5), 129.3 (dd, J_{C-P} = 20 Hz, J_{C-P} = 2 Hz, C_6H_5), 128.7 (s, C_6H_5), 128.6 (s, C_6H_5), 128.4 (s, C_6H_5), 49.1 (s, (d, satellite, $^1J_{C-Sn}$ = 290 Hz), Cδ), 32.3 (m, CH_2), 30.4 (dd, $^1J_{C-P}$ = 24 Hz, $^2J_{C-P}$ = 12 Hz, CH_2), 28.3 (dd, $^1J_{C-P}$ = 23 Hz, $^2J_{C-P}$ = 16 Hz, CH_2), 2.0 (s, $SiCH_3$), −7.0 (s, (d, satellite, $^1J_{C-Sn}$ = 310 Hz), $SnCH_3$).

[*cis*-W(CO)(dppe)$_2${C=C(SnMe$_3$)$_2$}] (6). An analogous procedure to **2** was applied starting from [*trans*-W(CO)(N_2)(dppe)$_2$] (20 mg, 0.0193 mmol) and $Me_3SnC{\equiv}CSnMe_3$ (7.4 mg, 0.021 mmol). A higher concentration of **4** and cooling were required to initialize crystallization of **4**. Yield: 8 mg (0.0059 mmol, 30%). Single crystals suitable for X-ray diffraction were grown by layering a benzene solution with pentane. Anal. Calcd for $C_{61}H_{67}OP_4Sn_2W$: C, 53.82; H, 4.96. Found: C, 54.02; H, 4.09. IR (cm^{-1}): ν = 1789 (CO). ^{1}H NMR (500 MHz, C_6D_6): δ 8.48 (t, J = 8 Hz, 2H, C_6H_5), 8.42 (t, J = 8 Hz, 2H, C_6H_5), 8.16 (t, J = 8 Hz, 2H, C_6H_5), 8.00 (t, J = 9 Hz, 2H, C_6H_5), 7.84 (t, J = 7 Hz, 2H, C_6H_5), 7.60 (t, J = 8 Hz, 2H, C_6H_5), 7.42 (t, J = 7 Hz, 2H, C_6H_5), 7.36 (t, J = 8 Hz, 4H, C_6H_5), 7.16 (m, 8H, C_6H_5), 7.00 (m, 8H, C_6H_5), 6.81 (t, J = 7 Hz, 2H, C_6H_5), 6.75 (t, J = 7 Hz, 2H, C_6H_5), 6.23 (m, 4H, C_6H_5), 2.65 (m, 2H, CH_2), 2.29−1.60 (m, 6H, CH_2), 0.28 (s, 18H, $SnCH_3$ (d, satellite, $^2J_{H-Sn}$ = 52 Hz)). ^{119}Sn NMR (184.6 MHz, C_6D_6): δ −32.2 (m, SnMe3). ^{31}P NMR (202 MHz, C_6D_6): δ 42.5 (m, 1P), 38.3 (m, 1P), 28.7 (m, 1P), 26.7 (m, 1P). ^{13}C NMR (125 MHz, C_6D_6): 297.6 (s, Cα), 226.2 (d, $^2J_{C-P}$ = 23 Hz, CO), 144.9 (d, $^1J_{C-P}$ = 34 Hz, ipso-C_6H_5), 142.6 (d, $^1J_{C-P}$ = 27 Hz, ipso-C_6H_5), 141.8 (d, $^1J_{C-P}$ = 27 Hz, ipso-C_6H_5), 141.5 (d, $^1J_{C-P}$ = 34 Hz, ipso-C_6H_5), 141.2 (d, $^1J_{C-P}$ = 27 Hz, ipso-C_6H_5), 140.4 (d, $^1J_{C-P}$ = 22 Hz, ipso-C_6H_5), 140.1 (d, $^1J_{C-P}$ = 18 Hz, ipso-C_6H_5), 138.7 (d, $^1J_{C-P}$ = 34 Hz, ipso-C_6H_5), 134.0 (d, J_{C-P} = 11 Hz, C_6H_5), 133.8 (d, J_{C-P} = 11 Hz, C_6H_5), 133.5 (d, J_{C-P} = 11 Hz, C_6H_5), 133.3 (d, J_{C-P} = 11 Hz, C_6H_5), 132.8 (d, J_{C-P} = 11 Hz, C_6H_5), 131.3 (d, J_{C-P} = 11 Hz, C_6H_5), 131.5 (d, J_{C-P} = 11 Hz, C_6H_5), 131.0 (d, J_{C-P} = 11 Hz, C_6H_5), 129.1 (s, C_6H_5), 128.8 (s, C_6H_5), 128.6 (s, C_6H_5), 128.5 (s, C_6H_5), 127.3 (s, C_6H_5), 127.2 (s, C_6H_5), 127.1 (s, C_6H_5), 90.8 (d, $^3J_{C-P}$ = 15 Hz, Cβ), 32.8 (dd, $^1J_{C-P}$ = 24 Hz, $^2J_{C-P}$ = 16 Hz, CH_2), 29.7 (m, CH_2), 28.1 (dd, $^1J_{C-P}$ = 22 Hz, $^2J_{C-P}$ = 12 Hz, CH_2), −3.2 (s, $SnCH_3$ (d, satellite $^1J_{C-Sn}$ = 313 Hz)).

[*cis*-W(CO)(dppe)$_2${C=C(SnMe$_3$)(Ph)}] (5). An analogous procedure to **2** was followed applying [*trans*-W(CO)(N_2)(dppe)$_2$] (20 mg, 0.0193 mmol) and $PhC{\equiv}CSnMe_3$ (5.6 mg, 0.021 mmol). Yield: 16 mg (0.0125 mmol, 65%). Anal. Calcd for $C_{64}H_{63}OP_4SnW$: C, 60.31; H, 4.98. Found: C, 60.55; H, 5.07. IR (cm^{-1}): ν = 1783 (CO). ^{1}H NMR (500 MHz, THF-d_8): δ 8.17 (t, J_{H-H} = 8 Hz, 2H, C_6H_5), 7.74 (m, 6H, C_6H_5), 7.25−7.00 (m, 25H, C_6H_5), 6.89 (q, J = 8 Hz, 4H, C_6H_5), 6.78 (t, J = 7 Hz, 2H, C_6H_5), 6.68 (t, J = 7 Hz, 2H, C_6H_5), 6.56 (t, J = 7 Hz, 1H, C_6H_5), 6.23 (t, J = 7 Hz, 2H, C_6H_5), 6.17 (t, J = 7 Hz, 2H, C_6H_5), 3.18 (m, 1H, CH_2), 3.18 (m, 1H, CH_2), 2.22−1.62 (m, 6H, CH_2), −0.46 (s, 9H, $SnCH_3$ (d, satellite, $^2J_{H-Sn}$ = 50 Hz)). ^{119}Sn NMR (184.6 MHz, THF-d_8): δ −41.4 (m, $SnMe_3$). ^{31}P NMR (202 MHz, C_6D_6): δ 40.4 (m, 1P), 38.0 (m, 1P), 24.1 (m, 1P), 21.8 (m, 1P). ^{13}C NMR (125 MHz, THF-d_8): 309.1 (dq, $^2J_{C-P(trans)}$ = 20 Hz, $^2J_{C-P(cis)}$ = 10 Hz, Cα), 225.3 (d, $^2J_{C-P}$ = 28 Hz, CO), 151.7 (s, ipso-C_6H_5), 142.2 (d, $^1J_{C-P}$ = 32 Hz, ipso-C_6H_5), 140.4 (d, $^1J_{C-P}$ = 35 Hz, ipso-C_6H_5), 139.1 (d, $^1J_{C-P}$ = 33 Hz, ipso-C_6H_5), 138.6 (s, C_6H_5), 138.4 (d, $^1J_{C-P}$ = 33 Hz, ipso-C_6H_5), 137.9 (d, $^1J_{C-P}$ = 26 Hz, ipso-C_6H_5), 136.0 (s, C_6H_5), 135.9 − 135.7 (m, C_6H_5), 132.1 (d, J_{C-P} = 11 Hz, C_6H_5), 131.5 (d, J_{C-P} = 11 Hz, C_6H_5), 131.3 (d, J_{C-P} = 11 Hz, C_6H_5), 131.0 (d, J_{C-P} = 11 Hz, C_6H_5), 130.5 (d, J_{C-P} = 11 Hz, C_6H_5), 129.6 (d, J_{C-P} = 11 Hz, C_6H_5), 129.4 (d, J_{C-P} = 11 Hz, C_6H_5), 129.3 (d, J_{C-P} = 11 Hz, C_6H_5), 127.2 (s, C_6H_5), 126.7 (s, C_6H_5), 126.4 (s, C_6H_5), 126.3 (s, C_6H_5), 126.0 (s, C_6H_5), 125.9 (s, C_6H_5), 125.8 (s, C_6H_5), 125.6 (s, C_6H_5), 125.5 (s, C_6H_5), 125.4 (s, C_6H_5), 125.3 (s, C_6H_5), 111.6 (d, $^3J_{C-P}$ = 14 Hz, Cβ), 29.8 (dd, $^1J_{C-P}$ = 23 Hz, $^2J_{C-P}$ = 15 Hz, CH_2), 27.3 (m, CH_2), 25.6 (dd, $^1J_{C-P}$ = 25 Hz, $^2J_{C-P}$ = 12 Hz, CH_2), −8.0 (s, $SnCH_3$ (d, satellite $^1J_{C-Sn}$ = 310 Hz)).

[*trans*-W(CO)(dppe)$_2$(C≡CPh)] (7). A solution of **5** (16 mg, 0.0125 mmol) in 0.5 mL of benzene was irradiated with an UV lamp for 5 min. The completeness of the reaction was assured by disappearance of the ^{31}P NMR signals of **5**. The resulting solution was concentrated to 0.3 mL and was layered with pentane to give crystals of **6**. Yield: 16 mg (0.0125 mmol, 65%). Anal. Calcd for $C_{61}H_{54}OP_4W$: C, 65.96; H, 4.90. Found: C, 66.02; H, 5.01. IR (cm^{-1}): ν = 1793 (CO). ^{1}H NMR (200 MHz, THF-d_8): δ 17.3 (br), 13.3 (br), 8.1 (br), 7.1 (br), 6.0 (br), 5.6 (br), 5.4 (br), 0.0 (br).

[*trans*-W(CO)(dppe)$_2$(C≡CSnMe$_3$)] (8). An analogous procedure to that for **7** was followed using [*trans*-W(CO)(N_2)(dppe)$_2$] (50 mg, 0.048 mmol) and $Me_3SnC{\equiv}CSnMe_3$ (18.5 mg, 0.053 mmol). Yield: 30 mg (0.0251 mmol, 52%). Anal. Calcd for $C_{58}H_{58}OP_4SnW$: C, 58.17; H, 4.88. Found: C, 58.49; H, 4.86. IR (cm^{-1}): ν = 1756 (CO). ^{1}H NMR (200 MHz, THF-d_8): δ 13.8 (br), 8.2 (br), 7.0 (br), 6.1 (br), 5.7 (br), 5.2 (br), −1.3 (br).

[*trans*-W(CO)(dppe)$_2$(C≡CSiMe$_3$)] (9). [*trans*-W(CO)(N_2)(dppe)$_2$] (100 mg, 0.096 mmol) and $Me_3SnC{\equiv}CSiMe_3$ (30 mg, 0.116 mmol) were placed in a Young-Schlenk tube in 6 mL of benzene. Three freeze−pump−thaw cycles was carried out to remove any dissolved nitrogen. The reaction mixture was heated under vacuum to 65 °C for 6 h. The freeze−pump−thaw cycles were repeated twice during the reaction. The resulting yellow solution was irradiated with an UV lamp for 5 min until the ^{31}P NMR signals of the vinylidene derivative disappeared. However, the vinylidene complex turned out to be unstable in this case, and irradiation was not required if the reaction was carried out overnight. Then the reaction mixture was concentrated to 1.5 mL *in vacuo* and layered with 10 mL of pentane. **7** crystallized as red prisms in 10 h. Yield: 50 mg (0.0452 mmol, 47%). Anal. Calcd for $C_{58}H_{58}OP_4SiW$: C, 62.93; H, 5.28. Found: C, 62.80; H, 5.13. IR (cm^{-1}): $\nu = 1756$ (CO). ^{1}H NMR (200 MHz, THF-d_8): δ 14.1 (br), 8.2 (br), 7.0 (br), 5.8 (br), 5.5 (br), 5.1 (br), 3.1 (br), 0.2 (br).

[*trans*-W(CO)(dppe)$_2$(C≡CC≡CH)][NBu$_4$] (10). A solution of **2** (20 mg, 0.01445 mmol) in 0.5 mL of THF-d_8 was mixed with a solution of NBu$_4$F·3H$_2$O (11 mg, 0.035 mmol) in 0.5 mL of THF-d_8 in a Young-Schlenk tube at −50 °C. Then the reaction mixture was transferred to a precooled NMR spectrometer. The temperature was raised to room temperature in approximately 1 h. The resulting mixture was kept at room temperature for one more hour and evaporated *in vacuo*. The residue was then washed with toluene three times to give **10**. Yield: 8 mg (0.0061 mmol, 42%). (A satisfactory elemental analysis could not be obtained due to thermal instability of this complex.) IR (cm^{-1}): $\nu = 3300$ (≡CH), 2056 (C≡C), 1709 (CO). ^{1}H NMR (500 MHz, THF-d_8): δ 7.41 (br, 8H, C$_6$H$_5$), 7.26 (br, 8H, C$_6$H$_5$), 6.93−6.88 (m, 24H, C$_6$H$_5$), 3.21 (t, $J_{H-H} = 8.5$ Hz, 8H, NCH$_2$), 2.38 (m, 4H, CH$_2$), 2.19 (m, 4H, CH$_2$), 1.63 (pent, $J_{H-H} = 8$ Hz, 8H, NCH$_2$C*H*$_2$), 1.36 (hex, $J_{H-H} = 7.5$ Hz, 8H, NCH$_2$CH$_2$C*H*$_2$), 1.25 (s, 1H, CH), 1.01 (s, $J_{H-H} = 7$ Hz, 12H NCH$_2$CH$_2$CH$_2$C*H*$_2$). ^{31}P NMR (81 MHz, C$_6$D$_6$): δ 45 br. ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): δ 213.1 (m, C$_\alpha$), 141.7 (br, C$_6$H$_5$-ipso), 139.9 (br, C$_6$H$_5$-ipso), 135.5 (s, C$_6$H$_5$), 134.0 (s, C$_6$H$_5$), 129.4 (s, C$_6$H$_5$), 126.8 (s, C$_6$H$_5$), 86.5 (s, C$_\beta$) 36.0 (m, CH$_2$).

Acknowledgment. Funding from the Swiss National Science Foundation (SNSF) and from the University of Zürich are gratefully acknowledged.

Supporting Information Available: Details of preparation of Me$_3$SnC≡CC≡CSnMe$_3$, CV studies of **2** and **4**, thermal ellipsoid plot for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.