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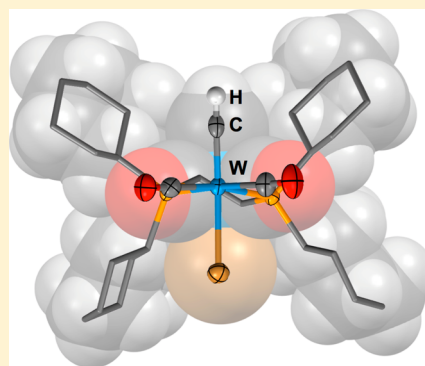
# Synthesis of a Stable Methylidyne Complex

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## S Supporting Information

**ABSTRACT:** The successive treatment of  $[\text{W}(\text{CO})_6]$  with  $\text{LiSiPh}_3$ ,  $(\text{OCBr})_2$ , and 4-picoline (pic) affords the silylcarbyne complex  $[\text{W}(\equiv\text{CSiPh}_3)\text{Br}(\text{CO})_2(\text{pic})_2]$ , which reacts with 1,2-bis(dicyclohexylphosphino)ethane (dcpe), 1,2-bis(diphenylphosphino)ethane (dppe), and tetramethylethylenediamine (tmeda) to provide the complexes  $[\text{W}(\equiv\text{CSiPh}_3)\text{Br}(\text{CO})_2(\text{L}_2)]$  ( $\text{L}_2 = \text{dcpe}, \text{dppe}, \text{tmeda}$ ). Fluoride-mediated protodesilylation of  $[\text{W}(\equiv\text{CSiPh}_3)\text{Br}(\text{CO})_2(\text{dcpe})]$  with moist  $[\text{Bu}_4\text{N}]\text{F}$  provides the stable and structurally characterized terminal methylidyne complex  $[\text{W}(\equiv\text{CH})\text{Br}(\text{CO})_2(\text{dcpe})]$  (shown) in addition to traces of the ethene-1,2-diylidyne complex  $\{\text{Br}(\text{dcpe})(\text{CO})_2\text{W}\}_2(\mu-\text{CCH}=\text{CHC}\equiv)$ .



## INTRODUCTION

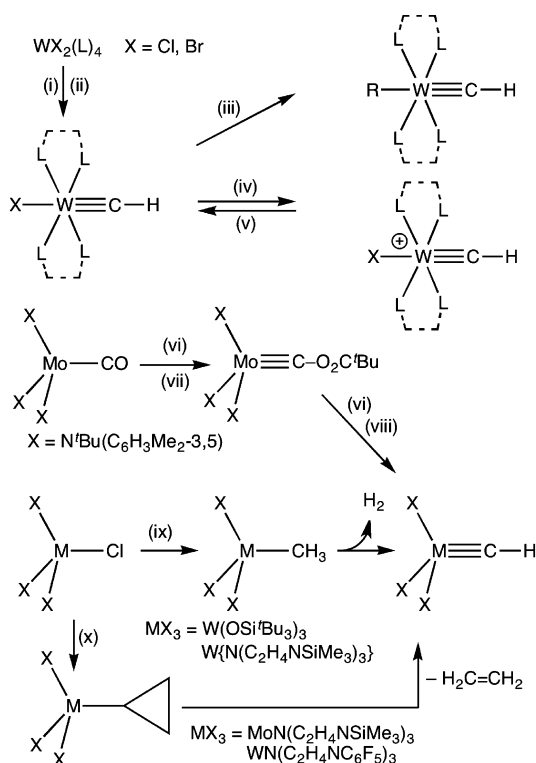
Although terminal methylidyne complexes  $\text{L}_n\text{M}\equiv\text{CH}_2$  are central to catalytic alkene metathesis,<sup>1</sup> they are generally prone to intermolecular decomposition routes. Accordingly, comparatively few isolable, structurally characterized examples are known<sup>2</sup> and the inclusion of steric bulk in coligands is a recurrent feature. Fewer complexes of methylidyne, the simplest organometallic ligand  $\text{L}_n\text{M}\equiv\text{CH}$ , have been structurally characterized,<sup>3,4</sup> and with the exception of  $[\text{W}(\equiv\text{CH})\{\text{N}^t\text{BuC}_6\text{H}_3\text{Me}_2-3,5\}_3]$ ,<sup>4</sup> all of these are variants of Schrock's archetypal complex  $[\text{W}(\equiv\text{CH})\text{Cl}(\text{PMe}_3)_4]$ <sup>3a</sup> via coligand substitution or redox processes (Scheme 1).<sup>3</sup> The vast majority of methylidyne complexes are obtained via elimination of dihydrogen or olefin extrusion from coordinatively unsaturated methyl, cyclopropyl, or norbornyl complexes.<sup>3,4</sup> An alternative route involves the protonation of the neutral terminal carbido complexes  $[\text{M}(\equiv\text{C})\text{Cl}_2\text{LL}']$  ( $\text{M} = \text{Ru}, \text{Os}$ ;  $\text{L}, \text{L}' = \text{PCy}_3, \text{NHC}$ ).<sup>5,6</sup> Thus, the reaction of  $[\text{Os}(\equiv\text{C})\text{Cl}_2(\text{PCy}_3)_2]$  with HOTf affords the thermally unstable salt  $[\text{Os}(\equiv\text{CH})\text{Cl}_2(\text{PCy}_3)_2][\text{OTf}]$ , which decomposes at ambient temperatures,<sup>6</sup> while similar intermediates account for the eventual formation of Piers' phosphoniocarbene salts  $[\text{Ru}(\equiv\text{CHPCy}_3)\text{Cl}_2(\text{L})]\text{BX}_4$  ( $\text{X} = \text{F}, \text{C}_6\text{F}_5$ ;  $\text{L} = \text{PCy}_3, \text{NHC}$ )<sup>7</sup> via migration (or dissociation/reattack) of a  $\text{PCy}_3$  ligand onto the methylidyne ligand. These salts are notable in serving as preactivated alkene metathesis initiators. Gas-phase methylidyne species, e.g.  $\text{Cl}_3\text{W}\equiv\text{CH}$ , are also proposed to form when various metals are laser ablated in the presence of halo-methanes.<sup>8</sup>

Perhaps the best studied methylidyne complexes are the thermally unstable species  $[\text{M}(\equiv\text{CH})(\text{CO})_2(\text{Tp}^*)]$  ( $\text{M} = \text{Mo}$  (**1a**),  $\text{W}$  (**1b**);  $\text{Tp}^* = \text{hydrotris(dimethylpyrazolyl)borate}$ ), which were first generated by Templeton via the fluoride-mediated protodesilylation of silylcarbynes  $[\text{M}(\equiv\text{CSiMe}_2\text{Ph})-$

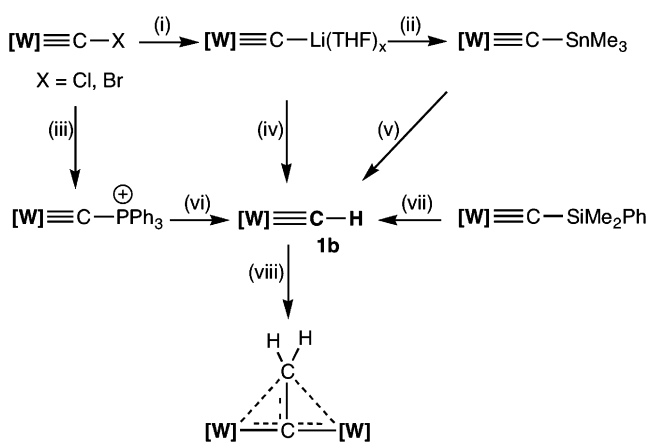
$(\text{CO})_2(\text{Tp}^*)]$ ,<sup>9</sup> a strategy to which we will return (vide infra). Although more concise routes to **1** have appeared in the interim,<sup>10,11</sup> the feature limiting more extensive investigations of these parent methylidyne is their spontaneous dimerization (rapid for molybdenum, slow for tungsten) to afford non-classical vinylidene-bridged bimetallic complexes (Scheme 2). Nevertheless, the most versatile aspect of the tungsten derivative involves its deprotonation to afford the anionic carbido species  $[\text{W}(\equiv\text{C})(\text{CO})_2(\text{Tp}^*)]^-$ , which allows the installation of a wide range of carbyne substituents via simple electrophilic attack.<sup>10,11</sup> This anion and its molybdenum analogue may be generated more conveniently via lithium/halogen exchange reactions of halocarbynes  $[\text{M}(\equiv\text{CX})(\text{CO})_2(\text{Tp}^*)]$  ( $\text{X} = \text{Cl}, \text{Br}$ ).<sup>11</sup> While these protocols have afforded access to a diverse range of unusually functionalized carbynes, each of the various routes proceed, directly or indirectly, from Lalor's halocarbyne complexes  $[\text{M}(\equiv\text{CX})(\text{CO})_2(\text{Tp}^*)]$ ,<sup>12</sup> which themselves result from a complex reaction manifold that has to date only been successfully applied to the " $\text{Tp}^*(\text{CO})_2\text{M}$ " platform. Given this limitation to the synthetic potential, we have therefore turned our attention to the synthesis of alternative parent methylidyne complexes that offer a more generalizable ligand set. In pursuit of such complexes, we have returned to Templeton's silylcarbyne desilylation strategy. We will report separately on more extensive studies on the synthesis of carbyne complexes with substituents based on the heavier tetrels; however, suffice it to say that we have now identified a high-yield entry point into silylcarbyne complexes of tungsten.

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Scheme 1. Synthetic Approaches to Terminal Methylidyne Complexes<sup>a</sup>

<sup>a</sup>L...L = (PMe<sub>3</sub>)<sub>2</sub>, dmpe; not all combinations. Legend: (i) AlMe<sub>3</sub>; (ii) tmeda; (iii) R<sup>−</sup>, R = F, I, OTf, CN, OSiMe<sub>3</sub>, <sup>n</sup>Bu; (iv) Ph<sub>3</sub>C<sup>+</sup>; (v) KCH<sub>2</sub>Ph; (vi) Na; (vii) <sup>n</sup>BuCOCl; (viii) MeCN; (ix) LiMe; (x) LiC<sub>3</sub>H<sub>3</sub>.

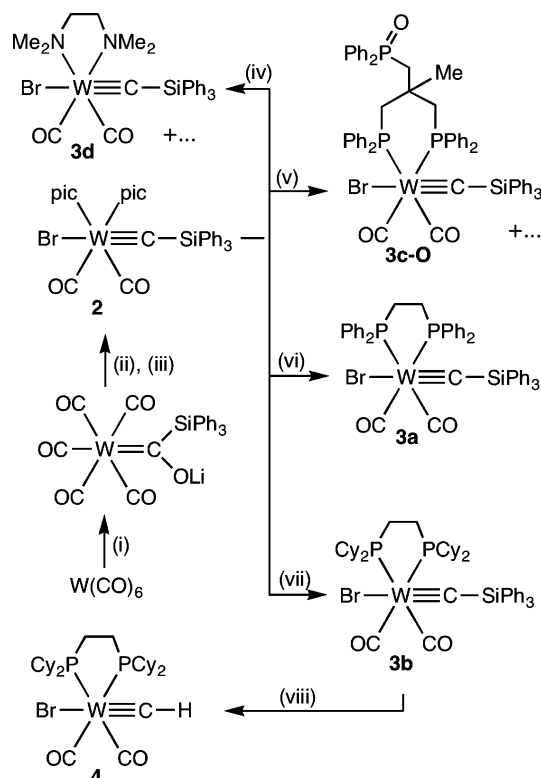
Scheme 2. Syntheses of Templeton's Parent Methylidyne Complex [W]≡CH (1b)<sup>a</sup>

<sup>a</sup>[W] = W(CO)<sub>2</sub>(Tp\*). Legend: (i) <sup>n</sup>BuLi; (ii) ClSnMe<sub>3</sub>; (iii) NaPF<sub>6</sub>, PPh<sub>3</sub>; (iv) H<sup>+</sup>; (v) H<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>; (vi) Li[Et<sub>3</sub>BH]; (vii) [<sup>n</sup>Bu<sub>4</sub>N]<sup>+</sup>F, H<sub>2</sub>O; (viii) room temperature.

## RESULTS AND DISCUSSION

The Fischer–Mayr acylate oxide abstraction protocol has been previously applied to the synthesis of silyl carbyne complexes of the form [M(≡CSiR<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)].<sup>9,11d</sup> In these previous reports, trifluoroacetic anhydride was deployed as the oxide abstracting agent, which we reasoned might account in part for the rather poor yields (7–20%). We therefore explored

alternative oxide abstractors, the side products of which we suspected might be less likely than a carboxylate to interact with the oxophilic silicon centers of intermediates or the final desired product. For this purpose, oxalyl bromide was found to be the most effective, perhaps reflecting the low enthalpies of Si–Br bonds. Thus, treating [W(CO)<sub>6</sub>] successively with LiSiPh<sub>3</sub> (25 °C), oxalyl bromide (−78 °C), and 4-picoline (pic; −78 → 25 °C) affords the complex [W(≡CSiPh<sub>3</sub>)Br(CO)<sub>2</sub>(pic)<sub>2</sub>] (2) (Scheme 3) in near-quantitative yields in a

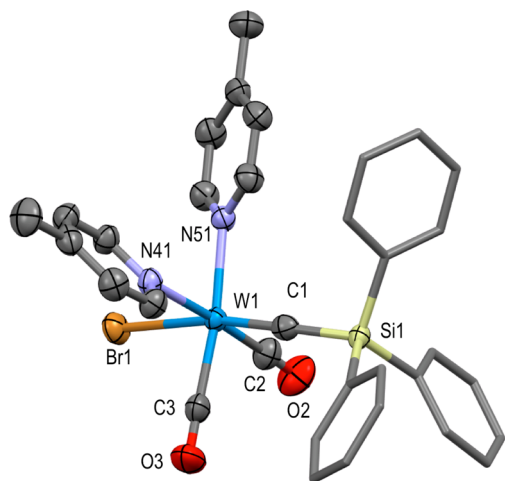
Scheme 3. Synthesis of Silylmethylidyne and Methylidyne Complexes<sup>a</sup>

<sup>a</sup>pic = 4-picoline. Legend: (i) LiSiPh<sub>3</sub>; (ii) (OCBr)<sub>2</sub>; (iii) pic; (iv) tmeda; (v) MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>, AgPF<sub>6</sub>; (vi) dppe; (vii) dcpe; (viii) [<sup>n</sup>Bu<sub>4</sub>N]<sup>+</sup>F, H<sub>2</sub>O.

“one-pot” procedure. Although the spectroscopically homogeneous material has not been obtained in analytical purity due to its slow decomposition during purification attempts (recrystallization, chromatography), spectroscopic and crystallographic data unequivocally confirm its identity. Sufficient examples of hydrocarbyl-substituted carbyne complexes of the form [M(≡CR)Br(CO)<sub>2</sub>(pic)<sub>2</sub>] (M = Mo, W) are known<sup>13</sup> to allow discussion here to focus on data associated with the W≡CSiPh<sub>3</sub> spine of interest. The trans influence of the carbyne ligand is reflected in the predominance of an [M – Br]<sup>+</sup> isotopic cluster (a recurrent observation for all derivatives of 2) in the ESI mass spectrum (MeCN matrix) accompanied by a less intense [M + H]<sup>+</sup> pattern.

The tungsten–carbon triple bond is evident from a <sup>13</sup>C{<sup>1</sup>H} NMR signal at characteristically low field (δ<sub>C</sub> 312.6 ppm) that is straddled by satellites with <sup>1</sup>J<sub>WC</sub> value of 184 Hz (<sup>183</sup>W: I = 1/2, 14.3% natural abundance). Though comparatively rare, in situations where data for pairs of otherwise identical silyl and hydrocarbyl carbyne complexes are available, the chemical shift

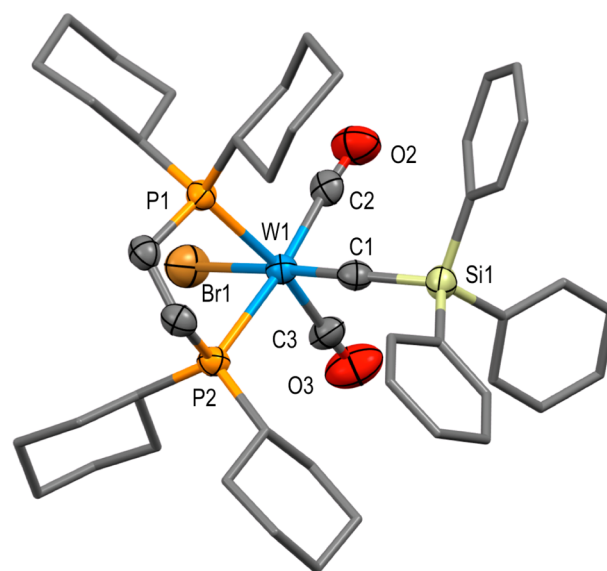
of the carbyne carbon for the former appears typically downfield of the latter: e.g.,  $[W(\equiv CMe_3)(CH_2AME_3)_3]$  ( $\delta_C$  317 (A = C),<sup>14</sup> 353 (A = Si)<sup>15</sup>) and  $[W(\equiv CAME_3)(OCMe_3)_3]$  ( $\delta_C$  271 (A = C), 292 (A = Si)).<sup>16</sup> The molecular structure of **2** is presented in Figure 1.



**Figure 1.** Molecular structure of **2** in a crystal (70% displacement ellipsoids, hydrogen atoms omitted, phenyl groups simplified for clarity). Selected bond lengths (Å) and angles (deg): Br1–W1 2.7113(3), N41–W1 2.249(2), N51–W1 2.251(2), Si1–C1 1.849(3), W1–C1 1.816(3); Si1–C1–W1 175.6(2).

The picoline ligands of **2** are labile under mild conditions, as illustrated by the reactions with a variety of chelating ligands to afford  $[W(\equiv CSiPh_3)Br(CO)_2(dppe)]$  (**3a**; dppe = 1,2-bis-(diphenylphosphino)ethane),  $[W(\equiv CSiPh_3)Br(CO)_2(dcpe)]$  (**3b**; dcpe = 1,2-bis(dicyclohexylphosphino)ethane),  $[W(\equiv CSiPh_3)Br(CO)_2(\kappa^2-P,P'$ -triphos)] (**3c**; triphos = MeC-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>), and  $[W(\equiv CSiPh_3)Br(CO)_2(tmeda)]$  (**3d**; tmeda = *N,N,N',N'*-tetramethylethylenediamine). The characterization of **3b–d** included crystallographic analyses, the results of which are discussed in the Supporting Information.

Due to various shortcomings (yields, stabilities, isomerism) associated with the syntheses of **3a,c,d** which are elaborated upon in the Supporting Information the more sterically encumbered derivative **3b** proved most amenable to further study and to complete characterization, including a crystallographic analysis (Figure 2). Thus, the gross composition follows from microanalytical and positive-ion ESI MS data. The latter includes a  $[M - Br]^+$  isotopic cluster as the base peak in addition to  $[M + Na]^+$  (24%). The two strong infrared carbonyl absorptions appear at 2009 and 1938 cm<sup>−1</sup> (CH<sub>2</sub>Cl<sub>2</sub>), somewhat lower in frequency than those for **3a** (CH<sub>2</sub>Cl<sub>2</sub>: 2018, 1952 cm<sup>−1</sup>), reflecting, as expected, a more  $\pi$ -basic tungsten. The carbyne carbon nucleus gives rise to a triplet resonance at  $\delta_C$  315.0 ppm ( $^1J_{CW} = 167.2$ ,  $^2J_{CP} = 14.6$  Hz), while the appearance of a single resonance in the  $^{31}P\{^1H\}$  NMR spectrum ( $\delta_C$  44.94,  $^1J_{PW} = 229.0$  Hz) reflects the chemical equivalence of the two phosphorus nuclei. The magnetic inequivalence of these is manifested, however, in the  $^{13}C\{^1H\}$  NMR spectrum for the CO resonance which appears as a doublet of doublets (215.7 ppm,  $^1J_{CW} = 152.9$ ,  $^2J_{PC} = 39.1$ , 6.6 Hz). Inversion ( $\delta/\lambda$ ) of the WP<sub>2</sub>C<sub>2</sub> metallacycle is rapid on the  $^1H$  and  $^{13}C$  NMR time scales ( $^1H/^{13}C$  HSQC, HMBC), resulting in nine  $^{13}C$  resonances for the dcpe ligand consistent with a time-averaged C<sub>s</sub> local symmetry (Cy syn to either W≡



**Figure 2.** Molecular structure of **3b** in a crystal (70% displacement ellipsoids, hydrogen atoms omitted, phenyl groups simplified for clarity). Selected bond lengths (Å) and angles (deg): Br1–W1 2.6899(5), P1–W1 2.562(1), P2–W1 2.549(1), Si1–C1 1.869(4), W1–C1 1.824(4); P1–W1–P2 80.18(3), Si1–C1–W1 167.3(2).

C or WBr). These data together indicate in solution the stereochemistry depicted in Scheme 3 and crystallographically confirmed in the solid state (Figure 2).

Selected structural data for published silylcarbynes<sup>17</sup> are given in Table S1 in the Supporting Information alongside those for the new complexes described herein. The tungsten atom in **3b** displays a distorted-octahedral coordination with the two axial positions occupied by a bromide ligand (W–Br = 2.6899(5) Å) and the carbyne carbon (W≡C = 1.824(4) Å). Despite the considerable steric clutter associated with both the dcpe and SiPh<sub>3</sub> groups, this bond length is essentially identical (3 esd) with that of the precursor **2** (1.816(3) Å) and comparable to the mean value for 118 tungsten carbyne complexes (1.8264 Å) archived in the Cambridge Crystallographic Data Centre.<sup>17a</sup> The W1≡C1–Si1 bond angle (167.3(2)°) deviates significantly from the sp-C ideal 180°; however, the mean W≡C–A angle (173.4°) of 118 mononuclear tungsten carbyne complexes<sup>17</sup> indicates that modest carbyne bending is commonplace and departures from linearity have generally been attributed to crystal-packing effects.<sup>18,19</sup> The angles between the carbon atoms of the carbyne and carbonyl ligands are very close to 90°, while those between the carbyne and the bulky phosphine are more obtuse (101.6(1), 95.3(1)°). Similarly obtuse angles are observed between the carbyne and picoline ligands in **2** (99.9(1), 99.4(1)°).

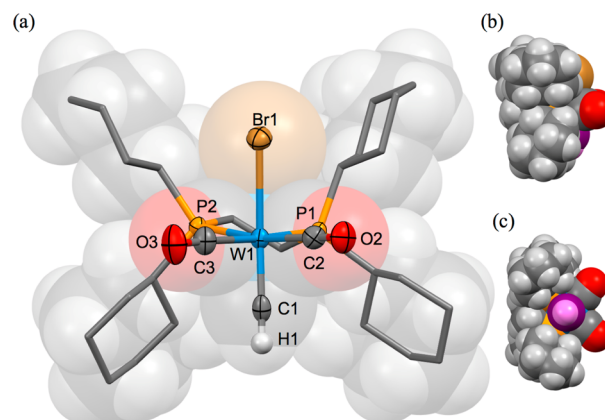
As noted above, the complex **3b** was chosen for desilylation studies, given the additional benefit of kinetic stabilization offered by the steric bulk of the dcpe ligand. Addition of tetra-*n*-butylammonium fluoride (TBAF) to a yellow THF solution of complex **3b** at −78 °C resulted in a rapid color change to orange. When the mixture was warmed to room temperature overnight, a yellow solution was obtained with essentially no change in the  $\nu_{CO}$  region of infrared spectrum. The isolated product was, however, the parent terminal methylidyne complex  $[W(\equiv CH)Br(CO)_2(dcpe)]$  (**4**) (THF: 2008, 1937 cm<sup>−1</sup>). Notably, there was very little difference observed



between the IR spectra of  $[\text{W}(\equiv\text{CSiMe}_2\text{Ph})(\text{CO})_2(\text{Tp}^*)]$  (THF: 1982, 1889  $\text{cm}^{-1}$ ) and  $[\text{W}(\equiv\text{CH})(\text{CO})_2(\text{Tp}^*)]$  (THF: 1986, 1891  $\text{cm}^{-1}$ ), indicating that the CH and  $\text{CSiR}_3$  carbyne ligands have comparable net acceptor ability and that IR spectroscopy is of little use in monitoring the reaction progress.<sup>9,10</sup> The complex could be isolated at ambient temperature and is remarkably stable. Aerobic solutions in  $\text{CDCl}_3$  undergo approximately 10% decomposition over 24 h at room temperature, while  $\text{CD}_2\text{Cl}_2$  solutions of pure **4** under argon show little spectroscopically discernible decomposition over 5 days. Very weak absorptions at 3063 and 918  $\text{cm}^{-1}$  are, with caution, tentatively assigned to the methylidyne  $\nu_{\text{CH}}$  and  $\nu_{\text{WC}}$  stretching modes, respectively. The reason for caution is that the region around 900  $\text{cm}^{-1}$  is heavily populated by more intense modes associated with the  $\text{W}(\text{dcpe})$  metallacycle, including P–C–H deformation modes. The calculated spectrum for the simpler model complex  $[\text{W}(\equiv\text{CH})\text{Br}(\text{CO})_2(\text{dmpe})]$  suggest the latter occurs at 899  $\text{cm}^{-1}$  in a region populated/obscured by more intense modes associated with the  $\text{W}(\text{dmpe})$  metallacycle ( $\delta_{\text{PCH}}$  and  $\delta_{\text{WPCCP}}$  modes). Notably, for the complex  $[\text{W}(\equiv\text{CH})\text{Cl}(\text{dmpe})_2]$ <sup>3a</sup> an absorption at 920  $\text{cm}^{-1}$  has been assigned to the  $\nu_{\text{WC}}$  mode;<sup>20</sup> however, the calculated IR spectrum (Supporting Information) indicates that the most intense band in this region by far (966  $\text{cm}^{-1}$ ,  $T = 100\%$ ) is a metallacycle mode, with the  $\nu_{\text{WC}}$  mode appearing as a very weak shoulder (974  $\text{cm}^{-1}$ ,  $T = 3\%$ ). That this absorption is strongly observed in the Raman spectrum but extremely weak in the IR spectrum points to an essentially nonpolar  $\text{W}\equiv\text{C}$  bond. A further caveat is that the  $\delta_{\text{WCH}}$  mode is calculated to appear in this region with similar intensity. The  $\nu_{\text{WC}}$  mode of  $[\text{W}(\equiv\text{CH})\text{Cl}(\text{PMe}_3\text{-}d_9)_4]$  was, however, unambiguously identified at 911  $\text{cm}^{-1}$  (5.9 N/cm) using Raman spectroscopy.<sup>4g</sup>

The formulation of **4** rests unambiguously upon spectroscopic and crystallographic data. The gross composition was established by elemental microanalytical data and ESI-MS HR-ESI-TOF spectrometry, including the observation of isotopic clusters attributable to  $[\text{M} - \text{Br}]^+$  and  $[\text{M} - \text{Br} + \text{MeCN}]^+$ . A characteristic carbyne resonance appears at 261.9 ppm (dt,  $^2J_{\text{PC}} = 10.6$ ,  $^1J_{\text{CH}} = 143.4$  Hz) in the proton-coupled  $^{13}\text{C}$  NMR spectrum that unequivocally identifies the methylidyne ligand. Of note is the small  $^1J_{\text{CH}}$  value, which contrasts with the large value of  $^1J_{\text{CH}}$  ( $\sim 250$  Hz) typical of terminal alkynes.<sup>21</sup> It has been suggested that the metal–carbon triple bond in methylidyne complexes substantially depletes the available carbon “s character” below what would be associated with a first-order sp hybrid, thereby lowering the  $^1J_{\text{CH}}$  coupling constant.<sup>9</sup> The magnitude is thus comparable with those of previously reported tungsten methylidyne complexes (Table S2 in the Supporting Information).<sup>3,4</sup> The assignment of the terminal proton nucleus followed from the  $^{13}\text{C}$ – $^1\text{H}$  HSQC spectrum, which indicated a correlation between the carbyne carbon resonance and a proton resonance at 6.66 ppm (t,  $^3J_{\text{PH}} = 1.6$  Hz). The complex displays the expected *cis*-dicarbonyl pattern in the IR ( $\nu_{\text{CO}}$  2008, 1937  $\text{cm}^{-1}$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (213.6 ppm, dd,  $^2J_{\text{PC}} = 40.7$ , 16.0,  $^1J_{\text{WC}} = 147.0$  Hz) spectra. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum comprises only a singlet resonance (47.2 ppm,  $^1J_{\text{WC}} = 228.9$  Hz), close to that of the precursor **3b** (45.0 ppm,  $^1J_{\text{WC}} = 229$  Hz).

Single crystals of complex **4** were obtained via vapor diffusion (*n*-pentane) into a  $\text{CH}_2\text{Cl}_2$  solution at 25 °C under argon. The molecular structure (Figure 3) confirmed the formulation surmised from spectroscopic data. Although it reveals gross



**Figure 3.** (a) Molecular structure of **4** in a crystal of  $4 \cdot 0.5\text{C}_6\text{H}_{14}$  (70% displacement ellipsoids, cyclohexyl hydrogen atoms and hexane solvate omitted for clarity, cyclohexyl groups simplified). Selected bond lengths (Å) and angles (deg): Br1–W1 2.6935(4), P1–W1 2.5293(7), P2–W1 2.5391(8), W1–C1 1.864(4), C1–H1 0.914;<sup>23</sup> P2–W1–P1 79.41(2), W1–C1–H1 178.6.<sup>23</sup> (b, c) Space-filling representations of **4** viewed (b) normal to and (c) along the C1–W1 vector (methylidyne in purple).

structural features similar to those of the precursor **3b**, the structure of **4** possesses a somewhat (10 esd) elongated  $\text{W}\equiv\text{C}$  bond (1.864(4) Å) in comparison to that of **3b** (1.824(4) Å). Indeed, the  $\text{W}\equiv\text{C}$  bond distance of complex **4** is the longest among those reported for methylidyne and carbido complexes.<sup>3,22</sup> The W1–C1–H1 angle of 178.7° is close to linear,<sup>23</sup> and a number of X-ray crystallographic studies of methylidyne complexes of the form  $[\text{W}(\equiv\text{CH})\text{X}(\text{PR}_3)_4]$  have suggested a proclivity toward bending. Detailed studies by Hopkins<sup>3c</sup> that included a comparison of neutron (100 K: W–C–H = 178.0(7)°) and X-ray (213 K: W–C–H = 164(6)°) diffraction data for  $[\text{W}(\equiv\text{CH})\text{Br}(\text{dmpe-}d_{12})_2]$ , however, point toward nonlinearity being a crystallographic artifact (heavy metal proximity, small scattering factor for hydrogen), in the absence of extenuating effects: e.g., intermolecular interactions. The exaggerated steric protection offered by the dcpe ligand in **4** obviates any such crystal-packing effects. The average W–CO and W–Br bond lengths are statistically identical for **3b** and **4**, and the C1–W1–P angles (92.4(1), 97.4(1)°) remain somewhat obtuse, suggesting that the steric bulk of the  $\text{SiPh}_3$  group does not significantly impinge on the geometry of the “ $\text{WBr}(\text{CO})_2(\text{dcpe})$ ” unit.

Spectra of crude **4** appear to contain a second methylidyne complex (9% by  $^1\text{H}$  or  $^{31}\text{P}$  NMR integration) with spectroscopic data remarkably similar to those of **4**: e.g.,  $\delta_{\text{C}}$  262.5 (t,  $^2J_{\text{PC}} = 10.6$ ,  $\text{W}\equiv\text{C}$ ), 214.8 (dd,  $J_{\text{PC}} = 42.3$ , 7.5 Hz, CO),  $\delta_{\text{H}}$  6.63 (t,  $J_{\text{PH}} = 1.8$  Hz), and  $\delta_{\text{P}}$  51.17 ( $^1J_{\text{WP}} = 229$  Hz). No additional  $\nu_{\text{CO}}$  infrared absorptions are resolvable, and we therefore attribute this second species to the chloro complex  $[\text{W}(\equiv\text{CH})\text{Cl}(\text{CO})_2(\text{dcpe})]$ , which would be expected to provide a mass spectrum identical with that of **4** under ESI conditions (MeCN), where halide dissociation prevails. From the crude reaction mixture, two further compounds were structurally characterized (see the Supporting Information). The first was the expected side product  $[\text{Bu}_4\text{N}][\text{SiF}_2\text{Ph}_3]$ ; however, the second was the intriguing binuclear ethenediylidyne complex  $(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}-\text{CH}=\text{CH}-\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)$  (**5**).<sup>24</sup> Because only sufficient material was obtained for crystallographic analysis, untested mechanistic

conjecture as to its mode of formation is relegated to the Supporting Information.

## CONCLUSIONS

The high-yield synthesis of the bis(picoline) complex **2** affords access to a range of silylcarbyne complexes via facile (room temperature) ligand substitution reactions. The variable yields obtained (nonoptimized) or the instability in solution precluded most from further study. One example, however, featuring the sterically demanding dcpe ligand,  $[W(\equiv\text{CSiPh}_3)\text{Br}(\text{CO})_2(\text{dcpe})]$  (**3b**), underwent clean desilylation to afford a rare example of a thermally stable methylidyne complex  $[W(\equiv\text{CH})\text{Br}(\text{CO})_2(\text{dcpe})]$  (**4**), which could be fully characterized.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line, and inert-atmosphere (argon) drybox techniques with dried and degassed solvents. NMR spectra were obtained at 25 °C on Bruker AVANCE 400 ( $^1\text{H}$  at 399.9 MHz,  $^{31}\text{P}$  at 162.0 MHz), AVANCE 600 ( $^1\text{H}$  NMR at 600.0 MHz,  $^{13}\text{C}$  NMR at 150.9 MHz), and AVANCE 800 ( $^1\text{H}$  NMR at 800.1 MHz,  $^{13}\text{C}$  NMR at 201.0 MHz) spectrometers. Chemical shifts ( $\delta$ ) are reported in ppm and are referenced to the solvent peak ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or external reference ( $^{31}\text{P}$ ,  $\text{H}_3\text{PO}_4$ ) with coupling constants given in Hz. Infrared spectra were obtained from solution and in the solid state (Nujol or KBr) using a PerkinElmer Spectrum One FT-IR spectrometer. Electrospray ionization mass spectrometry (ESI-MS, low and high resolution) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. In general, molecular ions  $[\text{M} + \text{H}]^+$  were not observed under ESI conditions (positive ion, MeCN matrix) due to facile halide loss. Elemental microanalytical data were provided by the Macquarie University Chemical Analysis Facility or the ANU Microanalytical Service. Crystallographic data were collected with an Agilent Supernova dual source (Cu, Mo) diffractometer. Reaction progress was typically monitored by in situ solution IR spectroscopy and thin-layer chromatography (silica gel).

**Synthesis of  $[W(\equiv\text{CSiPh}_3)\text{Br}(\text{CO})_2(\text{pic})_2]$  (**2**).** A solution of  $\text{Ph}_3\text{SiLi}$  was prepared by stirring  $\text{Ph}_3\text{SiCl}$  (3.541 g, 11.5 mmol) vigorously with finely cut lithium wire (0.5–1% Na content, 0.160 g, 23.1 mmol) in THF (150 mL) at room temperature for 24 h. The resulting reaction mixture was cannula filtered to give a brown solution, which was added to a solution of tungsten hexacarbonyl (4.047 g, 11.5 mmol) in THF (100 mL) at 0 °C. The resultant dark green suspension was cooled (dry ice, acetone bath) before a 2.0 M dichloromethane solution of oxalyl bromide (5.80 mL, 11.5 mmol) was added dropwise over 20 min. After 3 h of stirring at  $-78$  °C, the yellow suspension was treated with 4-picoline (2.20 mL, 23.1 mmol), during which time the suspension became bright orange. The orange suspension was warmed slowly to room temperature with the cooling bath in place overnight without replenishing the dry ice. The resultant dark brown solution was freed of volatiles under vacuum, and the residue was extracted with dichloromethane and filtered through diatomaceous earth to remove LiBr before the solvent was removed. The product was freed of traces of unreacted  $[W(\text{CO})_6]$  by sublimation (50 °C,  $\nu_{\text{CO}}$  1976  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ). Yield: 8.723 g (11.2 mmol, 97%). The compound should be stored under argon at  $-20$  °C. IR ( $\text{CH}_2\text{Cl}_2$ ): 2001, 1915 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ . IR (THF): 2001, 1918 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ . IR ( $\text{C}_6\text{H}_6$ ): 2004, 1921 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ . IR (KBr): 1996, 1910 ( $\nu_{\text{CO}}$ ), 1638, 1504, 1428, 1261, 1111, 802  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta_{\text{H}}$  8.77, 6.95 [AA'BB',  $^3J_{\text{HH}} = 6.0$ , 4 H  $\times$  2,  $\text{NC}_5\text{H}_4$ ], 7.8–7.3 [m, 15 H,  $\text{C}_6\text{H}_5$ ], 2.35 (s, 6 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta_{\text{C}}$  312.6 ( $^1J_{\text{WC}} = 183.9$ ,  $\text{W}\equiv\text{C}$ ), 222.0 ( $^1J_{\text{WC}} = 178.0$  Hz, CO), 152.2 [ $\text{C}^{2,6}(\text{NC}_5\text{H}_4)$ ], 150.4 [ $\text{C}^4(\text{NC}_5\text{H}_4)$ ], 136.0 [ $\text{C}^{2,6}(\text{C}_6\text{H}_5)$ ], 135.0 [ $\text{C}^1(\text{C}_6\text{H}_5)$ ], 129.6 [ $\text{C}^4(\text{C}_6\text{H}_5)$ ], 128.0 [ $\text{C}^{3,5}(\text{C}_6\text{H}_5)$ ], 125.9 [ $\text{C}^{3,5}(\text{NC}_5\text{H}_4)$ ], 21.3 ( $\text{CH}_3$ ). MS-ESI (positive ion, MeCN):  $m/z$  (%) 697.1521 (48)  $[\text{M} - \text{Br}]^+$ , 738.1829 (22)  $[\text{M} - \text{Br} + \text{MeCN}]^+$ ,

779.0750 (6)  $[\text{HM}]^+$ . HR ESI TOF MS: calcd for  $\text{C}_{33}\text{H}_{29}\text{N}_2\text{O}_2\text{Si}^{184}\text{W} [\text{M} - \text{Br}]^+$ , 697.1508; found, 697.1521; calcd for  $\text{C}_{33}\text{H}_{32}\text{N}_3\text{O}_2\text{Si}^{184}\text{W} [\text{M} - \text{Br} + \text{MeCN}]^+$ , 738.1773; found, 738.1788; calcd for  $\text{C}_{33}\text{H}_{30}\text{N}_2\text{O}_2\text{Si}^{79}\text{Br}^{184}\text{W} [\text{HM}]^+$ , 777.0769; found, 777.0771; calcd for  $\text{C}_{33}\text{H}_{30}\text{N}_2\text{O}_2\text{Si}^{81}\text{Br}^{184}\text{W} [\text{HM}]^+$ , 779.0749; found, 779.0750. Satisfactory elemental analytical data could not be obtained possibly due to lability during repeated recrystallization, even in the presence of additional picoline. Anal. Found (best result): C, 48.50; H, 4.33; N, 4.28. Calcd for  $\text{C}_{33}\text{H}_{29}\text{BrN}_2\text{O}_2\text{SiW}$ : C, 50.98; H, 3.76; N, 3.60. Crystals of **2** suitable for X-ray diffraction were obtained from vapor diffusion of  $\text{Et}_2\text{O}$  into a solution of **2** in  $\text{CH}_2\text{Cl}_2$  ( $-20$  °C, 7 days). Crystal data:  $\text{C}_{33}\text{H}_{29}\text{BrN}_2\text{O}_2\text{SiW}$ ,  $M_r = 777.44$ ,  $T = 150(2)$  K, triclinic, space group  $P\bar{1}$  (No. 2),  $a = 11.8049(3)$  Å,  $b = 11.8059(4)$  Å,  $c = 12.5211(3)$  Å,  $\alpha = 63.067(3)^\circ$ ,  $\beta = 76.1846(19)^\circ$ ,  $\gamma = 79.043(2)^\circ$ ,  $V = 1503.98(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.717$  Mg m<sup>-3</sup>,  $\mu(\text{Cu K}\alpha) = 9.31$  mm<sup>-1</sup>, brown plate,  $0.11 \times 0.10 \times 0.04$  mm, 15701 measured reflections with  $2\theta_{\text{max}} = 144^\circ$ , 5939 independent reflections, 5914 absorption-corrected data used in  $F^2$  refinement, 361 parameters,  $R_1 = 0.023$  for 5716 reflections with  $I > 2\sigma(I)$ ,  $wR_2 = 0.060$  for all data.

**Synthesis of  $[W(\equiv\text{CSiPh}_3)(\text{CO})_2(\text{dppe})\text{Br}]$  (**3a**).** Solid dppe (106 mg, 0.266 mmol) was added in one portion to a  $\text{CH}_2\text{Cl}_2$  solution (10 mL) of **2** (206 mg, 0.265 mmol), and the suspension was stirred at room temperature for 21 h. The resulting brown mixture was filtered (porosity 4, sintered glass) and the filtrate freed of volatiles under reduced pressure. The brown residue was then extracted with diethyl ether ( $3 \times 15$  mL), and the combined filtered extracts were reduced to dryness in vacuo. The yellow residue obtained was then washed with  $n$ -pentane ( $3 \times 15$  mL) and chromatographed on silica gel with 4/1  $\text{CH}_2\text{Cl}_2$ / $n$ -hexane as eluent. A yellow band was collected and freed of volatiles to provide a yellow solid. Yield: 95 mg (0.096 mmol, 36%). IR ( $\text{CH}_2\text{Cl}_2$ ): 2018, 1952 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ . IR (KBr): 2013, 1946, 1930sh, 1841 ( $\nu_{\text{CO}}$ ), 1483, 1429, 1264, 1107, 998, 871, 803  $\text{cm}^{-1}$ . NMR resonance assignments for the two Ph environments syn/anti to  $\text{W}\equiv\text{C}$  (A and B) were confirmed by  $^1\text{H}$ – $^{13}\text{C}$  HSQC and HMQC measurements.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta_{\text{H}}$  7.56, 7.46 [m  $\times$  2, 4 H  $\times$  2,  $\text{H}^{2,6}(\text{PC}_6\text{H}_5)$ ], 7.19 [dd,  $J_{\text{HH}} = 7.8$ , 1.8, 6 H,  $\text{H}^{2,6}(\text{SiC}_6\text{H}_5)$ ], 6.93 [tt,  $J_{\text{HH}} = 7.3$ , 1.2, 3 H,  $\text{H}^4(\text{SiC}_6\text{H}_5)$ ], 6.88 [t,  $J_{\text{HH}} = 7.2$  Hz, 6 H,  $\text{H}^{3,5}(\text{SiC}_6\text{H}_5)$ ], 6.82 [td,  $J_{\text{HH}} = 7.8$ , 1.8, 4H,  $\text{H}^{3,5}(\text{PC}_6\text{H}_5\text{-A})$ ], 6.72 [td,  $J = 7.2$ , 1.2, 2H,  $\text{H}^4(\text{PC}_6\text{H}_5\text{-A})$ ], 6.50 [td,  $J = 7.8$ , 1.2, 2 H,  $\text{H}^4(\text{PC}_6\text{H}_5\text{-B})$ ], 6.47 [td,  $J = 7.8$ , 1.8, 4 H,  $\text{H}^{3,5}(\text{PC}_6\text{H}_5\text{-B})$ ], 2.45, 1.96 (br. m  $\times$  2, 2 H  $\times$  2,  $\text{PCH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta_{\text{C}} = 318.1$  (t,  $^1J_{\text{WC}} = 164.5$ ,  $^2J_{\text{PC}} = 8.3$ ,  $\text{W}\equiv\text{C}$ ), 213.7 (dd,  $^1J_{\text{WC}} = 155.4$ ,  $^2J_{\text{PC}} = 42.3$ , 6.0, CO), 136.5 [ $\text{C}^{2,6}(\text{C}_6\text{H}_5)$ ], 136.1 [d,  $^1J_{\text{PC}} = 39.8$ ,  $\text{C}^1(\text{PC}_6\text{H}_5\text{-B})$ ], 135.1 [ $\text{C}^1(\text{SiC}_6\text{H}_5)$ ], 133.7 [d,  $^2J_{\text{PC}} = 12.4$ ,  $\text{C}^{2,6}(\text{PC}_6\text{H}_5\text{-B})$ ], 133.6 [d,  $^1J_{\text{PC}} = 37.4$ ,  $\text{C}^1(\text{PC}_6\text{H}_5\text{-A})$ ], 133.0 [d,  $^2J_{\text{PC}} = 10.4$ ,  $\text{C}^{3,5}(\text{PC}_6\text{H}_5\text{-A})$ ], 130.4 [ $\text{C}^4(\text{PC}_6\text{H}_5\text{-B})$ ], 130.2 [ $\text{C}^4(\text{PC}_6\text{H}_5\text{-A})$ ], 129.6 [ $\text{C}^4(\text{SiC}_6\text{H}_5)$ ], 128.8 [d,  $^2J_{\text{PC}} = 10.1$ ,  $\text{C}^{3,5}(\text{PC}_6\text{H}_5\text{-B})$ ], 128.5 [d,  $^2J_{\text{PC}} = 10.4$ ,  $\text{C}^{3,5}(\text{PC}_6\text{H}_5\text{-A})$ ], 128.1 [ $\text{C}^{3,5}(\text{SiC}_6\text{H}_5)$ ], 27.1 (dd,  $^1J_{\text{PC}} = 28.7$ , 12.1 Hz,  $\text{PCH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (25 °C):  $\delta_{\text{P}} = 38.2$  ( $\text{C}_6\text{D}_6$ ), 38.8 ( $\text{CDCl}_3$ ) ( $^1J_{\text{WP}} = 234.4$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C): 38.6 ( $^1J_{\text{WP}} = 234.4$  Hz). MS-ESI (positive, MeCN):  $m/z$  (%) 909.6 (68)  $[\text{M} - \text{Br}]^+$ , 950.7 (7)  $[\text{M} - \text{Br} + \text{MeCN}]^+$ . HR-ESI TOF MS: calcd for  $\text{C}_{47}\text{H}_{39}\text{O}_2\text{SiP}_2^{184}\text{W} [\text{M} - \text{Br}]^+$ , 909.1704; found, 909.1729. calcd for  $\text{C}_{49}\text{H}_{42}\text{NO}_2\text{SiP}_2^{184}\text{W} [\text{M} - \text{Br} + \text{MeCN}]^+$ , 950.1970; found, 950.1973. Satisfactory elemental microanalytical data were not obtained, most likely due to the presence of a second unidentified carbyne complex which was observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 25 °C) of the crude product mixture:  $\delta_{\text{C}}$  304.2 (br,  $\text{W}\equiv\text{C}$ ), 233.2 (dt,  $J = 39.7$ , 6.2 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): 38.2 (desired product, 47%), 37.1 (overlapping, 9%), 34.6 (dd,  $J = 18.2$ , 7.3, 9%), 23.8 (app. dd,  $J = 32.8$ , 18.6, 4%), 22.8 (app. dd,  $J = 32.8$ , 18.6, 4%),  $-9.7$  (d,  $J = 33.0$  Hz, 7%),  $-12.1$  (free dppe, 20%).

**Synthesis of  $[W(\equiv\text{CSiPh}_3)\text{Br}(\text{CO})_2(\text{dcpe})]$  (**3b**).** Solid dcpe (79 mg, 0.19 mmol) was added in one portion to a  $\text{CH}_2\text{Cl}_2$  solution (10 mL) of **2** (145 mg, 0.187 mmol), and the suspension was stirred at room temperature for 28 h. The resulting brown mixture was then filtered (porosity 4 sintered glass) and freed of volatiles. The brown residue was extracted with diethyl ether ( $3 \times 20$  mL), and the filtered extracts were reduced to dryness under vacuum. The yellow residue obtained was chromatographed on silica gel with 4/1  $\text{CH}_2\text{Cl}_2$ / $n$ -



hexane as eluent to remove a minor side product identified as  $[W(CO)_4(dcp)]$  ( $\delta_P = 48.6$ ,  $^1J_{WP} = 230.0$  Hz). A yellow band was collected and freed of volatiles to afford a yellow solid. Yield: 133 mg (0.131 mmol, 70%). IR ( $CH_2Cl_2$ ): 2009, 1938 ( $\nu_{CO}$ ). IR (THF): 2009, 1941 ( $\nu_{CO}$ )  $cm^{-1}$ . IR (KBr): 2004, 1934 ( $\nu_{CO}$ ), 1447, 1427, 1261, 1107, 1027, 800  $cm^{-1}$ . NMR resonance assignments for the two cyclohexyl environments syn/anti to  $W\equiv C$  (A and B) were confirmed by  $^1H$ - $^{13}C$  HSQC and HMBC measurements.  $^1H$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_H$  7.47 [d,  $^3J_{HH} = 6.7$ , 6 H,  $H^{2,6}(C_6H_5)$ ], 7.37 [t, 3 H,  $H^4(C_6H_5)$ ], 7.32 [d, 6 H,  $H^{3,5}(C_6H_5)$ ], 2.20 (m, 2 H, PCH), 2.11 (br, 4H,  $C_6H_{11}$ ), 1.93–1.86 (m, 10 H, PCH<sub>2</sub> and  $C_6H_{11}$ ), 1.78, 1.69 (m  $\times$  2, 4 H  $\times$  2,  $C_6H_{11}$ ), 1.55 (br d, 2 H,  $C_6H_{11}$ ), 1.84 (m, 4 H,  $C_6H_{11}$ ), 1.34 (m, 6 H,  $C_6H_{11}$ ), 0.88 [tq,  $J = 12.9$ , 3.0,  $H^{2,6}(C_6H_5)$ ], 0.75 (tq,  $J = 13.0$ , 4.8,  $C_6H_{11}$ ), 0.50 [tq,  $J = 12.9$ , 2.9 Hz,  $H^{2,6}(C_6H_5)$ ].  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_C$  315.0 (t,  $^1J_{WC} = 159.1$ ,  $^2J_{PC} = 7.1$ ,  $W\equiv C$ ), 215.7 (dd,  $^1J_{WC} = 152.9$ ,  $J_{PC} = 39.1$ , 6.6, CO), 136.1 [ $C^{2,6}(C_6H_5)$ ], 135.0 [ $C^1(C_6H_5)$ ], 129.5 [ $C^4(C_6H_5)$ ], 127.9 [ $C^{3,5}(C_6H_5)$ ], 40.8 [d,  $^1J_{PC} = 18.9$ ,  $C^1(C_6H_{11})$ ], 35.2 [d,  $^1J_{PC} = 18.9$ ,  $C^1(C_6H_{11})$ ], 30.4 [ $C^4(C_6H_{11})$ ], 30.3, 29.8 [ $C^{3,5}(C_6H_{11})$ ], 29.2 [ $C^1(C_6H_{11})$ ], 27.7 [d,  $^2J_{PC} = 12.7$ ,  $C^{2,6}(C_6H_{11})$ ], 27.6 [d,  $^2J_{PC} = 9.1$ ,  $C^{2,6}(C_6H_{11})$ ], 27.1 [d,  $^3J_{PC} = 9.7$ ,  $C^{2,6}(C_6H_{11})$ ], 26.9 [d,  $^2J_{PC} = 12.4$  Hz,  $C^{2,6}(C_6H_{11})$ ], 26.4, 25.8 [ $C^{3,5}(C_6H_{11})$ ], 22.6 (dd,  $J_{PC} = 22.6$ , 10.6 Hz, PCH<sub>2</sub>).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_P = 45.0$  ( $^1J_{WP} = 229.0$  Hz). MS-ESI (positive, MeCN):  $m/z$  (%) 933.8 (100) [ $M - Br$ ] $^+$ , 1035.5 (24) [ $M + Na$ ] $^+$ . HR-ESI TOF MS: found, 933.3586, 1037.2643; calcd for  $C_{47}H_{63}O_2SiP_2^{184}W$  [ $M - Br$ ] $^+$ , 933.3582; calcd for  $C_{47}H_{63}^{81}Br^{23}NaO_2SiP_2^{184}W$  [ $M + Na$ ] $^+$ , 1037.2643. Anal. Found: C, 55.86; H, 6.41; N, 0.00. Calcd for  $C_{47}H_{63}BrO_2P_2SiW$ : C, 55.68; H, 6.26; N, 0.00. Crystals of **3b** suitable for X-ray diffraction were obtained from vapor diffusion of *n*-hexane or *n*-pentane into solutions of **3a** in benzene or  $CH_2Cl_2$  (0  $^{\circ}C$ , 3 days). Crystal data:  $C_{47}H_{63}BrO_2P_2SiW$ ,  $M_r = 1013.80$ ,  $T = 200(2)$  K, monoclinic, space group  $P2_1/c$ ,  $a = 14.5120(1)$  Å,  $b = 18.8706(2)$  Å,  $c = 16.8137(2)$  Å,  $\beta = 95.4929(7)^{\circ}$ ,  $V = 4583.29(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{calcd} = 1.469$  Mg m<sup>-3</sup>,  $\mu(Mo K\alpha) = 3.52$  mm<sup>-1</sup>, yellow lath,  $0.57 \times 0.35 \times 0.18$  mm, 26410 measured reflections with  $2\theta_{max} = 60^{\circ}$ , 13398 independent reflections, 13395 absorption-corrected data used in  $F^2$  refinement, 487 parameters without restraints,  $R1 = 0.041$  for 9800 reflections with  $I > 2\sigma(I)$ ,  $wR2 = 0.097$  for all data.

**Synthesis of  $[W(\equiv CSiPh_3)Br(CO)_2(tmeda)]$  (**3d**).** Neat tmeda (0.040 mL, 0.29 mmol) was slowly added to a dichloromethane solution (10 mL) of **2** (224 mg, 0.29 mmol), and the solution was stirred at room temperature for 20 h. The resultant dark brown solution was freed of volatiles and the solid washed with Et<sub>2</sub>O to provide a brown residue. The product was crystallized from liquid–liquid diffusion in DCM/*n*-pentane to give a small amount of bright yellow needles and a yellow powder with the same IR spectrum. Combined yield: 0.174 g (0.25 mmol, 86%). IR ( $CH_2Cl_2$ ): 2001, 1910 ( $\nu_{CO}$ )  $cm^{-1}$ . IR (KBr): 1991, 1899 ( $\nu_{CO}$ ), 1465, 1428, 1261, 1111, 907, 806  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_H$  = 7.61, 7.58, 7.37 (m  $\times$  3, 15 H,  $C_6H_5$ ), 2.95, 2.87 (s  $\times$  2, 6 H  $\times$  2, NCH<sub>3</sub>), 2.80, 2.75 (m  $\times$  2, 2 H  $\times$  2, NCH<sub>2</sub>).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_C$  311.8 ( $W\equiv C$ ), 223.2 (CO), 135.9 [ $C^{2,6}(C_6H_5)$ ], 135.1 [ $C^1(C_6H_5)$ ], 129.6 [ $C^4(C_6H_5)$ ], 128.1 [ $C^{3,5}(C_6H_5)$ ], 61.2 (NCH<sub>2</sub>), 58.8, 52.7 (NCH<sub>3</sub>). HR-ESI TOF MS: calcd for  $C_{27}H_{31}N_2O_2Si^{184}W$  [ $M - Br$ ] $^+$ , 627.1664; found, 627.1667; calcd for  $C_{29}H_{34}N_3O_2Si^{184}W$  [ $M - Br + MeCN$ ] $^+$ , 668.1930; found, 668.1932. Crystals of **3d** suitable for X-ray diffraction were obtained from liquid diffusion of  $CH_2Cl_2$ /*n*-pentane at 25  $^{\circ}C$  over 18 h. Crystal data:  $C_{27}H_{31}BrN_2O_2SiW$ ,  $M_r = 707.39$ ,  $T = 200(2)$  K, monoclinic, space group  $P2_1/c$ ,  $a = 9.3085(3)$  Å,  $b = 15.1128(4)$  Å,  $c = 19.6064(4)$  Å,  $\beta = 96.3395(18)^{\circ}$ ,  $V = 2741.31(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{calcd} = 1.714$  Mg m<sup>-3</sup>,  $\mu(Mo K\alpha) = 5.74$  mm<sup>-1</sup>, yellow prism,  $0.32 \times 0.07 \times 0.06$  mm, 49557 measured reflections with  $2\theta_{max} = 55^{\circ}$ , 6276 independent reflections, 3865 absorption-corrected data used in  $F^2$  refinement, 308 parameters without restraints,  $R1 = 0.066$  for 6267 reflections with  $I > 2\sigma(I)$ ,  $wR2 = 0.191$  for all data.

**Synthesis of  $[W(\equiv CH)Br(CO)_2(dcp)]$  (**4**).** A THF solution (15 mL) of complex **3b** (0.535 g, 0.53 mmol) was cooled (dry ice, acetone) and treated with [<sup>n</sup>Bu<sub>4</sub>N]F (0.53 mL, 1.0 M in THF solution,

Sigma-Aldrich 2161433, ca. 5 wt % H<sub>2</sub>O), resulting in a rapid color change from yellow to orange. The solution was slowly warmed to room temperature overnight. The solvent was removed under reduced pressure, and the resulting residue was washed with diethyl ether (40 mL) and then extracted with toluene to provide a yellow solution and a white precipitate ([<sup>n</sup>Bu<sub>4</sub>N][SiF<sub>2</sub>Ph<sub>3</sub>] see below), which was removed by filtration. The solvent was removed from the filtrate and the residue recrystallized from a mixture of  $CH_2Cl_2$  and *n*-hexane to afford the hemisolvate **4**·0.5C<sub>6</sub>H<sub>14</sub> (solvate confirmed by elemental microanalysis and X-ray crystallography). Yield: 0.345 g (0.43 mmol, 80%). IR (THF): 2008, 1937 ( $\nu_{CO}$ )  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_H$  6.66 (t, 1 H,  $^3J_{PC} = 6.7$  Hz,  $W\equiv CH$ ), 2.48–0.92 (m, 48 H,  $C_6H_{11}$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_C$  261.9 (from  $^{13}C$  NMR spectrum, dt,  $^1J_{CH} = 143.4$ ,  $^2J_{PC} = 10.6$  Hz,  $W\equiv C$ ), 213.6 (dd,  $^1J_{WC} = 147.0$ ,  $J_{PC} = 40.7$ , 6.0, CO), 37.1 [d,  $^1J_{PC} = 21.6$ ,  $C^1(C_6H_{11})$ ], 35.0 [d,  $^1J_{PC} = 19.3$ ,  $C^1(C_6H_{11})$ ], 31.5 [ $C^1(C_6H_{11})$ ], 30.6, 28.6 [ $C^{3,5}(C_6H_{11})$ ], 28.3 [ $C^1(C_6H_{11})$ ], 27.6 [d,  $^2J_{PC} = 13.4$ ,  $C^{2,6}(C_6H_{11})$ ], 27.5 [d,  $^2J_{PC} = 10.6$ ,  $C^{2,6}(C_6H_{11})$ ], 27.4 [d,  $^3J_{PC} = 9.1$ ,  $C^{2,6}(C_6H_{11})$ ], 27.2 [d,  $^2J_{PC} = 12.74$  Hz,  $C^{2,6}(C_6H_{11})$ ], 26.4, 26.2 [ $C^{3,5}(C_6H_{11})$ ], 23.1 [dd,  $J_{PC} = 22.9$ , 11.5 Hz, PCH<sub>2</sub>].  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_P$  47.46 ( $^1J_{WP} = 228.0$  Hz). MS-ESI (positive):  $m/z$  (%) 675.2717 (5) [ $M - Br$ ] $^+$ , 716.3026 (3) [ $M - Br + MeCN$ ] $^+$ . HR-ESI TOF MS: found, 675.2717; calcd for  $C_{29}H_{49}O_2P_2^{184}W$  [ $M - Br$ ] $^+$ , 675.2717; found, 716.2990; calcd for  $C_{31}H_{52}NO_2P_2^{184}W$  [ $M - Br + MeCN$ ] $^+$ , 716.2983. Anal. Found: C, 50.33; H, 7.87; N, 0.00. Calcd for  $C_{33}H_{63}BrO_2P_2W$  (*n*-hexane solvate): C, 49.95; H, 7.55; N, 0.00. A second sample for analysis was ground and washed with *n*-pentane six times and then dried under high vacuum to apparently afford the nonsolvated form. Anal. Found: C, 46.02; H, 6.59; N, 0.00. Calcd for  $C_{29}H_{49}BrO_2P_2W$ : C, 46.11; H, 6.54; N, 0.00. Crystals of **4**·0.5C<sub>6</sub>H<sub>14</sub> suitable for X-ray diffraction were obtained from vapor diffusion of *n*-hexane into a solution of **4** in DCM (25  $^{\circ}C$ , 2 days). Crystal data:  $C_{29}H_{49}BrO_2P_2W \cdot (C_6H_{14})_{0.5}$ ,  $M_r = 798.5$ ,  $T = 150(2)$  K, monoclinic, space group  $P2_1/c$ ,  $a = 11.9089(1)$ ,  $b = 14.5019(1)$ ,  $c = 19.5129(1)$  Å,  $\beta = 94.9140(4)^{\circ}$ ,  $V = 3357.52(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{calcd} = 1.580$  Mg m<sup>-3</sup>,  $\mu(Cu K\alpha) = 1.541$  mm<sup>-1</sup>, orange prism,  $0.21 \times 0.10 \times 0.08$  mm, 66122 measured reflections with  $2\theta_{max} = 144^{\circ}$ , 6633 independent reflections, 18 restraints, 6606 absorption-corrected data used in  $F^2$  refinement, 343 parameters without restraints,  $R1 = 0.027$  for 6543 reflections with  $I > 2\sigma(I)$ ,  $wR2 = 0.057$  for all data.

The crude reaction mixture contained a second complex (ca. 9%) tentatively formulated as  $[W(\equiv CH)Cl(CO)_2(dcp)]$  with the following characteristic data. NMR ( $CDCl_3$ , 25  $^{\circ}C$ ):  $\delta_C$  262.5 (t,  $^2J_{PC} = 10.6$ ,  $W\equiv C$ ), 214.8 (dd,  $J_{PC} = 42.3$ , 7.5 Hz, CO),  $\delta_H$  = 6.63 (t,  $J_{PH} = 1.8$  Hz);  $\delta_P$  = 51.17 ( $^1J_{WP} = 229$  Hz).

## ■ ASSOCIATED CONTENT

### § Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00635.

Selected spectra for **2–4**, selected structural data for published silylcarbynes (Table S1),<sup>17</sup> selected spectroscopic data (Table S2) for previously reported methylidyne complexes, calculated IR spectra for  $[W(\equiv CH)Br(dmpe)_2]$ ,  $[W(\equiv CH)Br(CO)_4]$ , and  $[W(\equiv CH)Br(dmpe)(CO)_2]$  (PDF) Crystallographic data for **2** (CCDC 1413751), **3b** (CCDC 1413593) **3c-O** (CCDC 1413594), **3d** (CCDC 1413595), **4** (CCDC 1413752), **5** (CCDC 1413596), and [<sup>n</sup>Bu<sub>4</sub>N][SiF<sub>2</sub>Ph<sub>3</sub>] (CCDC 1413597) (CIF)

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## Notes

The authors declare no competing financial interest.

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(22) The thermal displacement parameters for Br1 in the structural model for **4** are unremarkable, suggesting that there is no chloride/bromide cocrystallization or halide/methyldiyne disorder: cf. [W(≡CH)Cl(PMe<sub>3</sub>)<sub>4</sub>].<sup>3b</sup>

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