

0.75 mmol, 70% (based on vanadium). The product 2 was identified by mass, infrared, and NMR spectroscopies and comparison with an authentic sample.<sup>23</sup>

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## Synthesis of Group 6 (Aryloxy)carbyne and Phosponiocarbyne Complexes from Chlorocarbyne Precursors

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Displacement of chloride from the group 6 chlorocarbyne complexes  $\text{Tp}'(\text{CO})_2\text{M}\equiv\text{CCl}$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Tp}' = \text{HB}[\text{N}_2\text{C}_3\text{Me}_2\text{H}]_3$ ) with aryloxy anions produces the neutral (aryloxy)carbynes  $\text{Tp}'(\text{CO})_2\text{M}\equiv\text{COAr}$  ( $\text{Ar} = \text{Ph}, 4\text{-C}_6\text{H}_4\text{CH}_3, 4\text{-C}_6\text{H}_4\text{OCH}_3$ ). Tertiary phosphines ( $\text{PMe}_2\text{Ph}, \text{PPh}_3, \text{PCy}_3$ ) also displace chloride from the tungsten halocarbyne precursor to give the cationic phosponiocarbynes  $[\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CPR}_3][\text{PF}_6]$ . Complex 5a,  $[\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CPMe}_2\text{Ph}][\text{PF}_6]$ , crystallizes in the triclinic space group  $\text{P}\bar{1}$  with unit cell dimensions  $a = 10.897$  (3) Å,  $b = 11.631$  (3) Å,  $c = 13.939$  (4) Å,  $\alpha = 102.96$  (2)°,  $\beta = 108.79$  (2)°,  $\gamma = 94.59$  (2)°,  $Z = 2$ , 4954 observed data,  $R = 0.039$  and  $R_w = 0.070$ . Although no one-bond coupling between phosphorus and the carbyne carbon was observed for the  $\text{PMe}_2\text{Ph}$  or  $\text{PPh}_3$  products, the tricyclohexyl derivative displays a small phosphorus-carbon one-bond coupling constant ( $^1J_{\text{P-C}} = 15$  Hz) in its <sup>13</sup>C NMR spectrum. All complexes have been characterized by <sup>1</sup>H and <sup>13</sup>C NMR and IR spectroscopy and by elemental analysis.

### Introduction

The stability imparted by heteroatom substituents bearing lone-pair electrons in low-oxidation-state Fischer-type carbene complexes, which tempers the characteristic electrophilic behavior of these compounds, has been documented by more than two decades of organometallics research.<sup>1</sup> The role of the transition metal is crucial in dictating the reactivity pattern accessible to the carbene carbon atom. While  $(\text{CO})_5\text{W}=\text{CHPh}$ , a low-oxidation-state Fischer carbene complex, is electrophilic at carbon, the carbene carbon in  $\text{Cp}_2(\text{R})\text{Ta}=\text{CHPh}$ , a high-oxidation-state Schrock alkylidene complex, is nucleophilic.<sup>1d</sup> The field of transition-metal carbyne chemistry, although less mature, has likewise provided numerous synthetic, theoretical, structural, and reactivity studies into the nature of the transition-metal-carbon multiple bond.<sup>2</sup> The only previously reported oxycarbyne complexes are the siloxycarbyne intermediates in the reductive coupling of

Chart I

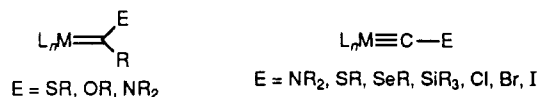
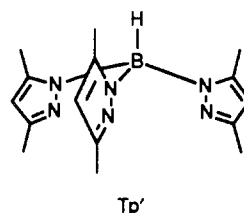
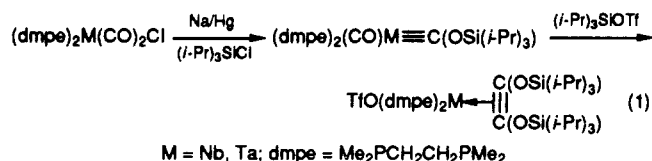


Chart II



$(\text{dmpe})_2\text{M}(\text{CO})_2\text{Cl}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) reported by Lippard et al. (eq 1).<sup>3</sup>

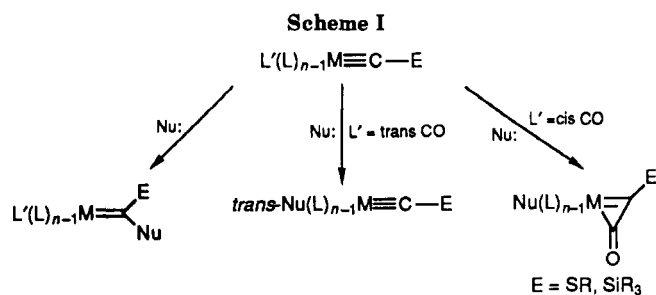


Substantive work has been devoted to carbyne complexes bearing other heteroatom substituents. Amino-carbynes comprise the majority of stable heteroatom-

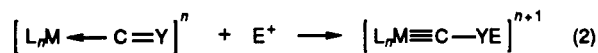
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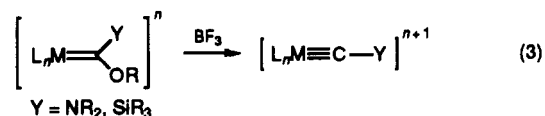
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substituted carbyne complexes. These complexes are accessible through electrophilic addition to isonitriles (eq 2)<sup>4</sup> or by Lewis-acid-promoted alkoxide abstraction from neutral or anionic metal carbamoyl precursors (eq 3).<sup>5,10e,f</sup>

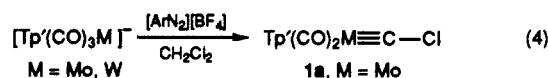


Y = NR, S



Angelici has shown that electrophiles add to electron-rich metal thiocarbonyls to generate (alkylthio)carbynes.<sup>6</sup> Fischer's abstraction methodology has been used in the preparation of two (triphenylsilyl)carbyne complexes of tungsten.<sup>7</sup>

Lalor has described the oxidation of anionic metal carbonyls in the presence of halocarbons to generate halocarbynes (eq 4) and the subsequent substitution of halide by non-first-row organochalcogenides to yield thio-, seleno-, and tellurocarbynes (eq 5).<sup>8</sup>

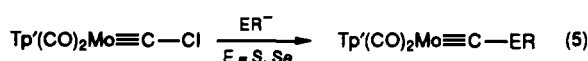


M = Mo, W

1a, M = Mo

b, M = W

Tp' = HB[3,5-Me<sub>2</sub>C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>]<sub>3</sub> (Chart II)



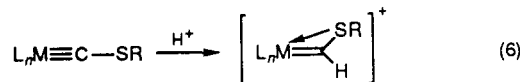
E = S<sup>2-</sup>, Se<sup>2-</sup>, Te<sup>2-</sup>



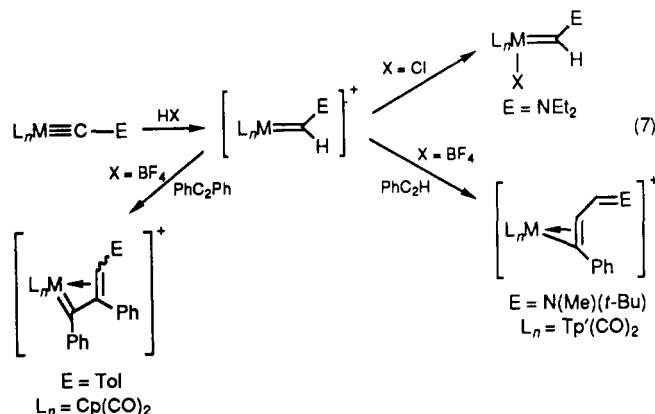
Recognized modes of reactivity for heteroatom-substituted carbynes include (i) nucleophilic attack at the methylidyne carbon, C<sub>α</sub>, in both neutral and cationic carbyne complexes,<sup>9,10d,e</sup> (ii) ligand substitution at the transition-

metal center,<sup>10</sup> and (iii) intramolecular ligand coupling in group 6 dicarbonyl thio- and silylcarbynes to form the corresponding thio- and silyl-substituted η<sup>2</sup>-ketenyl ligands (Scheme I).<sup>11</sup>

Charge-controlled<sup>12</sup> protonation of thiocarbynes at C<sub>α</sub> results in η<sup>2</sup>-thiocarbene formation (eq 6).<sup>13</sup> Both aryl-



carbynes<sup>14</sup> and aminocarbynes can be protonated at carbon and yield 7-coordinate HX addition products in cases where coordinating anions are employed;<sup>15</sup> with poorly coordinating anions, the cationic carbene intermediates can insert alkynes, ultimately yielding either a vinylcarbene<sup>16</sup> or, in the case of aminocarbynes, an η<sup>2</sup>-vinyliminium complex (eq 7).<sup>17</sup>



We report here the nucleophilic displacement of chloride from bulky molybdenum and tungsten chlorocarbyne complexes of the type Tp'(CO)<sub>2</sub>M≡CCl (Tp' = hydrido-tris(3,5-dimethylpyrazolyl)borate (Scheme I; M = Mo, W) by aryloxides to form stable, neutral (aryloxy)carbyne complexes, which have been characterized by elemental analysis and infrared and NMR spectroscopy (eq 8). Furthermore, addition of tertiary phosphines to the chlorocarbyne substrate gives cationic tungsten phosphino-carbynes, providing a viable route to multigram quantities of such complexes (eq 9).

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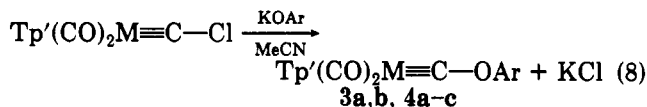
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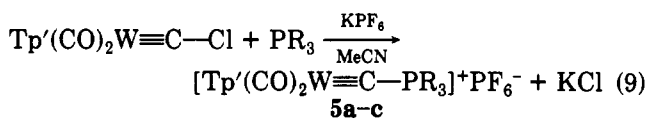
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**3a**, M = Mo, Ar = C<sub>6</sub>H<sub>5</sub>; **3b**, M = Mo, Ar = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; **4a**, M = W, Ar = C<sub>6</sub>H<sub>5</sub>; **4b**, M = W, Ar = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; **4c**, M = W, Ar = *p*-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>



**5a**, R<sub>3</sub> = Me<sub>2</sub>Ph; **5b**, R<sub>3</sub> = Ph<sub>3</sub>; **5c**, R<sub>3</sub> = (C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>

### Experimental Section

All reactions were run under dry nitrogen or argon with use of standard Schlenk techniques unless otherwise noted. Solvents were dried and distilled under nitrogen by standard methods.<sup>18</sup> Literature methods were used to prepare Tp'(CO)<sub>2</sub>M=CCl (M = Mo, W).<sup>8</sup> Liquid phosphines were freeze-thaw-degassed repeatedly prior to use; all other reagents were used as obtained from commercial sources.

Infrared spectra were obtained from a Mattson Polaris Fourier transform spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AC200, Bruker WM250, or Varian XL400 instrument; <sup>13</sup>C NMR spectra were obtained on a Varian XL400 instrument. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, Desert Analytics, Tucson, AZ, or Oneida Research Services, Whitesboro, NY.

**Synthesis of Tp'(CO)<sub>2</sub>Mo=COPh (3a).** A similar procedure was followed for all (aryloxy)carbyne preparations; only the reaction times varied, with the tungsten complexes requiring more vigorous conditions than their corresponding molybdenum analogues. An oven-dried Schlenk flask was charged with 0.44 g (11.0 mmol) of a 35% dispersion of KH in mineral oil. After thorough washes with dry THF, a 50-mL THF suspension of the KH was stirred with phenol (0.84 g, 8.93 mmol). Immediate gas evolution was observed. After it was stirred 30 min, the phenoxide solution was cannulated into a Schlenk flask containing a dry acetonitrile solution (200 mL) of Tp'(CO)<sub>2</sub>Mo=CCl (3.93 g, 7.92 mmol). The reaction mixture changed from bright yellow to brown-yellow, and a new dicarbonyl pattern appeared at  $\nu = 1982, 1889 \text{ cm}^{-1}$ . The reaction mixture was stirred for 10 h. Solvent was removed under vacuum after cooling, and the residue was chromatographed (alumina, eluted with 5:1 hexane-CH<sub>2</sub>Cl<sub>2</sub>) to give a bright yellow solution containing 1.47 g (34% yield) of Tp'(CO)<sub>2</sub>Mo=COPh following evaporation. IR (CH<sub>3</sub>CN): 1982, 1889 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.43, 7.29 (m, 5 H, Mo=COC<sub>6</sub>H<sub>5</sub>), 5.84, 5.82 (s, 2:1 H, Tp'CH), 2.43, 2.36, 2.35, 2.34 (s, 3:6:3:6 H, Tp'CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  225.4 (Mo(CO)), 218.0 (Mo=COPh), 154.8, 130.4, 126.3, 117.7 (Mo=COC<sub>6</sub>H<sub>5</sub>), 151.9, 151.5, 145.6, 145.2, (1:2:1:2 C, Tp'CCH<sub>3</sub>), 106.6, 106.4 (1:2 C, Tp'CH), 15.8, 14.9, 12.8 (Tp'CCH<sub>3</sub>). Anal. Calcd for C<sub>24</sub>H<sub>27</sub>BN<sub>6</sub>O<sub>3</sub>Mo: C, 52.03; H, 4.87; N, 15.16. Found: C, 52.44; H, 5.08; N, 14.82.

**Tp'(CO)<sub>2</sub>W=COPh (4a).** IR (CH<sub>3</sub>CN): 1967, 1870 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.42, 7.25 (m, 5 H, W=COC<sub>6</sub>H<sub>5</sub>), 5.92, 5.89 (s, 2:1 H, Tp'CH), 2.52, 2.42, 2.41, 2.40 (s, 3:6:6:3 H, Tp'CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  222.9 (<sup>1</sup>J<sub>W-C</sub> = 164 Hz, W(CO)), 219.3 (<sup>1</sup>J<sub>W-C</sub> = 242 Hz, W=COPh), 154.7, 130.3, 125.8, 117.3 (W=COC<sub>6</sub>H<sub>5</sub>), 152.8, 152.2, 145.7, 145.2 (1:2:1:2 C, Tp'CCH<sub>3</sub>), 106.9, 106.6 (1:2 C, Tp'CH), 16.6, 15.6, 12.8 (2:1:3 C, Tp'CCH<sub>3</sub>). Anal. Calcd for C<sub>24</sub>H<sub>27</sub>BN<sub>6</sub>O<sub>3</sub>W: C, 44.89; H, 4.24; N, 13.09. Found: C, 44.48; H, 4.24; N, 12.94. Yield: 83%.

**Tp'(CO)<sub>2</sub>Mo=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) (3b).** IR (CH<sub>3</sub>CN): 1980, 1887 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.29 (AA'BB', 4 H, Mo=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 5.90, 5.88 (s, 2:1 H, Tp'CH), 2.51, 2.44, 2.42, 2.39 (s, 3:6:9:3 H, Tp'CCH<sub>3</sub>, Mo=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  225.5 (Mo(CO)), 218.8 (Mo=COAr), 152.8, 136.3, 130.8, 117.5 (Mo=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 151.9, 151.5, 145.6, 145.2

(1:2:1:2 C, Tp'CCH<sub>3</sub>), 106.6, 106.4 (1:2 C, Tp'CH), 20.9 (Mo=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 15.8, 15.0, 12.9 (2:1:3 C, Tp'CCH<sub>3</sub>). Anal. Calcd for C<sub>25</sub>H<sub>29</sub>BN<sub>6</sub>O<sub>3</sub>Mo: C, 52.84; H, 5.14; N, 14.79. Found: C, 53.42; H, 5.23; N, 14.48. Yield: 46%.

**Tp'(CO)<sub>2</sub>W=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) (4b).** IR (CH<sub>3</sub>CN): 1966, 1870 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.25 (AA'BB', 4 H, W=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 5.88, 5.85 (s, 2:1 H, Tp'CH), 2.47, 2.37, 2.35, 2.34 (s, 3:12:3:3 H, Tp'CCH<sub>3</sub>, W=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  223.1 (<sup>1</sup>J<sub>W-C</sub> = 164 Hz, W(CO)), 220.2 (<sup>1</sup>J<sub>W-C</sub> = 245 Hz, W=COAr), 152.8, 136.0, 131.1, 117.5 (W=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 153.0, 152.4, 145.9, 145.3 (1:2:1:2 C, Tp'CCH<sub>3</sub>), 107.1, 106.8 (1:2 C, Tp'CH), 21.1 (W=CO(4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)), 16.8, 15.8, 13.0 (2:1:3 C, Tp'CCH<sub>3</sub>). Anal. Calcd for C<sub>25</sub>H<sub>29</sub>BN<sub>6</sub>O<sub>3</sub>W: C, 45.76; H, 4.46; N, 12.81. Found: C, 46.23; H, 4.48; N, 12.48. Yield: 94%.

**Tp'(CO)<sub>2</sub>W=CO(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>) (4c).** IR (CH<sub>3</sub>CN): 1965, 1866 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.30, 7.26, 6.91, 6.88 (AA'BB', 4 H, W=CO(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)), 5.87, 5.84 (s, 2:1 H, Tp'CH), 3.79 (s, 3 H, W=CO(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)), 2.47, 2.36, 2.35 (s, 3:12:3 H, Tp'CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  222.9 (<sup>1</sup>J<sub>W-C</sub> = 164 Hz, W(CO)), 220.5 (<sup>1</sup>J<sub>W-C</sub> = 244 Hz, W=COAr), 157.6, 148.4, 118.6, 115.1 (W=CO(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)), 152.7, 152.2, 145.6, 145.1 (1:2:1:2 C, Tp'CCH<sub>3</sub>), 106.9, 106.6 (1:2 C, Tp'CH), 56.0 (W=CO(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)), 16.5, 15.5, 12.8 (2:1:3 C, Tp'CCH<sub>3</sub>). Anal. Calcd for C<sub>25</sub>H<sub>29</sub>BN<sub>6</sub>O<sub>4</sub>W: C, 44.67; H, 4.35; N, 12.50. Found: C, 45.24; H, 4.43; N, 12.38. Yield: 81%.

**Synthesis of [Tp'(CO)<sub>2</sub>W=CPMe<sub>2</sub>Ph][PF<sub>6</sub>] (5a).** An oven-dried Schlenk flask was charged with 250 mL of acetonitrile, Tp'(CO)<sub>2</sub>W=CCl (2.00 g, 3.42 mmol), and KPF<sub>6</sub> (0.63 g, 3.42 mmol). PMe<sub>2</sub>Ph (0.48 mL, 3.35 mmol) was added dropwise, and the mixture was stirred at room temperature; a slow color change from yellow to deep red was observed. After 8 h, the solvent was removed under vacuum, and the residue was chromatographed on alumina by using CH<sub>2</sub>Cl<sub>2</sub> and gradually increasing the eluent polarity to 2:1 CH<sub>2</sub>Cl<sub>2</sub>-acetonitrile after residual starting chlorocarbene had been eluted. The phosphonio carbene was eluted as a dark red solution, which was stripped of solvent to yield 2.26 g (81% yield) of analytically pure [Tp'(CO)<sub>2</sub>W=CPMe<sub>2</sub>Ph][PF<sub>6</sub>] as a dark red, air-stable solid. IR (CH<sub>3</sub>CN): 2022, 1934 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.76 (m, 5 H, W=CPMe<sub>2</sub>Ph), 6.04, 5.87 (s, 2:1 H, Tp'CH), 2.41, 2.39, 2.33, 2.32 (s, 6:3:3:6 H, Tp'CCH<sub>3</sub>), 2.22 (d, 6 H, <sup>2</sup>J<sub>P-H</sub> = 13.5 Hz, W=CPMe<sub>2</sub>Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  245.9 (s, <sup>1</sup>J<sub>W-C</sub> = 207 Hz, W=CPMe<sub>2</sub>Ph), 223.0 (s, <sup>1</sup>J<sub>W-C</sub> = 155 Hz, W(CO)), 153.7, 151.6, 147.7, 146.8 (1:2:1:2 C, Tp'CCH<sub>3</sub>), 134.9, 131.1, 130.7, (d, W=CPMe<sub>2</sub>Ph), 121.9 (d, <sup>1</sup>J<sub>P-C</sub> = 88 Hz, C<sub>ipso</sub>, W=CPMe<sub>2</sub>Ph), 108.1, 107.6 (1:2 C, Tp'CH), 17.2, 15.5, 12.9, 12.7 (2:1:1:2 C, Tp'CCH<sub>3</sub>), 11.2 (d, <sup>1</sup>J<sub>P-C</sub> = 58 Hz, W=CPMe<sub>2</sub>Ph). Anal. Calcd for C<sub>26</sub>H<sub>33</sub>BF<sub>6</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>W: C, 37.52; H, 4.00; N, 10.09. Found: C, 37.10; H, 3.97; N, 9.73.

**Synthesis of [Tp'(CO)<sub>2</sub>W=CPPh<sub>3</sub>][PF<sub>6</sub>] (5b).** An oven-dried Schlenk flask was charged with 300 mL of dry acetonitrile, Tp'(CO)<sub>2</sub>W=CCl (1.58 g, 2.70 mmol), KPF<sub>6</sub> (0.50 g, 2.72 mmol), and PPh<sub>3</sub> (1.42 g, 5.41 mmol). The reaction mixture was refluxed for 2 days and then cooled and stripped of solvent. The residue was chromatographed on alumina (eluted with CH<sub>2</sub>Cl<sub>2</sub>, gradually changed to 9:1 CH<sub>2</sub>Cl<sub>2</sub>-acetonitrile). The product was collected as a purple solution, which was dried, leaving 1.60 g (62% yield) of [Tp'(CO)<sub>2</sub>W=CPPh<sub>3</sub>][PF<sub>6</sub>] as an analytically pure, air-stable purple solid. IR (CH<sub>3</sub>CN): 2026, 1940 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.79 (m, 15 H, W=CPPh<sub>3</sub>), 6.00, 5.86 (s, 2:1 H, Tp'CH), 2.43, 2.34, 2.33, 2.02 (s, 6:3:3:6 H, Tp'CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  242.1 (s, <sup>1</sup>J<sub>W-C</sub> = 212 Hz, W=CPPh<sub>3</sub>), 224.5 (s, <sup>1</sup>J<sub>W-C</sub> = 158 Hz, W(CO)), 153.6, 152.0, 147.7, 146.9 (1:2:1:2 C, Tp'CCH<sub>3</sub>), 135.2, 133.8, 130.7 (d, W=CP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), 120.9 (d, <sup>1</sup>J<sub>P-C</sub> = 90 Hz, W=CP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> ipso), 16.8, 15.5, 12.9, 12.8 (2:1:1:2 C, Tp'CCH<sub>3</sub>). Anal. Calcd for C<sub>36</sub>H<sub>37</sub>BF<sub>6</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>W: C, 45.21; H, 3.91; N, 8.78. Found: C, 44.90; H, 3.96; N, 9.08.

**Synthesis of [Tp'(CO)<sub>2</sub>W=CP(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>][PF<sub>6</sub>] (5c).** An oven-dried Schlenk flask was charged with 300 mL of dry propionitrile, Tp'(CO)<sub>2</sub>W=CCl (4.89 g, 8.37 mmol), KPF<sub>6</sub> (1.54 g, 8.37 mmol), and P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> (4.69 g, 16.7 mmol). The reaction mixture was refluxed for 4 days, giving a dark red solution. The solvent was removed under vacuum, leaving a dark red solid. Alumina chromatography (as described in the [Tp'(CO)<sub>2</sub>W=CPMe<sub>2</sub>Ph][PF<sub>6</sub>] preparation) gave 4.54 g (56% yield) of analytically pure [Tp'(CO)<sub>2</sub>W=CP(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>][PF<sub>6</sub>] as a dark red, air-stable solid. IR (CH<sub>3</sub>CN): 2020, 1933 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR

(18) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*, Wiley: New York, 1972.

Table I. Crystallographic Data Collection Parameters for 5a

Crystal Data	
mol formula	C <sub>26</sub> H <sub>33</sub> BF <sub>6</sub> N <sub>6</sub> O <sub>2</sub> P <sub>2</sub> W
fw	832.17
crystal dimens, mm	0.40 × 0.25 × 0.15
space group	P1
cell params	
a, Å	10.897 (3)
b, Å	11.631 (3)
c, Å	13.939 (4)
α, deg	102.96 (2)
β, deg	108.79 (2)
γ, deg	94.59 (2)
V, Å <sup>3</sup>	1607.4 (7)
Z	2
d(calcd), g/cm <sup>3</sup>	1.719
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.710 73)
monochromator	graphite
linear abs coeff, mm <sup>-1</sup>	3.84
scan mode	ω/2θ
bkgd	25% of full scan width on both sides
2θ limits, deg	2 < 2θ < 50
quadrant collected	±h,k,±l
total no. of reflns	5622
no. of data with I ≥ 2.5σ(I)	4954
R (including unobsds)	0.039 (0.047)
R <sub>w</sub> (including unobsds)	0.070 (0.070)
GOF	1.91
no. of params	451
largest param shift	0.002

(CD<sub>2</sub>Cl<sub>2</sub>): δ 6.08, 5.84 (s, 2:1 H, Tp'CH), 2.54, 2.43, 2.39, 2.31 (s, 6:6:3:3 H, Tp'CCH<sub>3</sub>), 2.2–1.2 (m, 33 H, W≡CP(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 251.1 (d, <sup>1</sup>J<sub>P-C</sub> = 15 Hz, W≡CP(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>), 226.1 (s, <sup>1</sup>J<sub>W-C</sub> = 163 Hz, W(CO)), 153.3, 151.8, 147.4, 147.1 (1:2:1:2 C, Tp'CCH<sub>3</sub>), 108.0, 107.6 (1:2 C, Tp'CH), 35.0 (d, <sup>1</sup>J<sub>P-C</sub> = 41 Hz, W≡CP(CH(CH<sub>2</sub>)<sub>5</sub>)), 27.7, 27.1, 25.7 (d, W≡CP(CH(CH<sub>2</sub>)<sub>5</sub>)), 17.6, 15.4, 12.9, 12.8 (2:1:2:1 C, Tp' CCH<sub>3</sub>). Anal. Calcd for C<sub>26</sub>H<sub>33</sub>BF<sub>6</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>W: C, 44.37; H, 5.64; N, 8.62. Found: C, 44.88; H, 5.96; N, 8.49.

**Collection of Diffraction Data for 5a.** A red crystal of dimensions 0.40 × 0.25 × 0.15 mm was selected, mounted on a glass fiber, and coated with epoxy. Diffraction data were collected on a Enraf-Nonius CAD-4 automated diffractometer. Cell parameters, listed in Table II, were refined by least squares from the positions of 25 well-centered reflections found in the region 30.0 < 2θ < 35.0° and indicated a triclinic cell.

Intensity data were collected in the quadrant ±h,k,±l under the conditions specified in Table I. Only data with I > 2.5σ(I) were used in the structure solution and refinement.<sup>19</sup>

**Solution and Refinement of the Structure of 5a.** The space group P1 was confirmed, and the position of the tungsten atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

The non-hydrogen atoms were refined anisotropically.<sup>20</sup> Hydrogen atom positions were calculated with use of a C–H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. Final least-squares refinement resulted in residuals of R = 3.9% and R<sub>w</sub> = 7.0%.<sup>21</sup> The final difference Fourier map had no peak greater than 1.26 e/Å<sup>3</sup>.<sup>22</sup>

(19) Programs used during solution and refinement were from the NRCVAX structure determination package: Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Chem.* 1989, 22, 384.

(20) The function minimized was Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup>, where w is based on counter statistics.

(21) R<sub>unweighted</sub> = Σ(|F<sub>o</sub>| - |F<sub>c</sub>|) / Σ|F<sub>o</sub>| and R<sub>weighted</sub> = [Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup> / ΣwF<sub>o</sub><sup>2</sup>]<sup>1/2</sup>.

(22) Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.

Table II. Complete Atomic Parameters (x, y, z, B<sub>iso</sub>) for 5a

	x	y	z	B <sub>iso</sub> , Å <sup>2</sup>
W(1)	0.07150 (3)	0.32588 (3)	0.209783 (23)	3.088 (17)
C(1)	-0.0099 (9)	0.1524 (8)	0.1393 (7)	4.3 (4)
O(1)	-0.0478 (8)	0.0556 (6)	0.1022 (7)	6.5 (4)
C(2)	0.1375 (10)	0.3207 (8)	0.0906 (8)	4.6 (5)
O(2)	0.1723 (11)	0.3180 (8)	0.0214 (7)	8.2 (6)
C(3)	0.2145 (8)	0.2591 (7)	0.2651 (6)	3.7 (4)
P(4)	0.34531 (21)	0.18011 (18)	0.29103 (17)	3.45 (9)
C(5)	0.4731 (11)	0.2496 (10)	0.4149 (8)	5.5 (5)
C(6)	0.2803 (10)	0.0342 (7)	0.2925 (8)	4.8 (5)
C(7)	0.4096 (8)	0.1691 (8)	0.1867 (7)	3.9 (4)
C(8)	0.3282 (9)	0.1110 (8)	0.0838 (7)	4.6 (4)
C(9)	0.3725 (12)	0.1086 (10)	0.0020 (9)	5.8 (6)
C(10)	0.4971 (15)	0.1621 (12)	0.0213 (11)	6.7 (8)
C(11)	0.5803 (12)	0.2217 (14)	0.1229 (12)	7.4 (8)
C(12)	0.5373 (10)	0.2269 (8)	0.2064 (8)	5.1 (5)
B(1)	-0.0965 (9)	0.5397 (8)	0.2693 (7)	3.3 (4)
N(21)	0.1358 (7)	0.5222 (6)	0.2800 (5)	3.4 (3)
N(22)	0.0470 (6)	0.5932 (5)	0.2901 (5)	3.2 (3)
C(23)	0.1069 (8)	0.7087 (7)	0.3235 (6)	3.4 (3)
C(24)	0.2350 (9)	0.7103 (8)	0.3344 (7)	4.1 (4)
C(25)	0.2508 (8)	0.5918 (7)	0.3048 (7)	3.7 (4)
C(26)	0.0341 (11)	0.8115 (7)	0.3383 (8)	4.9 (5)
C(27)	0.3747 (9)	0.5454 (9)	0.3038 (9)	5.1 (5)
N(31)	-0.1112 (7)	0.3801 (8)	0.1046 (6)	4.5 (4)
N(32)	-0.1613 (7)	0.4707 (5)	0.1498 (5)	3.2 (3)
C(33)	-0.2672 (8)	0.4917 (7)	0.0788 (6)	3.7 (4)
C(34)	-0.2875 (10)	0.4095 (9)	-0.0150 (7)	4.7 (5)
C(35)	-0.1895 (10)	0.3406 (8)	0.0034 (7)	4.4 (5)
C(36)	-0.3445 (10)	0.5883 (10)	0.1025 (9)	5.7 (6)
C(37)	-0.1702 (13)	0.2402 (12)	-0.0719 (8)	6.9 (7)
N(41)	-0.0378 (6)	0.3485 (5)	0.3172 (5)	3.3 (3)
N(42)	-0.0971 (6)	0.4471 (6)	0.3328 (5)	3.3 (3)
C(43)	-0.1606 (8)	0.4389 (8)	0.4005 (6)	3.8 (4)
C(44)	-0.1430 (9)	0.3343 (9)	0.4278 (7)	4.2 (4)
C(45)	-0.0667 (8)	0.2796 (8)	0.3759 (6)	3.8 (4)
C(46)	-0.2381 (10)	0.5317 (10)	0.4331 (8)	5.0 (5)
C(47)	-0.0200 (11)	0.1623 (9)	0.3771 (8)	5.2 (5)
P(11)	0.64020 (22)	0.89817 (20)	0.34964 (19)	4.60 (11)
F(11)	0.76832 (22)	0.94915 (20)	0.44749 (19)	10.39 (11)
F(12)	0.71930 (22)	0.87783 (20)	0.26974 (19)	8.83 (11)
F(13)	0.51092 (22)	0.84772 (20)	0.24976 (19)	10.99 (11)
F(14)	0.55501 (22)	0.92019 (20)	0.42410 (19)	9.74 (11)
F(15)	0.62834 (22)	1.02638 (20)	0.33922 (19)	10.47 (12)
F(16)	0.65554 (22)	0.76701 (20)	0.35861 (19)	12.16 (12)
F(21)	0.55628 (22)	0.96656 (20)	0.27117 (19)	9.85 (11)
F(22)	0.56655 (22)	0.77399 (20)	0.27600 (19)	11.63 (11)
F(23)	0.70950 (22)	0.83314 (20)	0.43734 (19)	11.59 (11)
F(24)	0.69916 (22)	1.03066 (20)	0.42285 (19)	12.48 (11)
F(25)	0.51958 (22)	0.87543 (20)	0.39102 (19)	7.69 (11)
F(26)	0.75585 (22)	0.90889 (20)	0.30819 (19)	13.31 (12)

<sup>a</sup> B<sub>iso</sub> is the mean of the principal axes of the thermal ellipsoid.

## Results and Discussion

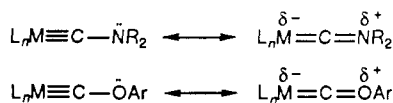
**Synthesis and Characterization of Molybdenum and Tungsten (Aryloxy)carbynes.** Halide displacement from mononuclear, η<sup>1</sup>-halocarbyne complexes constitutes an efficient route to a variety of carbyne complexes, presumably via frontier molecular orbital controlled nucleophilic attack at the methylidyne carbon atom.<sup>23</sup> While some nucleophilic attack at the metal center in L<sub>n</sub>M≡CCl might be expected, the bulky ligand sphere here may inhibit approach of the incoming nucleophile to the metal, resulting in clean reaction at C.<sup>9e,24</sup>

Deprotonation of phenol, or its 4-substituted derivatives *p*-cresol or *p*-methoxyphenol, with excess potassium hydride in THF generates the corresponding phenoxide anion, which smoothly displaces chloride from the chloro-

(23) (a) Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* 1981, 103, 4677. (b) Kostic, N. M.; Fenske, R. F. *Organometallics* 1982, 1, 489. (c) Ushio, J.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* 1984, 106, 5892.

(24) Desmond, T.; Lalor, F. J.; Parvez, M.; Ruhl, B. *J. Chem. Soc., Chem. Commun.* 1983, 55.

Scheme II



carbynes  $Tp'(CO)_2M \equiv CCl$  ( $M = Mo, W$ ;  $Tp' = HB-[N_2C_3Me_2H]_3^-$ ) in refluxing acetonitrile. A new class of carbynes, (aryloxy)carbynes **3a,b** and **4a-c**, are isolated in good yield (eq 8). No other products are detected by infrared spectroscopy during the reactions. Substitution of the molybdenum chlorocarbyne typically proceeds faster than with the analogous tungsten substrate. The new carbyne products are purified by alumina chromatography, yielding analytically pure bright yellow solids. Attempts at methoxide or *tert*-butoxide substitution on chlorocarbyne **1b** did not result in alkoxy-carbyne isolation.

The tungsten (aryloxy)carbynes **4a-c** are characterized by two strong carbonyl stretching frequencies in the infrared spectrum at approximately 1966 and 1868  $cm^{-1}$ , noticeably lower than the CO stretches of the chlorocarbyne precursor (1987, 1894  $cm^{-1}$ ). The corresponding molybdenum complexes display higher carbonyl stretching frequencies (by approximately 25–30  $cm^{-1}$ ).  $^1H$  NMR spectroscopy reveals that the compounds possess a symmetry plane, as the  $Tp'$  ligand displays a 2:1 out-of-plane-in-plane pattern. The symmetry plane contains the carbyne-metal bond and one dimethylpyrazole ring of the  $Tp'$  ligand and bisects the two terminal carbonyls. The aryloxy signals are easily assigned.

We observe a remarkably high-field chemical shift in the  $^{13}C$  NMR spectrum of each complex (even upfield from the terminal carbonyl signals), which is assigned to  $C_\alpha$ . This carbyne carbon signal is assigned on the basis of its chemical shift ( $\delta \approx 220$  ppm) and its large coupling to tungsten ( $^1J_{W-C} = 245$  Hz in **4b**, for example;  $^{183}W$  14%,  $I = 1/2$ ).<sup>2</sup> Only the family of group 6 halocarbynes displays similar high-field methylidyne chemical shifts. The chemical shift of the methylidyne carbon in these (aryloxy)carbyne complexes, upfield relative to the shifts of other group 6 carbynes, suggests that the oxygen atom acts to stabilize the electron-deficient<sup>23b</sup> methylidyne carbon. Conjugative interaction of the oxygen lone pairs with the  $d_\pi-p_\pi$  metal-methylidyne  $\pi$  bonds could influence the methylidyne chemical shift (Scheme II). A similar stabilization of the methylidyne center by the lone-pair-bearing nitrogen atom of related aminocarbyne complexes has been invoked to explain their long metal-carbon bond lengths and relatively high-field methylidyne chemical shifts, as well as to explain their reactivity (or lack thereof) under typical intramolecular ligand-coupling conditions.<sup>23b</sup>

**Synthesis and Characterization of Cationic Tungsten Phosphonocarbynes.** In an earlier report, we described that the tungsten thiocarbyne functionality served as a suitable precursor for cationic tertiary phosphonium carbynes, with  $C_\alpha$  attack made more likely by the bulky  $Tp'$  ligand sphere about the metal nucleus.<sup>9a</sup> Cationic phosphonocarbyne complexes have been observed by Schrock during attempts to oxidize  $(PMe_3)_4W(CH)Cl^{25}$  and more recently by Hillhouse and co-workers in their investigations of tungsten complexes bearing the carbon suboxide ligand.<sup>26</sup> Note that these complexes do not contain heteroatom lone-pair electrons and hence differ

Chart III

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for  $[Tp'(CO)_2W \equiv CPM_2Ph][PF_6]$ 

W(1)–C(1)	2.022 (9)	W(1)–N(41)	2.179 (6)
W(1)–C(2)	2.003 (9)	C(3)–P(4)	1.741 (9)
W(1)–C(3)	1.821 (9)	P(4)–C(5)	1.79 (1)
W(1)–N(21)	2.227 (6)	P(4)–C(6)	1.793 (8)
W(1)–N(31)	2.291 (7)	P(4)–C(7)	1.791 (9)
W(1)–C(3)–P(4)	168.1 (5)	C(3)–W(1)–N(31)	166.8 (3)
C(1)–W(1)–C(3)	81.9 (4)	N(21)–W(1)–N(31)	84.3 (3)
C(2)–W(1)–C(3)	85.1 (4)	N(21)–W(1)–N(41)	82.4 (2)
C(1)–W(1)–C(2)	86.9 (4)	N(31)–W(1)–N(41)	81.7 (3)

fundamentally from their (aryloxy)- and aminocarbyne relatives (Chart III).

Due to the limited quantities of thiocarbyne precursors that are available to produce the thiocarbyne reagent, a more efficient route to the group 6 pyrazolyborato phosphonocarbynes involves displacement of chloride from the Lalor chlorocarbynes in a process analogous to that for the (aryloxy)carbyne syntheses. Thus, reaction of  $PM_2Ph$ ,  $PPh_3$ , or  $PCy_3$  with a slight excess of  $Tp'(CO)_2W \equiv CCl/KPF_6$  in acetonitrile smoothly generates the cationic ( $\eta^1$ -phosphonio)carbynes **5a-c** (eq 9). The steric bulk of  $P(Cy)_3$  (cone angle 170°)<sup>27</sup> requires that a high-boiling solvent (in this case propionitrile) be used to facilitate chloride replacement. Chloride displacement is the only observable reaction, as indicated by infrared spectroscopy of the reaction mixture. Solvent evaporation followed by chromatography on alumina ( $CH_2Cl_2$  eluent) separates unreacted chlorocarbyne as a bright yellow band. As the eluent polarity is increased by adding  $CH_3CN$ , a deep red (purple in the case of  $PPh_3$  addition) band elutes. Evaporation of the red solution yields analytically pure, air-stable **5a-c** as a dark red (purple) air-stable powder in good yield.

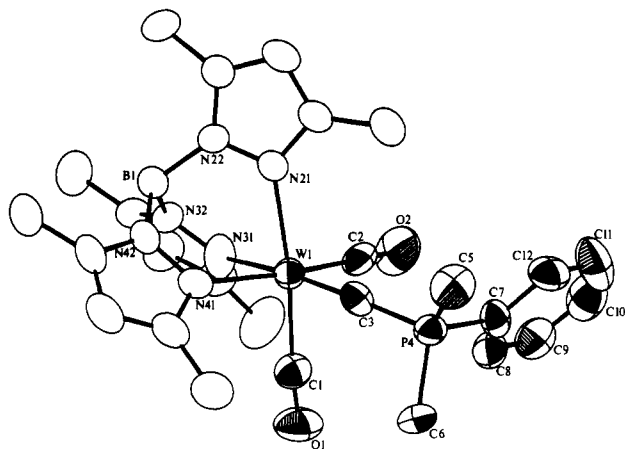
High-energy carbonyl stretching frequencies at approximately 2022 and 1934  $cm^{-1}$  reflect the cationic nature of the dicarbonyl products. Once again, the axially symmetric carbyne ligand contributes to a molecular  $C_\infty$  symmetry;  $^1H$  NMR spectroscopy displays a 2:1 pattern in the  $Tp'$  proton assignments. Aromatic resonances attributable to the phosphorus-bound phenyl groups in complexes **5a,b** are easily assignable, and a doublet resonance ( $^2J_{P-H} = 13.5$  Hz), assigned to the phosphorus-bound methyl group, appears at approximately 2.22 ppm in **5a**.

Whereas the  $^{13}C$  NMR  $C_{ipso}$  signal (and other carbon resonances of the phosphorus-bound phenyl groups) in compounds **5a,b** appear as doublets due to spin coupling to the phosphorus atom, the low-field  $^{13}C$  NMR carbyne resonances of **5a,b** (near 210 ppm) both display small satellites due to coupling to the tungsten nucleus ( $^1J_{W-C} = 210$  Hz) but appear as singlets with no observable coupling to the directly bound phosphorus atom. This is in agreement with previous descriptions of both neutral and cationic phosphonocarbyne complexes, as no coupling to the phosphonium substituent has been detected in  $^{13}C$  NMR spectra. However, we have been able to resolve a doublet resonance for the methylidyne carbon in (tricyclohexylphosphonio)carbyne complex **5c** ( $\delta = 251.1$  ppm,  $^1J_{P-C} = 15$  Hz). The magnitude of this coupling is far less than that observed in numerous alkenyl ( $[(Ph_3P)CH=$

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**Figure 1.** ORTEP representation of the cationic phosphonocarbyne complex **5a**.

CRR']<sup>+</sup>) and alkynyl [(Ph<sub>3</sub>P)C≡C(R)]<sup>+</sup> phosphonium salts<sup>28,29</sup> and even well below the observed coupling constant between the phosphorus and its aliphatic substituents in complexes **5a** (<sup>1</sup>J<sub>P-Me</sub> = 56 Hz) and **5c** (<sup>1</sup>J<sub>P-Cy</sub> = 41 Hz). It remains unclear to us why we should see coupling only in complex **5c** and not the arylated phosphonium derivatives **5a-b**.

**Molecular Structure of [Tp'(CO)<sub>2</sub>W≡CPMe<sub>2</sub>Ph]<sub>+</sub>[PF<sub>6</sub>]<sup>-</sup> (**5a**).** An ORTEP drawing of **5a** is shown in Figure 1; selected bond lengths and angles are shown in Table III. The complex is a monomeric cation that assumes a distorted-octahedral geometry. The bond angles between the carbyne and the two carbonyl ligands are slightly less than 90°, as are those between the three nitrogen donors of the Tp' ligand.

Relief of steric interactions between the Tp' ligand and the phosphorus-bound substituents of the methylidyne moiety manifests itself in a deviation from linearity in the bond angle at C<sub>3</sub>; the 168.1 (5)° W(1)-C(3)-P(4) bond angle is close enough to 180° to approximate sp hybridization at C(3), however. The phosphonium moiety is slightly directed toward the cavity defined by C(1)-W(1)-C(2). As reported for the other previously characterized phosphonocarbynes Cl<sub>2</sub>(CO)(PMePh<sub>2</sub>)<sub>2</sub>W≡C-(PPh<sub>3</sub>)<sup>26</sup> and [W<sub>2</sub>(≡CPMe<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>][AlCl<sub>4</sub>]<sub>2</sub>,<sup>25</sup> the short tungsten-methylidyne bond length of 1.821 (9) Å in **5a** confirms the triple bond that links the methylidyne

fragment to the metal nucleus. This geometrical feature agrees with other metal-carbyne bond distances, where the metal bears a relatively electron-rich ligand trans to the methylidyne ligand.<sup>15a,30</sup> The higher degree of s character at the methylidyne carbon relative to that for the other phosphorus substituents is translated into a slightly shorter C<sub>3</sub>-P bond distance; the carbon-phosphorus bond length of 1.741 (9) Å is 0.05 Å shorter than the bonds from phosphorus to its sp<sup>3</sup>-hybridized methyls (1.79 (1) Å) or the sp<sup>2</sup>-hybridized phenyl substituent (1.791 (9) Å). The trans influence of the carbyne ligand is reflected in the W(1)-N(31) bond length of 2.291 (7) Å, which is roughly 0.08 Å longer than the average of the W-N bonds that are trans to the carbonyl ligands (W(1)-N(21) = 2.227 (6) Å and W(1)-N(41) = 2.179 (6) Å).

## Conclusions

Air-stable, neutral (aryloxy)carbyne complexes of molybdenum and tungsten are accessible through nucleophilic displacement from bulky Tp' chlorocarbyne precursors. The five members of this new class of carbyne complexes reported here display relatively high field methylidyne resonances in their <sup>13</sup>C NMR spectra, presumably due to resonance stabilization by the aryloxy substituent. Similarly, tertiary phosphines can displace chloride from the tungsten chlorocarbyne precursor to yield air-stable, cationic phosphonocarbynes. The absence of a heteroatom lone pair on the carbyne substituent is a key feature of these complexes. In accord with other observations, we see no one-bond coupling between the methylidyne carbon and its directly bound phosphorus substituent except in the case of [Tp'(CO)<sub>2</sub>W≡CP(Cy)<sub>3</sub>][PF<sub>6</sub>]; however, the observed coupling is still strongly attenuated relative to that expected for a phosphonium-C<sub>sp</sub> linkage. Investigations into the reactivity of the neutral oxycarbynes are presently underway.

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**Supplementary Material Available:** Complete tables of anisotropic temperature factors, bond distances and bond angles, and calculated hydrogen positions for **5a** as well as a PLUTO drawing of **5a** with the complete numbering scheme (6 pages); a table of observed and calculated structure factors for **5a** (19 pages). Ordering information is given on any current masthead page.

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