

# Reactions of Tungsten Alkylidyne with Thionyl Chloride

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The reaction of  $[W(=CR)(CO)_2(\eta-C_5H_5)]$  ( $R = C_6H_3Me_{2-2,6}$ ) with thionyl chloride provides the metallacyclic alkylidene complex  $[W(=CRSCRS)Cl_3(\eta-C_5H_5)]$ , while similar treatment of  $[W(=CR)(CO)_2\{HB(pz)_3\}]$  ( $pz = \text{pyrazol-1-yl}$ ) provides the alkylidyne complex  $[W(=CR)Cl_2\{HB(pz)_3\}]$ , which is also obtained from the reaction of  $[W(=CR)(CO)_2\{HB(pz)_3\}]$  with  $[Fe(\eta-C_5H_5)_2]Cl$ . The crystal structures of  $[W(=CC_6H_2Me_{3-2,4,6})(CO)_2\{HB(pz)_3\}]$ ,  $[W(=CRSCRS)Cl_3(\eta-C_5H_5)]$ , and  $[W(=CR)Cl_2\{HB(pz)_3\}]$  ( $R = C_6H_3Me_{2-2,6}$ ) are reported.

## Introduction

The metal–carbon multiple bonds of alkylidyne (carbyne) complexes have been shown to enter into various C–S bond forming processes.<sup>1</sup> The first of such processes to be observed involved the addition of elemental chalcogens to the electron-rich alkylidyne complex  $[Os(=CC_6H_4Me-4)Cl(CO)(PPh_3)_2]$ , resulting in the formation of the first complete series of isostructural chalcocarbonyl complexes  $[Os(\eta^2-ECC_6H_4Me-4)Cl(CO)(PPh_3)_2]$  ( $E = S, Se, Te$ ).<sup>2</sup> The related thiocarbonyl complex  $[Ru(\eta^2-SCPh)Cl(CS)(PPh_3)_2]$  has been shown to arise from the addition of  $CS_2$  to  $[Ru(=CPh)Cl(CO)(PPh_3)_2]$ .<sup>3</sup> In contrast, the addition of sulfur or selenium to alkylidyne complexes of group 6 metals  $[M(=CR)L_2(\eta-C_5H_5)]$  [ $M = Mo, W; R = C_6H_4Me-4, CH_2CMe_3; L = CO, P(OMe)_3$ ] provides dichalcocarbonyl complexes  $[M(E_2CR)L_2(\eta-C_5H_5)]$  ( $E = S, Se$ ).<sup>4</sup> Similar compounds are obtained with cyclohexene episulfide in place of elemental sulfur,<sup>5</sup> however thioacyl complexes are the initial products with methylthiirane.<sup>6</sup> The electrophilic “ $SMe^+$ ” transfer re-

agent  $[Me_3S_2]BF_4$  has been employed by Kreissl to generate bidentate thiolatocarbene complexes.<sup>7</sup> Thioaldehyde complexes have been obtained from the reactions of  $[W(=CPh)Cl(CO)_2(py)_2]^{8a}$  or  $[W\{=CC_5H_4Mn(CO)_3\}(O_2CCF_3)(CO)_2(tmeda)]^{8b}$  with  $[Et_2NH_2][S_2CNMe_2]$ , although there are now indications that the actual C–S bond forming step may occur following initial conversion to an alkylidene intermediate.<sup>9,10</sup> Sulfur-containing heterocumulenes have also been shown to couple with alkylidyne complexes,<sup>11–16</sup> although not all cases involve C–S bond formation: The reactions of  $[M(=CPh)Cl(CO)(PPh_3)_2]$  ( $M = Ru, Os$ ) with  $SO_2$  or imino-oxosulfuranes lead to thermally unstable metallacyclic carbene complexes via C–O bond formation,<sup>14</sup> while the same complexes with  $CS_2$  ultimately provide thioacyl-thio-

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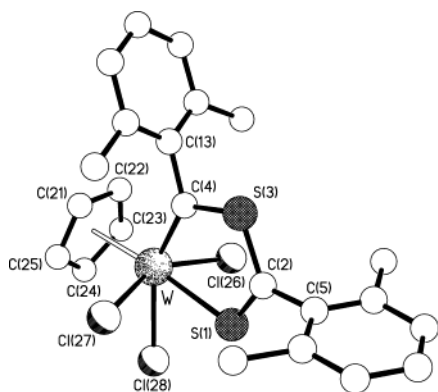
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**Figure 1.** Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): W–C(4) 2.043(6), C(4)–S(3) 1.740(6), S(3)–C(2) 1.701(6), C(2)–S(1) 1.626(6), W–S(1) 2.520(2), W–Cl(26) 2.453(2), W–Cl(27) 2.429(2), W–Cl(28) 2.479(2), W–Cp 2.032(4), S(3)–C(4)–W 126.4(3), C(2)–S(3)–C(4) 104.8(3), S(1)–C(2)–S(3) 120.2(4), C(2)–S(1)–W 107.7(2), C(4)–W–S(1) 80.6(2).

carbonyl complexes.<sup>3</sup> In contrast, group 6 alkylidyne complexes have been shown to react with CS<sub>2</sub> to provide thiolatoalkyne,<sup>11</sup> thioketenyl,<sup>11–13</sup> or thioketene complexes via putative thioketenyl intermediates.<sup>15</sup>

Herein, we report the reactions of a range of alkylidyne complexes of tungsten and molybdenum with thionyl chloride. Our original target was the preparation of metallasulfines via three-fragment oxidative addition across the metal–carbon triple bond. Metallasulfines have been described previously, but only for late transition metals.<sup>16</sup> Instead, we find that either oxidation of the metal center occurs or in one case an unusual metalacyclic alkylidene complex of high-valent tungsten [formally W(IV)]<sup>17</sup> is obtained, which is however consistent with the intermediacy of a metallasulfine.

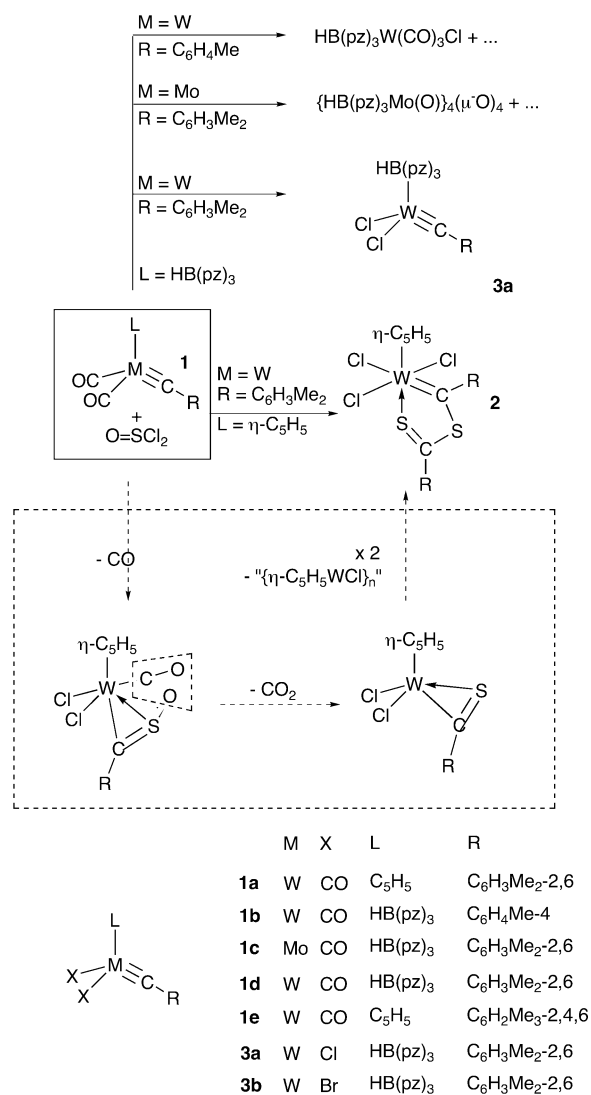
## Results and Discussion

The complex [W(≡CR)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (R = C<sub>6</sub>H<sub>3</sub>Me<sub>2-2,6</sub>) (**1a**)<sup>18</sup> reacts with thionyl chloride (diethyl ether, high dilution) to provide a purple complex [W(=CRS)Cl<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (**2**). The isotopic cluster of highest *m/z* in the FAB-MS spectrum is consistent with the composition "W(CR)<sub>2</sub>S<sub>3</sub>Cl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)" (subsequently assigned to [M – Cl]<sup>+</sup>), while elemental microanalytical data suggest "W(CR)<sub>2</sub>S<sub>3</sub>Cl<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>)". The presence of two xylyl groups within the one mononuclear complex was surprising but is confirmed by integrated NMR data for these substituents (Experimental Section). The absence of carbonyl ligands was indicated by the lack of characteristic ν(CO) infrared absorptions; however two low-field resonances (δ = 281.0 and 210.3) are apparent in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum in addition to two CH<sub>3</sub> resonances (δ 20.6, 20.4). These data failed to unambiguously identify the product, and accordingly the formulation was confirmed by a crystallographic study. The molecular geometry of **2** is depicted in Figure 1 and discussed below, establishing the complex as a metal-

(17) For the purposes of (arbitrary) oxidation state assignments, we ascribe a neutral charge to alkylidene ligands and a monopositive charge to alkylidyne. The alternative formalism ([=CR<sub>2</sub>]<sup>2-</sup>, [≡CR]<sup>3-</sup>) provides oxidation states two units higher than the assignments used here. Both formalisms have merit and advocates.

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## Scheme 1



acyclic dithiocarboxylatoalkylidene complex of tungsten(IV).<sup>17</sup> On the basis of the solid state structure, the low-field resonances are assigned to the alkylidene (δ 281.0) and dithiocarboxylate (δ 210.3) carbon nuclei, while the appearance of two methyl resonances indicates rapid rotation of the distinct xylyl groups.

The mechanism of formation of complex **2** remains obscure. In the absence of any isolable intermediates, we tentatively suggest the mechanism shown in Scheme 1. Thus three-fragment oxidative addition of thionyl chloride across the W≡C multiple bond could provide a metallasulfine which undergoes reduction, possibly by coordinated CO, to provide a thioacyl complex of tungsten(IV). As noted above, metallasulfines have precedent for later transition metals.<sup>16</sup> The reduction of co-ligands by coordinated CO also has considerable precedent, e.g., in the conversion of carbonyl-nitro complexes to CO<sub>2</sub> and coordinated NO.<sup>19</sup> Curiously, **2** is not observed when **1a** was treated with either SCl<sub>2</sub> or S<sub>2</sub>Cl<sub>2</sub>. The ultimate location of two xylyl groups on one metal requires a bimolecular head-to-tail thioacyl dimerization step. We have previously prepared binuclear complexes in which the metal–metal bond is supported by one thioacyl or selenoacyl ligand.<sup>4b,20</sup> The ultimate fate of the extruded

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"WCl( $\eta$ -C<sub>5</sub>H<sub>5</sub>)" group remains obscure, as the purple color of the product is evident prior to chromatographic purification. Clearly, alternative mechanisms can be proposed; however in the absence of further facts, that shown in Scheme 1 is at least plausible. The complex is however noteworthy in that high-valent alkylidene complexes typically have non-heteroatom carbene substituents and are, in most cases, coordinatively unsaturated or ligated by strong  $\pi$ -donor co-ligands, e.g., oxo, alkoxide, and/or imido ligands. Thus **2** provides a rare example<sup>21</sup> of a structurally characterized example of a coordinatively saturated high-valent carbene complex of tungsten, bearing a  $\pi$ -donative carbene substituent (a high-valent Fischer-type carbene).

The synthesis of **2** proved disappointingly unique. Attempts to prepare derivatives based on molybdenum or alkylidyne substituents with more modest steric profiles (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>Me-4) have so far met with failure. It was hoped that introducing more steric encumbrance at the metal center might allow the isolation of intermediates in the process, by disfavoring bimolecular steps. Toward this end the cyclopentadienyl ligand was replaced with the more bulky hydrotris(pyrazolyl)borate ligand.<sup>22</sup> The reaction of [W( $\equiv$ CC<sub>6</sub>H<sub>4</sub>Me-4)(CO)<sub>2</sub>{HB(pz)<sub>3</sub>}] (**1b**) (pz = pyrazol-1-yl) with thionyl chloride provided a mixture of compounds from which only unreacted starting material and the complex [WCl(CO)<sub>3</sub>{HB(pz)<sub>3</sub>}]<sup>23</sup> could be identified. Similarly the products of the reaction of [Mo( $\equiv$ CC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(CO)<sub>2</sub>{HB(pz)<sub>3</sub>}] (**1c**)<sup>18</sup> with thionyl chloride have so far eluded identification, other than the observation of traces of the complex [MoO{HB(pz)<sub>3</sub>}]<sub>4</sub>( $\mu$ -O)<sub>4</sub>. This tetramer has been previously obtained, among other products, from the reaction of [Et<sub>4</sub>N][Mo(CO)<sub>3</sub>{HB(pz)<sub>3</sub>}] with dimethyldioxirane.<sup>24</sup> The reaction of the tungsten analogue [W( $\equiv$ CC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(CO)<sub>2</sub>{HB(pz)<sub>3</sub>}] (**1d**) with thionyl chloride under strictly anhydrous conditions however provided a blue complex, [W( $\equiv$ CC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)Cl<sub>2</sub>{HB(pz)<sub>3</sub>}] (**3a**). The infrared spectrum is devoid of absorptions due to carbonyl ligands. The FAB-mass spectrum contains a molecular ion as base peak and fragmentations consistent with the formulation. Additionally, a second manifold of peaks is observed due to the molecular ion and fragmentations of the complex [W( $\equiv$ CHC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)Cl(=O){HB(pz)<sub>3</sub>}], which results from hydrolysis by the moist 3-nitrobenzyl alcohol matrix (vide infra). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum is most diagnostic: While lacking any resonances due to carbonyl ligands, a peak is observed at  $\delta$  326.6 attributable to the alkylidyne carbon, having been shifted some 50 ppm to lower field of that for the precursor. The formulation was confirmed by a crystallographic study, discussed below

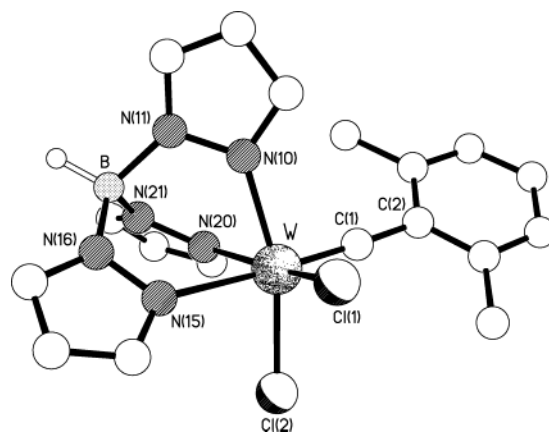
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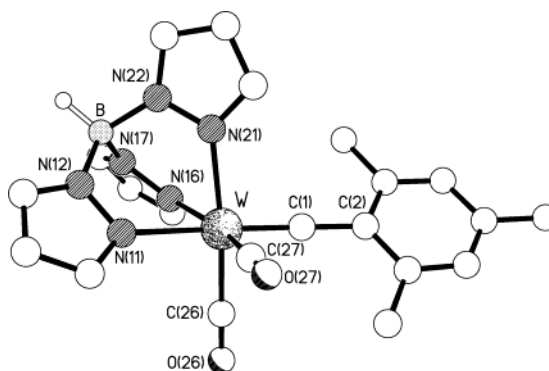
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**Figure 2.** Molecular structure of **3a**. Selected bond lengths (Å) and angles (deg): W–C(1) 1.800(11), C(1)–C(2) 1.44(2), W–Cl(1) 2.352(3), W–Cl(2) 2.336(3), W–N(10) 2.138(10), W–N(15) 2.359(11), W–N(20) 2.166(10), W–C(1)–C(2) 176.7(11), C(1)–W–Cl(1) 97.2(4), C(1)–W–Cl(2) 97.1(4), C(1)–W–N(20) 96.3(5), C(1)–W–N(10) 95.5(5).



**Figure 3.** Molecular structure of **1e**. Selected bond lengths (Å) and angles (deg): W–C(1) 1.826(5), C(1)–C(2) 1.449(7), W–C(26) 1.989(6), W–C(27) 1.978(5), W–N(11) 2.298(4), W–N(16) 2.214(4), W–N(21) 2.212(4), W–C(1)–C(2) 173.9(4), C(1)–W–C(26) 86.7(2), C(1)–W–C(27) 85.9(2), C(1)–W–N(16) 109.2(2), C(1)–W–N(21) 97.6(2).

(Figure 2). For comparative purposes the formally zerovalent alkylidyne complex [W( $\equiv$ CC<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)-(CO)<sub>2</sub>{HB(pz)<sub>3</sub>}] (**1e**) was also structurally characterized, as attempts to obtain crystallographic grade crystals of [W( $\equiv$ CC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(CO)<sub>2</sub>{HB(pz)<sub>3</sub>}] (**1c**) met with failure. The results of this study are discussed below (Figure 3). The complex **1e** was obtained in a manner similar to **1d**<sup>18</sup> (see Experimental Section).

The general class of alkylidyne complex [W( $\equiv$ CR)X<sub>2</sub>(L)] [X = anionic ligand, L = HB(pz)<sub>3</sub>, HB(pzMe<sub>2</sub>)<sub>2</sub>; pzMe<sub>2</sub> = 3,5-dimethylpyrazol-1-yl] has attracted attention<sup>25–29</sup> following Angelici's report of the first example [W( $\equiv$ CSMe)(SMe)<sub>2</sub>{HB(pz)<sub>3</sub>}].<sup>25</sup> This complex results from the thermally induced double  $\alpha$ -tungsten-thiolate elimination reaction of the complex [W( $\eta^2$ -MeSC(SMe)<sub>2</sub>)(CO)<sub>2</sub>{HB(pz)<sub>3</sub>}]. The dibromo complexes may be prepared by either bromination of dicarbonyl precursors<sup>26,27</sup>

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or alternatively reaction of  $[W(\equiv CPh)Br_3(dme)]$  with  $K[HB(pzMe_2)_3]$ .<sup>28</sup> Similar treatment of  $[W(\equiv CMe_3)Cl_2(dme)]$  provides  $[W(\equiv CMe_3)Cl_2\{HB(pzMe_2)_3\}]$ , hydrolysis of which affords the moisture stable alkene metathesis mediator  $[W(=CHCMe_3)(=O)Cl\{HB(pzMe_2)_3\}]$ .<sup>29</sup>

The yields of **3a** obtained from **1b** and thionyl chloride were modest unless the reaction was carried out under high dilution, and the product obtained also required chromatographic purification (silica gel,  $-40^\circ C$ ). An alternative approach was therefore developed. Chlorine adds across the  $Os\equiv C$  triple bond of  $[Os(\equiv CC_6H_4Me_4)Cl(CO)(PPh_3)_2]$ ,<sup>2</sup> while iodine adds to the metal center of  $[Ru(\equiv CPh)Cl(CO)(PPh_3)_2]$ ,<sup>1e,14a,30</sup> and accordingly we sought a "nonelectrophilic" chlorinating agent. The metal-based oxidation of carbyne complexes with retention of the metal-carbon triple bond was first demonstrated by Roper with the conversion of  $[Os(\equiv CR)Cl(CO)(PPh_3)_2]$  ( $R = C_6H_4NMe_2-4$ ) to  $[Os(\equiv CR)Cl(CO)(OH)_2(PPh_3)_2]^+$  via sequential treatment with oxygen and aqueous HCl.<sup>30</sup> Subsequently, Mayr showed that bromination of  $[W(\equiv CPh)Br(CO)_4]$  (generated in situ) in dme provided  $[W(\equiv CPh)Br_3(dme)]$  (dme = 1,2-dimethoxyethane).<sup>31</sup> These metal-based oxidation reactions were landmark discoveries in carbyne chemistry: the former in demonstrating the oxidation state dependence of the  $M\equiv C$  bond reactivity, the latter in interconverting classical Fischer and Schrock-type carbynes. In the interim, further examples of redox processes that leave the  $M\equiv C$  bond intact have followed.<sup>26,27</sup>

In recent times arylidonium dichlorides have been employed in organometallic chemistry as mild chlorinating agents; however we chose an alternative approach, which we suspect may prove more useful in a wider context. Ferrocenium salts are widely employed as one-electron oxidants; however, these are usually in the form of salts of innocent noncoordinating anions, e.g.,  $BF_4$ ,  $BPh_4$ , and  $PF_6$ . If however the anion is a potential nucleophile, then 2 equiv should lead *ultimately* to oxidative addition, wherein the incoming ligand at no time assumes electrophilic character. The complex **1a** reacts smoothly with 2 equiv of  $[Fe(\eta-C_5H_5)_2]Cl$  to provide  $[W(\equiv CC_6H_3Me_2-2,6)Cl_2\{HB(pz)_3\}]$  (**3a**), carbon monoxide, and (hexane-soluble) ferrocene as the only organometallic side product. The yields for this oxidation are consistently high and the crude product is formed in high purity, without recourse to cryostatic chromatography (**3a** is hydrolyzed by silica gel at room temperature). The complex  $[W(\equiv CC_6H_3Me_2-2,6)Br_2\{HB(pz)_3\}]$  (**3b**) was also obtained; however, in this case elemental bromine was employed, following Mayr's procedure for  $[W(\equiv CPh)Br_2\{HB(pz)_3\}]$ .<sup>26</sup>

**Molecular Structure of  $[W(=CRSCRS)Cl_3(\eta-C_5H_5)]$  (**2**)** (Figure 1). Considering the cyclopentadienyl ligand to occupy one coordination site, the geometry at tungsten can loosely be described as distorted octahedral, in that the angles between the remaining ligands lie in the range  $70.6-92.4^\circ$  including the bite of the metallacycle [ $S(1)-W-C(4)$   $80.6(2)^\circ$ ] despite the geometric constraints of chelation. The chloride and cyclopentadienyl ligands are unremarkable, other than to note that (i) the W is displaced from the plane defined by the

chlorides and carbene carbon by  $0.58 \text{ \AA}$  toward the cyclopentadienyl ligand and (ii) the tungsten-chlorine bond *trans* to the alkylidene carbon is somewhat longer [ $W-Cl(28)$   $2.479(2) \text{ \AA}$ ] relative to those of the "*trans*- $WCl_2$ " unit [ $2.429(2)$ ,  $2.453(2) \text{ \AA}$ ]. The feature of interest is the metallacyclic carbene motif, which adopts a shallow envelope, the tungsten atom lying  $0.14 \text{ \AA}$  out of the  $\{S(1),C(2),S(3),C(4)\}$  plane whose atoms are coplanar to better than  $0.01 \text{ \AA}$ . The xylyl substituents are however not in conjugation with the metallacycle, the torsional twists about the  $C(2)-C(5)$  and  $C(4)-C(13)$  bonds being ca.  $84^\circ$  and  $87^\circ$ , respectively. These essentially orthogonal orientations are probably a consequence of the steric profile of these groups rather than any electronic factors. The bond lengths within the metallacycle are consistent with its description as a dithiocarboxylate carbene chelated by a dative  $S(1)-W$  interaction [ $2.520(2) \text{ \AA}$ ]. To the best of our knowledge no previous example of such a metallacycle has been structurally characterized, and high-valent metal complexes of alkylidene ligands bearing  $\pi$ -dative substituents remain rare.<sup>32</sup> The  $W-C(4)$  separation at  $2.043(6) \text{ \AA}$  clearly reflects multiple bonding, but is significantly longer than for the alkylidene ligand in Schrock's benchmark complex  $[W(\equiv CBu^t)(=CHBu^t)(CH_2Bu^t)(dmpe)]$  [ $W=C$   $1.942(9) \text{ \AA}$ ].<sup>33,34</sup> The presence of  $\pi$ -dative carbene substituents is generally held to compromise metal-carbon  $d\pi-p\pi$  overlap, and this might be expected to be encouraged by electrophilic metal centers. The  $\pi$ -basicity of  $S(3)$  is however compromised by interaction with the dithiocarboxyl carbon  $C(2)$ , as indicated by the  $S(3)-C(2)$  bond length of  $1.701(6) \text{ \AA}$ , being noticeably shorter than that for  $S(3)-C(4)$  [ $1.740(6) \text{ \AA}$ ]. There are no intermolecular contacts of note.

**Molecular Structure of  $[W(\equiv CC_6H_2Me_3-2,4,6)(CO)_2\{HB(pz)_3\}]$  (**1e**)** (Figure 3). For the six-coordinate tungsten center, the primary deviation from ideal octahedral geometry arises from the geometrical constraints of scorpionate chelation by the  $HB(pz)_3$  ligand. Thus the angles between pyrazolyl nitrogen donors are each contracted from  $90^\circ$ , lying in the range  $80.4(1)-81.2(1)^\circ$  [angle sum =  $242.6^\circ$ ]. The tungsten carbonyl separations are unremarkable [ $1.989(6)$ ,  $1.978(6) \text{ \AA}$ ], although the angle they each make with the alkylidyne ligand is acute [ $86.7(2)^\circ$ ,  $85.9(2)^\circ$ ]. In contrast, the angles between the alkylidyne ligand and the two *cis*-coordinated pyrazolyls are obtuse [ $109.2(2)^\circ$ ,  $97.6(2)^\circ$ ]. Thus the alkylidyne ligand, while close to linear [ $W-C(1)-C(2)$   $173.9(4)^\circ$ ], is skewed away from the pocket formed by the two pyrazolyls, toward that between the carbonyls. The alkylidyne-tungsten separation of  $1.826(5) \text{ \AA}$  is typical of  $W\equiv C$  triple bonds,<sup>1</sup> and this multiple bonding is manifest in an appreciable *trans* influence, causing a lengthening in  $W-N(11)$  [ $2.298(4) \text{ \AA}$ ] relative to the two remaining pyrazolyl groups [ $2.214(4)$ ,  $2.212-$

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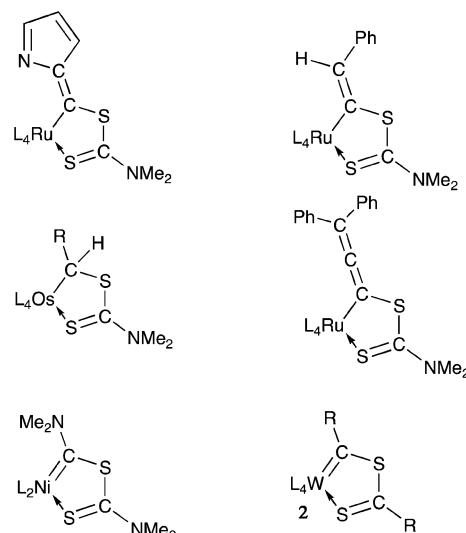
(4) Å, respectively]. The orientation of the carbyne substituent, such that it fits between the two carbonyl ligands and between the two pyrazolyls, serves to minimize steric interactions between the co-ligands and the sterically cumbersome 2-xylyl substituent. The N(11)- and N(21)-containing pyrazole rings enter into  $\pi$ -stacking interactions with their centrosymmetrically related counterparts to form continuous chains of molecules. The centroid...centroid and mean interplanar separations are 3.66, 3.50 Å and 3.49, 3.40 Å for the two ring systems, respectively. These stacking interactions are supplemented by additional C–H... $\pi$  interactions involving both the pyrazole rings and the 2,4,6-trimethylphenyl ring.

**Molecular Structure of [W(≡CC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)Cl<sub>2</sub>{HB(pz)<sub>3</sub>}] (3a)** (Figure 2). As with the previous complex, the geometry at tungsten is distorted octahedral with *cis* inter-ligand angles in the range 78.5(3)–98.0(1)°. However in contrast, in **3a** each of the *cis* angles involving the carbyne carbon C(1) is obtuse such that the tungsten lies 0.26 Å above the plane defined by the four *cis*-donor atoms Cl(1), Cl(2), N(10), and N(20), which are coplanar to 0.01 Å. Furthermore, the Cl(1)–W–Cl(2) angle of 97.97(12)° reflects the steric bulk of chloride atoms relative to the remaining donors. As in the previous example, the alkylidyne exerts an appreciable *trans* influence, such that the W–N(15) separation [2.359(11) Å] is significantly longer than the W–N(10) and W–N(20) bond lengths of 2.138(10) and 2.166(10) Å, respectively. Thus  $\pi$ -donor ligands appear to contract *trans*-M–pz bonds. The alkylidyne ligand is essentially linear at C(1) [176.7(11)°] with W–C(1) at 1.800(11) Å, not differing significantly from that in the previous example, despite the change in the oxidation state of tungsten and substantial change in chemical shift for the alkylidyne carbon. The orientation of the xylyl substituent is analogous to that in **1e**, once again allowing a minimization of steric interactions between the ortho methyl groups and the co-ligands. This orientation would, however, appear to be a solid-state phenomenon since **1a**, **3a**, and **3b** all give rise to a single resonance for the ortho methyl protons in their <sup>1</sup>H NMR spectra; that is, carbyne rotation is rapid in solution. Thus oxidation of the metal center and replacement of  $\pi$ -acid carbonyls with  $\pi$ -donative chloride ligands have little effect on the geometrical features of the alkylidyne complex other than those attributable to steric effects. There is an intermolecular  $\pi$ -stacking interaction between the N(10)-containing pyrazole ring in one molecule and the N(20)-containing ring of another; the centroid...centroid and mean interplanar separations are 3.64 and 3.48 Å, respectively, the rings being inclined by ca. 4°. There is also a parallel and overlapping arrangement of centrosymmetrically related pairs of 2,6-dimethylphenyl rings, but the interplanar separation of 3.88 Å is too long for any significant  $\pi$ -stacking interaction.

### Concluding Remarks

We have previously characterized the first examples of a range of metallacycles derived from the coupling reactions of various "C<sub>1</sub>" multiply bonded ligands with dithiocarbamates including alkylidenes,<sup>35</sup> vinylidenes, and allenylidenes<sup>36</sup> (Chart 1). A related metallacycle has

**Chart 1. Dithiocarbamate- and Dichalcocarbonylate-Derived Metallacycles**



been reported to result from the coupling of two thio-carbamoyl groups on nickel,<sup>37</sup> and Roper has obtained an unusual metallacycle from the reaction of dithiocarbamate salts with a chloro(pyrolyl)carbene complex of ruthenium.<sup>38</sup> We have previously suggested that such metallacycles are important intermediates in Mayr's thiobenzaldehyde synthesis, by way of subsequent thermolytic C–S bond cleavage.<sup>35</sup> Although the present example is not derived from a dithiocarbamate, it does provide a further example of such a metallacycle derived in this case from alkylidyne and dithiocarbonylate units, thereby extending the series (Chart 1).

### Experimental Section

The compounds [W(≡CC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(CO)<sub>2</sub>(L)] (L = C<sub>5</sub>H<sub>5</sub>, HB(pz)<sub>3</sub>)<sup>18</sup> and [W(≡CC<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)Br(CO)<sub>2</sub>( $\gamma$ -pic)<sub>2</sub>]<sup>39</sup> have been described previously. All manipulations were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube and vacuum line techniques. Solvents were purified by distillation from an appropriate drying agent and degassed prior to use. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a JEOL JNM EX270 NMR spectrometer and calibrated against internal SiMe<sub>4</sub> (<sup>1</sup>H) or CDCl<sub>3</sub> (<sup>13</sup>C). Infrared spectra were recorded from dichloromethane solutions and Nujol mulls using a Perkin-Elmer 1725-X FT-IR spectrometer. FAB mass spectrometry was carried out using an Autospec Q mass spectrometer with 3-nitrobenzyl alcohol as matrix. Abundances are given for the major peak of isotopic envelopes confirmed by simulation. Elemental microanalytical data were obtained from the ICL microanalytical service.

**Preparation of [W(≡CC<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)(CO)<sub>2</sub>{HB(pz)<sub>3</sub>}] (1e).** [W(≡CC<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)Br(CO)<sub>2</sub>( $\gamma$ -pic)<sub>2</sub>]<sup>39</sup> (1.30 g, 2.00 mmol)

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was dissolved in dichloromethane (30 mL) and  $K[HB(pz)_3]^{22}$  (0.50 g, 2.00 mmol) added. The mixture was stirred for 20 h and then the resulting red solution concentrated under reduced pressure to ca. 10 mL. This mixture was then chromatographed on silica gel (20 × 300 mm, 25 °C) eluting with a 1:2 mixture of dichloromethane and light petroleum (60–80). The second and major red fraction was collected and freed of volatiles under reduced pressure. The resultant red oil was redissolved in the minimum amount of dichloromethane and layered with hexane. This solution was cooled to –10 °C, whereupon after inter-diffusion of the two solvents a red crystalline solid was obtained and dried in vacuo. Yield: 1.00 g (87%). IR  $CH_2Cl_2$ : 1975, 1888 [ $\nu(CO)$ ]  $cm^{-1}$ . Nujol: 2462 [ $\nu(BH)$ ], 1971, 1874 [ $\nu(CO)$ ]  $cm^{-1}$ . NMR ( $CDCl_3$ , 25 °C)  $^1H$ :  $\delta$  2.22 [s, 3 H,  $Me^4(C_6H_2Me_3)$ ], 2.48, [s, 6 H,  $Me^{2,6}(C_6H_3Me_3)$ ], 6.19 [t, 1 H,  $H^4(pz)$ ],  $^3J(HH) = 2.3$ ], 6.23 [t, 2 H,  $H^4(pz)$ ],  $^3J(HH) = 2.3$ ], 7.26 [s, 2 H,  $C_6H_2$ ], 7.65 (1 H), 7.69 (2 H), 7.72 (1 H), 8.04 (2 H) [d × 4, 6 H,  $H^{3,5}(pz)$ ],  $^3J(HH) = 2.3$  Hz].  $^{13}C$ -{ $^1H$ }:  $\delta$  288.5 [W≡C],  $^1J(WC) = 193$ ], 226.3 [WCO],  $^1J(WC) = 165$  Hz], 145.1 [ $C^{3,5}(C_6H_3)$ ], 143.7 [ $C^{2,6}(C_6H_3)$ ], 140.6, 137.8 [ $C^{1,4}(C_6H_3)$ ], 135.3 (3 C), 128.0 (3 C) [ $C^{3,5}(pz)$ ], 105.8 (2C), 105.6 (1C) [ $C^4(pz)$ ], 21.5 [ $Me^{2,6}(C_6H_2Me_3)$ ], 20.5 [ $Me^4(C_6H_2Me_3)$ ] ppm. FAB-MS:  $m/z$  (%) 584 (16) [ $M$ ] $^+$ , 556 (30) [ $M - CO$ ] $^+$ , 528 (15) [ $M - 2CO$ ] $^+$ . Anal. Found: C, 43.0; H, 3.6; N, 13.9. Calcd for  $C_{21}H_{21}BN_6O_2W$ : C, 43.2; H, 3.6; N, 14.4. *Crystal data for 1e*:  $C_{21}H_{21}N_6O_2BW$ ,  $M = 584.1$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 8.543(2)$  Å,  $b = 11.608(3)$  Å,  $c = 11.779(2)$  Å,  $\alpha = 76.26(2)^\circ$ ,  $\beta = 83.80(2)^\circ$ ,  $\gamma = 83.00(2)^\circ$ ,  $V = 1122.5(4)$  Å $^3$ ,  $Z = 2$ ,  $D_c = 1.728$  g  $cm^{-3}$ ,  $\mu(Mo K\alpha) = 5.18$  mm $^{-1}$ ,  $T = 293$  K, yellow-brown blocks; 3920 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.028$ ,  $wR_2 = 0.066$ , 3437 independent observed absorption corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ,  $2\theta_{max} = 50^\circ$ ], 280 parameters. CCDC 226000.

**Preparation of  $[W(=CRSCRS)Cl_3(\eta-C_5H_5)]$  (**2**;  $R = C_6H_3Me_2-2,6$ ).** A solution of  $[W(=CC_6H_3Me_2-2,6)(CO)_2(\eta-C_5H_5)]$  (1.00 g, 2.4 mmol) in diethyl ether (300 mL) was treated with a dilute solution of thionyl chloride (100 mL, 0.025 mol  $dm^{-3}$ , 2.5 mmol) over a period of 2 h. The resulting dark solution was freed of solvent under reduced pressure and the residue chromatographed on silica gel (20 × 300 mm, –40 °C). Initial elution with dichloromethane provided unreacted starting material. Subsequent elution with a 10:1 mixture of dichloromethane and tetrahydrofuran provided the violet product, which was crystallized from a mixture of dichloromethane and hexane at –20 °C. Yield: 0.60 g (78%, based on "R"). NMR ( $CDCl_3$ , 25 °C)  $^1H$ :  $\delta$  2.40, 2.51 [2 × s, 6 H × 2,  $CH_3$ ], 6.08 [s, 5 H,  $C_5H_5$ ], 7.09–7.26 [ $C_6H_3$ ] ppm.  $^{13}C$ { $^1H$ }:  $\delta$  281.0 [W=C], 210.3 [ $S_2C$ ], 149.4, 135.8, 135.3, 131.7, 130.1, 128.8, 127.7 [ $C_6H_3$ ], 113.9 [ $C_5H_5$ ], 20.6, 20.4 [ $CH_3$ ]. FAB-MS:  $m/z$  (%) 614 (3) [ $M - Cl$ ] $^+$ , 582 (6) [ $M - 2Cl$ ] $^+$ , 465 (3) [ $M - 2Cl - RCS_2$ ] $^+$ , 316 (45) [ $WScI(C_5H_5)$ ] $^+$ , 149 (100) [ $RCS$ ] $^+$ . Anal. Found: C, 41.9; H, 4.1. Calcd for  $C_{23}H_{23}Cl_3S_2W$ : C, 42.3; H, 3.9. *Crystal data for 2*:  $C_{23}H_{23}S_2Cl_3W$ ,  $M = 653.7$ , monoclinic,  $C2/c$  (no. 15),  $a = 18.858(6)$  Å,  $b = 8.336(2)$  Å,  $c = 30.285(6)$  Å,  $\beta = 92.30(3)^\circ$ ,  $V = 4757(2)$  Å $^3$ ,  $Z = 8$ ,  $D_c = 1.826$  g  $cm^{-3}$ ,  $\mu(Mo K\alpha) = 5.38$  mm $^{-1}$ ,  $T = 293$  K, burgundy prisms; 4186 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.032$ ,  $wR_2 = 0.075$ , 3377 independent observed absorption corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ,  $2\theta_{max} = 50^\circ$ ], 254 parameters. CCDC 226001.

**Preparation of  $[W(=CC_6H_3Me_2-2,6)Cl_2\{HB(pz)_3\}]$  (**3a**).** (a)  $[W(=CC_6H_3Me_2-2,6)(CO)_2\{HB(pz)_3\}]$  (**1d**, 0.50 g, 0.84 mmol) was dissolved in dichloromethane (30 mL) and cooled (dry ice/propanone). Ferrocenium chloride (0.36 g, 1.60 mmol) was added and the solution allowed to warm gradually to room temperature with stirring. The resulting blue solution was reduced to ca. 10 mL and chromatographed on silica gel (20 × 300 mm, –40 °C, NB: hydrolysis occurs at room temperature)

eluting with a mixture (1:1) of dichloromethane and light petroleum (60–80). The resulting blue eluate was reduced in vacuo to dryness. The residue was dissolved in the minimum volume of dichloromethane and layered with light petroleum. This solution was cooled to –10 °C, whereupon blue crystals were obtained, which were isolated and dried in vacuo. Yield: 0.40 g (90%). The procedure has on one occasion been scaled up to 10 mmol with the product being purified by recrystallization ( $CH_2Cl_2$ , hexane, –20 °C) rather than chromatography and an attendant reduction in yield to 72%. (b) A solution of  $[W(=CC_6H_3Me_2-2,6)(CO)_2\{HB(pz)_3\}]$  (1.24 g, 2.18 mmol) in diethyl ether (60 mL) was treated with a solution of thionyl chloride in dichloromethane (9.8 mL, 0.27 mol  $dm^{-3}$ , 2.6 mmol) that was added dropwise over a period of 80 min. The mixture was then stirred for a further 2 h. The solvent was removed in vacuo and the product isolated by cryostatic column chromatography as described in (a) above. Yield: 0.47 g (37%). NMR ( $CDCl_3$ , 25 °C)  $^1H$ :  $\delta$  3.05 [s, 6 H,  $CH_3$ ], 6.27 [m, 3 H,  $H^4(pz)$ ], 7.20–7.24 [m, 3 H,  $C_6H_3$ ], 7.66, 7.80 [d × 2, 3 H,  $H^5(pz)$ ],  $^3J(HH) = 2.3$  Hz], 7.94, 8.25 [d × 2, 3 H,  $H^3(pz)$ ],  $^3J(HH) = 2.3$  Hz].  $^{13}C$ { $^1H$ }:  $\delta$  326.5 [W≡C], 147.7, 147.4 [ $C^5(pz)$ ], 143.1 [ $C^3(pz)$ ], 137.3 [ $C^1(C_6H_3)$ ], 136.1 [ $C^3(pz)$ ], 134.2 [ $C^4(C_6H_3)$ ], 130.9 [ $C^{2,6}(C_6H_3)$ ], 124.4 [ $C^{3,5}(C_6H_3)$ ], 107.4, 106.2 [ $C^4(pz)$ ], 18.7 [ $CH_3$ ]. FAB-MS:  $m/z$  (%) 594 (100) [ $M$ ] $^+$ , 641 (28) [ $M - Cl + H_2O$ ] $^+$ , 614 (40) [ $M - Cl$ ] $^+$ , 588 (20) [ $M - 2Cl$ ] $^+$ . Anal. Found: C, 35.8; H, 3.5; N, 12.9. Calcd for  $C_{18}H_{19}BCl_2N_6W \cdot 0.5CH_2Cl_2$ : C, 35.4; H, 3.2; N, 13.4. Dichloromethane of solvation confirmed by  $^1H$  NMR integration and X-ray crystallography. *Crystal data for 3a*:  $C_{18}H_{19}N_6BCl_2W \cdot 0.5CH_2Cl_2$ ,  $M = 627.4$ , monoclinic,  $P2_1/c$  (no. 14),  $a = 8.704(4)$  Å,  $b = 13.587(4)$  Å,  $c = 20.393(7)$  Å,  $\beta = 98.00(3)^\circ$ ,  $V = 2388(2)$  Å $^3$ ,  $Z = 4$ ,  $D_c = 1.745$  g  $cm^{-3}$ ,  $\mu(Mo K\alpha) = 5.19$  mm $^{-1}$ ,  $T = 293$  K, blue-green dichroic plates; 4197 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.053$ ,  $wR_2 = 0.104$ , 2700 independent observed absorption corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ,  $2\theta_{max} = 50^\circ$ ], 289 parameters. CCDC 226002.

**Preparation of  $[W(=CC_6H_3Me_2-2,6)Br_2\{HB(pz)_3\}]$  (**3b**).** (a)  $[W(=CC_6H_3Me_2-2,6)(CO)_2\{HB(pz)_3\}]$  (**1d**, 0.50 g, 0.84 mmol) was dissolved in dichloromethane (30 mL) and cooled (dry ice/propanone). A solution of bromine in dichloromethane was then added dropwise (9.0 mL, 0.10 mol  $dm^{-3}$ ) and the mixture stirred for 15 min before being allowed to warm slowly to room temperature. The solvent was removed in vacuo and the green residue washed with hexane (2 × 10 mL) and then recrystallized from a mixture of dichloromethane and hexane at –20 °C. Yield: 0.51 g (87%). NMR ( $CDCl_3$ , 25 °C)  $^1H$ :  $\delta$  3.14 [s, 6 H,  $CH_3$ ], 6.34 m 7.27 [m × 2, 6 H,  $H^4(C_6H_3)$  and  $H^4(pz)$ ], 7.70, 7.81 [d × 2, 3 H,  $H^5(pz)$ ],  $J(HH) = 2.3$  Hz], 8.14, 8.22 [d × 2, 3 H,  $H^3(pz)$ ],  $J(HH) = 2.3$  Hz].  $^{13}C$ { $^1H$ }:  $\delta$  335.5 [W≡C], 148.2, 148.1 [ $C^5(pz)$ ], 144.5 [ $C^3(pz)$ ], 136.6 [ $C^1(C_6H_3)$ ], 135.6 [ $C^3(pz)$ ], 134.4 [ $C^4(C_6H_3)$ ], 131.2 [ $C^{2,6}(C_6H_3)$ ], 124.2 [ $C^4(pz)$ ], 107.4, 106.3 [ $C^5(pz)$ ], 18.7 [ $CH_3$ ] ppm. FAB-MS:  $m/z$  (%) 674 (46) [ $M$ ] $^+$ , 610 (57) [ $M - Br + H_2O$ ] $^+$ , 595 (18) [ $M - Br$ ] $^+$ , 492 (33) [ $M + H_2O - RCH_3 - Br$ ] $^+$ . Anal. Found: C, 32.0; H, 3.0; N, 12.1. Calcd for  $C_{18}H_{19}BBR_2N_6W$ : C, 32.1; H, 2.8; N, 12.5.

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**Supporting Information Available:** Details of the crystal structure determinations and ORTEP representations of compounds **1e**, **2**, and **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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