

# Unexpected Reactivity of $\text{CH}(3,5\text{-Me}_2\text{Pz})_2(\text{CO})_3\text{WSnAr}_3$ ( $\text{Pz}$ = pyrazol-1-yl; $\text{Ar}$ = phenyl or $p$ -tolyl) toward Hydrogen Halide

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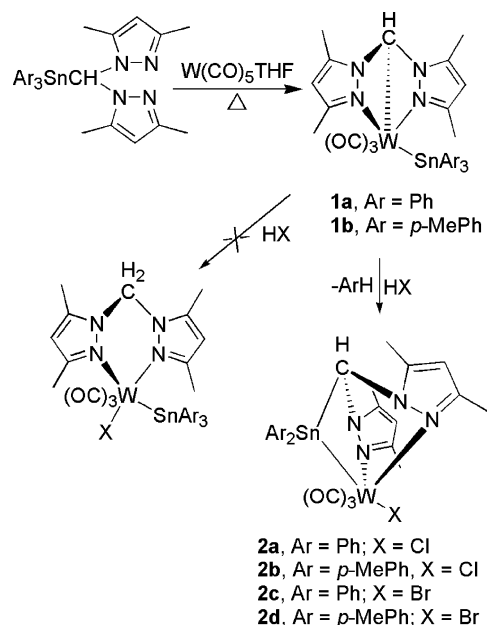
Reaction of  $\text{CH}(3,5\text{-Me}_2\text{Pz})_2(\text{CO})_3\text{WSnAr}_3$  ( $\text{Pz}$  = pyrazol-1-yl;  $\text{Ar}$  = phenyl or  $p$ -tolyl) with hydrogen halide results in the formation of one  $\text{Sn}-\text{C}_{\text{sp}^3}$  bond with the cleavage of one  $\text{Sn}-\text{C}_{\text{Ar}}$  bond as well as the  $\text{W}-\text{C}_{\text{sp}^3}$  bond to give novel heterodinuclear complexes  $\text{Ar}_2\text{SnCH}(3,5\text{-Me}_2\text{Pz})_2(\text{CO})_3\text{WX}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), in which an intriguing  $\kappa^3\text{-[N,Sn,N]}$  coordination mode as well as an unsymmetrically semibridging carbonyl between the  $\text{W}-\text{Sn}$  bond is observed.

## Introduction

Poly(pyrazol-1-yl)alkane, especially bis(pyrazol-1-yl)-methane, has drawn extensive attention and inspired a great deal of studies as one of the most popular polydentate nitrogen donor ligands since Trofimenko's first<sup>1</sup> report and especially Julia's later modification.<sup>2</sup> Recent investigations have shown that the bridging carbon atom can also be modified with organic functional groups to expand this promising category of ligands to novel heteroscorpionate ligands.<sup>3</sup> Our recent investigations on bis(pyrazol-1-yl)methanes have demonstrated that the modification of these ligands with organometallic groups on the bridging carbon atom may provide unusual reactivity.<sup>4</sup> For example, treatment of triarylstannylbis(pyrazol-1-yl)methane with  $\text{W}(\text{CO})_5\text{THF}$  leads to the oxidative addition of the  $\text{Sn}-\text{C}_{\text{sp}^3}$  bond to the tungsten(0) atom, yielding heterodinuclear complexes  $\text{CH}(3,5\text{-Me}_2\text{Pz})_2(\text{CO})_3\text{WSnAr}_3$  ( $\text{Pz}$  = pyrazol-1-yl;  $\text{Ar}$  = phenyl or  $p$ -tolyl) (Scheme 1).<sup>4a</sup>

Complexes **1a** and **1b** have structural characteristics similar to other heterodinuclear complexes containing  $\text{Sn}-\text{M}$  bonds,<sup>5</sup> such as cyclopentadienyl derivatives  $\text{CpW}(\text{CO})_3\text{SnAr}_3$ . Comparable  $\text{W}-\text{Sn}$  and  $\text{Sn}-\text{C}_{\text{Ar}}$  bond distances are also observed in both compounds, with bis-(pyrazol-1-yl)methide and cyclopentadienyl groups acting as a tridentate monoanionic ligands.<sup>6</sup> These structural features inspired us to further investigate whether

## Scheme 1. Formation and Reaction with Hydrogen Halide of **1a** and **1b**



the  $\text{Sn}-\text{C}_{\text{Ar}}$  and  $\text{W}-\text{Sn}$  bonds in these compounds have similar reactivities toward electrophilic reagents. It is generally accepted that the tin-transition-metal bond or the tin-aryl bond in tin-transition-metal bonded compounds can be cleaved, and the preference of one type of bond over the other depends on the different reaction conditions and electrophilic reagents.<sup>7</sup> Furthermore, the  $\text{W}-\text{C}_{\text{sp}^3}$  bond in the small four-membered metallacycles of **1a** and **1b** should have unusual reactivity owing to the ring strain and the high polarity of the metal-carbon bond. These make us believe that reactions involving cleavage of the tin-transition-metal bond or the tin-phenyl bond coupled with  $\text{W}-\text{C}_{\text{sp}^3}$  bond

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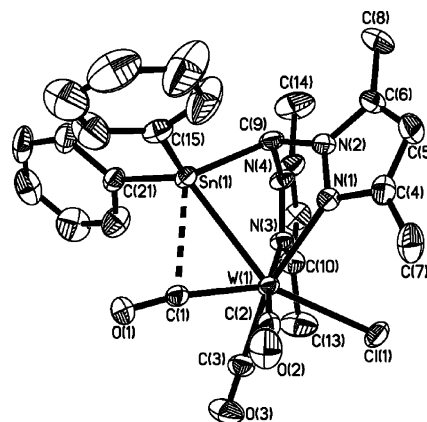
breaking could take place in this category of compounds. In this paper we report the reaction of  $\text{CH}(\text{3,5-Me}_2\text{Pz})_2(\text{CO})_3\text{WSnAr}_3$  with  $\text{HX}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) leading to the formation of the  $\text{Sn}-\text{C}_{\text{sp}^3}$  bond involving the cleavage of one  $\text{Sn}-\text{C}_{\text{Ar}}$  bond coupled with the  $\text{W}-\text{C}_{\text{sp}^3}$  bond breaking as a supportive example of our idea.

## Results and Discussion

**Reaction of  $\text{CH}(\text{3,5-Me}_2\text{Pz})_2(\text{CO})_3\text{WSnAr}_3$  toward Hydrogen Halide.** It is well-known that the reaction of  $\text{CpW}(\text{CO})_3\text{SnAr}_3$  with gaseous  $\text{HCl}$  leads to the cleavage of all three  $\text{Sn}-\text{C}_{\text{Ar}}$  bonds to give  $\text{CpW}(\text{CO})_3\text{SnCl}_3$ .<sup>8</sup> Similarly, treatment of gaseous  $\text{HCl}$  on the phenyltin compounds also results in the substitution of the phenyl groups by chlorine atoms to afford organotin chloride.<sup>9</sup> However, it is surprisingly observed that the reaction of **1a** and **1b** with  $\text{HX}$  is remarkably different from these above-mentioned reactions. Instead of breaking all three  $\text{Sn}-\text{C}_{\text{Ar}}$  bonds, this reaction involves the cleavage of only one  $\text{Sn}-\text{C}_{\text{Ar}}$  bond. Furthermore, the bridging carbon atom is linked to the tin atom again with the  $\text{W}-\text{C}_{\text{sp}^3}$  bond broken to give novel heterodinuclear complexes **2a–2d**, which are characterized by  $^1\text{H}$  NMR spectroscopy, IR spectra, and elemental analyses, and the structure is confirmed by X-ray structural analyses of **2a**. It is also worthy of note that the polar  $\text{W}-\text{C}_{\text{sp}^3}$  bond exists in **1a** and **1b**, but the proton at first does not attack the nucleophilic carbon atom of this bond (see Scheme 1).

An intriguing characteristic of complexes **2a–2d** is the unusual stability. They are air-stable in the solid state, and even their solution can be manipulated in air without notable decomposition. Furthermore, these complexes are insensitive to water and can even survive the severe conditions in the reaction of **1a** and **1b** with concentrated hydrochloric acid and 48% hydrobromic acid. The proton signal of the CH group in **2a–2d** (6.25–6.37 ppm) is considerably shifted to lower field than that in **1a** and **1b** (4.32 ppm),<sup>4b</sup> due to less shielding by the relatively more electronegative tin atom. These values are very close to those in ligands  $\text{Ph}_3\text{SnCH}(\text{3,5-Me}_2\text{Pz})_2$  (6.72 ppm) and  $(p\text{-MePh})_3\text{SnCH}(\text{3,5-Me}_2\text{Pz})_2$  (6.64 ppm), consistent with the fact that the CH group is linked to the tin atom instead of the tungsten atom. Two strong  $\nu(\text{CO})$  bands in the range 1989–1885  $\text{cm}^{-1}$  and one significant low-frequency absorption band of  $\nu(\text{CO})$  at ca. 1780–1769  $\text{cm}^{-1}$  are observed in the IR spectra of **2a–2d**, indicating that the semibridging carbonyl probably exists, which is confirmed by the results of X-ray structural analyses of **2a**.

The crystal structure of **2a** presented in Figure 1 clearly shows that the tin atom is integrated with the bridging carbon of bis(pyrazol-1-yl)methide again, as in ligands  $\text{Ar}_3\text{SnCH}(\text{3,5-Me}_2\text{Pz})_2$ , the  $\text{Sn}-\text{W}$  distance is



**Figure 1.** Molecular structure of **2a**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg):  $\text{W}(1)-\text{C}(1)$  1.950(5),  $\text{W}(1)-\text{C}(2)$  1.970(5),  $\text{W}(1)-\text{C}(3)$  1.989(5),  $\text{W}(1)-\text{N}(1)$  2.263(4),  $\text{W}(1)-\text{N}(3)$  2.268(3),  $\text{W}(1)-\text{Cl}(1)$  2.525(1),  $\text{W}(1)-\text{Sn}(1)$  2.8547(9),  $\text{Sn}(1)-\text{C}(9)$  2.204(4),  $\text{Sn}(1)\cdots\text{C}(1)$  2.527(4),  $\text{C}(1)-\text{O}(1)$  1.177(5),  $\text{C}(2)-\text{O}(2)$  1.149(5),  $\text{C}(3)-\text{O}(3)$  1.144(5);  $\text{N}(1)-\text{W}(1)-\text{Sn}(1)$  72.35(9),  $\text{N}(3)-\text{W}(1)-\text{Sn}(1)$  75.12(8),  $\text{Cl}(1)-\text{W}(1)-\text{Sn}(1)$  150.16(3),  $\text{N}(1)-\text{W}(1)-\text{N}(3)$  82.5(1),  $\text{N}(4)-\text{C}(9)-\text{N}(2)$  110.9(3),  $\text{C}(1)-\text{W}(1)-\text{Cl}(1)$  149.8(1),  $\text{N}(4)-\text{C}(9)-\text{Sn}(1)$  107.1(3),  $\text{N}(2)-\text{C}(9)-\text{Sn}(1)$  106.4(3),  $\text{W}(1)-\text{C}(1)-\text{O}(1)$  170.9(4).

still in the bonding range, but the  $\text{W}-\text{C}_{\text{sp}^3}$  bond is broken. The molecular fundamental framework of **2a** is similar to that in  $(t\text{-Bu})_2\text{SnCH}(\text{3,5-Me}_2\text{Pz})_2\text{W}(\text{CO})_3(\text{Ph})$ .<sup>4b</sup> A compelling feature is that a novel  $\kappa^3\text{-[N,Sn,N]}$  coordination mode as well as an unsymmetrically semibridging carbonyl between the  $\text{W}-\text{Sn}$  bond is observed in both complexes. The chlorine atom is *trans* to the organotin group with the angle  $\angle\text{Cl}(1)-\text{W}(1)-\text{Sn}(1)$  of 150.16(3)° in **2a**. The  $\text{W}-\text{Sn}$  distance is 2.8547(9) Å, comparable to that in  $(t\text{-Bu})_2\text{SnCH}(\text{3,5-Me}_2\text{Pz})_2\text{W}(\text{CO})_3(\text{Ph})$  (2.8778(12) Å), but slightly longer than those in the analogous starting reactant  $\text{CH}(\text{3,4,5-Me}_3\text{Pz})_2\text{W}(\text{CO})_3\text{SnPh}_3$  (2.7795(4) Å)<sup>4a</sup> and the neutral bis(pyrazol-1-yl)methane complex  $\text{CH}_2(\text{3,5-Me}_2\text{Pz})_2\text{W}(\text{CO})_3(\text{Cl})\text{SnCl}_3$  (2.741(1) Å).<sup>10</sup> It is also noteworthy that the  $\text{W}-\text{Cl}$  distance in **2a** is 2.525(1) Å, slightly longer than that in the neutral bis(pyrazol-1-yl)methane complex  $\text{CH}_2(\text{3,5-Me}_2\text{Pz})_2\text{W}(\text{CO})_3(\text{Cl})\text{SnCl}_3$  (2.425(3) Å), possibly owing to the differently electronegative organotin groups attached to the tungsten atom ( $\text{SnPh}_2\text{R}$  for the former and  $\text{SnCl}_3$  for the latter, respectively). Another considerable result from the existence of the semibridging carbonyl is the deviation of the angle  $\angle\text{W}(1)-\text{C}(1)-\text{O}(1)$  from linearity, which is 170.9(4)° and slightly larger than the corresponding angle in  $(t\text{-Bu})_2\text{SnCH}(\text{3,5-Me}_2\text{Pz})_2\text{W}(\text{CO})_3(\text{Ph})$  (167.8(8)°).

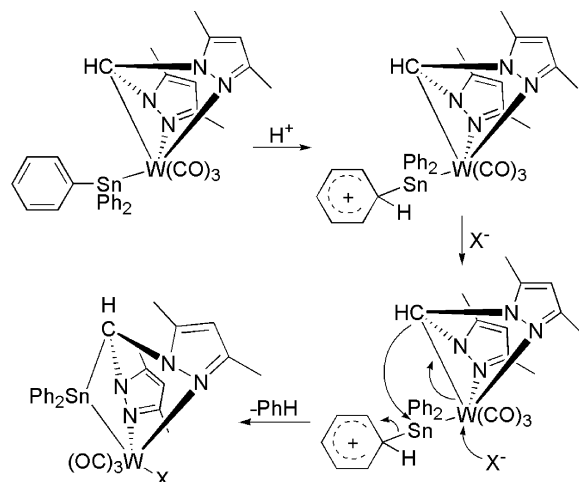
### Possible Pathways of the Formation of **2a–2d**.

To elucidate if the cleavage of the  $\text{W}-\text{C}_{\text{sp}^3}$  bond with the formation of the  $\text{Sn}-\text{C}_{\text{sp}^3}$  bond is concerted, we carried out the reaction of **1a** and **1b** with gaseous  $\text{HCl}$  in the presence of benzaldehyde or benzyl chloride, but no other products were obtained. Eaborn has proposed that the mechanism of acid cleavage of aryl–silicon and aryl–tin bonds is analogous to familiar electrophilic aromatic substitutions, proceeding through an *ipso*-

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**Scheme 2. Possible Pathways of the Formation of 2a–2d**

oriented  $\sigma$ -complex.<sup>11</sup> Combined with the above investigations and Eaborn's work, a plausible mechanism for the formation of **2a–2d** is depicted as in Scheme 2. The first step of the formation of **2a–2d** may undergo the same process as that in the reaction of the acid cleavage of aryl–silicon and aryl–tin bonds, namely, proton transfer to the aromatic ring to give the  $\sigma$ -complex. In the second step the halide anion attacks the tungsten atom instead of the tin atom, probably due to the driving force of releasing the ring strain of the four-membered metallacycle by breaking the W–C bond.

In conclusion, the present result exhibits distinctive reactivity of **1a** and **1b** with HX, compared with other heterodinuclear complexes containing Sn–M bonds. Further investigations on the reactions of **1a** and **1b** with other electrophilic reagents, such as halogens or Lewis acids, are in progress.

## Experimental Section

**General Considerations.** Solvents were dried and distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of argon. <sup>1</sup>H NMR spectra were recorded on a Bruker AV300 spectrometer using CDCl<sub>3</sub> as solvent unless otherwise noted. IR spectra were recorded as KBr pellets on a Bruker Equinox55 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400C analyzer. Compounds **1a** and **1b** were prepared according to the literature methods.<sup>4b</sup>

**Reaction of 1a and 1b with Gaseous Hydrogen Halide.** **1a** or **1b** (20 mg) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and the solution was cooled in an ice bath while gaseous HX was passed through (2–3 bubbles per second, 5 min for HCl and 2 h for HBr). A yellow-green solution was obtained. After removing the solvent under reduced pressure, and the residual solid was purified through a short column of silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The eluate was concentrated to dryness under reduced pressure, and the residual solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give yellow-green crystals.

**Synthesis of 2a.** This complex was obtained by the reaction of **1a** (20 mg, 0.024 mmol) with gaseous HCl. Yield: 15.6 mg (82%). Anal. Found: C, 40.13; H, 3.18; N, 7.12. Calcd for C<sub>26</sub>H<sub>25</sub>ClN<sub>4</sub>O<sub>3</sub>SnW: C, 40.06; H, 3.23; N, 7.19. IR (KBr, cm<sup>-1</sup>): 1984 vs, 1886 vs, 1776 s ( $\nu(\text{CO})$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300

MHz):  $\delta$  2.32, 2.75 (s, s, 6H, 6H, CH<sub>3</sub>), 5.98 (s, 2H, hydrogen in 4-position of pyrazole), 6.33 (s, 1H, CH), 7.26–7.35 (m, 10H, C<sub>6</sub>H<sub>5</sub>).

**Synthesis of 2b.** This complex was obtained by the reaction of **1b** (20 mg, 0.023 mmol) with gaseous HCl. Yield: 15 mg (80%). Anal. Found: C, 41.52; H, 3.75; N, 7.02. Calcd for C<sub>28</sub>H<sub>29</sub>ClN<sub>4</sub>O<sub>3</sub>SnW: C, 41.64; H, 3.62; N, 6.94. IR (KBr, cm<sup>-1</sup>): 1989 vs, 1898 vs, 1771 s ( $\nu(\text{CO})$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.32, 2.33, 2.70 (s, s, s, 6H, 6H, 6H, CH<sub>3</sub>), 5.96 (s, 2H, hydrogen in 4-position of pyrazole), 6.32 (s, 1H, CH), 7.05, 7.14 (d, d, 4H, 4H, C<sub>6</sub>H<sub>4</sub>).

**Synthesis of 2c.** This complex was obtained by the reaction of **1a** (20 mg, 0.024 mmol) with gaseous HBr. Yield: 15 mg (75%). Anal. Found: C, 37.49; H, 3.03; N, 7.11. Calcd for C<sub>26</sub>H<sub>25</sub>BrN<sub>4</sub>O<sub>3</sub>SnW: C, 37.88; H, 3.04; N, 6.80. IR (KBr, cm<sup>-1</sup>): 1985 vs, 1888 vs, 1780 s ( $\nu(\text{CO})$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.36, 2.75 (s, s, 6H, 6H, CH<sub>3</sub>), 5.99 (s, 2H, hydrogen in 4-position of pyrazole), 6.37 (s, 1H, CH), 7.30–7.41 (m, 10H, C<sub>6</sub>H<sub>5</sub>).

**Synthesis of 2d.** This complex was obtained by the reaction of **1b** (20 mg, 0.023 mmol) with gaseous HBr. Yield: 15.3 mg (78%). Anal. Found: C, 39.57; H, 3.35; N, 6.72. Calcd for C<sub>28</sub>H<sub>29</sub>BrN<sub>4</sub>O<sub>3</sub>SnW: C, 39.45; H, 3.40; N, 6.58. IR (KBr, cm<sup>-1</sup>): 1989 vs, 1900 vs, 1769 s ( $\nu(\text{CO})$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.26, 2.27, 2.66 (s, s, s, 6H, 6H, 6H, CH<sub>3</sub>), 5.90 (s, 2H, hydrogen in 4-position of pyrazole), 6.25 (s, 1H, CH), 6.96, 7.01 (d, d, 4H, 4H, C<sub>6</sub>H<sub>4</sub>).

**Reaction of 1a and 1b with Gaseous Hydrogen Halide in the Presence of Benzaldehyde or Benzyl Chloride.** Besides 0.2 mL of benzaldehyde or benzyl chloride added, other reagents and conditions as well as the workup were the same as above-mentioned in the reaction with gaseous hydrogen halide, but only complexes **2a–2d** were obtained in good yields.

**Reaction of 1a and 1b with Concentrated Hydrochloric or Hydrobromic Acid.** The mixture of **1a** or **1b** (20 mg) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and 0.2 mL of concentrated hydrochloric acid or 48% hydrobromic acid was stirred at room temperature for 5 min (hydrochloric acid) or 2 h (48% hydrobromic acid). A yellow-green solution was obtained. After workup similar to that in the reaction with gaseous hydrogen halide, **2a–2d** were obtained in similar yield.

**X-ray Crystallographic Determination of 2a.** Yellow-green crystals of **2a** suitable for X-ray analyses were grown by slow diffusion of hexane into the CH<sub>2</sub>Cl<sub>2</sub> solution of **2a** at –10 °C. All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were resolved by the direct method and refined by full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically. Crystallographic data for **2a**: monoclinic,  $P2_1/n$ ,  $a = 10.446(4)$  Å,  $b = 16.222(5)$  Å,  $c = 16.152(4)$  Å,  $\beta = 91.231(3)^\circ$ ,  $V = 2736.4(15)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd}} = 1.892$  g cm<sup>-3</sup>,  $T = 293(2)$  K, 6540 unique reflections, 4720 with  $I > 2\sigma(I)$ ,  $R$  ( $R_w$ ) = 0.0323 (0.0494).

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**Supporting Information Available:** Tables of crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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