Bis(3,5-dimethylpyrazol-1-yl)acyl and Bis(3,5-dimethylpyrazol-1-yl)methide Carbonyl Tungsten Derivatives

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Reaction of (isopropyl)diphenylstannylbis(3,5-dimethylpyrazol-1-yl)methane [(*i*-Pr)Ph_2SnCH(3,5-$Me_2Pz)_2$] and tricyclohexylstannylbis(3,5-dimethylpyrazol-1-yl)methane [Cy_3SnCH(3,5-$Me_2Pz)_2$] with $W(CO)_5$THF in refluxing THF yields heterobimetallic complexes (*i*-Pr)Ph_2SnCH(3,5-$Me_2Pz)_2W(CO)_4$ and Cy_3SnCH(3,5-$Me_2Pz)_2W(CO)_4$, respectively. Treatment of these heterobimetallic complexes, R_3SnCH(3,5-$Me_2Pz)_2W(CO)_4$ (R_3 = (*i*-Pr)Ph_2, Cy_3, Et_3), with I_2 results in the formation of a novel η^1-bis(pyrazol-1-yl)acyl complex CHC(O)(3,5-$Me_2Pz)_2W(CO)_3I$, with the loss of the organotin group from the methine carbon. In addition, the reaction of R_3SnCH(3,5-$Me_2Pz)_2W(CO)_4$ with $SnCl_4$ in a 1:1 molar ratio gives heterotrimetallic complexes R_3SnCH(3,5-$Me_2Pz)_2W(Cl)(CO)_3SnCl_3$ (R = Cy, Et). It is unexpected that these heterotrimetallic complexes are also reactive in solution. They change to a novel four-membered heterometallacyclic complex CH(3,5-$Me_2Pz)_2W(CO)_3Cl$ in dichloromethane solution at room temperature. Furthermore, this complex can also be obtained by the selective cleavage of the W−Sn bond in complexes CH(3,5-$Me_2Pz)_2W(CO)_3SnAr_3$ with $SnCl_4$.

Introduction

Bis(pyrazol-1-yl)methane, modified by organic functional groups on the bridging carbon atom to form heteroscorpionate ligands, is currently drawing extensive attention,[1,2] and its application has also been increasingly exploited in recent years.[3−5] Our recent investigations on bis(pyrazol-1-yl)methane indicate that the modification of this ligand with organometallic groups on the methine carbon atom can provide unusual reactivity.[6] For example, the reaction of triarylstannylbis(3,5-dimethylpyrazol-1-yl)methane with $W(CO)_5$THF results in the oxidative addition of the $Sn-C_{sp3}$ bond to the tungsten(0) atom to give the novel four-membered metallacyclic complex, while the analogous reaction of di(*tert*-butyl)phenylstannylbis(3,5-dimethylpyrazol-1-yl)methane results in the oxidative addition of the $Sn-C_{sp2}$ bond to the tungsten(0) atom. Interestingly, the similar reaction of trialkylstannylbis(3,5-dimethylpyrazol-1-yl)methane with $W(CO)_5$THF gives only heterobimetallic complexes R_3SnCH(3,5-$Me_2Pz)_2W(CO)_4$ (R = alkyl).[6b] These facts suggest that the electronic and steric effects of substitutions on the tin atom play a key role in these reactions. To gain further

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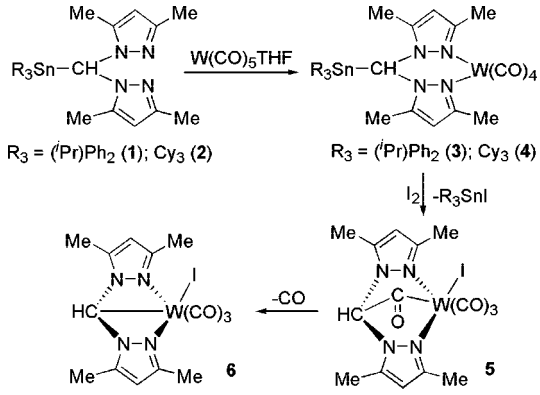
Scheme 1. Synthesis of Bis(3,5-dimethylpyrazol-1-yl)acyl Tungsten Derivative



understanding of the influence of the nature of substitutions on the tin atom on these reactions, in this paper we synthesize bis(3,5-methylpyrazol-1-yl)methanes modified with the bulky (isopropyl)diphenyltin and tricyclohexyltin groups on the methine carbon and study their related reactivities. Some novel bis(3,5-dimethylpyrazol-1-yl)acyl and bis(3,5-dimethylpyrazol-1-yl)methide carbonyl tungsten derivatives are obtained by the reaction of heterobimetallic complexes $R_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ with I_2 and $SnCl_4$.

Results and Discussion

Synthesis of Bis(3,5-dimethylpyrazol-1-yl)acyl Tungsten Derivative. Treatment of (isopropyl)diphenylstannylbis(3,5-dimethylpyrazol-1-yl)methane (**1**) and tricyclohexylstannylbis(3,5-dimethylpyrazol-1-yl)methane (**2**), prepared by the reactions of bis(3,5-dimethylpyrazol-1-yl)methyl lithium with the corresponding organotin halide, with $W(CO)_5THF$ in refluxing THF yields heterobimetallic complexes **3** and **4** (Scheme 1). No oxidative addition of the $Sn-C_{sp3}$ or $Sn-C_{sp2}$ bond to the tungsten(0) atom is observed. These two complexes have been characterized by spectroscopic methods. Their $^{119}Sn\{^1H\}$ NMR signals are very similar to those in free ligands **1** and **2**, consistent with the reaction position away from the tin atom. In addition, their IR spectra also display a typical *cis*-tetracarbonyl arrangement around the tungsten atom.

The structure of complex **3**, presented in Figure 1, has been further confirmed by X-ray crystallography. As shown in Figure 1, the organotin group is still connected to the methine carbon and lies in the axial position of the ligand. The fundamental molecular framework is similar to that in $(p\text{-}MeC_6H_4)_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$.[6b] It is worth noting that two *cis*-carbonyl groups are markedly distorted with the O(4)−C(4)−W(1) angle of 166.5(9)° and O(2)−C(2)−W(1) angle of 169.5(10)°, and some angles around the Sn(1) and C(41) atoms (such as the C(18)−Sn(1)−C(41) angle of 93.3(3)° and N(4)−C(41)−Sn(1) angle of 123.9(6)°) significantly deviate from the tetrahedral geometry of the sp^3-hybridized Sn(1) and C(41). These geometric parameters suggest a large steric repulsion in this complex, as expected.

It is known that the reaction of tetraorganotin derivatives with halogen leads to the cleavage of the Sn−C bond to give organotin halide.[7] In addition, the oxidation of group 6 metal carbonyl derivatives of poly(pyrazol-1-yl)methane by halogen, forming six- and seven-coordinate group 6 metal (0−VI) halides of poly(pyrazol-1-yl)methane, has also been reported in the literature.[8] Although no oxidative addition reaction of the $Sn-C_{sp3}$ or $Sn-C_{sp2}$ bond to the tungsten(0) atom takes place during the reaction of ligands **1** and **2** with $W(CO)_5THF$, the products **3** and **4** are fascinating owing to their having two reactive centers as described above. Thus these two complexes are expected to display some markedly different reactivities compared with the corresponding mononuclear complexes possibly owing to the cooperative effects of two different metal centers.[9]

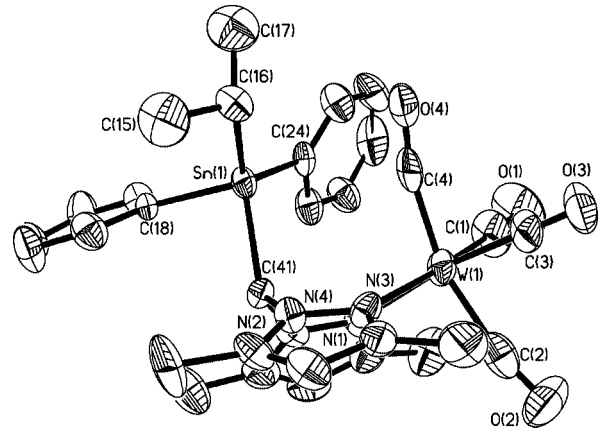


Figure 1. Molecular structure of **3**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)−C(41) 2.236(9), Sn(1)−C(18) 2.151(9), N(4)−C(41) 1.452(11), N(2)−C(41) 1.441(11), W(1)−N(1) 2.289(8), W(1)−N(3) 2.260(8); C(24)−Sn(1)−C(16) 119.6(4), C(18)−Sn(1)−C(41) 93.3(3), N(4)−C(41)−Sn(1) 123.9(6), O(4)−C(4)−W(1) 166.5(9), O(2)−C(2)−W(1) 169.5(10), N(3)−W(1)−N(1) 80.3(3), N(2)−C(41)−N(4) 110.8(7), C(4)−W(1)−C(2) 163.4(4), C(1)−W(1)−N(3) 174.0(4).

It is interesting that treatment of complexes **3** and **4** with I_2 leads to the novel η^1-bis(pyrazol-1-yl)acyl complex $CHC(O)(3,5\text{-}Me_2Pz)_2W(CO)_3I$ (**5**) (Scheme 1), with the loss of the organotin group from the methine carbon. To investigate if the bulky substituents on the tin atom are necessary for the novel reaction, $Et_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ is also treated with I_2 under the same conditions, which yields the same complex **5**. The IR spectrum of **5** clearly shows that this complex has a η^1-acyl coordinate mode with the characteristic carbonyl absorption at 1676.6 cm^{-1}. The structure of **5** is further confirmed by X-ray single-crystal diffraction, as shown in Figure 2. The carbonyl group is bound to the tungsten in an η^1-fashion, resulting in bis(pyrazol-1-yl)acyl acting as a novel tridentate κ^3-[N,C,N] chelating ligand. The C(6)−C(9) bond length of 1.608(10) Å is somewhat longer than other η^1-acyl complexes of tungsten,[10] possibly owing to the large strain originating from the chelating

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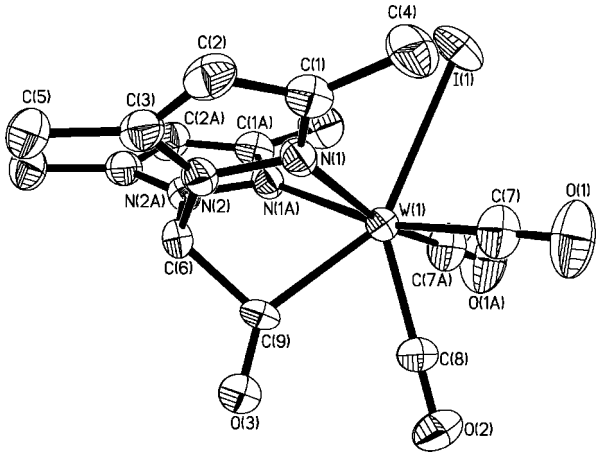

Figure 2. Molecular structure of **5**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): W(1)−C(9) 2.231(7), W(1)−I(1) 2.8732(7), W(1)−N(1) 2.253(4), O(3)−C(9) 1.169(9), C(6)−C(9) 1.608(10), N(2)−C(6) 1.430(5); C(6)−C(9)−W(1) 101.6(4), O(3)−C(9)−C(6) 117.6(7), N(1)−W(1)−N(1A) 84.7(2), N(2A)-C(6)−N(2) 112.9(6) (symmetric code A: x, $-y + 1/2$, z).

effect of the bis(pyrazol-1-yl)acyl ligand. In addition, the C(6)−C(9)−W(1) angle of 101.6(4)° significantly deviates from the trigonal and planar C(9) atom of the sp^2 hybridization, probably influenced by the same factor. The long C(6)−C(9) bond distance as well as the large strain makes this complex unstable, which slowly loses the acyl group to yield four-membered heterometallacyclic complex **6**.

The M−acyl complexes are key intermediates in many catalytic carbonylation reactions. Capturing these key species and obtaining their structural parameters play an important role in understanding the catalytic mechanism and improving the activity of the catalyst. Although there are some examples of η^1-acyl tungsten complexes of scorpionate ligands in the literature,[11] the related acyl complexes of anionic heteroscorpionate ligands prior to our work are unknown. Herein we present a case of the novel acyl complex of the heteroscorpionate ligand.

Possible Pathways of the Formation of 5. The high reaction rate, even at −50 °C, prevents us from obtaining any intermediate as the direct evidence for supporting the reaction pathways, though several possible pathways to form complex **5** are reasoned (Scheme 2). According to the known knowledge, the initial reaction possibly takes place on the tin atom to form intermediate **A**;[7] subsequently the oxidative addition of the C−I bond to the tungsten(0) atom gives **6**.[12] In the alternative possible pathway, **6** is yielded via intermediate **B**,[8b] formed from the initial reaction of $R_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ with I_2. The lone electron pair on the iodine atom in **B** attacks the tin atom to facilitate the cleavage of the $Sn-C_{sp3}$ bond, and subsequently the resulting anion attacks the tungsten atom to result in the cleavage of this W−I bond, yielding **6**. Although **6** cannot be obtained from the reaction of $R_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ with I_2, fortunately it can be prepared by the selective cleavage of the W−Sn bond in $CH(3,5\text{-}Me_2Pz)_2W(CO)_3SnPh_3$ with I_2. However, no migratory insertion reaction is observed when the solution of **6** is treated with CO under similar experimental conditions in which **5** is formed. Thus an alternative mechanism is suggested to interpret the formation of the bridging carbonyl.

It is known that the carbonyl group in cationic carbonyl metal complexes is strongly activated toward nucleophilic attack owing to the positive charge on the metal.[13] The nucleophilic attack at the carbonyl carbon in cationic carbonyl tungsten complexes has been observed.[14] In addition, the oxidative addition of carbonyl tungsten derivatives of poly(pyrazol-1-yl)methane with I_2 yielding cationic carbonyl tungsten complexes is also known.[15] Taking into consideration the above facts, the initial reaction to form complex **5** is more likely to take place on the tungsten(0) atom to yield cationic intermediate **C**. Subsequently the iodide anion attacks the tin atom to lead to the cleavage of the $Sn-C_{sp3}$ bond, and the nucleophilic attack of the resulting anion on the carbonyl carbon atom gives complex **5**.

Synthesis of Bis(3,5-dimethylpyrazol-1-yl)methide Tungsten Derivative. The above novel reaction mode of heterobimetallic complexes $R_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ with I_2 inspires us to expand the investigations on reactivities of these complexes. The oxidative addition of the tin(IV)−halogen bond to low-valent group 6 metals has been well-established.[16] Our previous investigations indicated that the reaction with $SnCl_4$ of group 6 metal carbonyl complexes with bis(pyrazol-1-yl)-methane gives heterobimetallic M−Sn complexes in good yields.[17] Herein, treatment of heterobimetallic complexes $R_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (R = Cy or Et) with $SnCl_4$ in a 1:1 molar ratio similarly gives the oxidative addition products **7** and **8** (Scheme 3), as expected. What is beyond expectation is that these two complexes are also reactive in solution. Complex **7** slowly converts to four-membered heterometallacyclic complex **9** in CH_2Cl_2 solution at room temperature. We are unable to obtain **8** in pure form because it exhibits a higher reactivity compared with **7** in solution. In addition, when the reaction of **4** with $SnCl_4$ is carried out in a 1:2 molar ratio, complex **9** is yielded directly. At the same time, complex **9** is also obtained by the selective cleavage of the W−Sn bond in $CH(3,5\text{-}Me_2Pz)_2W(CO)_3SnAr_3$ (Ar = C_6H_5 or p-$CH_3C_6H_4$) with $SnCl_4$.

Complexes **7** and **9** have been characterized by IR and ^1H NMR spectroscopy, and their structures have been further confirmed by X-ray structural analyses. The proton signal of the CH group in complex **9** (5.55 ppm) is markedly shifted to higher field, compared with those in **7** (6.08 ppm) and **4** (6.18), but similar to that in **6** (5.41 ppm). Furthermore, complexes **6** and **9** have very similar IR spectra, indicating that they possibly have analogous structures.

The crystal structure of complex **7** is presented in Figure 3. One chlorine-bridged W−Sn bond is observed in this complex, which is similar to other W(Mo)−Sn systems, such as $(L_2)W(Cl)(CO)_3(SnCl_3)$ (L = CH_3CN, PPh_3, dppe, and bipy)[18]

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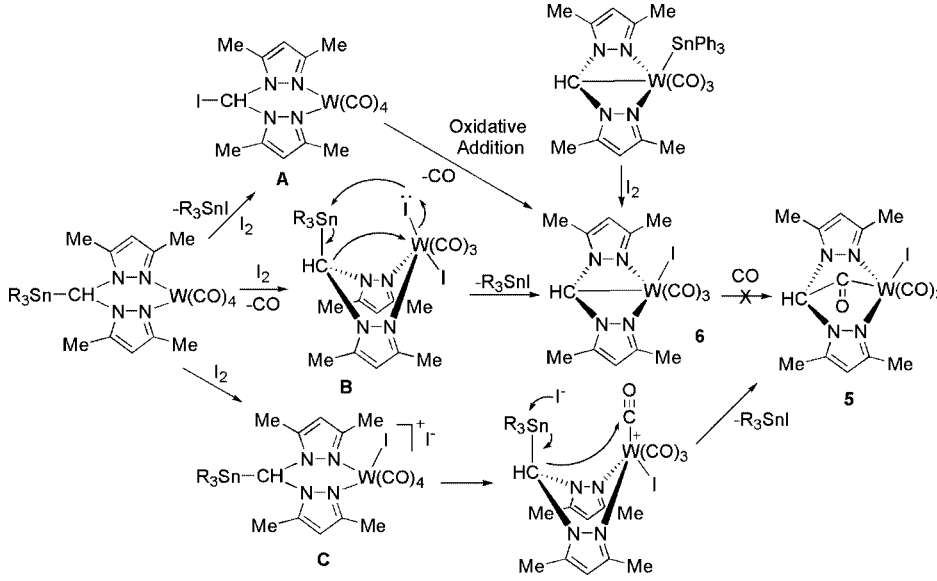
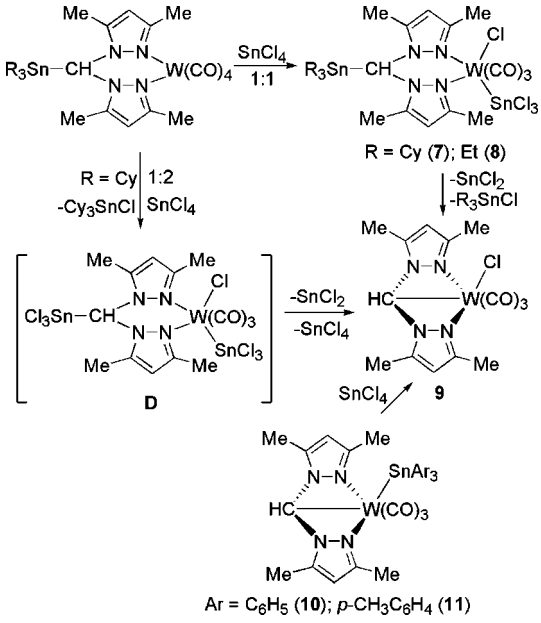
Scheme 2. Possible Pathways of the Formation of 5



Scheme 3. Reaction of $R_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (R = Cy, Et) with $SnCl_4$



and $CH_2(4\text{-}BrPz)_2Mo(CO)_3(Cl)(SnCl_2Ph)$.[17a] The Sn(1)−Cl(1) distance (2.831(2) Å) is markedly longer than the terminal Sn−Cl bond lengths (2.324(2)−2.336(2) Å), indicating that this bond is relatively weak and possibly dissociates in solution. It is also noted that the Sn(2)−C(9) bond length is longer than those of the other three Sn−C bonds. In addition, some angles around the Sn(2) and C(9) atoms (such as the C(9)−Sn(2)−C(21) angle of 97.1(3)° and N(2)−C(9)−Sn(2) angle of 125.8(5)°) significantly deviate from the tetrahedral geometry of the sp^3-hybridized Sn(2) and C(9), suggesting a large steric repulsion in this complex. These structural parameters should be in favor of the intramolecular redistribution reaction of the tricyclohexyltin group with the $SnCl_3$ group to yield complex **9**.

The X-ray crystal structure of complex **9** consists of two crystallographically independent molecules with similar structural parameters. One of them is presented in Figure 4, which clearly shows that the bridging carbon of bis(pyrazol-1-yl)methide is integrated with the tungsten atom to form two four-membered heterometallacycles, as in complexes $CH(3,4,5\text{-}Me_3Pz)_2W(CO)_3SnPh_3$[6a] and $CH(3,5\text{-}^iPr_2Pz)_2W(CO)_3SnPh_3$.[6b] The average W−N distance is 2.2345 Å, similar to those in $CH(3,5\text{-}^iPr_2Pz)_2W(CO)_3SnPh_3$ (2.217 Å) and $CH(3,4,5\text{-}Me_3Pz)_2W(CO)_3SnPh_3$ (2.2325 Å). The W−C_{sp3} bond distance is 2.296(13) Å, comparable to the corresponding bonds in $CH(3,5\text{-}^iPr_2Pz)_2W(CO)_3SnPh_3$ (2.343(6) Å) and $CH(3,4,5\text{-}Me_3Pz)_2W(CO)_3SnPh_3$ (2.326(5) Å). In addition, the W−Cl bond distance is 2.462(4) Å, slightly shorter than that in complex **7** (2.545(2) Å).

Although the chlorine bridge repels the $SnCl_3$ group away from the $SnCy_3$ group in the solid **7**, the approach of the chlorine atom on the $SnCl_3$ group to the tin atom of the $SnCy_3$ group should be possible in solution by the dissociation of this bridge owing to the weak Sn(1)···Cl(1) interactions. Furthermore, in the nonbridged W−$SnCl_3$ complexes with bis(pyrazol-1-yl)-methane ligands,[17] the $SnCl_3$ group close to the bridging carbon has been observed. Thus, the possible formation pathway of **9** from **7** and **8** may be similar to that of the formation of **6** from

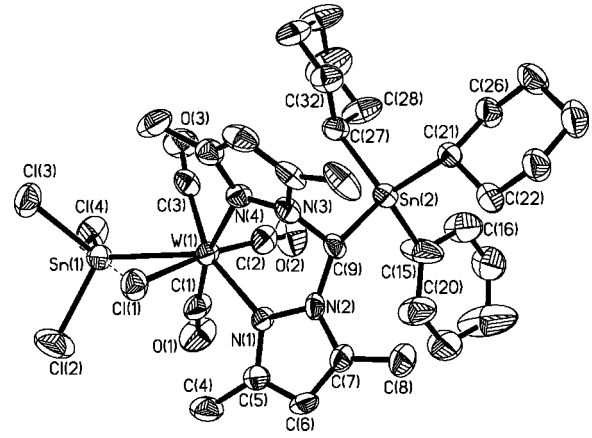


Figure 3. Molecular structure of **7**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): W(1)−N(1) 2.241(5), W(1)−N(4) 2.253(5), W(1)−Cl(1) 2.545(2), W(1)−Sn(1) 2.7187(7), Sn(1)···Cl(1) 2.831(2), Sn(1)−Cl(2) 2.336(2), Sn(1)−Cl(3) 2.324(2), Sn(1)−Cl(4) 2.369(2), Sn(2)−C(9) 2.264(7), Sn(2)−C(15) 2.125(8), N(2)−C(9) 1.447(8), N(3)−C(9) 1.459(9); N(1)−W(1)−N(4) 81.6(2), Cl(1)−W(1)−Sn(1) 64.96(4), N(2)−C(9)−N(3) 110.1(5), N(2)−C(9)−Sn(2) 125.8(5), C(15)−Sn-(2)−C(27) 117.6(4), C(9)−Sn(2)−C(21) 97.1(3), C(21)−Sn(2)−C(27) 106.4(3), Cl(2)−Sn(1)−Cl(4) 98.13(10), Cl(3)−Sn(1)−W(1) 121.15(6), Cl(3)−Sn(1)−Cl(2) 101.74(10).

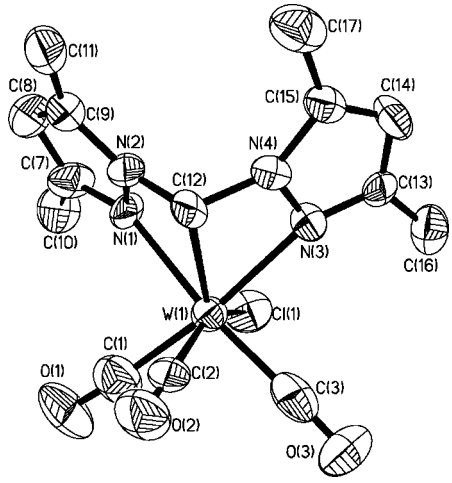


Figure 4. Molecular structure of **9**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): W(1)−C(12) 2.296(13), W(1)−Cl(1) 2.462(4), W(1)−N(1) 2.242(10), W(1)−N(3) 2.227(11), N(2)−C(12) 1.450(15), N(4)−C(12) 1.433(14); N(1)−W(1)−N(3) 87.9(4), N(1)−W(1)−C(12) 60.2(4), N(3)−W(1)−C(12) 60.2(4), N(2)−C(12)−N(4) 109.5(10), N(4)−C(12)−W(1) 92.4(8), N(2)−C(12)−W(1) 92.4(7).

the intermediate **B** in Scheme 2, with the attack by the chlorine atom on the $SnCl_3$ group instead of the iodine atom. Namely, the lone electron pair on one chlorine atom connected to the Sn(1) atom attacks the Sn(2) atom to lead to the cleavage of the Sn(2)−C(9) bond. Subsequently, the resulting anion attacks the tungsten atom to result in the cleavage of the W−Sn bond to complete the related reactions. Intermediate **D** is possibly formed when **4** reacts with $SnCl_4$ in a 1:2 molar ratio.[19] The stronger Lewis acidity of the tin atom on the methine atom in intermediate **D**, compared with the corresponding tin atom in **4**, possibly favors the attack of the chlorine atom on W−$SnCl_3$, which leads to quick formation of complex **9**.

In conclusion, novel bis(3,5-dimethylpyrazol-1-yl)acyl and bis(3,5-dimethylpyrazol-1-yl)methide carbonyl tungsten derivatives can be easily synthesized by treatment of heterobimetallic complexes $R_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ with I_2 or $SnCl_4$. Although strains exist in four-membered metallacycles of complexes $CH(3,5\text{-}Me_2Pz)_2W(CO)_3X$ (X = Cl or I), these complexes are easily obtained and stable. The strong W−C_{sp3} bond possibly plays the key role in the formation of these four-membered metallacycles.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled prior to use according to standard procedures. NMR spectra were recorded on a Bruker AV300 or Mercury 400BB spectrometer using $CDCl_3$ as solvent unless otherwise noted, and the chemical shifts are reported in ppm with respect to the reference (internal $SiMe_4$ for ^1H NMR and $^{13}C\{^1H\}$ NMR spectra, external $SnMe_4$ for $^{119}Sn\{^1H\}$ NMR). IR spectra were recorded as KBr pellets on a Bruker Equinox55 spectrometer. Elemental analyses were carried out on an Elementar Vairo EL analyzer. $CH(3,5\text{-}Me_2Pz)_2W(CO)_3SnAr_3$ (Ar = Ph (**10**) and *p*-$CH_3C_6H_4$ (**11**)),[6b] $Et_3SnCH(3,5\text{-}Me_2Pz)_2$-$W(CO)_4$,[6b] and (*i*-Pr)$Ph_2SnI$[20] were prepared according to the literature methods. Melting points were measured with an X-4 digital micro melting-point apparatus and are uncorrected.

(19) Elhamzaoui, H.; Jousseaume, B.; Toupance, T.; Allouchi, H. *Organometallics* **2007**, *26*, 3908.

(20) Abel, E. W.; Brady, D. B. *J. Chem. Soc.* **1965**, 1192.

Synthesis of (*i*-Pr)$Ph_2SnCH(3,5\text{-}Me_2Pz)_2$ (1). To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (0.41 g, 2.0 mmol) in THF (30 mL) was added a hexane solution of *n*-BuLi (2.5 M, 0.80 mL) at −70 °C, and the mixture was stirred for 1 h at that temperature. To the mixture was added a solution of the (*i*-Pr)Ph_2SnI (0.89 g, 2.0 mmol) in THF (10 mL). The reaction mixture was stirred at −70 °C for 1 h, allowed to slowly reach room temperature, and stirred overnight. The solvent was removed under reduced pressure, and the residual solid was recrystallized from hexane to yield white crystals of **1**. Yield: 0.65 g, 63%, mp 69−71 °C. ^1H NMR: δ 1.29 (d, J = 7.5 Hz, 6H, $(CH_3)_2CH$), 1.91 (m, 1H, $(CH_3)_2CH$), 1.81, 2.11 (s, s, 6H, 6H, CH_3), 5.65 (s, 2H, 4-position hydrogen of pyrazole ring), 6.34 (s, 1H, C*H*N), 7.18−7.33 (m, 10H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ 11.0, 13.5 (3 and 5-CH_3), 20.8 ($(CH_3)_2CH$), 21.6 ($(CH_3)_2CH$), 70.2 (*C*HN), 106.9 (4-position carbon of pyrazole ring), 141.7, 147.0 (3- or 5-position carbon of pyrazole ring), 128.0, 128.3, 137.6, 139.7 (C_6H_5). $^{119}Sn\{^1H\}$ NMR: δ −128.1. Anal. Found: C, 60.35; H, 6.04; N, 10.97. Calcd for $C_{26}H_{32}N_4Sn$: C, 60.14; H, 6.21; N, 10.79.

Synthesis of $Cy_3SnCH(3,5\text{-}Me_2Pz)_2$ (2). This ligand was similarly obtained as above-mentioned for **1**, but (*i*-Pr)Ph_2SnI was replaced by Cy_3SnCl. Yield: 53%, mp 73−75 °C. ^1H NMR: δ 1.36−1.78 (m, 33H, C_6H_{11}), 1.96, 2.09 (s, s, 6H, 6H, CH_3), 5.61 (s, 2H, 4-position hydrogen of pyrazole ring), 6.18 (s, 1H, C*H*). $^{13}C\{^1H\}$ NMR: δ 11.1, 13.4 (3 and 5-CH_3), 27.3, 29.5, 30.3, 31.8 (C_6H_{11}), 67.9 (*C*HN), 106.4 (4-position carbon of pyrazole ring), 138.9, 146.1 (3- or 5-position carbon of pyrazole ring). $^{119}Sn\{^1H\}$ NMR: δ −85.9. Anal. Found: C, 60.80; H, 8.68; N, 9.46. Calcd for $C_{29}H_{48}N_4Sn$: C, 60.95; H, 8.47; N, 9.80.

Reaction of 1 and 2 with $W(CO)_5THF$. Ligand **1** or **2** (0.3 mmol) was added to a solution of $W(CO)_5THF$ in THF, prepared in situ by the irradiation of a solution of $W(CO)_6$ (0.11 g, 0.30 mmol) in THF (20 mL) for 8 h, and the mixture was stirred and heated at reflux for 5 h. After the reaction was complete, the solvent was removed under reduced pressure. The residual solid was purified by column chromatography on silica using CH_2Cl_2/hexane (1:1 v/v) as eluent. The eluate was concentrated to dryness again, and the residual solid was recrystallized from CH_2Cl_2/hexane to give yellow-green crystals.

Synthesis of (*i*-Pr)$Ph_2SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (3). This complex was obtained by the reaction of **1** with $W(CO)_5THF$. Yield: 55%. ^1H NMR: δ 1.21 (d, J = 7.5 Hz, 6H, $(CH_3)_2CH$), 2.20 (m, 1H, $(CH_3)_2CH$), 2.15, 2.52 (s, s, 6H, 6H, CH_3), 6.02 (s, 2H, 4-position hydrogen of pyrazole ring), 6.56 (s, 1H, C*H*N), 7.12−7.36 (m, 10H, C_6H_5). $^{13}C\{^1H\}$ NMR: δ 11.8, 17.1 (3 and 5-CH_3), 21.4 ($(CH_3)_2CH$), 24.3 ($(CH_3)_2CH$), 64.7 (*C*HN), 107.8 (4-position carbon of pyrazole ring), 140.1, 157.8 (3- or 5-position carbon of pyrazole ring), 128.6, 129.3, 136.6, 139.1 (C_6H_5), 206.8, 211.2 (*C*O). $^{119}Sn\{^1H\}$ NMR: δ −124.2. IR (cm^{-1}): ν_{CO} = 1997.6 vs, 1886.1 vs, 1844.8 vs, 1829.7 vs. Anal. Found: C, 44.39; H, 3.75; N, 6.68. Calcd for $C_{30}H_{32}N_4O_4SnW$: C, 44.20; H, 3.96; N, 6.87.

Synthesis of $Cy_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (4). This complex was obtained by the reaction of **2** with $W(CO)_5THF$. Yield: 62%. ^1H NMR: δ 1.24−1.29, 1.52−1.61, 1.64−1.89 (m, m, m, 15H, 12H, 6H, C_6H_{11}), 1.97, 2.10 (s, s, 6H, 6H, CH_3), 5.69 (s, 2H, 4-position hydrogen of pyrazole ring), 6.18 (s, 1H, C*H*N). $^{13}C\{^1H\}$ NMR: δ 11.2, 13.4 (3- and 5-CH_3), 27.3, 29.4, 30.4, 31.7 (C_6H_{11}), 67.9 (*C*HN), 106.3 (4-position carbon of pyrazole ring), 139.0, 146.0 (3- or 5-position carbon of pyrazole ring), 201.8, 206.1, 211.4 (*C*O). $^{119}Sn\{^1H\}$ NMR: δ −86.0. IR (cm^{-1}): ν_{CO} = 1996.2, 1873.7, 1831.0 (br, vs). Anal. Found: C, 45.48; H, 5.74; N, 6.58. Calcd for $C_{33}H_{48}N_4O_4SnW$: C, 45.70; H, 5.58; N, 6.46.

Reaction of 3 and 4 as well as $Et_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ with I_2. To a stirred solution of **3**, **4**, or $Et_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (0.058 mmol) in CH_2Cl_2 (15 mL) was added dropwise at room temperature a CH_2Cl_2 solution (15 mL) of I_2 (0.058 mmol). After addition was complete, the reaction mixture

Table 1. Crystallographic Data for Complexes 3, 5, 7, and 9

	3	5	7	9
formula	$C_{30}H_{32}N_4O_4SnW$	$C_{15}H_{15}IN_4O_4W$	$C_{32}H_{48}Cl_4N_4O_3Sn_2W$	$C_{14}H_{15}ClN_4O_3W$
fw	815.14	626.06	1099.77	506.60
cryst size, mm	0.30 × 0.10 × 0.10	0.20 × 0.18 × 0.14	0.18 × 0.16 × 0.14	0.14 × 0.10 × 0.08
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/m$	$P\bar{1}$	$P\bar{1}$
cell params				
a, Å	8.607(6)	7.1875(13)	10.6878(16)	9.196(2)
b, Å	10.833(8)	14.160(3)	12.4245(18)	14.033(3)
c, Å	17.866(12)	9.0408(16)	17.410(3)	14.305(3)
α, deg	93.782(11)	90	74.486(3)	81.941(5)
β, deg	92.825(12)	97.959(3)	75.947(3)	81.338(4)
γ, deg	112.388(11)	90	65.769(2)	73.698(4)
V, Å^3	1531.9(18)	911.2(3)	2008.0(5)	1742.3(7)
Z	2	2	2	4
T, K	293(2)	294(2)	294(2)	294(2)
calcd density, Mg/m^{-3}	1.767	2.282	1.819	1.931
F(000)	792	584	1068	968
μ, mm^{-1}	4.606	8.059	4.393	6.801
no. of rflns collcd/unique	7526/5181	5927/2498	10 282/7037	9929/7025
(R_{int})	(0.0578)	(0.0336)	(0.0338)	(0.0708)
no. of rflns obsd with ($I \geq 2\sigma(I)$)	3179	2003	5005	3162
no. of params	367	126	419	423
R, R_w ($I \geq 2\sigma(I)$)	0.0516, 0.0806	0.0354, 0.0693	0.0398, 0.0787	0.0566, 0.0850
goodness-of-fit on F^2	0.925	1.025	0.984	0.891

was stirred for an additional 1 h. The solvent was removed under reduced pressure, and the residual solid was recrystallized from CH_2Cl_2/hexane at −18 °C to give yellow crystals of CH(CO)(3,5-$Me_2Pz)_2W(CO)_3$I (**5**). Yield: 45% from **3**, 40% from **4**, and 50% from $Et_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$. ^{1}H NMR: δ 2.44, 2.73 (s, s, 6H, 6H, C*H*$_3$), 5.82 (s, 1H, C*H*), 6.05 (s, 2H, 4-position hydrogen of pyrazole ring). IR (cm^{-1}): ν_{CO} = 2019.1 vs, 1919.2 vs; $\nu_{C=O}$ = 1676.6 s. Anal. Found: C, 28.96; H, 2.25; N, 9.11. Calcd for $C_{15}H_{15}IN_4O_4W$: C, 28.78; H, 2.42; N, 8.95. In addition, this reaction was also carried out at −50 °C; only complex **5** was obtained. During storage, this complex slowly lost the acyl group to yield $CH(3,5\text{-}Me_2Pz)_2W(CO)_3$I (**6**), which also can be obtained as follows.

Reaction of $CH(3,5\text{-}Me_2Pz)_2W(CO)_3SnPh_3$ (10) with I_2 to Yield 6. To a stirred solution of **10** (110 mg, 0.134 mmol) in CH_2Cl_2 (15 mL) at 10 °C was dropwise added a solution of I_2 (34.0 mg, 0.134 mmol) in CH_2Cl_2 (10 mL). After addition was complete, the reaction mixture was stirred for an additional 2 h at room temperature. The solvent was removed under reduced pressure, and the residual solid was recrystallized from CH_2Cl_2/hexane to yield 52 mg (65%) of **6** as orange-red crystals. ^{1}H NMR: δ 2.20, 2.43 (s, s, 6H, 6H, C*H*$_3$), 5.67 (s, 2H, 4-position hydrogen of pyrazole ring), 5.41 (s, 1H, C*H*). ^{13}C{^{1}H} NMR: δ 9.0, 13.0 (3- or 5-*C*H$_3$), 40.3 (*C*H), 106.3 (4-position carbon of pyrazole ring), 141.9, 152.4 (3- or 5-position carbon of pyrazole ring), 220.5, 240.0 (*C*O). IR (cm^{-1}): ν_{CO} = 2023.4 s, 1926.1 vs, 1898.8 vs. Anal. Found: C, 28.16; H, 2.52; N, 9.51. Calcd for $C_{14}H_{15}IN_4O_3W$: C, 28.12; H, 2.53; N, 9.37.

Attempted Reaction of 6 with CO. In a Schlenk flask, the solution of **6** (20 mg, 0.033 mmol) in CH_2Cl_2 (10 mL) was degassed by multiple freeze−pump−thaw cycles. The flask was refilled with CO. The reaction mixture was warmed to room temperature and stirred for additional 5 h under a CO atmosphere. After the solvent was removed under reduced pressure, the residue was analyzed by ^{1}H NMR spectroscopy, indicating that no reaction took place; only starting material **6** was observed.

Reaction of 4 with $SnCl_4$ in 1:1 Molar Ratio. To a vigorously stirred solution of $Cy_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (43 mg, 0.050 mmol) in CH_2Cl_2 (15 mL) at room temperature was added dropwise a solution of $SnCl_4$ (0.050 mmol) in CH_2Cl_2 (5 mL). The color of the solution changed from green-yellow to orange-red. After addition was complete, the reaction mixture was stirred for an additional 1 h. The solvent was removed under reduced pressure, and the residual solid was recrystallized from CH_2Cl_2/hexane at −18 °C to give red crystals of $Cy_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_3$-(Cl)$SnCl_3$ (**7**). Yield: 32 mg, 58%. ^{1}H NMR: δ 1.62−1.97 (m, 33H, C_6H_{11}), 2.35, 2.70 (s, s, 6H, 6H, 3- or 5-C*H*$_3$), 6.08 (s, 2H, 4-position hydrogen of pyrazole ring), 6.37 (s, 1H, C*H*). ^{13}C{^{1}H} NMR: δ 12.2, 17.5 (3- or 5-*C*H$_3$), 26.9, 29.2, 32.3, 33.8 (C_6H_{11}), 59.3 (*C*H), 110.0 (4-position carbon of pyrazole ring), 140.3, 155.1 (3- or 5-position carbon of pyrazole ring). The carbonyl carbon signals are not observed possibly due to the lower signal intensity and the low solubility of complex **7**. IR (cm^{-1}): ν_{CO} = 2020.7 s, 1996.5 vs, 1899.6 vs. Anal. Found: C, 34.61; H, 4.55; N, 4.92. Calcd for $C_{32}H_{48}Cl_4N_4O_3Sn_2W$: C, 34.95; H, 4.40; N, 5.09. In addition, when stirring the CH_2Cl_2 solution of **7** for 24 h at room temperature, this complex slowly transformed to complex $CH(3,5\text{-}Me_2Pz)_2W(CO)_3Cl$ (**9**). ^{1}H NMR: δ 2.29, 2.47 (s, s, 6H, 6H, 3- or 5-C*H*$_3$), 5.55 (s, 1H, C*H*), 5.76 (s, 2H, 4-position hydrogen of pyrazole ring). IR (cm^{-1}): ν_{CO} = 2028.0 s, 1929.0 vs, 1892.0 s. Anal. Found: C, 32.86; H, 2.60; N, 10.80. Calcd for $C_{14}H_{15}ClN_4O_3W$: C, 33.19; H, 2.98; N, 11.06.

Reaction of $Et_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ with $SnCl_4$. To a vigorously stirred solution of $Et_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (57 mg, 0.080 mmol) in CH_2Cl_2 (20 mL) cooled to 0 °C was slowly added dropwise a solution of $SnCl_4$ (0.080 mmol) in CH_2Cl_2 (5 mL). After addition was complete, the reaction mixture was stirred for an additional 1 h to 0 °C. The solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H NMR spectroscopy, indicating that no starting material was observed, and complexes $Et_3SnCH(3,5\text{-}Me_2Pz)_2W(CO)_3(Cl)SnCl_3$ (**8**) and **9** were formed. The ratio was estimated to be ca. 3:1 (**8**:**9**) according to the integration of the CH resonance. Unfortunately, we were unable to isolate complex **8** in pure form owing to its instability in solution. In fact, when the reaction mixture was stirred overnight, only complex **9** was observed by ^{1}H NMR spectroscopy, and it was isolated in ca. 21% yield by silica column chromatography. ^{1}H NMR data for **8**: δ 1.08−1.15 (m, 15H, C_2H_5), 2.29, 2.61 (s, s, 6H, 6H, 3- or 5-C*H*$_3$), 6.06 (s, 2H, 4-position hydrogen of pyrazole ring), 6.33 (s, 1H, C*H*).

Reaction of 4 with $SnCl_4$ in 1:2 Molar Ratio. This reaction was carried out similarly to that described above for the reaction in 1:1 molar ratio, using $SnCl_4$ (0.10 mmol) instead. During the reaction, some white solids precipitated. After the reaction was complete, the solution was filtered off. With a similar workup, red crystals of **9** were obtained. Yield: 45%.

In addition, this complex can also be obtained by the reaction of $CH(3,5\text{-}Me_2Pz)_2W(CO)_3SnAr_3$ (Ar = C_6H_5 (**10**) or *p*-$CH_3C_6H_4$

(**11**)) with $SnCl_4$ as follows. To a stirred solution of **10** or **11** (0.05 mmol) in CH_2Cl_2 (10 mL) at 10 °C was added dropwise a solution of $SnCl_4$ (0.05 mmol) in CH_2Cl_2 (5 mL). After addition was complete, the reaction mixture was stirred for an additional 2 h at room temperature. The solvent was removed under reduced pressure, and the residual solid was purified by short column chromatography on silica using CH_2Cl_2 as eluent. After removing the solvent, the residual solid was recrystallized from CH_2Cl_2/hexane to yield **9** as red crystals. Yield: 60% from **10** and 48% from **11**, respectively.

X-ray Crystallographic Determinations of 3, 5, 7, and 9. Green-yellow crystals of **3** as well as red crystals of **5**, **7**, and **9** suitable for X-ray analyses were grown by diffusion of hexane into their CH_2Cl_2 solutions at −18 °C. All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite-monochromated Mo Kα 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. A summary of the fundamental crystal data for these complexes is listed in Table 1.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for **3**, **5**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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