

Reaction of Bis(pyrazol-1-yl)methanes Modified by Organotin Groups on the Methine Carbon with $W(CO)_5THF$ to Give Novel Heterodinuclear Organometallic Complexes

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A series of new bis(pyrazol-1-yl)methanes with organotin groups on the methine carbon have been synthesized by the reaction of bis(pyrazol-1-yl)methyl lithium with organotin halide. Their reactions with $W(CO)_5THF$ have been investigated in detail, indicating that these new ligands display versatile reactivities upon treatment with $W(CO)_5THF$, depending on the properties of the substituents on the tin atom. Treatment of triarylstannylbis(pyrazol-1-yl)methanes, $Ar_3SnCHPz_2$ (Ar = phenyl or *p*-tolyl; Pz = substituted pyrazole), with $W(CO)_5THF$ results in the oxidative addition of the tin–carbon(sp^3) bond to the tungsten(0) center to yield novel metal–metal bonded complexes $CHPz_2(CO)_3W-SnAr_3$, in which four-membered metallacycles are found and bis(pyrazol-1-yl)methide acts as a tridentate monoanionic κ^3 -[N,C,N] chelating ligand. When there are alkyl substituents in the 4-position of pyrazole rings, some decarbonylation intermediates $Ar_3SnCHPz_2W(CO)_4$ can be isolated. Sequentially heating these intermediates can also result in the oxidative addition of the tin–carbon(sp^3) bond to the tungsten(0) center, implying that the oxidative addition reaction of the tin–carbon(sp^3) bond may form these decarbonylation intermediates. While the reactions of trialkylstannylbis(pyrazol-1-yl)methanes, $R_3SnCHPz_2$ (R = Et or *i*Pr), with $W(CO)_5THF$ yield only the decarbonylation heterodinuclear complexes $R_3SnCHPz_2W(CO)_4$, in which bis(pyrazol-1-yl)methanes act as N,N-chelating bidentate ligands, no analogous oxidative addition products are obtained. However, treatment of phenyl(*tert*-butyl)stannylbis(pyrazol-1-yl)methanes, $(tBu)_2PhSnCHPz_2$ (Pz = 3,5-dimethylpyrazole or 3,4,5-trimethylpyrazole), with $W(CO)_5THF$ results in the oxidative addition of the tin–carbon(sp^2) bond instead of the tin–carbon(sp^3) bond to the tungsten(0) center to yield metal–metal bonded complexes $(tBu)_2SnCHPz_2W(CO)_3(Ph)$, in which a novel κ^3 -[N,Sn,N] coordination mode as well as asymmetric semibridging carbonyl between the W–Sn bond is observed. In addition, the reactions of trivinylstannylbis(pyrazol-1-yl)methanes, $(CH_2=CH)_3SnCHPz_2$, with $W(CO)_5THF$ result in a vinyl group bonded to the tungsten center in η^2 -fashion to give a tridentate κ^3 -(π ,N,N) coordination mode.

Introduction

Poly(pyrazol-1-yl)alkanes, especially bis(pyrazol-1-yl)methane, have been popular polydentate nitrogen donor ligands since Trofimenko's first report¹ and especially Julia's later modification.² Their coordination chemistry toward main group and transition metals has received increasing attention,^{3–5} a number of main group⁶ and transition metal⁷ complexes containing poly(pyrazol-1-yl)alkanes have been synthesized and characterized in

recent years. Their coordination behaviors can easily be adjusted by changing the electronic and steric characteristics of substituents on the pyrazole rings. Recent

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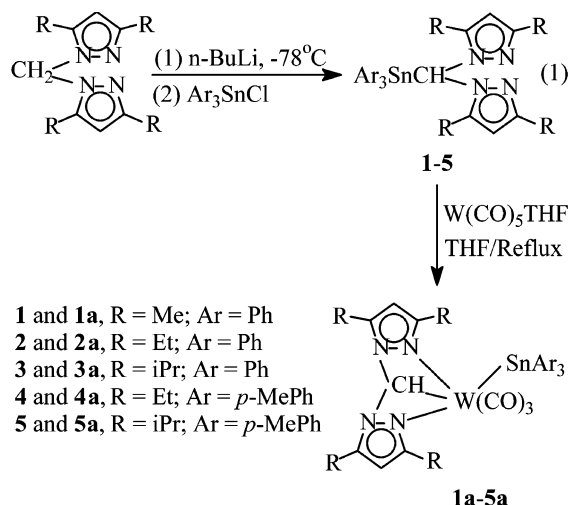
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investigations show that the bridging carbon atom can also be modified by organic functional groups to form novel heteroscorpionate ligands, which usually have asymmetric N_2O ,⁸ N_2S ,⁹ N_3S ,¹⁰ or N_3O ¹¹ coordination environments. These ligands have been of considerable interest owing to their important usage in biological enzyme models. In addition, the replacement of the bridging atom by the silicon atom to form poly(pyrazol-1-yl)silanes has also been successful.¹² However, the modification of poly(pyrazol-1-yl)alkanes by organometallic groups on the bridging carbon atom is rare.¹³ Our recent investigation on poly(pyrazol-1-yl)methanes reveals that such modification may result in unusual reactivity.¹⁴ Now we continue our investigation on the modification of poly(pyrazol-1-yl)alkanes by introducing organotin groups on the methine carbon and observing their reactions with $W(CO)_5THF$. These organometallic ligands react with $W(CO)_5THF$ to give markedly different heterodinuclear complexes, depending on the properties of substituents on the tin atom.

Results and Discussion

Modification of Bis(pyrazol-1-yl)methanes with Triarylstannyl Groups on the Methine Carbon and Their Reactions with $W(CO)_5THF$. When bis(pyrazol-1-yl)methanes were treated with butyllithium at $-78^\circ C$, their central carbon atom of the CH_2 group was deprotonated to give bis(pyrazol-1-yl)methylolithium.^{14,15} The appropriate triaryltin chloride was then added to yield products **1–5** (eq 1).



Treatment of **1–5** with $W(CO)_5THF$ in refluxing THF resulted in the oxidative addition of the $Sn-C(sp^3)$ bond

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to the tungsten(0) center to yield novel four-membered metallacyclic complexes **1a–5a**, which were characterized by 1H NMR spectroscopy, IR spectra, and elemental analyses, as well as X-ray structure analyses. The oxidative addition of a $Sn-C(sp^3)$ bond to a tungsten(0) center to yield $W-Sn$ bonded complexes with a κ^3 -[C,N,N'] ligand is known,¹⁶ but there is no prior report of tungsten complexes containing the sp^3 hybridized carbon in κ^3 -[N,C,N] ligands.¹⁷ The present results also exhibit a novel coordination mode for poly(pyrazol-1-yl)alkanes.

Complexes **1a–5a** are air-stable in the solid state, and even their solutions can be manipulated in air. They are moderately soluble in chlorinated solvents, but insoluble in alkanes and ether. The proton signals of the CH group (4.32–4.63 ppm) are considerably shifted to higher field, compared with those in **1–5**, which appear between 6.71 and 6.92 ppm. In addition, four sets of proton signals of isopropyl methyl groups have been observed in ligands **3** and **5** as well as complexes **3a** and **5a**, possibly as a result of these groups being diastereotopic, which is due to the bulky isopropyl groups in the pyrazole rings, which prevent their free rotation. Three strong $\nu(CO)$ bands in the range 1970–1830 cm^{-1} are observed in the IR spectra of **1a–5a**, which is consistent with the tricarbonyltungsten species.

The structure of **3a** has also been confirmed by X-ray crystallography as shown in Figure 1, which clearly shows that the triphenylstannyl group has been transferred to the tungsten center and that new tungsten-saturated carbon and tungsten–tin bonds have been formed. Bis(3,5-diisopropylpyrazol-1-yl)methide acts as a tridentate, monoanionic κ^3 -[N,C,N] chelating ligand, resulting in the formation of two novel four-membered metallaheterocycles. It is noteworthy that in the four-membered metallaheterocycles the angles $N-C-W$ are very close to 90° . The geometry of the seven-coordinate tungsten atom is best described as a capped octahedron with the triphenylstannyl groups in the capping position. The capped face is made up of C(2), C(3), and C(13) atoms. The $W-Sn$ distance is 2.7712(8) Å, which is similar with that in $CH(3,4,5-Me_3Pz)_2W(CO)_3SnPh_3$ (2.7795(4) Å)^{14a} and within the normal range for $W-Sn$ bonds.¹⁸ The isopropyl methyl groups are away from the metal tungsten, which is analogous to the case in hydrotris(3,5-diisopropylpyrazol-1-yl)borate complexes.¹⁹

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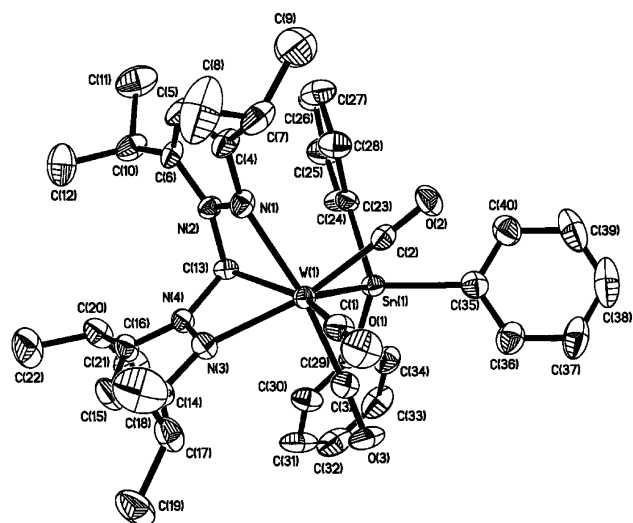
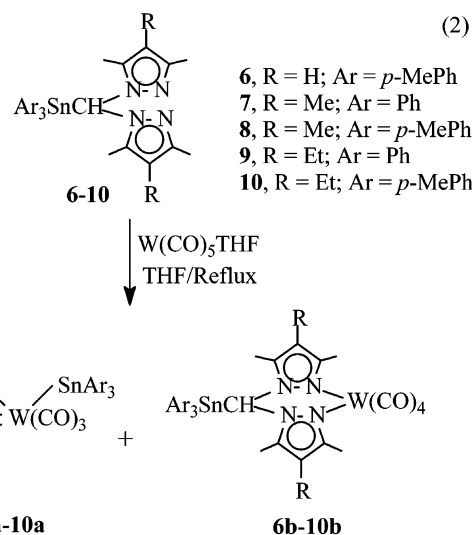


Figure 1. Molecular structure of **3a**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): W(1)–N(1) = 2.222(5), W(1)–N(3) = 2.212(5), W(1)–C(13) = 2.343(6), W(1)–Sn(1) = 2.7712(8), N(2)–C(13) = 1.463(7); N(3)–W(1)–N(1) = 81.81(19), C(13)–W(1)–Sn(1) = 76.98(15), N(1)–W(1)–C(13) = 60.41(19), C(3)–W(1)–N(1) = 170.8(2), N(4)–C(13)–N(2) = 109.5(5), C(4)–C(7)–C(9) = 111.2(7), N(2)–C(13)–W(1) = 91.4(3), N(4)–C(13)–W(1) = 91.2(3).

It has been found that the coordination behavior of poly(pyrazol-1-yl)alkanes can easily be adjusted by changing the electronic and steric characteristics of substituents in the 3-, 4-, and 5-positions of the pyrazole rings. Bulky substituents in the 3- and 5-positions of pyrazole rings prevent the accessibility of the metals to the coordinated nitrogen atoms owing to their strong steric repulsion. Equation 1 shows that stable oxidative addition products **3a** and **5a** can be formed even with bulky isopropyl groups in the 3- and 5-positions of the pyrazole rings. To investigate the influence of substituents in the 4-position of the pyrazole rings on the oxidative addition reaction, ligands **6–10** were synthesized. Treatment of these ligands with $W(CO)_5THF$ under the same experiment conditions as the above reactions of ligands **1–5** with $W(CO)_5THF$ yielded the analogous oxidative addition products **6a–10a**, accompanied by the decarbonylation complexes **6b–10b** at the same time (eq 2). It seems that the alkyl substituents in the 4-position of the pyrazole rings can stabilize the decarbonylation intermediates **7b–10b** via their electron-donating properties to increase the overall electron density of the ligands. Sequentially heating complexes **6b–10b** resulted in the oxidative addition of the Sn–C(sp³) bond to the tungsten(0) center to form complexes **6a–10a**. In addition, when heating ligands **6–10** and $W(CO)_5THF$ at reflux in THF for a long time or the reactions of these ligands with $W(CO)_6$ in dioxane at reflux yielded only complexes **6a–10a**; complexes **6b–10b** could not be obtained. The above results show that the oxidative addition reaction of the Sn–C(sp³) bond to the tungsten(0) center may form the decarbonylation intermediates **6b–10b**.

Complexes **6a–10a** and **6b–10b** have also been characterized by elemental analysis, IR, ¹H NMR spectroscopies, and for **6b** X-ray diffraction analyses. The



IR and ¹H NMR spectroscopic data of **6a–10a** are similar to those of **1a–5a**, indicating that they should have analogous structures. For example, in the ¹H NMR spectra of **6a–10a**, the proton signal of the CH group appears at ca. 4.32 ppm, and for **1a–5a** it appears between 4.32 and 4.63 ppm. However, the proton signal of the CH group in **6b–10b** is significantly different from that in **1a–10a**, which appears in the range 6.57–6.70 ppm, but is similar to that of the corresponding free ligands (6.50–6.70 ppm). The IR spectra of **6b–10b** are also different from those of **1a–10a**. Four bands in the carbonyl stretching region are observed in **6b–10b**, and these values of $\nu(CO)$ can also be compared with those reported for (N–N)M(CO)₄ complexes (N–N represents substituted bis(pyrazol-1-yl)methane),^{14b,20} indicating a typical *cis*-tetracarbonyl arrangement.

The molecular structure of **6b** has been confirmed by X-ray diffraction analyses as shown in Figure 2. As seen in Figure 2, the tungsten atom is six-coordinate with a quasi-octahedral coordination geometry; ligand **6** acts as a chelating bidentate ligand in the complex, and the tri(*p*-tolyl)stannyl group on the methine carbon lies in the axial position so as to reduce steric repulsion with the methyl groups in the 5-position of the pyrazole rings. The metallacyclic ring W–N–N–C–N–N adopts a boat conformation. The average W–N distance is 2.2715 Å, which is slightly longer than that in **3a** (2.217 Å), but comparable to those found for Ph₃GeCH(3,5-Me₂Pz)₂W(CO)₄ (2.25 Å) and Me₃SiCH(3,5-Me₂Pz)₂W(CO)₄ (2.269 Å).^{14b} In addition, the angles N(1)–W(1)–N(3) (80.8(2)°), C(1)–W(1)–C(4) (161.6(3)°), and N(2)–C(15)–N(4) (111.0(5)°) are also similar to the corresponding angles in Ph₃GeCH(3,5-Me₂Pz)₂W(CO)₄ (80.2(4)°, 160.4(3)°, and 111.1(8)°, respectively) and Me₃SiCH(3,5-Me₂Pz)₂W(CO)₄ (80.55(15)°, 162.4(2)°, and 111.6(4)°, respectively). Two *cis*-carbonyl groups are markedly distorted, with angles W(1)–C(1)–O(1) of 165.9(6)° and W(1)–C(4)–O(4) of 171.1(9)°, possibly owing to the steric repulsion between the ligand with two *cis*-carbonyls. It is worth noting that some angles around the Sn(1) and C(15) atoms (such as the angles C(23)–Sn(1)–C(15) of 98.0(3)° and N(2)–C(15)–Sn(1) of 120.0(4)°) significantly deviate from the tetrahedral geometry of the sp³ hybridized Sn(1) and

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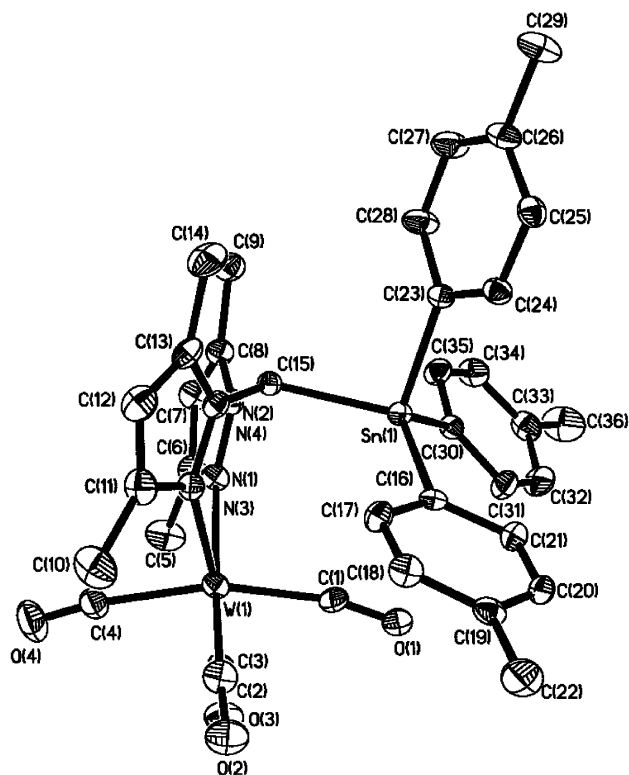


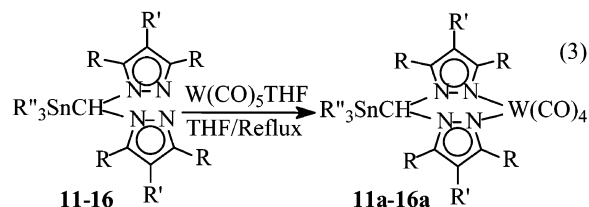
Figure 2. Molecular structure of **6b**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): W(1)–N(1) = 2.259(6), W(1)–N(3) = 2.284(6), Sn(1)–C(15) = 2.221(7), N(2)–C(15) = 1.447(8), N(4)–C(15) = 1.455(8), Sn(1)–C(16) = 2.133(6); N(1)–W(1)–N(3) = 80.8(2), C(1)–W(1)–C(4) = 161.6(3), N(2)–C(15)–N(4) = 111.0(5), W(1)–C(1)–O(1) = 165.9(6), W(1)–C(4)–O(4) = 171.1(9), C(16)–Sn(1)–C(30) = 119.5(3), C(23)–Sn(1)–C(15) = 98.0(3), N(2)–C(15)–Sn(1) = 120.0(4).

C(15) atoms, possibly owing to the repulsion among the *p*-tolyl groups and between the tri(*p*-tolyl)stannyl group and the CH(3,5-Me₂Pz)₂W(CO)₄ unit.

It is also noteworthy that despite the similar structural features between **6b**, Ph₃GeCH(3,5-Me₂Pz)₂W(CO)₄, and Me₃SiCH(3,5-Me₂Pz)₂W(CO)₄,^{14b} and even larger steric effects of the Ph₃Ge group,²¹ the analogous oxidative addition reaction of the Ge–C or Si–C bond in Ph₃GeCH(3,5-Me₂Pz)₂W(CO)₄ and Me₃SiCH(3,5-Me₂Pz)₂W(CO)₄ to the tungsten(0) center did not take place, which may be related to the lower reactivity of the Ge–C and Si–C bonds²² as well as the lower stability of the W–Ge and W–Si bonds, compared with the Sn–C and W–Sn bonds, respectively.²³

Modification of Bis(pyrazol-1-yl)methanes with Trialkylstannyl Groups on the Methine Carbon and Their Reactions with W(CO)₅THF. Ligands **11–16** were readily obtained using trialkyltin chloride instead of triaryltin chloride as described in eq 1. Treatment of these ligands with W(CO)₅THF under experimental conditions similar to those described in eq 1 yielded only heterobimetallic complexes **11a–16a**

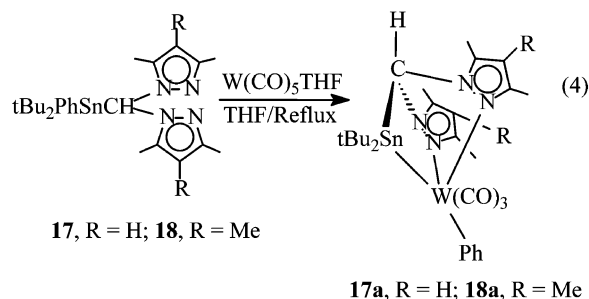
(eq 3), which were characterized by elemental analysis



- 11** and **11a**, R = Me; R' = H; R'' = Et
12 and **12a**, R = R' = Me; R'' = Et
13 and **13a**, R = Me; R' = R'' = Et
14 and **14a**, R = Et; R' = H; R'' = Et
15 and **15a**, R = *i*Pr; R' = H; R'' = Et
16 and **16a**, R = Me; R' = H; R'' = *i*Pr

and IR and ¹H NMR spectroscopies. Their IR and ¹H NMR spectroscopic data are similar to those of **6b–10b**, indicating that they have analogous structures. The analogous oxidative addition products were not obtained. Furthermore, the oxidative addition reaction of the Sn–C bond to the tungsten(0) center did not take place, even with raising the reaction temperature or prolongating the reaction time. The steric effects of substituents attached to the tin atom may not be mainly responsible for the oxidative addition reaction of the Sn–C bond to the tungsten(0) center owing to the larger steric hindrance of the ⁱPr₃Sn group in **16** than that of the Ph₃Sn group in **1**.²¹ It seems that the electronic effects of substituents attached to the tin atom play a key role. Compared to the electron-donating alkyl groups, the aryl groups have strong electron-withdrawing ability, which may decrease the electron density around the tin atom in the Ar₃Sn groups, resulting in the higher oxidative addition reactivity of the Ar₃Sn–C(sp³) bond than that of the R₃Sn–C(sp³) to the tungsten(0) center.

To verify if the aryl group is necessary for the oxidative addition reaction, ligands **17** and **18** have been synthesized (eq 4). It is interesting that treatment of



ligands **17** and **18** results in the oxidative addition reaction of the Sn–C(sp²) bond instead of the Sn–C(sp³) bond to the tungsten(0) center to yield novel complexes **17a** and **18a** in good yield. Unlike the results reported,¹⁶ the phenyl groups in **17** and **18** have no chelate-assisted effects during the oxidative addition reaction of the Sn–C(sp²) bond to the tungsten(0) center. It is likely that bulky substituents on the tin atom decrease the reactivity of the Sn–C(sp³) bond,²⁴ strengthening the reactivity of the Sn–C(sp²) bond in **17** and **18**.

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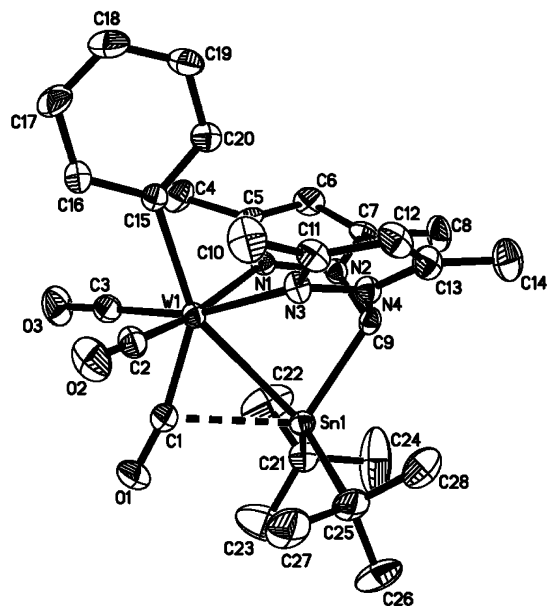
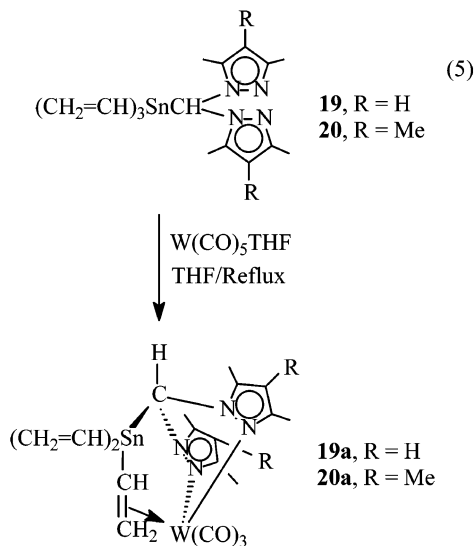


Figure 3. Molecular structure of **17a**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): W(1)–C(1) = 1.947(10), W(1)–C(2) = 1.971(10), W(1)–C(15) = 2.247(9), C(1)–O(1) = 1.185(11), C(2)–O(2) = 1.135(10), W(1)–N(1) = 2.262(6), W(1)–N(3) = 2.254(7), N(2)–C(9) = 1.453(10), N(4)–C(9) = 1.428(10), W(1)–Sn(1) = 2.8778(12), Sn(1)–C(9) = 2.237(9), Sn(1)···C(1) = 2.541(11); C(15)–W(1)–Sn(1) = 154.0(2), W(1)–C(1)–O(1) = 167.8(8), W(1)–C(2)–O(2) = 177.3(9), W(1)–C(3)–O(3) = 176.9(9), N(3)–W(1)–N(1) = 81.5(2), N(4)–C(9)–N(2) = 109.2(7), C(9)–Sn(1)–W(1) = 78.2(2).

Both complexes **17a** and **18a** have been characterized by ^1H NMR and IR spectra. They have very similar spectroscopic data. The molecular structure of **17a** has also been confirmed by X-ray diffraction analyses as shown in Figure 3. As seen in Figure 3, the phenyl group has been transferred to the tungsten center, resulting in a novel $\kappa^3\text{-(N,Sn,N)}$ coordination mode, and the phenyl group is *trans* to the organotin group with the angle C(15)–W(1)–Sn(1) of 154.0(2)°. The tungsten atom is seven-coordinate, close to the distorted capped-octahedral geometry, with the Sn(1) atom in the unique capping position and the capped face made up of N(1), N(3), and C(1) atoms. The W–Sn distance is 2.8778(12) Å, which is longer than that in **3a** (2.7712(8) Å). It is interesting to note that an asymmetric semibridging carbonyl is observed between the W–Sn bond, while such a semibridging carbonyl between the transition metal and main group metal bond is rare.²⁵ The angle W(1)–C(1)–O(1) of 167.8(8)° is significantly smaller than the angles W(1)–C(2)–O(2) of 177.3(9)° and W(1)–C(3)–O(3) of 176.9(9)° possibly owing to the existence of the semibridging carbonyl. The asymmetric parameter α for C(1)O(1) is 0.31, which falls within the range of α values for semibridging carbonyls.²⁵ In addition, the existence of the semibridging carbonyl is also in good agreement with the fact that the IR spectra of **17a** and **18a** show a low-frequency absorption band at 1783.9 cm^{-1} for **17a** and 1781.6 cm^{-1} for **18a**, respectively.

It is known that organotin compounds containing unsaturated organic groups often show special reactivi-

ties and structural features. The above results also show that bis(pyrazol-1-yl)methanes modified by organotin groups containing unsaturated aryl groups on the methine carbon display unusual reactivities. To detect if bis(pyrazol-1-yl)methanes modified by unsaturated vinyltin groups on the methine carbon have analogous reactivity, ligands **19** and **20** have been prepared (eq 5). Treatment of **19** and **20** with $\text{W}(\text{CO})_5\text{THF}$ in reflux-



ing THF yielded heterobimetallic complexes **19a** and **20a**, which were confirmed by IR and ^1H NMR spectra, as well as X-ray diffraction analyses of **19a**. The analogous oxidative addition reaction of the Sn–C(sp³) or Sn–C(sp²) bond did not take place. The proton signals of a vinyl group in **19a** and **20a** are considerably shifted to higher field compared with those of the other two vinyl groups and those in free ligands **19** and **20**, indicating that this vinyl group may be bonded to the metal.²⁶ In addition, two sets of proton signals of uncoordinated vinyl groups and bis(pyrazol-1-yl)methane ligands have been observed in complexes **19a** and **20a**, possibly owing to the steric repulsion of substituents as well as the rigidity caused by the coordination of an olefinic double bond to the tungsten center, inhibiting their free rotation in solution, or as a result of these groups being diastereotopic.

Although a number of group 6 metal carbonyl complexes containing an alkene unit as part of a polydentate ligand have been reported, most of them involve P-donors as the other chelate-assisted groups.²⁷ Complexes with chelating alkene ligands and N-donors as the other ligating groups are rare. Some group 6 metal carbonyl complexes containing intramolecular η^2 -bound arene as well as N-donor chelate ligands are known, but the η^2 -arene bonding interaction is relatively weak in these complexes.^{28,29}

To confirm the metal–olefin coordination mode, the structure of complex **19a** was determined by X-ray

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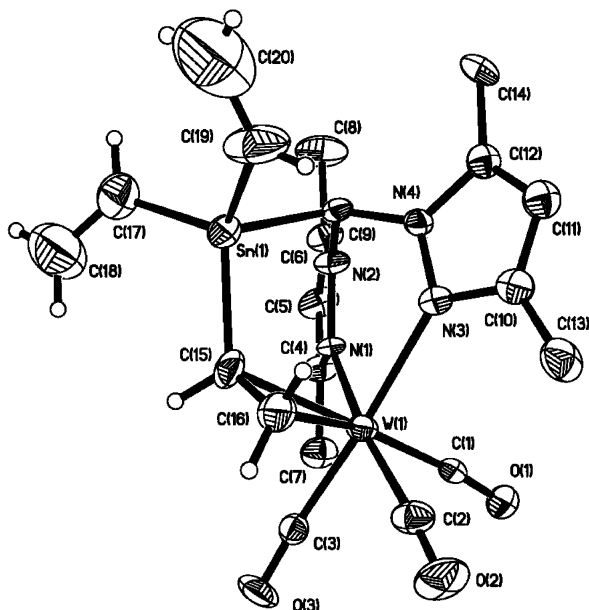


Figure 4. Molecular structure of **19a**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): W(1)–N(1) = 2.288(9), W(1)–N(3) = 2.295(9), W(1)–C(15) = 2.385(10), W(1)–C(16) = 2.361(12), C(15)–C(16) = 1.392(18), C(19)–C(20) = 1.362(10), N(2)–C(9) = 1.451(13), Sn(1)–C(9) = 2.192(11), Sn(1)–C(17) = 2.119(16), Sn(1)–C(15) = 2.070(12); C(19)–Sn(1)–C(9) = 101.9(5), C(17)–Sn(1)–C(19) = 118.8(7), N(4)–C(9)–N(2) = 112.5(9), N(2)–C(9)–Sn(1) = 112.0(7), C(15)–Sn(1)–C(9) = 104.2(4), C(16)–C(15)–Sn(1) = 124.4(11), C(18)–C(17)–Sn(1) = 125.7(14), N(1)–W(1)–N(3) = 82.6(3).

crystallography, which shows that there are two crystallographically independent molecules in the unit cell with very similar crystallographic data. For simplicity only one of them is given in Figure 4. As shown in Figure 4, a vinyl group is bound to the tungsten in η^2 -fashion, resulting in a κ^3 -(π ,N,N) coordination mode. The significantly short W–C(sp²) bond distances of 2.385(10) Å for W(1)–C(15) and 2.361(12) Å for W(1)–C(16), compared to those in PhP(3,5-Me₂Pz)₂W(CO)₃ (2.58(2) and 2.82(3) Å),^{29a} but relatively close to the value of 2.247(9) Å for the W–C(sp²) σ bond in **17a**, indicate the strong metal– π bonding interactions in **19a**, which is in good agreement with the markedly upfield shift of a vinyl group in the ¹H NMR spectrum. It is noteworthy that some angles around the Sn(1) atom (such as the angles C(19)–Sn(1)–C(9) of 101.9(5)° and C(17)–Sn(1)–C(19) of 118.8(7)°) significantly deviate from the tetrahedral geometry of the sp³ hybridized Sn(1) atom, possibly owing to the repulsion among the vinyl groups as well as between the vinyl groups with the pyrazole ligands.

Conclusions

The modification of bis(pyrazol-1-yl)methane by the substitution of organotin groups on the methine carbon atom is readily carried out. These new ligands display versatile reactivities upon treatment with W(CO)₅THF, depending on the properties of the substituents on the tin atom. The reactions of triarylstannylbis(pyrazol-1-yl)methanes with W(CO)₅THF result in the oxidative addition of the Sn–C(sp³) bond to the tungsten(0) center

to give novel four-membered metallacyclic complexes, while the analogous reactions of trialkylbis(pyrazol-1-yl)methanes with W(CO)₅THF do not take place. However, the reactions of phenyldi(*tert*-butyl)stannylbis(pyrazol-1-yl)methanes with W(CO)₅THF result in the oxidative addition reaction of the Sn–C(sp²) bond instead of the Sn–C(sp³) bond to the tungsten(0) center. In addition, the reactions of trivinylstannylbis(pyrazol-1-yl)methanes with W(CO)₅THF result in a vinyl group bonded to the tungsten center in η^2 -fashion to give a κ^3 -(π ,N,N) coordination mode.

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. ¹H NMR spectra were recorded on a Mercury 300 spectrometer using CDCl₃ as solvent unless otherwise noted. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 170SX spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240C analyzer. The preparation and spectroscopic data of **7** and **7a**, as well as **8** and **8a**, have been reported in a previous paper.^{14a} ¹³⁷Pr₃SnCl,³⁰ ¹³⁷Bu₂PhSnCl,³¹ (CH₂=CH)₃SnCl,³² bis(3,5-dimethylpyrazol-1-yl)methane,^{6a} and bis(3,4,5-trimethylpyrazol-1-yl)methane^{6a} were prepared according to the literature methods.

Preparation of Bis(3,5-diisopropylpyrazol-1-yl)methane, Bis(3,5-diethylpyrazol-1-yl)methane, and Bis(3,5-dimethyl-4-ethylpyrazol-1-yl)methane. These ligands were prepared similarly using the appropriate pyrazole with CH₂Br₂ as described for bis(pyrazol-1-yl)methane.³³ Data for bis(3,5-diisopropylpyrazol-1-yl)methane: yield 61%, mp 47–49 °C. ¹H NMR: δ 1.00, 1.18 (d, d, 12H, 12H, CH(CH₃)₂), 2.88, 3.40 (m, m, 2H, 2H, CH(CH₃)₂), 5.79 (s, 2H, H^a of pyrazole ring), 6.17 (s, 2H, CH₂). Data for bis(3,5-diethylpyrazol-1-yl)methane: yield 71%, mp 34–36 °C. ¹H NMR: δ 1.18, 1.21 (t, t, 6H, 6H, CH₂CH₃), 2.59, 2.83 (q, q, 4H, 4H, CH₂CH₃), 5.85 (s, 2H, H^a of pyrazole ring), 6.11 (s, 2H, CH₂). Data for bis(3,5-dimethyl-4-ethylpyrazol-1-yl)methane: yield 75%, mp 99–101 °C. ¹H NMR: δ 1.02 (t, 6H, CH₂CH₃), 2.15, 2.34 (s, s, 6H, 6H, CH₃), 2.29 (q, 4H, CH₂CH₃), 6.05 (s, 2H, CH₂).

Preparation of Ph₃SnCH(3,5-Me₂Pz)₂ (1). To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (0.408 g, 2 mmol) in THF (40 mL) under Ar was added a hexane solution of ⁿBuLi (2 M, 1.0 mL) at –78 °C, and the mixture was stirred for 1 h at that temperature. To the mixture was added a solution of triphenyltin chloride (0.77 g, 2 mmol) in THF (10 mL). The reaction mixture was stirred at –78 °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 0.46 g (42%) of **1** as white crystals, mp 126–128 °C. ¹H NMR: δ 1.93, 2.20 (s, s, 6H, 6H, CH₃), 5.77 (s, 2H, H^a of pyrazole ring), 6.72 (s, 1H, CH), 7.48–7.60 (m, 15H, C₆H₅). Anal. Found: C, 62.93; H, 5.42; N, 10.11. Calcd for C₂₉H₃₀N₄Sn: C, 62.96; H, 5.47; N, 10.13.

Preparation of Ph₃SnCH(3,5-Et₂Pz)₂ (2). This ligand was obtained similarly using bis(3,5-diethylpyrazol-1-yl)methane (0.52 g, 2 mmol) instead of bis(3,5-dimethylpyrazol-1-yl)methane as described above for **1**. Yield: 0.49 g (40%), mp 64–66 °C. ¹H NMR: δ 0.88, 1.11 (t, t, 6H, 6H, CH₂CH₃), 2.29, 2.57 (q, q, 4H, 4H, CH₂CH₃), 5.81 (s, 2H, H^a of pyrazole ring), 6.71 (s, 1H, CH), 7.29–7.54 (m, 15H, C₆H₅). Anal. Found: C, 65.31; H, 5.96; N, 9.56. Calcd for C₃₃H₃₈N₄Sn: C, 65.04; H, 6.28; N, 9.19.

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Preparation of $\text{Ph}_3\text{SnCH}(3,5\text{-}^i\text{Pr}_2\text{Pz})_2$ (3). This ligand was obtained as an oil, similarly using bis(3,5-diisopropylpyrazol-1-yl)methane (0.63 g, 2 mmol) instead of bis(3,5-dimethylpyrazol-1-yl)methane as described above for **1**. Yield: 0.57 g (43%). $^1\text{H NMR}$: δ 0.64, 0.76, 1.17, 1.20 (d, d, d, d, 6H, 6H, 6H, 6H, $\text{CH}(\text{CH}_3)_2$), 2.91–3.02 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 5.82 (s, 2H, H^f of pyrazole ring), 6.92 (s, 1H, CH), 7.30, 7.52 (m, m, 9H, 6H, C_6H_5).

Preparation of $(p\text{-CH}_3\text{Ph})_3\text{SnCH}(3,5\text{-Et}_2\text{Pz})_2$ (4). This ligand was obtained similarly by the reaction of bis(3,5-diethylpyrazol-1-yl)methane (0.52 g, 2 mmol) with tri(*p*-methylphenyl)tin chloride (0.855 g, 2 mmol) as described above for **1**. Yield: 0.48 g (37%), mp 81–83 °C. $^1\text{H NMR}$: δ 0.88, 1.18 (t, t, 6H, 6H, CH_2CH_3), 2.21, 2.56 (q, q, 4H, 4H, CH_2CH_3), 2.31 (s, 9H, $\text{C}_6\text{H}_4\text{CH}_3$), 5.80 (s, 2H, H^f of pyrazole ring), 6.71 (s, 1H, CH), 7.17, 7.41 (d, d, 6H, 6H, C_6H_4). Anal. Found: C, 66.15; H, 6.89; N, 8.73. Calcd for $\text{C}_{36}\text{H}_{44}\text{N}_4\text{Sn}$: C, 66.37; H, 6.81; N, 8.60.

Preparation of $(p\text{-CH}_3\text{Ph})_3\text{SnCH}(3,5\text{-}^i\text{Pr}_2\text{Pz})_2$ (5). This ligand was obtained similarly by the reaction of bis(3,5-diisopropylpyrazol-1-yl)methane (0.63 g, 2 mmol) with tri(*p*-methylphenyl)tin chloride (0.855 g, 2 mmol) as described above for **1**. Yield: 0.45 g (32%), mp 75–77 °C. $^1\text{H NMR}$: δ 0.60, 0.74, 1.20, 1.26 (d, d, d, d, 6H, 6H, 6H, 6H, $\text{CH}(\text{CH}_3)_2$), 2.34 (s, 9H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.93–3.01 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 5.80 (s, 2H, H^f of pyrazole ring), 6.91 (s, 1H, CH), 7.18, 7.46 (d, d, 6H, 6H, C_6H_4). Anal. Found: C, 67.57; H, 7.58; N, 7.65. Calcd for $\text{C}_{40}\text{H}_{52}\text{N}_4\text{Sn}$: C, 67.89; H, 7.41; N, 7.92.

Preparation of $(p\text{-CH}_3\text{Ph})_3\text{SnCH}(3,5\text{-Me}_2\text{Pz})_2$ (6). This ligand was obtained similarly using tri(*p*-methylphenyl)tin chloride (0.855 g, 2 mmol) instead of triphenyltin chloride as described above for **1**. Yield: 0.55 g (46%), mp 122–124 °C. $^1\text{H NMR}$: δ 1.64, 2.16 (s, s, 6H, 6H, CH_3), 2.30 (s, 9H, $\text{C}_6\text{H}_4\text{CH}_3$), 5.71 (s, 2H, H^f of pyrazole ring), 6.64 (s, 1H, CH), 7.12, 7.42 (d, d, 6H, 6H, C_6H_4). Anal. Found: C, 64.54; H, 6.05; N, 9.46. Calcd for $\text{C}_{32}\text{H}_{36}\text{N}_4\text{Sn}$: C, 64.56; H, 6.09; N, 9.41.

Preparation of $\text{Ph}_3\text{SnCH}(3,5\text{-Me}_2\text{-4-EtPz})_2$ (9). This ligand was obtained similarly using bis(3,5-dimethyl-4-ethylpyrazol-1-yl)methane (0.52 g, 2 mmol) instead of bis(3,5-dimethylpyrazol-1-yl)methane as described above for **1**. Yield: 0.55 g (45%), mp 99–101 °C. $^1\text{H NMR}$: δ 0.97 (t, 6H, CH_2CH_3), 1.86, 2.15 (s, s, 6H, 6H, 3 or 5- CH_3), 2.26 (q, 4H, CH_2CH_3), 6.65 (s, 1H, CH), 7.31, 7.55 (m, m, 9H, 6H, C_6H_5). Anal. Found: C, 65.28; H, 6.35; N, 9.46. Calcd for $\text{C}_{33}\text{H}_{38}\text{N}_4\text{Sn}$: C, 65.04; H, 6.29; N, 9.19.

Preparation of $(p\text{-CH}_3\text{Ph})_3\text{SnCH}(3,5\text{-Me}_2\text{-4-EtPz})_2$ (10). This ligand was obtained similarly by the reaction of bis(3,5-dimethyl-4-ethylpyrazol-1-yl)methane (0.52 g, 2 mmol) with tri(*p*-methylphenyl)tin chloride (0.855 g, 2 mmol) as described above for **1**. Yield: 0.55 g (42%), mp 81–83 °C. $^1\text{H NMR}$: δ 0.89 (t, 6H, CH_2CH_3), 1.81, 2.14 (s, s, 6H, 6H, 3 or 5- CH_3), 2.22 (q, 4H CH_2CH_3), 2.31 (s, 9H, $\text{C}_6\text{H}_4\text{CH}_3$), 6.64 (s, 1H, CH), 7.25, 7.52 (d, d, 6H, 6H, C_6H_4). Anal. Found: C, 66.61; H, 6.82; N, 8.85. Calcd for $\text{C}_{36}\text{H}_{44}\text{N}_4\text{Sn}$: C, 66.37; H, 6.81; N, 8.60.

Preparation of $\text{Et}_3\text{SnCH}(3,5\text{-Me}_2\text{Pz})_2$ (11). This ligand was obtained similarly using triethyltin chloride (0.48 g, 2 mmol) instead of triphenyltin chloride as described above for **1**. After the hexane solvent was removed under reduced pressure, a viscous oil was obtained. Yield: 0.38 g (47%). $^1\text{H NMR}$: δ 0.97 (t, 9H, CH_2CH_3), 1.12 (q, 6H, CH_2CH_3), 1.98, 2.13 (s, s, 6H, 6H, 3 or 5- CH_3), 5.73 (s, 2H, H^f of pyrazole ring), 6.18 (s, 1H, CH).

Preparation of $\text{Et}_3\text{SnCH}(3,4,5\text{-Me}_3\text{Pz})_2$ (12). This ligand was obtained similarly by the reaction of bis(3,4,5-trimethylpyrazol-1-yl)methane (0.46 g, 2 mmol) with triethyltin chloride (0.48 g, 2 mmol) as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.35 g (40%). $^1\text{H NMR}$: δ 0.91 (t, 9H, CH_2CH_3), 1.11 (q, 6H, CH_2CH_3), 1.80, 1.90, 2.07 (s, s, s, 6H, 6H, 6H, 3, 4 or 5- CH_3), 6.18 (s, 1H, CH).

Preparation of $\text{Et}_3\text{SnCH}(3,5\text{-Me}_2\text{-4-EtPz})_2$ (13). This ligand was obtained similarly by the reaction of bis(3,5-

dimethyl-4-ethylpyrazol-1-yl)methane (0.52 g, 2 mmol) with triethyltin chloride (0.48 g, 2 mmol) as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.34 g (37%). $^1\text{H NMR}$: δ 0.96 (t, 9H, SnCH_2CH_3), 1.13 (t, 6H, 4- CH_2CH_3 on pyrazole ring), 1.31 (q, 6H, SnCH_2CH_3), 1.92, 2.13 (s, s, 6H, 6H, 3 or 5- CH_3), 2.32 (q, 4H, 4- CH_2CH_3 on pyrazole ring), 6.21 (s, 1H, CH).

Preparation of $\text{Et}_3\text{SnCH}(3,5\text{-Et}_2\text{Pz})_2$ (14). This ligand was obtained similarly by the reaction of bis(3,5-diethylpyrazol-1-yl)methane (0.52 g, 2 mmol) with triethyltin chloride (0.48 g, 2 mmol) as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.37 g (40%). $^1\text{H NMR}$: δ 0.92 (t, 9H, SnCH_2CH_3), 1.02 (q, 6H, SnCH_2CH_3), 1.17, 1.23 (t, t, 6H, 6H, 3 or 5- CH_2CH_3), 2.41, 2.59 (q, q, 4H, 4H, 3 or 5- CH_2CH_3), 5.85 (s, 2H, H^f of pyrazole ring), 6.29 (s, 1H, CH).

Preparation of $\text{Et}_3\text{SnCH}(3,5\text{-}^i\text{Pr}_2\text{Pz})_2$ (15). This ligand was obtained similarly by the reaction of bis(3,5-diisopropylpyrazol-1-yl)methane (0.63 g, 2 mmol) with triethyltin chloride (0.48 g, 2 mmol) as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.4 g (38%). $^1\text{H NMR}$: δ 0.79, 0.86, 1.22 (d, d, d, 6H, 6H, 12H, $\text{CH}(\text{CH}_3)_2$), 0.95 (t, 9H, SnCH_2CH_3), 1.10 (q, 6H, SnCH_2CH_3), 2.88, 3.10 (m, m, 2H, 2H, $\text{CH}(\text{CH}_3)_2$), 5.80 (s, 2H, H^f of pyrazole ring), 6.44 (s, 1H, CH).

Preparation of $^i\text{Pr}_3\text{SnCH}(3,5\text{-Me}_2\text{Pz})_2$ (16). This ligand was obtained similarly by the reaction of bis(3,5-dimethylpyrazol-1-yl)methane (0.408 g, 2 mmol) with triisopropyltin chloride (0.57 g, 2 mmol) as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.39 g (43%). $^1\text{H NMR}$: δ 1.24 (d, 18H, $\text{CH}(\text{CH}_3)_2$), 1.47 (m, 3H, $\text{CH}(\text{CH}_3)_2$), 2.08, 2.16 (s, s, 6H, 6H, 3 or 5- CH_3), 5.76 (s, 2H, H^f of pyrazole ring), 6.24 (s, 1H, CH).

Preparation of $^t\text{Bu}_2\text{PhSnCH}(3,5\text{-Me}_2\text{Pz})_2$ (17). This ligand was obtained similarly by the reaction of bis(3,5-dimethylpyrazol-1-yl)methane (0.408 g, 2 mmol) with phenyldi(*tert*-butyl)tin chloride (0.69 g, 2 mmol) as described above for **1**. Yield: 0.46 g (45%), mp 70–72 °C. $^1\text{H NMR}$: δ 1.24 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.99, 2.16 (s, s, 6H, 6H, 3 or 5- CH_3), 5.72 (s, 2H, H^f of pyrazole ring), 6.30 (s, 1H, CH), 7.23, 7.36 (m, m, 3H, 2H, C_6H_5). Anal. Found: C, 58.61; H, 7.82; N, 10.57. Calcd for $\text{C}_{25}\text{H}_{38}\text{N}_4\text{Sn}$: C, 58.50; H, 7.46; N, 10.91.

Preparation of $^t\text{Bu}_2\text{PhSnCH}(3,4,5\text{-Me}_3\text{Pz})_2$ (18). This ligand was obtained similarly by the reaction of bis(3,4,5-trimethylpyrazol-1-yl)methane (0.46 g, 2 mmol) with phenyldi(*tert*-butyl)tin chloride (0.69 g, 2 mmol) as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.41 g (38%). $^1\text{H NMR}$: δ 1.25 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.81, 1.92, 2.12 (s, s, s, 6H, 6H, 6H, 3, 4, or 5- CH_3), 6.36 (s, 1H, CH), 7.23, 7.34 (m, m, 3H, 2H, C_6H_5).

Preparation of $(\text{CH}_2=\text{CH})_3\text{SnCH}(3,5\text{-Me}_2\text{Pz})_2$ (19). This ligand was obtained similarly using trivinyltin chloride (0.47 g, 2 mmol) instead of triphenyltin chloride as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.28 g (35%). $^1\text{H NMR}$: δ 1.98, 2.17 (s, s, 6H, 6H, 3 or 5- CH_3), 5.81 (s, 2H, H^f of pyrazole ring), 6.32 (s, 1H, CH), 5.75, 5.78, 6.16, 6.20, 6.42–6.54 (d, d, d, d, m, $\text{CH}=\text{CH}_2$).

Preparation of $(\text{CH}_2=\text{CH})_3\text{SnCH}(3,4,5\text{-Me}_3\text{Pz})_2$ (20). This ligand was obtained similarly by the reaction of trivinyltin chloride (0.47 g, 2 mmol) with bis(3,4,5-trimethylpyrazol-1-yl)methane (0.46 g, 2 mmol) as described above for **1**. A viscous oil was obtained after the hexane solvent was removed. Yield: 0.28 g (32%). $^1\text{H NMR}$: δ 1.82, 1.89, 2.11 (s, s, s, 6H, 6H, 6H, 3, 4, or 5- CH_3), 6.34 (s, 1H, CH), 5.68, 5.75, 6.14, 6.18, 6.42–6.53 (d, d, d, d, m, $\text{CH}=\text{CH}_2$).

Reactions of 1–5 with $\text{W}(\text{CO})_5\text{THF}$ to Give $\text{CH}(3,5\text{-Me}_2\text{Pz})_2\text{W}(\text{CO})_3\text{SnPh}_3$ (1a), $\text{CH}(3,5\text{-Et}_2\text{Pz})_2\text{W}(\text{CO})_3\text{SnPh}_3$ (2a), $\text{CH}(3,5\text{-}^i\text{Pr}_2\text{Pz})_2\text{W}(\text{CO})_3\text{SnPh}_3$ (3a), $\text{CH}(3,5\text{-Et}_2\text{Pz})_2\text{W}(\text{CO})_3\text{Sn}(p\text{-MePh})_3$ (4a), and $\text{CH}(3,5\text{-}^i\text{Pr}_2\text{Pz})_2\text{W}(\text{CO})_3\text{Sn}(p\text{-MePh})_3$ (5a). Since all reactions were run similarly, a general procedure was described. Ligand (0.3 mmol) was added to a solution of $\text{W}(\text{CO})_5\text{THF}$ in THF, prepared in situ by the

irradiation of a solution of $W(CO)_6$ (0.3 mmol) in THF (20 mL) for 8 h, and the mixture was stirred and heated at reflux for 2 h. After the reaction was completed, the solvent was removed under reduced pressure, and the residual solid was purified by column chromatography on alumina using CH_2Cl_2 /hexane (1:2 v/v) as eluent. The eluate was concentrated to dryness again, and the residual solid was recrystallized from CH_2Cl_2 /hexane to give orange-red crystals.

Spectroscopic Data for 1a. Yield: 36%. 1H NMR: δ 1.80, 2.32 (s, s, 6H, 6H, 3 or 5- CH_3), 4.32 (s, 1H, CH), 5.59 (s, 2H, H^f of pyrazole ring), 7.23–7.34 (m, 15H, C_6H_5). IR (cm^{-1}): 1970.5 vs, 1879.4 s, 1849.6 vs [ν (CO)]. Anal. Found: C, 47.06; H, 3.59; N, 6.59. Calcd for $C_{32}H_{30}N_4O_3SnW$: C, 46.81; H, 3.68; N, 6.82.

Spectroscopic Data for 2a. Yield: 34%. 1H NMR: δ 1.07, 1.32 (t, t, 6H, 6H, CH_2CH_3), 2.15, 2.73 (q, q, 4H, 4H, CH_2CH_3), 4.41 (s, 1H, CH), 5.67 (s, 2H, H^f of pyrazole ring), 7.21, 7.41 (m, m, 9H, 6H, C_6H_5). IR (cm^{-1}): 1967.0 vs, 1875.3 vs, 1850.8 vs [ν (CO)]. Anal. Found: C, 49.61; H, 4.18; N, 6.69. Calcd for $C_{36}H_{38}N_4O_3SnW$: C, 49.29; H, 4.37; N, 6.39.

Spectroscopic Data for 3a. Yield: 41%. 1H NMR: δ 0.87, 1.10, 1.31, 1.38 (d, d, d, d, 6H, 6H, 6H, 6H, $CH(CH_3)_2$), 2.54–2.63, 3.06–3.16 (m, m, 2H, 2H, $CH(CH_3)_2$), 4.63 (s, 1H, CH), 5.63 (s, 2H, H^f of pyrazole ring), 7.22, 7.45 (m, m, 9H, 6H, C_6H_5). IR (cm^{-1}): 1971.4 vs, 1879.4 vs, 1862.9 vs, 1831.9 sh [ν (CO)]. Anal. Found: C, 50.75; H, 5.08; N, 6.29. Calcd for $C_{40}H_{46}N_4O_3SnW$: C, 51.47; H, 4.97; N, 6.01.

Spectroscopic Data for 4a. Yield: 28%. 1H NMR: δ 0.87, 1.20 (t, t, 6H, 6H, CH_2CH_3), 2.15, 2.70 (q, q, 4H, 4H, CH_2CH_3), 4.39 (s, 1H, CH), 5.65 (s, 2H, H^f of pyrazole ring), 7.06, 7.30 (d, d, 6H, 6H, C_6H_4). IR (cm^{-1}): 1968.1 s, 1878.1 s, 1856.1 vs [ν (CO)]. Anal. Found: C, 50.68; H, 4.94; N, 6.15. Calcd for $C_{39}H_{44}N_4O_3SnW$: C, 50.95; H, 4.82; N, 6.09.

Spectroscopic Data for 5a. Yield: 35%. 1H NMR: δ 0.87, 1.08, 1.25, 1.35, (d, d, d, d, 6H, 6H, 6H, 6H, $CH(CH_3)_2$), 2.28 (s, 9H, $C_6H_4CH_3$), 2.60, 3.10 (m, m, 2H, 2H, $CH(CH_3)_2$), 4.59 (s, 1H, CH), 5.62 (s, 2H, H^f of pyrazole ring), 7.03, 7.32 (d, d, 6H, 6H, C_6H_4). IR (cm^{-1}): 1964.7 vs, 1875.4 s, 1854.4 vs, 1824.1 sh [ν (CO)]. Anal. Found: C, 52.83; H, 5.31; N, 5.74. Calcd for $C_{43}H_{52}N_4O_3SnW$: C, 52.94; H, 5.37; N, 5.74.

Reactions of 6–10 with $W(CO)_5$ THF to Give $CH(3,5-Me_2Pz)_2W(CO)_3Sn(p-MePh)_3$ (6a), $(p-MePh)_3SnCH(3,5-Me_2Pz)_2W(CO)_4$ (6b), $CH(3,4,5-Me_3Pz)_2W(CO)_3SnPh_3$ (7a), $Ph_3SnCH(3,4,5-Me_3Pz)_2W(CO)_4$ (7b), $CH(3,4,5-Me_3Pz)_2W(CO)_3Sn(p-MePh)_3$ (8a), $(p-MePh)_3SnCH(3,4,5-Me_3Pz)_2W(CO)_4$ (8b), $CH(3,5-Me_2-4-EtPz)_2W(CO)_3SnPh_3$ (9a), $Ph_3SnCH(3,5-Me_2-4-EtPz)_2W(CO)_4$ (9b), $CH(3,5-Me_2-4-EtPz)_2W(CO)_3Sn(p-MePh)_3$ (10a), and $(p-MePh)_3SnCH(3,5-Me_2-4-EtPz)_2W(CO)_4$ (10b). The reactions were carried out similarly as described above for the reactions of 1–5 with $W(CO)_5$ THF. After the reaction was complete, the solvent was removed under reduced pressure. The residual solid was purified by column chromatography on alumina using CH_2Cl_2 /hexane (1:2 v/v) as eluent to yield two products. The first orange-red band was confirmed as compounds 6a–10a, respectively, and the second green-yellow band was confirmed as compounds 6b–10b, respectively, by their spectroscopic data as well as X-ray crystal diffraction.

Spectroscopic Data for 6a and 6b. 6a: Yield: 30%. 1H NMR: δ 1.81, 2.28 (s, s, 6H, 6H, 3 or 5- CH_3), 2.31 (s, 9H, $C_6H_4CH_3$), 4.32 (s, 1H, CH), 5.60 (s, 2H, H^f of pyrazole ring), 7.01, 7.27 (d, d, 6H, 6H, C_6H_4). IR (cm^{-1}): 1937.9 vs, 1875.9 s, 1855.5 vs [ν (CO)]. Anal. Found: C, 48.67; H, 4.07; N, 6.43. Calcd for $C_{35}H_{36}N_4O_3SnW$: C, 48.70; H, 4.20; N, 6.49. 6b: Yield: 8%. 1H NMR: δ 2.03, 2.55 (s, s, 6H, 6H, 3 or 5- CH_3), 2.31 (s, 9H, $C_6H_4CH_3$), 6.01 (s, 2H, H^f of pyrazole ring), 6.57 (s, 1H, CH), 7.01, 7.09 (d, d, 6H, 6H, C_6H_4). IR (cm^{-1}): 2005.7 m, 1888.4 s, 1850.0 vs, 1822.9 vs [ν (CO)]. Anal. Found: C, 48.73; H, 4.25; N, 6.18. Calcd for $C_{36}H_{36}N_4O_4SnW$: C, 48.52; H, 4.07; N, 6.29.

Spectroscopic Data for 7b. Yield: 9%. 1H NMR: δ 1.94, 1.96, 2.51 (s, s, s, 6H, 6H, 6H, 3, 4, or 5- CH_3), 6.70 (s, 1H,

CH), 7.14, 7.33 (m, m, 6H, 9H, C_6H_5). IR (cm^{-1}): 1995.6 vs, 1878.9 sh, 1850.8 vs, 1835.2 vs [ν (CO)]. Anal. Found: C, 47.86; H, 3.87; N, 6.61. Calcd for $C_{35}H_{34}N_4O_4SnW$: C, 47.92; H, 3.91; N, 6.39.

Spectroscopic Data for 8b. Yield: 13%. 1H NMR: δ 1.93, 1.96, 2.51 (s, s, s, 6H, 6H, 6H, 3, 4, or 5- CH_3), 2.31 (s, 9H, $C_6H_4CH_3$), 6.66 (s, 1H, CH), 7.08, 7.13 (d, d, 6H, 6H, C_6H_4). IR (cm^{-1}): 1994.6 s, 1859.4 (br) vs, 1834.6 s [ν (CO)]. Anal. Found: C, 49.51; H, 4.21; N, 5.98. Calcd for $C_{38}H_{40}N_4O_4SnW$: C, 49.65; H, 4.39; N, 6.09.

Spectroscopic Data for 9a and 9b. 9a: Yield: 34%. 1H NMR: δ 0.98 (t, 6H, CH_2CH_3), 1.78, 2.29 (s, s, 6H, 6H, 3 or 5- CH_3), 2.34 (q, 4H, CH_2CH_3), 4.31 (s, 1H, CH), 7.22, 7.39 (m, m, 9H, 6H, C_6H_5). IR (cm^{-1}): 1968.3 vs, 1875.7 s, 1842.3 vs [ν (CO)]. Anal. Found: C, 48.22; H, 3.97; N, 6.28. Calcd for $C_{36}H_{38}N_4O_3SnW \cdot 0.25CH_2Cl_2$: C, 48.46; H, 4.29; N, 6.24. 9b: Yield: 10%. 1H NMR: δ 1.08 (t, 6H, CH_2CH_3), 1.98, 2.42 (s, s, 6H, 6H, 3 or 5- CH_3), 2.39 (q, 4H, CH_2CH_3), 6.69 (s, 1H, CH), 7.12, 7.36 (m, m, 6H, 9H, C_6H_5). IR (cm^{-1}): 1997.3 s, 1883.4 s, 1868 s, 1844.8 sh, 1832.3 vs [ν (CO)]. Anal. Found: C, 48.86; H, 4.52; N, 6.38. Calcd for $C_{37}H_{38}N_4O_4SnW$: C, 49.09; H, 4.23; N, 6.19.

Spectroscopic Data for 10a and 10b. 10a: Yield: 32%. 1H NMR: δ 1.03 (t, 6H, CH_2CH_3), 1.74 (s, 6H, 3 or 5- CH_3), 2.25–2.28 (m, 19H, 3 or 5- CH_3 , CH_2CH_3 and $C_6H_4CH_3$), 4.34 (s, 1H, CH), 7.03, 7.24 (d, d, 6H, 6H, C_6H_4). IR (cm^{-1}): 1972.4 s, 1929.3 m, 1882.6 s, 1858.7 s [ν (CO)]. Anal. Found: C, 50.68; H, 4.54; N, 6.47. Calcd for $C_{39}H_{44}N_4O_3SnW$: C, 50.95; H, 4.82; N, 6.09. 10b: Yield: 10%. 1H NMR: δ 1.08 (t, 6H, CH_2CH_3), 1.99, 2.33 (s, s, 6H, 6H, 3 or 5- CH_3), 2.41 (q, 4H, CH_2CH_3), 2.55 (s, 9H, $C_6H_4CH_3$), 6.66 (s, 1H, CH), 6.99, 7.13 (d, d, 6H, 6H, C_6H_4). IR (cm^{-1}): 1999.5 s, 1882.0 sh, 1868.1 s, 1851.5 vs, 1831.8 vs, [ν (CO)]. Anal. Found: C, 50.85; H, 4.92; N, 6.26. Calcd for $C_{40}H_{44}N_4O_4SnW$: C, 50.71; H, 4.68; N, 5.91.

The reaction of ligands 6–10 with $W(CO)_6$ in dioxane at reflux for 12 h directly yielded complexes 6a–10a, and complexes 6b–10b could not be obtained.

Heating Complexes 9b and 10b at 60 °C in $CDCl_3$. First, the 1H NMR spectra of 9b and 10b (15 mg) in $CDCl_3$ (0.6 mL) were recorded; then, the solution was heated at 60 °C for 30 min. After cooling to room temperature, the 1H NMR spectra were recorded again. The results showed that the signal of protons at 6.69 ppm for 9b and 6.66 ppm for 10b disappeared, and a new proton signal at 4.31 ppm for 9b and 4.34 ppm for 10b was observed, respectively.

Reactions of 11–16 with $W(CO)_5$ THF to Give $Et_3SnCH(3,5-Me_2Pz)_2W(CO)_4$ (11a), $Et_3SnCH(3,4,5-Me_3Pz)_2W(CO)_4$ (12a), $Et_3SnCH(3,5-Me_2-4-EtPz)_2W(CO)_4$ (13a), $Et_3SnCH(3,5-Et_2Pz)_2W(CO)_4$ (14a), $Et_3SnCH(3,5-Pr_2Pz)_2W(CO)_4$ (15a), and $Pr_3SnCH(3,5-Me_2Pz)_2W(CO)_4$ (16a). The same procedure was followed as described above for the reactions of 1–5 with $W(CO)_5$ THF. Only complexes 11a–16a were obtained as green-yellow solids; no analogous oxidative addition products of 1a were obtained.

Spectroscopic Data for 11a. Yield: 48%. 1H NMR: δ 1.03 (t, 9H, CH_2CH_3), 1.21 (q, 6H, CH_2CH_3), 2.32, 2.50 (s, s, 6H, 6H, 3 or 5- CH_3), 5.95 (s, 2H, H^f of pyrazole ring), 6.25 (s, 1H, CH). IR (cm^{-1}): 1999.6 s, 1879.0 vs, 1860.4 vs, 1822.5 vs [ν (CO)]. Anal. Found: C, 35.64; H, 4.35; N, 7.72. Calcd for $C_{21}H_{30}N_4O_4SnW$: C, 35.78; H, 4.29; N, 7.95.

Spectroscopic Data for 12a. Yield: 52%. 1H NMR: δ 1.02 (t, 9H, CH_2CH_3), 1.18 (q, 6H, CH_2CH_3), 1.91, 2.25, 2.45 (s, s, s, 6H, 6H, 6H, 3, 4, or 5- CH_3), 6.33 (s, 1H, CH). IR (cm^{-1}): 1991.9 s, 1925.9 w, 1864.9 vs, 1832.4 vs [ν (CO)]. Anal. Found: C, 37.48; H, 4.56; N, 7.77. Calcd for $C_{23}H_{34}N_4O_4SnW$: C, 37.68; H, 4.67; N, 7.64.

Spectroscopic Data for 13a. Yield: 42%. 1H NMR: δ 0.98–1.12 (m, 21H, $SnCH_2CH_3$ and 4- CH_2CH_3 of pyrazole ring), 2.28, 2.50 (s, s, 6H, 6H, 3 or 5- CH_3), 2.41 (q, 4H, 4- CH_2CH_3 of pyrazole ring), 6.34 (s, 1H, CH). IR (cm^{-1}): 1997.3 s, 1878.8 s, 1862.6 s, 1822.7 s [ν (CO)]. Anal. Found: C, 39.68;

Table 1. Crystallographic Data for Compounds 3a, 6b, 17a, and 19a

	3a	6b ·H ₂ O	17a ·2CH ₂ Cl ₂	19a
formula	C ₄₀ H ₄₆ N ₄ O ₃ SnW	C ₃₆ H ₃₈ N ₄ O ₅ SnW	C ₃₀ H ₄₂ Cl ₄ N ₄ O ₃ SnW	C ₂₀ H ₂₄ N ₄ O ₃ SnW
fw	933.35	909.24	951.02	670.97
cryst size, mm	0.22 × 0.20 × 0.16	0.30 × 0.25 × 0.05	0.25 × 0.20 × 0.20	0.16 × 0.10 × 0.06
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
cell params				
<i>a</i> (Å)	11.050(3)	11.467(3)	14.224(7)	9.463(3)
<i>b</i> (Å)	21.455(6)	22.037(6)	15.507(8)	14.280(5)
<i>c</i> (Å)	17.805(5)	15.422(4)	17.597(9)	34.137(9)
β (deg)	107.101(5)	100.008(5)	106.315(8)	94.382(7)
<i>V</i> , Å ³	4035(2)	3837.6(17)	3725(3)	4600(2)
<i>Z</i>	4	4	4	8
<i>T</i> (K)	293	293	293	293
calcd density (Mg m ⁻³)	1.536	1.574	1.696	1.938
<i>F</i> (000)	1848	1784	1864	2560
μ , mm ⁻¹	3.507	3.689	4.077	6.110
no. of reflns colld	18 932	15 735	15 634	26 238
no. of reflns obsd with (<i>I</i> ≥ 2σ(<i>I</i>))	8253	6723	7455	9460
no. of params	443	432	416	514
<i>R</i> , <i>R</i> _w (<i>I</i> ≥ 2σ(<i>I</i>))	0.0497, 0.0634	0.0413, 0.0810	0.0484, 0.0892	0.0638, 0.0895
goodness-of-fit on <i>F</i> ²	0.950	0.918	1.030	1.021

H, 5.31; N, 7.54. Calcd for C₂₅H₃₈N₄O₄SnW: C, 39.45; H, 5.03; N, 7.36.

Spectroscopic Data for 14a. Yield: 36%. ¹H NMR: δ 0.99–1.13 (m, 15H, SnCH₂CH₃), 1.27, 1.33 (t, t, 6H, 6H, 3 or 5-CH₂CH₃), 2.59–2.86 (m, 8H, 3 or 5-CH₂CH₃), 6.03 (s, 2H, H^β of pyrazole ring), 6.31 (s, 1H, CH). IR (cm⁻¹): 1998.4 s, 1877.8 vs, 1846.9 vs, 1820.5 vs [ν (CO)]. Anal. Found: C, 39.78; H, 5.34; N, 7.63. Calcd for C₂₅H₃₈N₄O₄SnW: C, 39.45; H, 5.03; N, 7.36.

Spectroscopic Data for 15a. Yield: 41%. ¹H NMR: δ 0.81, 0.89, 1.24 (d, d, d, 6H, 6H, 12H, 6H, CH(CH₃)₂), 1.01 (t, 9H, SnCH₂CH₃), 1.12 (q, 6H, SnCH₂CH₃), 2.88, 3.10 (m, m, 2H, 2H, CH(CH₃)₂), 5.81 (s, 2H, H^β of pyrazole ring), 6.44 (s, 1H, CH). IR (cm⁻¹): 2002.0 s, 1924.0 m, 1858.9 vs, 1830.7 vs [ν (CO)]. Anal. Found: C, 42.30; H, 5.77; N, 7.23. Calcd for C₂₆H₄₆N₄O₄SnW: C, 42.62; H, 5.67; N, 6.85.

Spectroscopic Data for 16a. Yield: 44%. ¹H NMR: δ 1.16 (d, 18H, SnCH(CH₃)₂), 1.89 (m, 3H, SnCH(CH₃)₂), 2.38, 2.53 (s, s, 6H, 6H, 3 or 5-CH₃), 5.96 (s, 2H, H^β of pyrazole ring), 6.36 (s, 1H, CH). IR (cm⁻¹): 1997.8 s, 1882.3 s, 1854.6 s, 1823.6 s [ν (CO)]. Anal. Found: C, 38.35; H, 4.56; N, 7.83. Calcd for C₂₄H₃₆N₄O₄SnW: C, 38.58; H, 4.86; N, 7.50.

Reactions of 11 and 12 with W(CO)₆. These reactions were carried out in dioxane at reflux for 12 h to give compounds **11a** and **12a**.

Reactions of 17 and 18 with W(CO)₅THF to Give **Bu₂SnCH(3,5-Me₂Pz)₂W(CO)₃Ph (17a) and **Bu₂SnCH(3,4,5-Me₃Pz)₂W(CO)₃Ph (18a)**.** The same procedure was followed as described above for the reactions of **1–5** with W(CO)₅THF, but the reaction time was 4 h. After recrystallized from CH₂Cl₂/hexane, compounds **17a** and **18a** were obtained as green-yellow crystals.

Spectroscopic Data for 17a. Yield: 53%. ¹H NMR: δ 1.10 (s, 18H, C(CH₃)₃), 1.82, 2.46 (s, s, 6H, 6H, 3 or 5-CH₃), 5.86 (s, 2H, H^β of pyrazole ring), 6.19 (s, 1H, CH), 6.85, 7.23 (m, m, 3H, 2H, C₆H₅). IR (cm⁻¹): 1966.6 vs, 1878.1 vs, 1783.9 s [ν (CO)]. Anal. Found: C, 42.83; H, 4.66; N, 6.84. Calcd for C₂₈H₃₈N₄O₃SnW: C, 43.05; H, 4.90; N, 7.17.

Spectroscopic Data for 18a. Yield: 48%. ¹H NMR: δ 1.19 (s, 18H, C(CH₃)₃), 1.76, 1.85, 2.39 (s, s, s, 6H, 6H, 6H, 3, 4, or 5-CH₃), 6.23 (s, 1H, CH), 6.86, 7.22 (m, m, 3H, 2H, C₆H₅). IR (cm⁻¹): 1959.1 s, 1861.1 s, 1781.6 s [ν (CO)]. Anal. Found: C, 44.23; H, 5.34; N, 7.04. Calcd for C₃₀H₄₂N₄O₃SnW: C, 44.52; H, 5.23; N, 6.92.

Reactions of 19 and 20 with W(CO)₅THF to Give (CH₂=CH)₃SnCH(3,5-Me₂Pz)₂W(CO)₃ (19a) and **(CH₂=CH)₃SnCH(3,4,5-Me₃Pz)₂W(CO)₃ (20a)**. The same procedure was followed as described above for the reactions of **1–5** with W(CO)₅THF, but the reaction time was 12 h. After recrystallization from CH₂Cl₂/hexane, compounds **19a** and **20a** were obtained as orange-red crystals.

Spectroscopic Data for 19a. Yield: 35%. ¹H NMR: δ 2.30, 2.38, 2.42, 2.61 (s, s, s, s, 3H, 3H, 3H, 3H, 3 or 5-CH₃), 2.49, 3.40, 4.70 (dd, d, d, 1H, 1H, 1H, η²-CH=CH₂), 5.20, 5.38, 6.10–6.26 (dd, dd, m, 1H, 1H, 4H, CH=CH₂), 5.84, 6.03–6.08 (s, m, 1H, 2H, H^β of pyrazole ring and CH). IR (cm⁻¹): 1930.6 vs, 1846.9 m, 1830.7 s, 1824.0 s, 1780.2 vs [ν (CO)]. Anal. Found: C, 35.43; H, 3.43; N, 8.14. Calcd for C₂₀H₂₄N₄O₃SnW: C, 35.80; H, 3.61; N, 8.35.

Spectroscopic Data for 20a. Yield: 30%. ¹H NMR: δ 1.85, 1.95 (s, s, 3H, 3H, 4-CH₃), 2.22, 2.30, 2.37, 2.56 (s, s, s, s, 3H, 3H, 3H, 3H, 3 or 5-CH₃), 2.49, 3.41, 4.72 (dd, d, d, 1H, 1H, 1H, η²-CH=CH₂), 5.21, 5.40, 5.94–6.01, 6.08–6.24 (dd, dd, m, m, 1H, 1H, 2H, 2H, CH=CH₂), 6.05 (s, 1H, CH). IR (cm⁻¹): 1931.6 s, 1848.5 sh, 1832.7 s, 1789.2 s [ν (CO)]. Anal. Found: C, 36.65; H, 4.24; N, 7.93. Calcd for C₂₂H₂₈N₄O₃SnW·0.5CH₂Cl₂: C, 36.44; H, 3.94; N, 7.56.

X-ray Crystallographic Determination of 3a, 6b, 17a, and 19a. Orange-red crystals of **3a** and **19a** as well as green-yellow crystals of **6b** suitable for X-ray analyses were grown by slow diffusion of hexane into the CH₂Cl₂ solution of **3a**, **19a**, and **6b** at –10 °C. Green-yellow crystals of **17a** suitable for X-ray analyses were obtained by slowly evaporating the CH₂Cl₂/hexane solution of **17a** at 4 °C. The crystals of complex **17a** quickly eliminated the partly incorporated solvents when taken out of the solvent phase, so the single crystal of complex **17a** was sealed in a capillary tube. In **17a** the methyl carbon atoms of a *tert*-butyl group (C(26), C(27), and C(28)) were found to be disordered. Satisfactory results were obtained when C(26), C(27), and C(28) were given occupancy factors of 0.58 and C(26)', C(27)', and C(28)' were given occupancy factors of 0.42. All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 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 complexes **3a**, **6b**, **17a**, and **19a** is listed in Table 1.

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Supporting Information Available: Table of crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for **3a**, **6b**, **17a**, and **19a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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