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# The modification of bis(pyrazol-1-yl)methanes by chalcogen (S and Se) and their related reactions with organotin chloride and M(CO)$_5$THF (M = Mo and W)

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## Abstract

The modification of bis(pyrazol-1-yl)methane by sulfur or selenium on the methine carbon has been successfully carried out by the reaction of the bis(pyrazol-1-yl)methide anion, prepared in situ by the reaction of bis(pyrazol-1-yl)methane with *n*-BuLi, with elemental sulfur or selenium. These bis(pyrazol-1-yl)methylthiolate or selenolate anions reacted with Ph$_2$SnCl$_2$ to form new organotin derivatives CH(3,5-Me$_2$Pz)$_2$ESnPh$_2$Cl (Pz = pyrazol-1-yl, E = S (**1**) or Se (**2**)), which have been characterized by NMR, IR and elemental analysis. The molecular structure of **2** determined by X-ray structure analysis indicates that bis(3,5-dimethylpyrazol-1-yl)methylselenolate is a bidentate monoanionic κ$^2$-[N,Se] chelating ligand. The treatment of CH(3,5-Me$_2$Pz)$_2$ESnPh$_2$Cl with W(CO)$_5$THF resulted in the decomposition of ligands to yield pyrazole derivative of (3,5-Me$_2$PzH)W(CO)$_5$, while direct treatment of bis(pyrazol-1-yl)methylthiolate or selenolate anions with M(CO)$_5$THF (M = Mo or W) formed their tricarbonyl metal anions CH(Pz)$_2$EM(CO)$_3^-$. Succedent reaction of these carbonyl metal anions with Ph$_2$SnCl$_2$ or Ph$_3$SnCl yielded heterobimetalic compounds CH(Pz)$_2$EM(CO)$_3$SnPh$_n$Cl$_{3-n}$ (*n* = 2 or 3), which have also been characterized by $^1$H NMR, IR and elemental analysis. The structure of CH(3,4,5-Me$_3$Pz)$_2$SW(CO)$_3$SnPh$_3$ (**8**) has been confirmed by X-ray single crystal diffraction, showing that bis(3,4,5-trimethylpyrazol-1-yl)methylthiolate acts as a tridentate, monoanionic κ$^3$-[N,S,N] chelating ligand.
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*Keywords:* Bis(pyrazol-1-yl)methane; Organotin; Group 6 metal carbonyl complex; Chalcogen

## 1. Introduction

Bis(pyrazol-1-yl)methane has been one of the most popular nitrogen-containing donor ligands since Trofimenko's first report [1] and especially Julia's later modification [2]. Its coordination behavior towards main group and transition metal has been extensively investigated [3]. In recent years, the modification of bis(pyrazol-1-yl)methane by organic functional groups on the bridging carbon atom to form new heteroscorpionate ligand has also drawn extensive attention, and these new heteroscorpionate ligands have been extensively exploited to form various main group and transition metal complexes [3,4]. Our recent investigations on bis(pyrazol-1-yl)methane indicate that the modification of this ligand with organotin groups on the methine carbon atom can provide unusual reactivity [5–7]. For example, the reaction of triarylstannyl-bis(pyrazol-1-yl)methane with W(CO)$_5$THF results in oxidative addition of the Sn–C$_{sp^3}$ bond to the tungsten(0) center, while the analogous reaction of trialkylstannyl-bis(pyrazol-1-yl)methane with W(CO)$_5$THF does not take place [5]. On the other hand, chalcogene-containing ligands are good donors owing to the high affinity of chalcogen elements for many transition and main group metal atoms. Because of their various potential applications in synthetic and technical chemistry, metal–chalcogenolate complexes have received increasing attention [8]. Some bis(pyrazol-1-yl)methanes with sulfur and their complexes have also been prepared and exhibited unusual structure and proper-

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ties [9–18], which encourages us to continue our investigation of the modification of bis(pyrazol-1-yl)methane by introducing chalcogen elements on the methine carbon. In the present work we report the direct modification of bis(pyrazol-1-yl)methane by sulfur and selenium on the bridging carbon atom, and their related reactions with organotin chloride and M(CO)$_5$THF (M = Mo or W).

## 2. Results and discussion

### 2.1. Reaction of lithium bis(3,5-dimethylpyrazol-1-yl)methylthiolate or selenolate with organotin chloride

It is well-known that the reaction of the carbon anions with chalcogen such as sulfur or selenium gives alkylthiolate or alkylselenolate anions [8]. Similarly, treatment of bis(3,5-dimethylpyrazol-1-yl)methide anion, prepared in situ by the reaction of bis(3,5-dimethylpyrazol-1-yl)methane with *n*-BuLi at −70 °C, with sulfur or selenium yielded lithium bis(3,5-dimethylpyrazol-1-yl)methylthiolate or selenolate. These thiolate and selenolate anions were stable at room temperature, and easily reacted with Ph$_2$SnCl$_2$ to form compounds **1** and **2** (Scheme 1). We recently found that bis(pyrazol-1-yl)methane modified by organotin groups on the methine carbon may provide unusual reactivity [5]. Furthermore, the oxidative addition of the Sn–E (E = S or Se) bond to low oxidative transition metal complexes is known [19]. Herein, when compounds **1** and **2** were treated with W(CO)$_5$(THF) under the same experimental conditions as the reaction of Ph$_3$SnCHPz$_2$ with W(CO)$_5$(THF) [5], only known compound **3** was isolated with the decomposition of compounds **1** and **2**, no similar reaction taking place. The pentacoordinated tin possibly leads to the low reactivity of the Sn–E bond to tungsten carbonyl. In addition, the cleavage of the N–C$_{sp^3}$ bond of poly(pyrazol-1-yl)alkane has also been observed in other coordinative reactions [6,20–22].

Compounds **1** and **2** have been characterized by elemental analyses, as well as NMR spectra. One proton signal of CH group is observed in **1** (7.49 ppm) and **2** (7.57 ppm), respectively, markedly shifted to the lower field than that of the methylene group in bis(3,5-dimethylpyrazol-1-

yl)methane (5.94 ppm), due to the deshielding effect by the electronegative nitrogen and sulfur atoms. In addition, the $^{119}$Sn NMR signals of the two compounds in CDCl$_3$ occur at −226.0 ppm for **1** and −253.5 ppm for **2**, respectively, which are comparable to the reported values for pentacoordinated organotin derivatives [23–25].

The structure of **2**, presented in Fig. 1, has been confirmed further by X-ray single crystal diffraction analyses, which clearly shows that the bis(3,5-dimethylpyrazol-1-yl)methylselenolate anion is a bidentate $\kappa^2$-[N,Se] chelating ligand, which coordinates to the tin atom by only one nitrogen atom and the selenium atom. The tin atom adopts a five-coordinate distorted trigonal bipyramidal geometry with the N(4) and Cl(1) atoms occupying the axial positions, and the axial angle of N(4)–Sn(1)–Cl(1) is 166.4(1)°. The Sn–N bond distance of 2.373(4) Å is similar with that in organotin derivatives containing anionic heteroscorpionate ligands, such as (3,5-Me$_2$Pz)$_2$CHCO$_2$SnPh$_2$Cl (av. 2.357 Å, Pz = pyrazol-1-yl) [26], but slightly shorter than those in organotin derivatives containing neutral bis(pyrazol-1-yl)methane ligands, such as CH$_2$(4-MePz)$_2$SnMe$_2$Cl$_2$ (2.436 Å) [21] and CH$_2$(3-$^i$PrPz)$_2$SnPh$_2$Br$_2$ (2.435 Å) [27] as well as that in Me$_2$N(CH$_2$)$_3$SnPh$_2$Cl (2.578(4) Å) [28], and longer than the reported data for organotin derivatives containing anionic poly(pyrazol-1-yl)borate ligands [29].

It is also noted that although two different pyrazole rings exist in solid, only one set of NMR signals for the bis(pyrazol-1-yl)methide group in this compound are observed, possibly due to the result of the fast exchange in the coordination behavior of two pyrazole ligands on the NMR time scale in solution. This type of fast exchange has already been extensively observed for other poly(pyrazol-1-yl)alkane complexes [30,31].
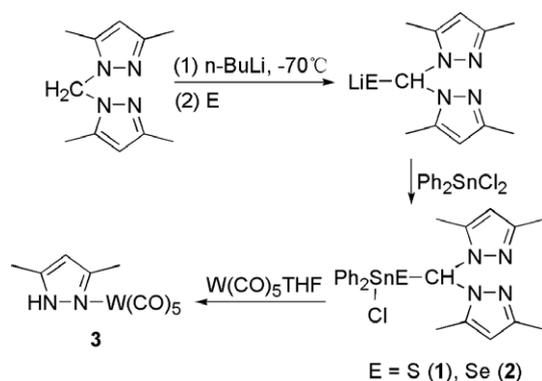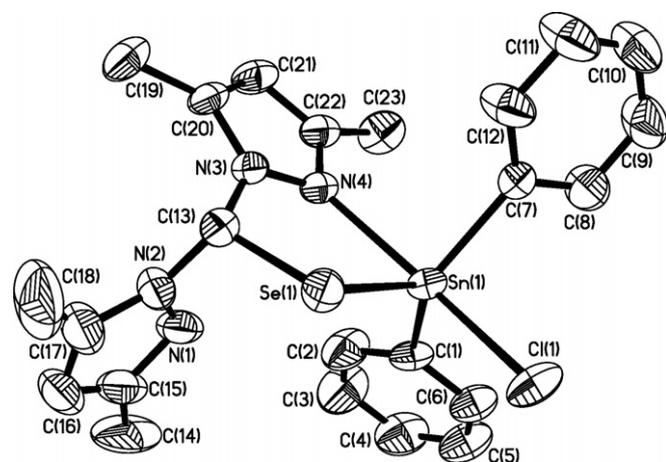
Fig. 1. The molecular structure of compound **2**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Sn(1)–C(7) 2.130(5), Sn(1)–C(1) 2.144(5), Sn(1)–N(4) 2.373(4), Sn(1)–Cl(1) 2.473(1), Sn(1)–Se(1) 2.5346(7), Se(1)–C(13) 1.973(5), N(2)–C(13) 1.448(7) Å; C(7)–Sn(1)–C(1) 119.2(2), N(4)–Sn(1)–Cl(1) 166.4(1), C(1)–Sn(1)–Se(1) 125.1(1), C(13)–Se(1)–Sn(1) 98.9(1), N(3)–C(13)–N(2) 110.4(4), N(3)–C(13)–Se(1) 112.5(3)°.

Scheme 1.

## 2.2. Reaction of lithium bis(pyrazol-1-yl)methylthiolate or selenolate with $M(CO)_5THF$ (M = Mo or W)

Although the reaction of compounds **1** and **2** with $W(CO)_5THF$ leads to the decomposition of bis(3,5-dimethylpyrazol-1-yl)methylthiolate or selenolate ligand, they should be good donors for transition metal atoms owing to the high affinity of sulfur and selenium for many metals. Upon treatment of bis(pyrazol-1-yl)methylthiolate or selenolate anions with $M(CO)_5THF$ (M = Mo or W) at 60 °C, their tricarbonyl metal anions could be formed. These metal anions, unstable over 60 °C, reacted with phenyltin chloride to yield heterobimetalic compounds **4–8** (Scheme 2).

These new compounds have moderate solubility in chlorinated solvents and acetone. Molybdenum complexes are slightly air-sensitive in solution, but all complexes are stable in the air in solid, and can be stored for several months at low temperature in the air. Compounds **4–8** have also been characterized by elemental analysis, IR and $^1$H NMR spectra. They provide the analogous IR spectra in solid. The metal carbonyl stretching bands have been observed in the region of 1989.6–1846.8 cm$^{-1}$. Their $^1$H NMR spectra demonstrate the structures by exhibiting the expected proton signals. Two equivalent pyrazole rings are observed.

The structure of compound **8** determined by single crystal X-ray diffraction is presented in Fig. 2. Selected distances and angles are listed in Table 1. As seen in Fig. 2, bis(3,4,5-trimethylpyrazol-1-yl)methylthiolate acts as a tridentate, monoanionic $\kappa^3$-[N,S,N] chelating ligand. 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(1), C(3) and S(1) atoms. The W–Sn bond distance is 2.8357(6) Å, which is similar to those in other cyclopenta-
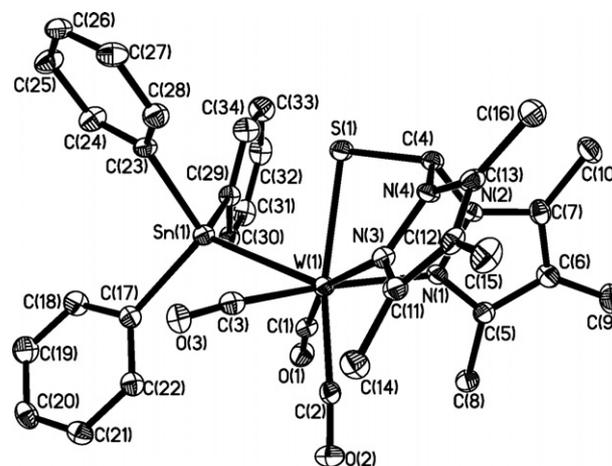


Fig. 2. The molecular structure of compound **8**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated solvent molecule has been omitted for clarity.

Table 1
Selected bond length (Å) and angles (°) for **8**

| W(1)–C(2) | 1.971(6) | W(1)–Sn(1) | 2.8357(6) |
|---|---|---|---|
| W(1)–C(3) | 1.973(6) | S(1)–C(4) | 1.810(6) |
| W(1)–C(1) | 1.983(6) | O(1)–C(1) | 1.157(7) |
| W(1)–N(1) | 2.226(5) | O(2)–C(2) | 1.154(7) |
| W(1)–N(3) | 2.233(5) | O(3)–C(3) | 1.157(8) |
| W(1)–S(1) | 2.538(1) | N(2)–C(4) | 1.451(7) |
|  |  |  |  |
| C(2)–W(1)–N(1) | 95.2(2) | C(23)–Sn(1)–C(29) | 102.4(2) |
| C(3)–W(1)–N(1) | 163.6(2) | C(17)–Sn(1)–C(23) | 107.4(2) |
| C(1)–W(1)–N(3) | 159.9(2) | W(1)–Sn(1)–C(23) | 114.9(1) |
| N(1)–W(1)–N(3) | 77.3(1) | W(1)–S(1)–C(4) | 87.7(1) |
| C(2)–W(1)–S(1) | 167.4(1) | W(1)–N(3)–C(11) | 137.9(4) |
| C(1)–W(1)–S(1) | 111.5(1) | C(13)–N(4)–C(4) | 132.1(5) |
| N(1)–W(1)–S(1) | 76.2(1) | W(1)–C(1)–O(1) | 173.2(5) |
| C(2)–W(1)–Sn(1) | 117.8(1) | W(1)–C(2)–O(2) | 176.0(5) |
| C(1)–W(1)–Sn(1) | 64.8(1) | W(1)–C(3)–O(3) | 173.9(5) |
| N(3)–W(1)–Sn(1) | 134.9(1) | N(2)–C(4)–N(4) | 107.4(4) |
| S(1)–W(1)–Sn(1) | 74.77(4) | N(4)–C(4)–S(1) | 109.5(4) |
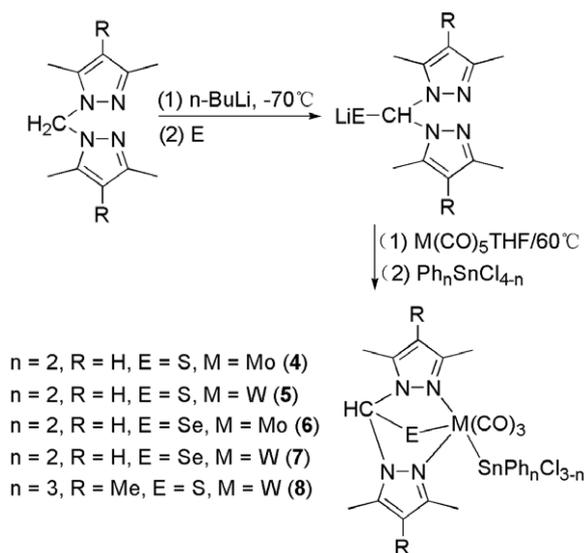
dienyl W–Sn complexes [32], such as $CH_3C_5H_4W$-$(CO)_3SnPh_3$ (2.8322(4) Å) [33], but slightly longer those in other W–Sn complexes with similar structural characters, such as $CH(3,4,5-Me_3Pz)_2W(CO)_3SnPh_3$ (2.7795(4) Å) [34]. The average W–N bond distance of 2.230 Å is comparable to the corresponding values found in other tungsten complexes with neutral bis(pyrazol-1-yl)methane ligands (such as av. 2.262 Å in $CH_2(3,4,5-Me_3Pz)_2W(CO)_3Br_2$ [35], 2.2575(5) Å in $CH_2(3-SMe-5-Bu^tPz)_2W(CO)_4$ [16]), as well as with anionic bis(pyrazol-1-yl)methide ligands (such as av. 2.233 Å in $CH(3,4,5-Me_3Pz)_2W(CO)_3SnPh_3$ [34]). It is also noteworthy that two carbonyl groups significantly deviate from linearity with the angles ∠W(1)–C(1)–O(1) of 173.2(5)° and ∠W(1)–C(3)–O(3) of 173.9(5)°. In addition, some angles around the Sn(1) atom (such as the angle ∠C(23)–Sn(1)–C(29) of 102.4(2)°) also significantly deviate from the tetrahedral geometry of the sp$^3$ hybridized tin atom. These structural parameters show the presence of



n = 2, R = H, E = S, M = Mo (**4**)
n = 2, R = H, E = S, M = W (**5**)
n = 2, R = H, E = Se, M = Mo (**6**)
n = 2, R = H, E = Se, M = W (**7**)
n = 3, R = Me, E = S, M = W (**8**)

Scheme 2.

the steric repulsion between the SnPh$_3$ group with the (3,4,5-Me$_3$Pz)$_2$CHSW(CO)$_3$ fragment.

In conclusion, the modification of bis(pyrazol-1-yl)methane by sulfur or selenium on the methine carbon atom has been successfully carried out. In their organotin derivatives, bis(3,5-dimethylpyrazol-1-yl)methylthiolate or selenolate is a bidentate monoanionic $\kappa^2$-[N,E] (E = S or Se) chelating ligand. The treatment of these organotin derivatives of bis(pyrazol-1-yl)methylthiolate or selenolate with W(CO)$_5$THF results in the decomposition of ligands. While the direct reaction of bis(pyrazol-1-yl)methylthiolate or selenolate anions with M(CO)$_5$THF gives their tricarbonyl metal anions. Succedent reaction of these carbonyl metal anions with phenyltin chloride yields heterobimetalic M–Sn compounds, in which bis(pyrazol-1-yl)methylthiolate or selenolate acts as a tridentate, monoanionic $\kappa^3$-[N,E,N] chelating ligand.

## 3. Experimental

Solvents were dried by the standard methods prior to use. All reactions were carried out under an argon atmosphere using standard Schlenk and Cannula techniques. NMR spectra were obtained with a Mercury 300BB or Bruker AV300 spectrometer using CDCl$_3$ as solvent unless otherwise noted, and the chemical shifts were reported in ppm with respect to the reference (internal SiMe$_4$ for $^1$H NMR and $^{13}$C NMR spectra, external SnMe$_4$ for $^{119}$Sn NMR). IR spectra data were obtained from a Bio-Rad FTS 6000 spectrometer using KBr discs. Element analyses were carried out on an Elementar Vairo EL analyzer.

### 3.1. Synthesis of compound 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 *n*-BuLi (2.5 M, 0.8 ml) at −70 °C, and the mixture was stirred for 1 h at that temperature. Then, sulfur (64 mg, 2 mmol) was added to the mixture. The reaction mixture was stirred at −70 °C for 1 h, and allowed to slowly reach room temperature during *ca.* 3 h, and stirred continuously for another 2 h to give a yellow solution. Then, Ph$_2$SnCl$_2$ (0.688 g, 2 mmol) were added to the above solution, and the reaction mixture was stirred overnight. The solvent was removed under a reduced pressure, and the residual solid was recrystallized from hot benzene/hexane to yield 0.36 g (33 %) of **1** as slightly yellow needle crystals, mp 194–196 °C. $^1$H NMR: $\delta$ 8.04–7.90, 7.40–7.35 (m, m, 4H, 6H, C$_6$H$_5$), 7.49 (s, 1H, C*H*), 5.89 (s, 2H, *H*$^4$ of pyrazole ring), 2.30, 1.80 (s, s, 3H, 3H, C*H*$_3$). $^{13}$C NMR: $\delta$ 10.61, 13.41 (3 or 5-CH$_3$), 69.40 (*C*H), 108.67 (4-position carbon of pyrazole ring), 128.59, 129.52, 135.66, 139.85 (*C*$_6$H$_5$), 143.86, 149.23 (3 or 5-position carbon of pyrazole ring). $^{119}$Sn NMR: $\delta$ −226.0. Anal. Calc. for C$_{23}$H$_{25}$ClN$_4$SSn: C, 50.78; H, 4.60; N, 10.30. Found: C, 50.67; H, 4.92; N, 9.95%.

### 3.2. Synthesis of compound 2

This compound was obtained similarly using selenium instead of sulfur as described above for **1**. After similar workup, slightly yellow crystals of **2** were obtained. Yield: 0.52 g (44%), mp 203–205 °C. $^1$H NMR: $\delta$ 8.07–7.79, 7.43–7.38 (m, m, 4H, 6H, C$_6$H$_5$), 7.57 (s, 1H, C*H*), 5.92 (s, 2H, *H*$^4$ of pyrazole ring), 2.28, 1.79 (s, s, 3H, 3H, C*H*$_3$). $^{13}$C NMR: $\delta$ 10.91, 13.45 (3 or 5-CH$_3$), 60.06 (*C*H), 108.64 (4-position carbon of pyrazole ring), 128.38, 129.52, 135.67, 140.17 (*C$_6$H$_5$*), 143.49, 149.53 (3 or 5-position carbon of pyrazole ring). $^{119}$Sn NMR: $\delta$ −253.5. Anal. Calc. for C$_{23}$H$_{25}$ClN$_4$SeSn: C, 46.74; H, 4.23; N, 9.48. Found: C, 47.20; H, 4.21; N, 9.28%.

### 3.3. Reactions of 1 and 2 with W(CO)$_5$THF

Compound **1** (0.3 mmol) was added to a solution of W(CO)$_5$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 under reflux for 6 h. Then, the solvent was removed under a reduced pressure, and the residual solid was purified by column chromatography on silica using CH$_2$Cl$_2$/hexane (1/1 v/v) as eluent. The eluate was concentrated to dryness again, and the residual solid was recrystallized from CH$_2$Cl$_2$/hexane to give green-yellow crystals of **3**. Yield: 10%. $^1$H NMR: $\delta$ 2.24 (s, 6H, C*H*$_3$), 5.85 (s, 1H, *H*$^4$ of pyrazole ring), 9.25 (s, br, 1H, N*H*). IR (nujol mull): $v_{NH}$ = 3387.0 (m), $v_{CO}$ = 2071.5 (w), 1927.8 (s), 1851.7 (m), 1838.2 (m) cm$^{-1}$.

The similar reaction of **2** with W(CO)$_5$THF also gave compound **3** at *ca.* 15% yield.

### 3.4. Synthesis of compound 4

To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (0.204 g, 1 mmol) in THF (20 ml) under Ar was added a hexane solution of *n*-BuLi (2.5 M, 0.4 ml) at −70 °C, the mixture was stirred for 1 h at that temperature, and sulfur (32 mg, 1 mmol) was added to the mixture. The reaction mixture was stirred at −70 °C for 1 h, and allowed to slowly reach room temperature during *ca.* 3 h, and stirred continuously for 2 h. Then, Mo(CO)$_5$THF prepared in situ by the irradiation of a solution of Mo(CO)$_6$ (0.264 g, 1 mmol) in THF (20 ml) for 8 h, was added to the above solution, and the reaction mixture was stirred and heated at 60 °C for 6 h to give a deep red solution. After cooling to room temperature, Ph$_2$SnCl$_2$ (0.344 g, 1 mmol) was added. The reaction mixture was stirred continuously overnight. Then, the solvent was removed *in vacuo*, and the residual solid was purified by column chromatography on silica using CH$_2$Cl$_2$/hexane (3/1 v/v) as eluent. The eluate was concentrated to dryness again, and the residual solid was recrystallized from CH$_2$Cl$_2$/hexane to give 0.21 g (30%) yellow crystals of **4**. $^1$H NMR: $\delta$ 2.34, 2.55 (s, s, 6H, 6H, C*H*$_3$), 5.84 (s, 2H, *H*$^4$ of pyrazole ring), 7.16 (1H, C*H*), 7.36–7.33, 7.71–7.74 (m, m, 6H, 4H, C$_6$H$_5$).

IR: $\nu_{CO}$ = 1989.6 (vs), 1885.3 (vs, br) cm$^{-1}$. Anal. Calc. for C$_{26}$H$_{25}$ClMoN$_4$O$_3$SSn · 0.5CH$_2$Cl$_2$: C, 41.51; H, 3.39; N, 7.31. Found: C, 41.02; H, 3.58; N, 7.52%.

### 3.5. Synthesis of compound 5

This compound was obtained similarly using W(CO)$_5$THF instead of Mo(CO)$_5$THF as described above for **4**. After similar workup, bright yellow crystals of **5** were obtained. Yield: 32%. $^1$H NMR: $\delta$ 2.36, 2.55 (s, s, 6H, 6H, C$H_3$), 5.85 (s, 2H, $H^4$ of pyrazole ring), 7.16 (1H, C$H$), 7.31–7.37, 7.71–7.74 (m, m, 7H, 4H, C$H$ and C$_6H_5$). IR: $\nu_{CO}$ = 1982.0 (vs), 1883.8 (sh), 1875.6 (vs) cm$^{-1}$. Anal. Calc. for C$_{26}$H$_{25}$ClN$_4$O$_3$SSnW: C, 38.45; H, 3.08; N, 6.90. Found: C, 38.12; H, 3.26; N, 7.39%.

### 3.6. Synthesis of compound 6

This compound was obtained similarly using selenium instead of sulfur as described above for **4**. After similar workup, yellow crystals of **6** were obtained. Yield: 31%. $^1$H NMR: $\delta$ 1.74, 2.23 (s, s, 6H, 6H, C$H_3$), 5.89 (s, 2H, $H^4$ of pyrazole ring), 7.51 (1H, C$H$), 7.35–7.37, 7.78–7.89 (m, m, 6H, 4H, C$_6H_5$). IR: $\nu_{CO}$ = 1967.2 (vs), 1942.6 (s), 1860.9 (s) cm$^{-1}$. Anal. Calc. for C$_{26}$H$_{25}$ClMoN$_4$O$_3$SeSn: C, 40.49; H, 3.24; N, 7.27. Found: C, 40.38; H, 3.19; N, 7.18%.

### 3.7. Synthesis of compound 7

This compound was obtained similarly using selenium instead of sulfur, and W(CO)$_5$THF instead of Mo(CO)$_5$THF as described above for **4**. After similar workup, yellow crystals of **7** were obtained. Yield: 33%. $^1$H NMR: $\delta$ 2.32, 2.54 (s, s, 6H, 6H, C$H_3$), 5.85 (s, 2H, $H^4$ of pyrazole ring), 7.34–7.37, 7.72–7.74 (m, m, 7H, 4H, C$H$ and C$_6H_5$). IR: $\nu_{CO}$ = 1980.8 (vs), 1874.8 (vs, br) cm$^{-1}$. Anal. Calc. for C$_{26}$H$_{25}$ClN$_4$O$_3$SeSnW · 2CH$_2$Cl$_2$: C, 32.67; H, 2.82; N, 5.44. Found: C, 33.15; H, 2.60; N, 5.82%.

### 3.8. Synthesis of compound 8

This compound was obtained similarly using bis(3,4,5-tirmethylpyrazol-1-yl)methane instead of bis(3,5-dimethylpyrazol-1-yl)methane, and W(CO)$_5$THF instead of Mo(CO)$_5$THF as described above for **4**. After similar workup, yellow crystals of **8** were obtained. Yield: 29%. $^1$H NMR: $\delta$ 1.81, 2.20, 2.41 (s, s, s, 6H, 6H, 6H, C$H_3$), 7.11–7.24, 7.53–7.58 (m, m, 7H, 4H, C$H$ and C$_6H_5$). IR: $\nu_{CO}$ = 1958.6 (vs), 1873.5 (vs), 1846.8 (vs) cm$^{-1}$. Anal. Calc. for C$_{34}$H$_{34}$N$_4$O$_3$SSnW · CH$_2$Cl$_2$: C, 43.48; H, 3.73; N, 5.80. Found: C, 43.12; H, 3.75; N, 5.53%.

### 3.9. X-ray crystallography

Crystals of compound **2** suitable for X-ray analysis were obtained by slowly cooling its hot benzene/hexane solution, while crystals of compound **8** were obtained by slow

**Table 2**
Crystallographic data for compounds **2** and **8**

| Compound | **2** | **8** · CH$_2$Cl$_2$ |
|---|---|---|
| Formula | C$_{23}$H$_{25}$ClN$_4$SeSn | C$_{35}$H$_{36}$Cl$_2$N$_4$O$_3$SSnW |
| Formula weigh | 590.57 | 966.18 |
| Temperature ($K$) | 294(2) | 113(2) |
| Wavelength (Å) | 0.71073 | 0.71070 |
| Crystal size (mm) | 0.22 × 0.20 × 0.16 | 0.26 × 0.22 × 0.06 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $C_2/c$ | $P2_1/n$ |
| $a$ (Å) | 17.590(3) | 12.369(2) |
| $b$ (Å) | 15.712(2) | 14.352(3) |
| $c$ (Å) | 20.021(3) | 21.200(4) |
| $\beta$ (°) | 114.443(2) | 104.915(3) |
| $V$ (Å$^3$) | 5037.5(13) | 3636.4(12) |
| $D_{calc}$ (g cm$^{-3}$) | 1.557 | 1.765 |
| $\mu$ (mm$^{-1}$) | 2.582 | 4.092 |
| Absorption correction | Semi-empirical from equivalents | Numerical |
| $2\theta$ Range (°) | 3.64–50.04 | 3.46–55.76 |
| $Z$ | 8 | 4 |
| $F(000)$ | 2336 | 1888 |
| Reflections collected | 12 666 | 44 705 |
| Independent reflections ($R_{int}$) | 4448 (0.0406) | 8653 (0.0560) |
| Number of parameters | 275 | 425 |
| $R$, $R_w[I > 2\sigma(I)]$ | 0.0350, 0.0678 | 0.0516, 0.1267 |
| Goodness-of-fit on $F^2$ | 1.026 | 1.081 |

diffusion of hexane into the CH$_2$Cl$_2$ solution of this compound at $-18\,°$C, and crystallized with one molecular CH$_2$Cl$_2$. Intensity data were collected on a Bruker SMART CCD diffractometer for compound **2** and Rigaku Saturn CCD area detector for compound **8**, respectively. The structures were solved by direct methods 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 **2** and **8** is listed in Table 2.

### Appendix A. Supplementary information

CCDC 616063 and 616064 contain the supplementary crystallographic data for **2** and **8**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.003.

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