Functionalized bis(pyrazol-1-yl)methanes by organotin halide on the methine carbon atom and their related reactions

Zhen-Kang Wen, Yun-Fu Xie, Shu-Bin Zhao, Run-Yu Tan, Liang-Fu Tang *

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Abstract

The modification of bis(pyrazol-1-yl)methanes by organotin halide on the methine carbon atom has been successfully carried out, and their related reactions have also been studied. Bis(3,5-dimethylpyrazol-1-yl)(iododiphenylstannyl)methane [$Ph_2ISnCH(3,5-Me_2Pz)_2$] can be obtained by the selective cleavage of the $Sn–C_{sp^2}$ bond in bis(3,5-dimethylpyrazol-1-yl)triphenylstannylmethane with I_2 in a 1:1 molar ratio, while {di(*tert*-butyl)chlorostannyl}bis(3,5-dimethylpyrazol-1-yl)methane [$(t$-Bu$)_2$ClSnCH(3,5-Me$_2$Pz)$_2$] and {di(*tert*-butyl)chlorostannyl}bis(3,4,5-trimethylpyrazol-1-yl)methane [$(t$-Bu$)_2$ClSnCH(3,4,5-Me$_3$Pz)$_2$] are easily prepared by the reaction of the bis(3,5-dimethylpyrazol-1-yl)methide or bis(3,4,5-trimethylpyrazol-1-yl)methide anion with di(*tert*-butyl)tin dichloride. The molecular structure of [$(t$-Bu$)_2$ClSnCH(3,5-Me$_2$Pz)$_2$] determined by X-ray structure analysis indicates that bis(3,5-dimethylpyrazol-1-yl)methide acts as a bidentate monoanionic κ^2-[C,N] chelating ligand. Reaction of these bis(pyrazol-1-yl)methanes functionalized by organotin halide with $W(CO)_5THF$ results in the oxidative addition of the relative electrophilic Sn–X (X = Cl or I) bond instead of the $Sn–C_{sp^3}$ bond to the tungsten(0) atom, yielding new metal–metal bonded complexes $R_2SnCHPz_2W(CO)_3X$ (R = Ph or *t*-Bu, Pz represents substituted pyrazol-1-yl). Furthermore, treatment of the oxidative addition product $(t$-Bu$)_2$SnCH(3,5-Me$_2$Pz)$_2$W(CO)$_3$Cl with *n*-BuLi results in known complex $CH_2(3,5-Me_2Pz)_2W(CO)_4$ with the loss of the organotin fragment. In addition, reaction of $Ph_2ISnCH(3,5-Me_2Pz)_2$ with 2-PySNa (Py = pyridyl) leads to the replacement of iodide by 2-PyS$^-$ anion to give $Ph_2(2$-PyS)SnCH(3,5-Me$_2$Pz)$_2$, which subsequently reacts with $W(CO)_5THF$ to result in the decomposition of this ligand, also yielding the known bis(3,5-dimethylpyrazol-1-yl)methane derivative of $CH_2(3,5-Me_2Pz)_2W(CO)_4$.
© 2008 Elsevier B.V. All rights reserved.

Keywords: Bis(pyrazol-1-yl)methane; Organotin halide; Tungsten carbonyl; Oxidative addition

1. Introduction

Poly(pyrazol-1-yl)alkanes, such as tris(pyrazol-1-yl)methane [1] and bis(pyrazol-1-yl)methane [2], have been performing as one of the most popular nitrogen-containing donor ligands in recent years. Their coordination chemistry towards main group and transition metals has been widely exploited. Furthermore, the modification of poly(pyrazol-1-yl)methanes by organic functional groups on the bridging carbon atom to form novel heteroscorpionate ligands is currently drawing extensive attention [1–3]. These intrigu-ing heteroscorpionate ligands usually have N_2O [4], N_2S [5] or N_2N' [6] coordination environments, which render them the potential to form novel complexes with various main group and transition metals. In addition, the modifi-cation of bis(pyrazol-1-yl)methane by organometallic groups has also successfully broadened the scope of the application of these novel ligands [7]. Our recent investiga-tions on bis(pyrazol-1-yl)methane indicate that the modifi-cation of this ligand with organotin groups on the methine carbon atom can provide unusual reactivity [8]. For exam-ple, the reaction of bis(pyrazol-1-yl)(triarylstannyl)meth-ane with $W(CO)_5THF$ results in the oxidative addition of the $Sn–C_{sp^3}$ bond to the tungsten(0) atom to give novel four-membered metallacyclic complex, while the analogous

---

reaction of bis(pyrazol-1-yl)(trialkylstannyl)methane with W(CO)₅THF does not take place [8b]. Furthermore, the similar reaction of {di(*tert*-butyl)phenylstannyl}bis(pyrazol-1-yl)methane results in the oxidative addition of the Sn–C_{sp^2} bond to the tungsten(0) center [8b]. To gain further understanding of the influence of the nature of substitutions on the tin atom on the reaction, in this paper we have synthesized bis(pyrazol-1-yl)methanes modified by organotin halide on the methine carbon, and studied their related reactivities.

2. Results and discussion

2.1. Modification of bis(pyrazol-1-yl)methanes with organotin halide

Bis(3,5-dimethylpyrazol-1-yl)(iododiphenylstannyl)methane (**1**) is prepared by the selective cleavage of the Sn–C_{sp^2} bond in bis(3,5-dimethylpyrazol-1-yl)triphenylstannylmethane with I₂ in a 1:1 molar ratio at room temperature in good yield (Scheme 1). Whereas {di(*tert*-butyl)chlorostannyl}bis(3,5-dimethylpyrazol-1-yl)methane (**2**) and {di-(*tert*-butyl)chlorostannyl}bis(3,4,5-trimethylpyrazol-1-yl)methane (**3**) can be easily obtained by the reaction of the bis(3,5-dimethylpyrazol-1-yl)methide or bis(3,4,5-trimethylpyrazol-1-yl)methide anion with di(*tert*-butyl)tin dichloride, attributed to the steric hindrance around the tin atom preventing the replacement of another chloride.

Ligands **1**–**3** have been characterized by elemental analyses and NMR spectra, and the structure of **2** is further confirmed by X-ray structural analysis. The molecular structure of **2** is presented in Fig. 1, which shows that the bis(3,5-dimethylpyrazol-1-yl)methide anion is a bidentate κ^2-[C,N] chelating ligand, which coordinates to the tin atom by only one nitrogen atom and the carbon atom to form a new four-membered heterometallacycle. The tin atom adopts a five-coordinate markedly distorted trigonal bipyramidal geometry with the N(1) and Cl(1) atoms occupying the axial positions, and the axial angle of
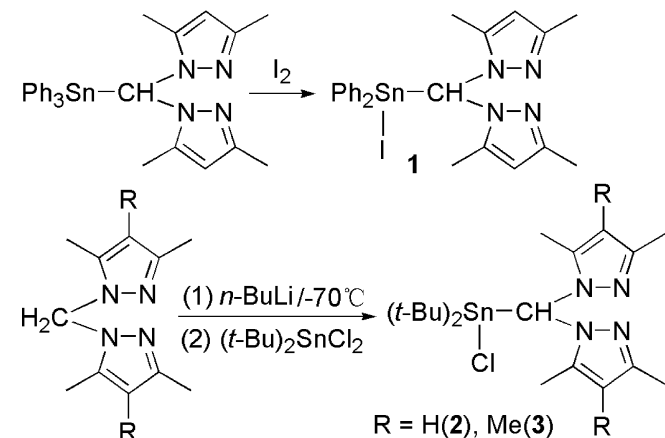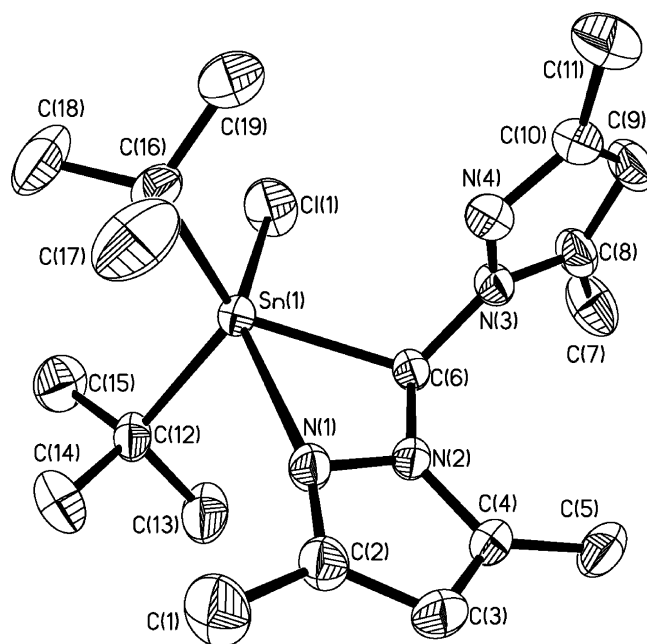

Fig. 1. The molecular structure of **2**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Sn(1)–C(6) 2.196(3), Sn(1)–C(16) 2.175(4), Sn(1)–Cl(1) 2.445(1), Sn(1)–N(1) 2.572(3), N(2)–C(6) 1.443(4), N(3)–C(6) 1.446(4) Å; N(1)–Sn(1)–Cl(1) 149.80(7), C(12)–Sn(1)–C(6) 111.7(1), C(6)–Sn(1)–N(1) 58.9(1), N(2)–C(6)–N(3) 111.8(3), N(2)–C(6)–Sn(1) 99.7(1); N(1)–Sn(1)–C(6)–N(2) 4.5(1), Sn(1)–N(1)–N(2)–C(6) 6.7(3)°.

N(1)–Sn(1)–Cl(1) is 149.80(7)°. The Sn–N bond distance is 2.572(3) Å, slightly longer than those in other triorganotin complexes with a bidentate κ^2-[C,N] chelating ligand (such as 2.4899(14) Å in LSnMe₂F [9], 2.519 Å in LSnPh₂Cl [10], L = 2-(*N,N*-dimethylaminomethyl)phenyl), but markedly shorter than those in bulky di(*tert*-butyl)tin chloride derivatives (such as 2.904(14) Å in LSn(*t*-Bu)₂Cl [11]). It is also worthy of note that although two different pyrazole rings exist in solid, only one set of NMR signals for the bis(pyrazol-1-yl)methide group is observed in solution, possibly as the result of the fast exchange in the coordination behavior of two pyrazole ligands on the NMR time scale. This type of fast exchange has already been extensively observed for other poly(pyrazol-1-yl)methane complexes [4c,5d,12].

2.2. Reaction of ligands **1**–**3** with W(CO)₅THF

The oxidative addition of the tin(IV)–halogen bond to low-valent group 6 metals to give heterobimetallic M–Sn complexes has been well-established [13]. Furthermore, the reactivity of the tin(IV)–halogen bond in R_nSnX_{4-n} (R = alkyl or aryl, n = 0–3) markedly decreases with the increasing of the number of the organic substituents, which leads to the increasing of the electron density on the tin atom [14]. Thus, the oxidative addition reaction of the Sn–X bond in triorganotin halide is rare. Combined with our previous works [8], ligands **1**–**3** possibly have

Scheme 1. Modification of bis(pyrazol-1-yl)methane by organotin halide.

two different reactivity patterns with $W(CO)_5THF$, namely the oxidative addition of the Sn–X (X = Cl or I) bond or the Sn–C_{sp^3} bond to the tungsten(0) atom. To confirm the reaction modes, ligands **1–3** are treated with $W(CO)_5THF$ under the similar experimental conditions as the reaction of bis(3,5-dimethylpyrazol-1-yl)(triarylstannyl)methane with $W(CO)_5(THF)$ [8b], and only the oxidative addition of the Sn–X bond is observed instead of the Sn–C_{sp^3} bond to the tungsten(0) atom to yield complexes **4–6** (Scheme 2), possibly owing to the higher electrophilic nature of the Sn–X bond compared to the Sn–C_{sp^3} bond. Furthermore, this reaction is markedly different from the reaction of $Ph_2ClSnSCH(3,5-Me_2Pz)_2$ with $W(CO)_5THF$ [5d]. The latter yields pyrazole derivative of $(3,5-Me_2PzH)W(CO)_5$ with the decomposition of the ligand and no oxidative addition product of the Sn–Cl or Sn–S bond to the tungsten atom is obtained.

Complexes **4–6** have been characterized by IR and NMR spectra as well as elemental analyses, and the structures of complexes **4** and **5** are further confirmed by X-ray structural analyses. Their IR spectra show one significant low-frequency absorption band of v (CO) at 1787 cm^{-1} for **4**, 1773 cm^{-1} for **5** and 1774 cm^{-1} for **6**, implying that the semibridging carbonyl probably exists, consistent with the results of their X-ray structural analyses. The ^{13}C signal of the CH group in complexes slightly shifts to the higher field than that in the corresponding ligands. In addition, the ^{119}Sn NMR signals of complexes also markedly downfield shift than those in the corresponding ligands, indicating that the chemical environment around the tin atom is significantly changed. These NMR spectral data support the conclusion that the oxidative addition of the Sn–X bond has taken place.

The crystal structures of **4** and **5** are presented in Figs. 2 and 3, respectively. Their molecular fundamental frameworks are similar, and analogous to those in $Ph_2SnCH(3,5-Me_2Pz)_2(CO)_3WCl$ [15] and $(t-Bu)_2SnCH(3,5-Me_2Pz)_2W(CO)_3(Ph)$ [8b]. For example, a novel κ^3-[N, Sn, N] coordination mode as well as an unsymmetrically semi-
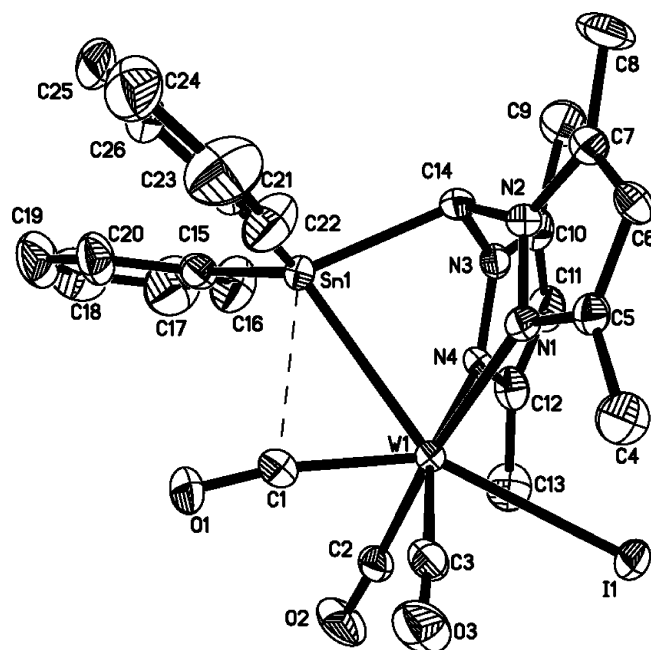

Fig. 2. The molecular structure of **4**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–Sn(1) 2.839(1), W(1)–I(1) 2.8576(8), Sn(1)–C(14) 2.221(7), Sn(1)···C(1) 2.538(7), W(1)–C(1) 1.944(8), W(1)–C(2) 1.971(8), W(1)–N(1) 2.274(6), W(1)–N(4) 2.276(5), C(1)–O(1) 1.170(8), C(2)–O(2) 1.142(8) Å; N(1)–W(1)–N(4) 83.6(2), C(1)–W(1)–Sn(1) 60.7(2), C(3)–W(1)–Sn(1) 121.4(2), C(1)–W(1)–I(1) 147.7(2), Sn(1)–W(1)–I(1) 151.52(2), C(14)–Sn(1)–W(1) 79.3(1), N(2)–C(14)–N(3) 111.5(6), O(1)–C(1)–W(1) 170.9(7), O(2)–C(2)–W(1) 176.5(7)°.

bridging carbonyl between the W–Sn bond is observed in these complexes. Their structural parameters are also very analogous (Table 1), such as similar Sn···C distance. Complex **5** has a slightly longer W–Sn distance than complex **4**, and longer values than the reported cyclopentadienyl heterobimetallic derivatives with the W–Sn bond (such as 2.7681(8) Å in $Cp_2HWSnCl(t-Bu)_2$) [16].

2.3. Reaction of complex 5 with n-BuLi

The alkylation reaction of organometal halide with alkyllithium has been widely used to synthesize alkyl metal complexes with catalytic activities. Herein, treatment of **5** with *n*-BuLi leads to the known complex $CH_2(3,5-Me_2Pz)_2W(CO)_4$ [17] with the loss of the organotin fragment. Although the mechanism is unclear at present, the formation of this complex should be partially attributed to the reductivity of *n*-BuLi as well as the strong Lewis acidity of the tungsten atom in complex **5**, led by the large electronegative chlorine. In addition, one carbonyl group in this complex should origin from absorbing the CO sourced from the decomposition of some of complex **5**.

2.4. Reaction of ligand 1 with 2-PySNa (Py = pyridyl)

To investigate the reactivity of the Sn–X bond with other nucleophiles and obtain polyfunctional bis(pyrazol-
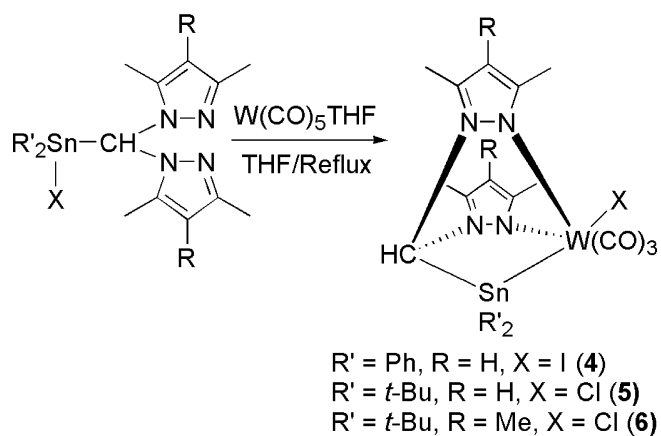
Scheme 2. Reaction of functionalized bis(pyrazol-1-yl)methane with $W(CO)_5THF$.

R' = Ph, R = H, X = I (**4**)
R' = *t*-Bu, R = H, X = Cl (**5**)
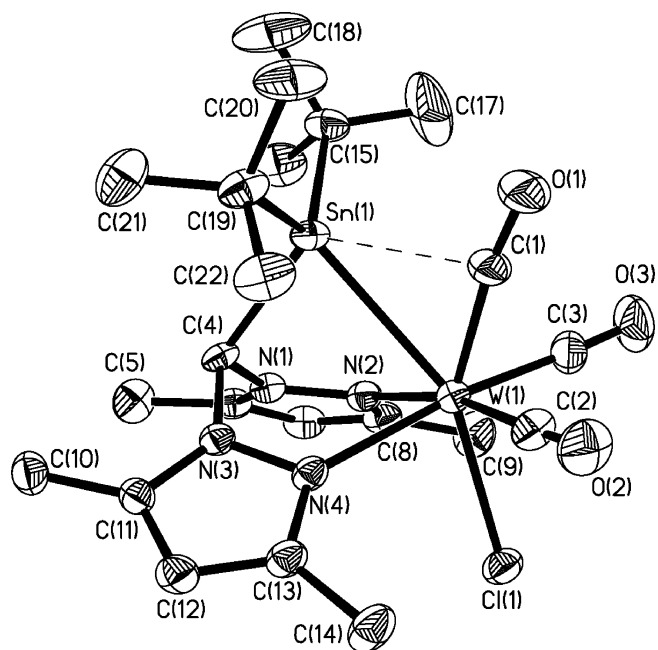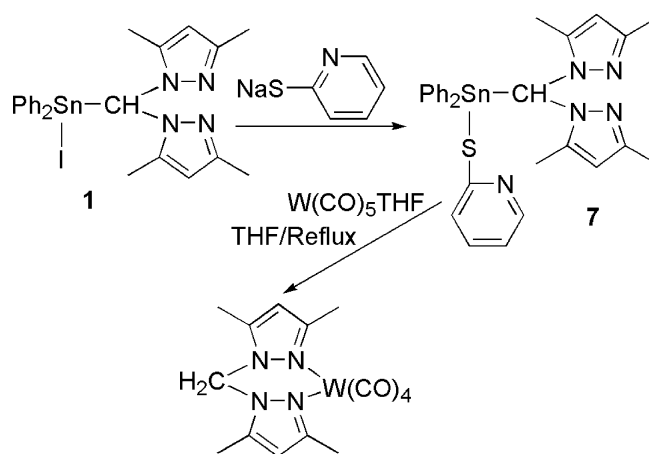R' = *t*-Bu, R = Me, X = Cl (**6**)

Fig. 3. The molecular structure of **5**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–Sn(1) 2.8865(5), W(1)–Cl(1) 2.514(1), W(1)–N(2) 2.268(4), W(1)–N(4) 2.269(4), W(1)–C(1) 1.941(6), Sn(1)–C(4) 2.204(5), Sn(1)···C(1) 2.484(6), C(1)–O(1) 1.175(7), N(3)–C(4) 1.455(5), N(1)–C(4) 1.445(5) Å; N(2)–W(1)–N(4) 80.5(1), C(3)–W(1)–N(4) 168.9(2), Cl(1)–W(1)–Sn(1) 152.84(3), C(4)–Sn(1)–W(1) 78.6(1), C(4)–Sn(1)–C(1) 120.0(1), O(1)–C(1)–W(1) 171.1(5), N(1)–C(4)–N(3) 109.5(3), C(17)–C(15)–C(18) 113.5(7)°.

Scheme 3. Synthesis and reaction of Ph₂(2-PyS)SnCH(3,5-Me₂Pz)₂.

position of this ligand, and no product of oxidative addition to the tungsten atom is observed.

In summary, bis(pyrazol-1-yl)methanes functionalized by organotin halide on the methine carbon atom can easily be obtained. Treatment of these ligands with W(CO)$_5$THF results in the oxidative addition of the Sn–X (X = Cl or I) bond with relative high electrophilic nature to the tungsten(0) atom, instead of the Sn–C$_{sp^2}$ or Sn–C$_{sp^3}$ bond. Combined with our previous works [8], the suggestion is made that the electronic effect of the substituents on the tin atom plays the major role in the oxidative addition reactions of functionalized bis(pyrazol-1-yl)methanes with W(CO)$_5$-THF. For example, the relative electronegative substituents on the tin atom such as halogen or aryl groups are favor of the oxidative addition reactions. Furthermore, the ligands are inclined to decomposition in the reactions of bis(pyrazol-1-yl)methanes modified by organotin groups with heteroatom on the bridge with W(CO)$_5$THF [5d]. In addition, preliminary investigations show that treatment of the oxidative addition product with *n*-BuLi leads to the loss of the organotin fragment.

3. Experimental

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 300BB spectrometer using CDCl₃ as solvent unless otherwise noted, and the chemical shifts were reported in ppm with respect to the reference (internal SiMe₄ for ¹H NMR and ¹³C NMR spec-

1-yl)methane ligands, the reaction of ligand **1** with 2-PySNa (Py = pyridyl) has been carried out, which yields ligand **7** in good yield (Scheme 3). This ligand has also been characterized by NMR spectra and X-ray single crystal diffraction. Its ¹¹⁹Sn NMR signal in CDCl₃ occurs at −156.6 ppm, markedly shifts to the lower field than that in **1** (−193 ppm). The crystal structure of **7**, presented in Fig. 4, shows that the tin atom is four-coordinate with a distorted tetrahedral geometry. The pyridyl and pyrazolyl nitrogen atoms as well as sulfur atom do not coordinate to the tin atom. This ligand is expected to act as an unsymmetric multidentate N,N,S or N,N,N′ ligand for other metal atoms. In addition, the oxidative addition of the Sn–S bond to low-oxidative transition-metal complexes is also observed [18]. However, upon treatment of **7** with W(CO)$_5$(THF) under similar experimental conditions as the reaction of **1** with W(CO)$_5$(THF), only known complex CH₂(3,5-Me₂Pz)₂W(CO)₄ [17] is isolated with the decom-

Table 1
Comparison of some key bond distances (Å) and angles (°) in semibridging carbonyl complexes

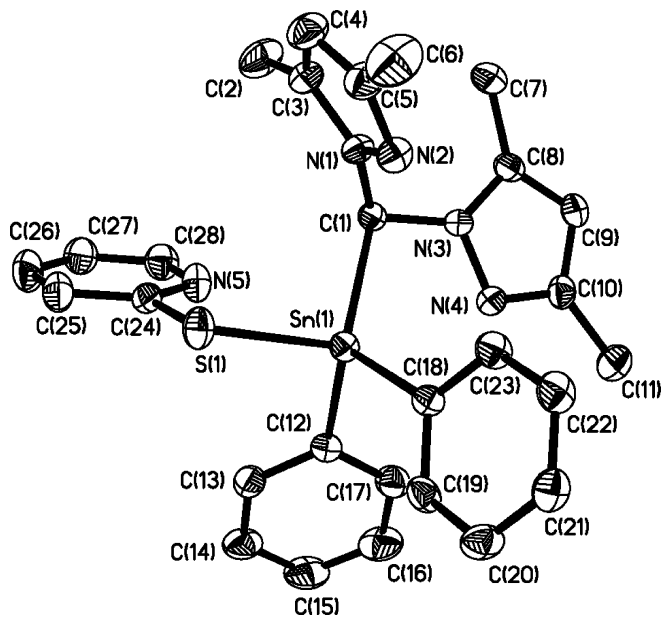| Complex	W–Sn	Sn···C	Sn–C$_{sp^3}$	N–W–N	W–C–O	W–Sn–C$_{sp^3}$	Ref.
Ph₂SnCHPz₂W(CO)₃I (**4**)	2.839(1)	2.538(7)	2.221(7)	83.6(2)	170.9(7)	79.3(1)	This work
(*t*-Bu)₂SnCHPz₂W(CO)₃Cl (**5**)	2.8865(5)	2.484(6)	2.204(5)	80.5(1)	171.1(5)	78.6(1)	This work
Ph₂SnCHPz₂W(CO)₃Cl	2.8547(9)	2.527(4)	2.204(4)	82.5(1)	170.9(4)	79.2(1)	[15]
(*t*-Bu)₂SnCHPz₂W(CO)₃Ph	2.8778(12)	2.541(11)	2.237(9)	81.5(2)	167.8(8)	78.2(2)	[8b]

Fig. 4. The molecular structure of **7**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Sn(1)–C(1) 2.215(5), Sn(1)–S(1) 2.481(1), Sn(1)–C(12) 2.149(5), Sn(1)–C(18) 2.162(5), S(1)–C(24) 1.766(5), N(1)–C(1) 1.430(6), N(3)–C(1) 1.458(6) Å; C(12)–Sn(1)–C(18) 105.5(1), C(12)–Sn(1)–C(1) 122.5(1), C(24)–S(1)–Sn(1) 96.1(1), N(1)–C(1)–N(3) 113.7(4)°.

tra, external SnMe$_4$ for ^{119}Sn NMR). IR spectra were recorded as KBr pellets on a Bruker Equinox55 spectrometer. Element analyses were carried out on an Elementar Vairo EL analyzer. Ph$_3$SnCH(3,5-Me$_2$Pz)$_2$ [8b] and (t-Bu)$_2$SnCl$_2$ [19] were prepared according to the literature methods. Melting points were measured with an X-4 digital micro melting-point apparatus and were uncorrected.

3.1. Synthesis of Ph$_2$ISnCH(3,5-Me$_2$Pz)$_2$ (1)

A solution of I$_2$ (0.51 g, 2.0 mmol) in CHCl$_3$ (40 ml) was dropwise added to a stirred solution of Ph$_3$SnCH(3,5-Me$_2$Pz)$_2$ (1.11 g, 2.00 mmol) in CHCl$_3$ (30 ml) at 10 °C. After addition completed, the reaction mixture was continuously stirred for 1 h at room temperature. The solvent was removed under a reduced pressure, and the residual solid was recrystallized from hot hexane to yield 0.91 g (75%) of **1** as white crystals, mp 164–166 °C. ^{1}H NMR: δ 2.09, 2.11 (s, s, 6H, 6H, CH_3), 5.80 (s, 2H, H^4 of pyrazole ring), 6.34 (s, 1H, CH), 7.26–7.34, 7.78–7.82 (m, m, 6H, 4H, C$_6H_5$). ^{13}C NMR: δ 11.2, 13.4 (3 or 5-CH$_3$), 75.4 (CH), 107.6 (4-position carbon of pyrazole ring), 128.4, 129.4, 136.3, 140.6 (C$_6$H$_5$), 139.9, 145.0 (3 or 5-position carbon of pyrazole ring). ^{119}Sn NMR: δ −193.0. Anal. Calc. for C$_{23}$H$_{25}$IN$_4$Sn: C, 45.81; H, 4.18; N, 9.29. Found: C, 45.78; H, 4.32; N, 9.56%.

3.2. Synthesis of (t-Bu)$_2$ClSnCH(3,5-Me$_2$Pz)$_2$ (2)

To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (0.41 g, 2.0 mmol) in THF (40 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 this mixture was added a solution of di(tert-butyl)tin chloride (0.76 g, 2.5 mmol) in THF (10 ml). The reaction mixture was stirred at −70 °C for 1.5 h, and allowed to slowly approach room temperature and stirred overnight. The solvent was removed under a reduced pressure, and the residual solid was recrystallized from hot hexane to yield 0.60 g (64%) of **2** as white crystals, mp 140–142 °C. ^{1}H NMR: δ 1.29 (s, 18H, (CH_3)$_3$C), 2.09, 2.10 (s, s, 6H, 6H, CH_3), 5.75 (s, 2H, H^4 of pyrazole ring), 6.06 (s, 1H, CH). ^{13}C NMR: δ 11.0, 13.5 (3 or 5-CH$_3$), 30.4 ((CH$_3$)$_3$C), 38.2 ((CH$_3$)$_3$C), 72.8 (CH), 107.0 (4-position carbon of pyrazole ring), 139.9, 147.3 (3 or 5-position carbon of pyrazole ring). ^{119}Sn NMR: δ −69.9. Anal. Calc. for C$_{19}$H$_{33}$ClN$_4$Sn: C, 48.38; H, 7.05; N, 11.88. Found: C, 48.26; H, 7.35; N, 11.65%.

3.3. Synthesis of (t-Bu)$_2$ClSnCH(3,4,5-Me$_3$Pz)$_2$ (3)

This ligand was obtained similarly using bis(3,4,5-trimethylpyrazol-1-yl)methane (0.47 g, 2.0 mmol) instead of bis(3,5-dimethylpyrazol-1-yl)methane as described above for **2**. Yield: 0.49 g (49%), white crystals, mp 141–143 °C. ^{1}H NMR: δ 1.28 (s, 18H, (CH_3)$_3$C), 1.80, 2.00, 2.03 (s, s, s, 6H, 6H, 6H, CH_3), 6.08 (s, 1H, CH). ^{13}C NMR: δ 7.2, 8.5, 10.9 (3, 4 or 5-CH$_3$), 29.4 ((CH$_3$)$_3$C), 36.9 ((CH$_3$)$_3$C), 72.3 (CH), 112.1 (4-position carbon of pyrazole ring), 135.1, 145.0 (3 or 5-position carbon of pyrazole ring). ^{119}Sn NMR: δ −72.8. Anal. Calc. for C$_{21}$H$_{37}$ClN$_4$Sn: C, 50.47; H, 7.46; N, 11.21. Found: C, 50.25; H, 7.26; N, 11.01%.

3.4. Reaction of ligands 1–3 with W(CO)$_5$THF

Ligand (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 at reflux for 5 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 (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 green-yellow crystals.

3.4.1. Ph$_2$SnCH(3,5-Me$_2$Pz)$_2$W(CO)$_3$I (4)

This complex was obtained by the reaction of ligand **1** with W(CO)$_5$THF. The reaction mixture was stirred and heated at reflux for 3 h. Yield: 45%. ^{1}H NMR: δ 2.31, 2.69 (s, s, 6H, 6H, CH_3), 5.91 (s, 2H, H^4 of pyrazole ring), 6.27 (s, 1H, CH), 7.04–7.06, 7.25–7.30 (m, m, 4H, 6H, C$_6H_5$). ^{119}Sn NMR (DMSO-d_6): δ −207.3. IR (cm^{-1}): ν_{CO} = 1985 (vs), 1892 (vs), 1787 (s). Anal. Calc. for C$_{26}$H$_{25}$IN$_4$O$_3$SnW: C, 35.85; H, 2.89; N, 6.43. Found: C, 35.75; H, 2.78; N, 6.59%.

3.4.2. (t-Bu)₂SnCH(3,5-Me₂Pz)₂W(CO)₃Cl (5)

This complex was obtained by the reaction of ligand **2** with W(CO)₅THF. Yield: 45%. ¹H NMR: δ 1.09 (s, 18H, (CH_3)₃C), 2.43, 2.70 (s, s, 6H, 6H, CH_3), 6.00 (s, 2H, H^4 of pyrazole ring), 6.08 (s, 1H, CH). ¹³C NMR: δ 12.9, 16.8 (3 or 5-CH_3), 31.6 ((CH₃)₃C), 36.9 ((CH₃)₃C), 61.6 (CH), 109.3 (4-position carbon of pyrazole ring), 139.0, 156.0 (3 or 5-position carbon of pyrazole ring), 214.3 (CO). Only one signal of carbonyl carbon was observed possibly due to the low signal intensity and the limited solubility of **5**. ¹¹⁹Sn NMR: δ −72.6. IR (KBr, cm⁻¹): v_{CO} = 1974 (vs), 1891 (vs), 1773 (s); (CH₂Cl₂, cm⁻¹): v_{CO} = 1989 (vs), 1898 (vs), 1786 (s). Anal. Calc. for C₂₂H₃₃ClN₄O₃SnW: C, 35.73; H, 4.50; N, 7.58. Found: C, 35.56; H, 4.29; N, 7.69%.

3.4.3. (t-Bu)₂SnCH(3,4,5-Me₃Pz)₂W(CO)₃Cl (6)

This complex was obtained by the reaction of ligand **3** with W(CO)₅THF. Yield: 40%. ¹H NMR: δ 1.08 (s, 18H, (CH_3)₃C), 1.92, 2.31, 2.58 (s, s, s, 6H, 6H, 6H, CH_3), 6.15 (s, 1H, CH). ¹³C NMR: δ 8.5, 10.7, 14.0 (3, 4 or 5-CH_3), 31.4 ((CH₃)₃C), 36.2 ((CH₃)₃C), 61.6 (CH), 115.1 (4-position carbon of pyrazole ring), 135.8, 153.9 (3 or 5-position carbon of pyrazole ring), 214.6 (CO). Only one signal of carbonyl carbon was observed possibly due to the low signal intensity and the limited solubility of **6**. ¹¹⁹Sn NMR: δ −65.5. IR (KBr, cm⁻¹): v_{CO} = 1983 (vs), 1894 (vs), 1868 (sh), 1774 (s); (CH₂Cl₂, cm⁻¹): v_{CO} = 1987 (vs), 1895 (vs), 1782 (s). Anal. Calc. for C₂₄H₃₇ClN₄O₃SnW: C, 37.55; H, 4.86; N, 7.30. Found: C, 37.61; H, 4.78; N, 7.39%.

3.5. Reaction of complex 5 with n-BuLi

To a solution of **5** (85.0 mg, 0.115 mmol) in THF (10 ml) was added a hexane solution of n-BuLi (2.5 M, 0.050 ml) at −50 °C. The mixture was stirred for 0.5 h at that temperature, and allowed to slowly reach room temperature and stirred for 2 h. After the solvent was removed under a reduced pressure, the residual solid was purified by column chromatography on silica using CH₂Cl₂ as eluent. The eluate was concentrated to dryness again, and the residual solid was recrystallized from CH₂Cl₂/hexane to give green-yellow crystals, which was identified as complex CH₂(3,5-Me₂Pz)₂W(CO)₄ according to its ¹H NMR and IR spectra. Yield: 12%. ¹H NMR: δ 2.42, 2.48 (s, s, 6H, 6H, CH_3), 6.01 (m, 3H, H^4 of pyrazole ring and one of hydrogen of CH_2), 6.39 (d, J = 14.7 Hz, 1H, one of hydrogen of CH_2). IR (cm⁻¹): v_{CO} = 2002 (s), 1876 (vs), 1852 (vs), 1829 (vs).

3.6. Reaction of 1 with 2-PySNa (Py = pyridyl)

NaH (8.0 mg, 0.33 mmol) was added to a solution of 2-pyridinethiol (37 mg, 0.33 mmol) in benzene (10 ml) at room temperature. The reaction mixture was stirred for 2 h, and then a solution of **1** (0.20 g, 0.33 mmol) in benzene (10 ml) was added to the above solution. The reaction mixture was stirred overnight at room temperature, and filtered off. The solvent was removed under a reduced pressure, and the residual solid was recrystallized from hot hexane to give 0.11 g (57%) of **7** as pale yellow crystals, mp 146–148 °C. ¹H NMR: δ 1.81, 2.07 (s, s, 6 H, 6H, CH_3),

Table 2
Crystallographic data and refinement parameters for compounds **2**, **4**, **5** and **7**

Compound	2	4	5	7
Formula	C₁₉H₃₃ClN₄Sn	C₂₆H₂₅IN₄O₃SnW	C₂₂H₃₃ClN₄O₃SnW	C₂₈H₂₉N₅SSn
Formula weight	471.63	870.94	739.51	586.31
Crystal size (mm)	0.30 × 0.26 × 0.18	0.20 × 0.16 × 0.12	0.22 × 0.20 × 0.14	0.24 × 0.20 × 0.14
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P2₁/c	P2₁/n	P2₁/n	P1̄
Cell parameters				
a (Å)	10.476(1)	10.319(3)	9.787(1)	8.543(3)
b (Å)	24.089(4)	16.716(5)	17.206(1)	12.136(4)
c (Å)	10.405(1)	16.115(5)	16.281(1)	13.568(4)
α (°)	90	90	90	85.751(6)
β (°)	116.130(2)	90.633(5)	102.272(2)	83.467(6)
γ (°)	90	90	90	81.616(6)
V (Å³)	2357.4(6)	2779.6(14)	2679.1(5)	1380.3(8)
Z	4	4	4	2
T (K)	294(2)	293(2)	294(2)	293(2)
D_{calc} (g cm⁻³)	1.329	2.081	1.833	1.411
2θ Range (°)	3.38–52.76	3.52–52.94	3.48–52.74	3.02–52.96
F(0 0 0)	968	1640	1432	596
μ (mm⁻¹)	1.206	6.178	5.351	1.026
Number of reflections measured	13148	15898	14918	8027
Number of reflections observed [R_{int}]	4805 [0.0341]	5705 [0.0541]	5453 [0.0434]	5635 [0.0379]
Number of reflections observed with (I ⩾ 2σ(I))	3416	3981	4096	3986
Number of parameters	236	329	299	320
Residuals R, R_w (I ⩾ 2σ(I))	0.032, 0.068	0.036, 0.051	0.030, 0.059	0.046, 0.086
Goodness-of-fit	0.988	1.033	1.033	1.022

5.68 (s, 2H, H^4 of pyrazole ring), 6.73 (s, 1H, CH), 6.66 (m, 1H, C_5H_4N), 7.17–7.30, 7.71–7.84 (m, m, 7H, 6H, C_6H_5 and C_5H_4N). ^{13}C NMR: δ 10.7, 13.4 (3 or 5-CH_3), 74.5 (CH), 107.1 (4-position carbon of pyrazole ring), 118.1, 124.4, 128.0, 128.5, 135.8, 136.3, 136.6, 139.3, 143.5, 147.1, 147.7 (C_6H_5, C_5H_4N and 3 or 5-position carbon of pyrazole ring). ^{119}Sn NMR: δ −156.6. Anal. Calc. for $C_{28}H_{29}N_5SSn$: C, 57.36; H, 4.99; N, 11.94. Found: C, 57.64; H, 5.35; N, 11.78%.

3.7. Reaction of 7 with W(CO)₅THF

This reaction was carried out similarly using **7** instead of **1** as described above for **4**. After the reaction completed, the reaction mixture was isolated by column chromatography on silica using CH_2Cl_2 as eluent. The eluate was concentrated to dryness again, and the residual solid was recrystallized from CH_2Cl_2/hexane to give green-yellow crystals, which was identified as complex $CH_2(3,5\text{-}Me_2Pz)_2W(CO)_4$ according to its ^{1}H NMR and IR spectra. Yield: 10%.

3.8. X-ray crystallography

Colorless crystals of **2** as well as pale yellow crystals of **7** suitable for X-ray analysis were obtained by slow cooling their hot hexane solutions. While green-yellow crystals of **4** and **5** suitable for X-ray analysis were grown by slow diffusion of hexane into their CH_2Cl_2 solutions at −10 °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 2.

Acknowledgements

Appendix A. Supplementary material

CCDC 666272, 666273, 666274 and 666275 contain the supplementary crystallographic data for **2**, **4**, **5** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.041.

References

[1] (a) C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 525;
(b) H.R. Bigmore, S.C. Lawrence, P. Mountford, C.S. Tredget, Dalton Trans. (2005) 635.

[2] (a) C. Pettinari, R. Pettinari, Coord. Chem. Rev. 249 (2005) 663;
(b) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, Dalton Trans. (2004) 1499.

[3] (a) T.C. Higgs, C.J. Carrano, Inorg. Chem. 36 (1997) 291;
(b) A. Otero, J. Fernández-Baeza, J. Tejeda, A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, A. Lara-Sánchez, M. Fernández-López, M. Lanfranchi, M.A. Pellinghelli, J. Chem. Soc., Dalton Trans. (1999) 3537;
(c) W. Kläui, M. Berghahn, G. Rheinwald, H. Lang, Angew. Chem. Int. Ed. 39 (2000) 2464;
(d) A. Beck, B. Weibert, N. Burzlaff, Eur. J. Inorg. Chem. (2001) 521;
(e) D.L. Reger, T.C. Grattan, Synthesis (2003) 350;
(f) D.L. Reger, R.P. Watson, M.D. Smith, P.J. Pellechia, Organometallics 25 (2006) 743;
(g) G.A. Santillan, C.J. Carrano, Inorg. Chem. 46 (2007) 1751;
(h) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L.F. Sánchez-Barba, M. Sánchez-Molina, A.M. Rodríguez, C. Bo, M. Urbano-Cuadrado, Organometallics 26 (2007) 4310;
(i) D.L. Reger, R.P. Watson, M.D. Smith, J. Organomet. Chem. 692 (2007) 3094;
(j) A. Sánchez-Méndez, E. de Jesús, J.C. Flores, P. Gómez-Sal, Inorg. Chem. 46 (2007) 4793.

[4] (a) R. Eaves, S. Parkin, F.T. Ladipo, Inorg. Chem. 46 (2007) 9495;
(b) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L.F. Sánchez-Barba, M. Sánchez-Molina, S. Franco, M.I. López-Solera, A.M. Rodríguez, Inorg. Chem. 46 (2007) 8475;
(c) S. Milione, F. Grisi, R. Centore, A. Tuzi, Organometallics 25 (2006) 266;
(d) J.T. Hoffman, Ba.L. Tran, C.J. Carrano, Dalton Trans. (2006) 3822;
(e) F. Mohr, E. Cerrada, M. Laguna, Dalton Trans. (2006) 5567;
(f) E.C.B. Alegria, L.M.D.R.S. Martins, M. Haukka, A.J.L. Pombeiro, Dalton Trans. (2006) 4954;
(g) E. Hübner, T. Haas, N. Burzlaff, Eur. J. Inorg. Chem. (2006) 4989;
(h) E.T. Papish, M.T. Taylor, F.E. Jernigan III, M.J. Rodig, R.R. Shawhan, G.P.A. Yap, F.A. Jové, Inorg. Chem. 45 (2006) 2242;
(i) S. Milione, V. Bertolasi, T. Cuenca, A. Grassi, Organometallics 24 (2005) 4915;
(j) M. Porchia, G. Papini, C. Santini, G.G. Lobbia, M. Pellei, F. Tisato, G. Bandoli, A. Dolmella, Inorg. Chem. 44 (2005) 4045;
(k) B.S. Hammes, B.S. Chohan, J.T. Hoffman, S. Einwächter, C.J. Carrano, Inorg. Chem. 43 (2004) 7800;
(l) I. Hegelmann, N. Burzlaff, Eur. J. Inorg. Chem. (2003) 409;
(m) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L. Sánchez-Barba, M.T. Expósito, A.M. Rodríguez, Dalton Trans. (2003) 1614.

[5] (a) B.S. Hammes, C.J. Carrano, J. Chem. Soc., Dalton Trans. (2000) 3304;
(b) A. Otero, J. Fernández-Baeza, A. Antiñolo, F. Carrillo-Hermosilla, J. Tejeda, A. Lara-Sánchez, L. Sánchez-Barba, M. Fernández-López, A.M. Rodríguez, I. López-Solera, Inorg. Chem. 41 (2002) 5193;
(c) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L. Sánchez-Barba, M. Sánchez-Molina, S. Franco, I. López-Solera, A.M. Rodríguez, Dalton Trans. (2006) 4359;
(d) R.-Y. Tan, H.-B. Song, L.-F. Tang, J. Organomet. Chem. 691 (2006) 5964;
(e) R.-Y. Tan, J. Hong, M. Du, L.-F. Tang, J. Organomet. Chem. 692 (2007) 1708.

[6] (a) L. Maria, S. Cunha, M. Videira, L. Gano, A. Paulo, I.C. Santos, I. Santos, Dalton Trans. (2007) 3010;
(b) A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejeda, A. Lara-Sánchez, L.F. Sánchez-Barba, I. López-Solera, A.M. Rodríguez, Inorg. Chem. 46 (2007) 1760;
(c) D. Adhikari, G. Zhao, F. Basuli, J. Tomaszewski, J.C. Huffman, D.J. Mindiola, Inorg. Chem. 45 (2006) 1604;
(d) D.L. Reger, R.F. Semeniuc, J.R. Gardinier, J. O'Neal, B. Reinecke, M.D. Smith, Inorg. Chem. 45 (2006) 4337;

(e) W. Kläui, M. Berghahn, W. Frank, G.J. Reiß, T. Schönherr, G. Rheinwald, H. Lang, Eur. J. Inorg. Chem. (2003) 2059.

[7] (a) R.G. Howe, C.S. Tredget, S.C. Lawrence, S. Subongkoj, A.R. Cowley, P. Mountford, Chem. Commun. (2006) 223;
(b) A. Sánchez-Méndez, J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, Dalton Trans. (2006) 5379;
(c) A. Sánchez-Méndez, G.F. Silvestri, de E. Jesús, de la F.J. Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, Eur. J. Inorg. Chem. (2004) 3287;
(d) L.-F. Tang, W.-L. Jia, X.-M. Zhao, P. Yang, J.-T. Wang, J. Organomet. Chem. 658 (2002) 198;
(e) A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, J. Fernández-Baeza, M. Fernández-López, A. Lara-Sánchez, A. Moreno, A. Otero, A.M. Rodriguez, J. Tejeda, J. Chem. Soc., Dalton Trans. (1998) 3737;
(f) A.R. Katritzky, A.E. Abdel-Rahman, D.E. Leahy, O.A. Schwarz, Tetrahedron 39 (1983) 4133.

[8] (a) L.-F. Tang, W.-L. Jia, D.-T. Song, Z.-H. Wang, J.-F. Chai, J.-T. Wang, Organometallics 21 (2002) 445;
(b) L.-F. Tang, S.-B. Zhao, W.-L. Jia, Z. Yang, D.-T. Song, J.-T. Wang, Organometallics 22 (2003) 3290;
(c) S.-B. Zhao, Z.-K. Wen, J.-T. Wang, L.-F. Tang, Chem. J. Chinese Univ. 26 (2005) 1062.

[9] J. Bareš, P. Novák, M. Nádvorník, R. Jambor, T. Lébl, I. Císařová, A. Růžička, J. Holeček, Organometallics 23 (2004) 2967.

[10] R.A. Varga, M. Schürmann, C. Silvestru, J. Organomet. Chem. 623 (2001) 161.

[11] P. Novák, I. Císařová, R. Jambor, A. Růžička, J. Holeček, Appl. Organomet. Chem. 18 (2004) 241.

[12] A. Macchioni, G. Bellachioma, G. Cardaci, V. Gramlich, H. Rüegger, S. Terenzi, L.M. Venanzi, Organometallics 16 (1997) 2139.

[13] T. Szymańska-Buzar, Coord. Chem. Rev. 249 (2005) 2195.

[14] (a) M. Panizo, M. Cano, J. Organomet. Chem. 287 (1985) 221;
(b) D. Miguel, J.A. Pérez-Martínez, V. Riera, S. García-Granda, Polyhedron 10 (1991) 1717.

[15] L.-F. Tang, J. Hong, Z.-K. Wen, Organometallics 24 (2005) 4451.

[16] T.A. Mobley, R. Gandour, E.P. Gillis, K. Nti-Addae, R. Palchaudhuri, P. Rajbhandari, N. Tomson, A. Vargas, Q. Zheng, Organometallics 24 (2005) 3897.

[17] (a) K.-B. Shiu, C.-J. Chang, J. Chin. Chem. Soc. 34 (1987) 297;
(b) L.-F. Tang, Z.-H. Wang, Y.-M. Xu, J.-T. Wang, H.-G. Wang, X.-K. Yao, Polyhedron 17 (1998) 3765.

[18] M.C. Janzen, H.A. Jenkins, L.M. Rendina, J.J. Vittal, R.J. Puddephatt, Inorg. Chem. 38 (1999) 2123.

[19] A.L. Albert, S.A. Kandil, J. Chem. Soc. (A) (1970) 2987.