

以 2-(1-吡唑基甲基)吡啶类化合物为配体的羰基钼、 钨衍生物的合成及结构

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摘要: 合成了 2-[1-(3-叔丁基)吡唑基甲基]吡啶($\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})$), 并研究了羰基钼(钨)与该配体及其类似物 2-(1-吡唑基甲基)吡啶($\text{CH}_2(\text{Py})(\text{Pz})$)和 2-[1-(3,5-二甲基)吡唑基甲基]吡啶($\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})$)的反应, 合成了 6 个含双齿螯合的 2-(1-吡唑基甲基)吡啶类配体的四羰基金属衍生物 $\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})\text{M}(\text{CO})_4$, $\text{CH}_2(\text{Py})(\text{Pz})\text{M}(\text{CO})_4$ 和 $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_4$ ($\text{M}=\text{Mo}$ 或 W)。当用 SnCl_4 处理 $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_4$ 时, Sn-Cl 键对金属中心发生氧化加成得到 2 个杂双核金属有机化合物 $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_3(\text{Cl})\text{SnCl}_3$ 。所有新化合物均通过了红外和核磁的表征, $\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})\text{W}(\text{CO})_4$ 和 $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_3(\text{Cl})\text{SnCl}_3$ 的结构还得到了 X-射线单晶衍射的确定。用循环伏安法测定了四羰基金属衍生物的电化学性质。

关键词: 吡唑; 吡啶; 2-(1-吡唑基甲基)吡啶; 第六族羰基金属化合物

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Synthesis and Structure of Carbonyl Molybdenum and Tungsten Derivatives Containing 2-(Pyrazol-1-ylmethyl)pyridine

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Abstract: 2-(3-*tert*-Butylpyrazol-1-ylmethyl)pyridine ($\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})$, $\text{Py}=2\text{-pyridyl}$ and $\text{Pz}=\text{pyrazol-1-yl}$) has been prepared by the reaction of 3-*tert*-butylpyrazole and 2-chloromethylpyridine-HCl under basic conditions. Reaction of $\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})$ and its analogs, namely $\text{CH}_2(\text{Py})(\text{Pz})$ and $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})$, with $\text{M}(\text{CO})_6$ ($\text{M}=\text{Mo}$ or W) has been investigated, which yields six bidentate chelating complexes $\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})\text{M}(\text{CO})_4$, $\text{CH}_2(\text{Py})(\text{Pz})\text{M}(\text{CO})_4$ and $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_4$. Treatment of $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_4$ with SnCl_4 gives heterobimetallic complexes $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_3(\text{Cl})\text{SnCl}_3$. These newly synthesized complexes have been characterized by IR and NMR spectroscopy, and the structures of $\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})\text{W}(\text{CO})_4$ and $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_3(\text{Cl})\text{SnCl}_3$ have been further confirmed by X-ray crystal diffraction. The electrochemical behavior of $\text{CH}_2(\text{Py})(3\text{-Bu}^t\text{Pz})\text{M}(\text{CO})_4$, $\text{CH}_2(\text{Py})(\text{Pz})\text{M}(\text{CO})_4$ and $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_4$ has been investigated by cyclic voltammetry. CCDC: 820993, 6; 820994, 8.

Key words: pyrazole; pyridine; 2-(pyrazol-1-ylmethyl)pyridine; group 6 metal carbonyl complex

Bis(pyrazol-1-yl)methanes have been extensively used in inorganic and organometallic chemistry in recent years, owing to their versatile coordination

chemistry towards main group and transition metals^[1-5]. The modification of bis(pyrazol-1-yl)methanes on the bridgehead carbon atom has been successfully

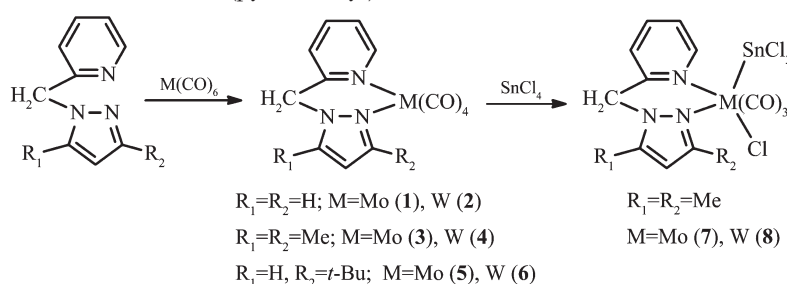
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exploited and widely broadened their applicable fields^[1-2,6-7]. The replacement of one pyrazol-1-yl group in bis(pyrazol-1-yl)methanes by pyridyl to form 2-(pyrazol-1-ylmethyl)pyridine has been reported in the literature^[8]. Owing to some analogous structural features with bis(pyrazol-1-yl)methanes, such as acting as *N,N*-chelating bidentate ligands, 2-(pyrazol-1-ylmethyl)pyridine has been explored to act as a good donor to various main group^[9] and transition metals^[10-14]. On the other hand, these two kinds of ligands also show significant structural difference. Bis(pyrazol-1-yl)

methanes provide two same nitrogen donors to metal centers, while 2-(pyrazol-1-ylmethyl)pyridine contains a hard donor (pyrazolyl nitrogen) and a relative soft donor (pyridyl nitrogen) in a given ligand system, which makes it convenient and facile to control the coordination environments around metal centers. As an extension of our investigations on bis(pyrazol-1-yl)methanes, herein we report the reaction of 2-(pyrazol-1-ylmethyl)pyridine with group VIB metal carbonyl complexes (Scheme 1).



Scheme 1 Reactions of 2-(pyrazol-1-ylmethyl)pyridine with $M(CO)_6$ ($M=Mo$ or W)

1 Experimental

Solvents were dried by standard methods and distilled prior to use. All reactions were carried out under an argon atmosphere. NMR spectra were recorded in $CDCl_3$ unless otherwise indicated on a Bruker 400 spectrometer, and the chemical shifts are reported in ppm with respect to the reference (internal $SiMe_4$ for 1H and ^{13}C NMR). IR spectroscopic data were obtained from a Bio-Rad FTS 6000 spectrometer as KBr pellets. Elemental analyses were carried out on a Yanaco CHN Corder MT-3 elemental analyzer. HR mass spectra were carried out on a Varian QFT-ESI spectrometer. Cyclic voltammetric experiments were performed on a LK 2005 electrochemical analyzer equipped with a three-electrode assembly. The working electrode was a Pt disk ($\varphi=2$ mm), and the reference was a SCE electrode. A Pt filament was used as an auxiliary electrode. 3-*tert*-Butylpyrazole^[15], 2-(pyrazol-1-ylmethyl)pyridine $[(CH_2(Py)Pz)]^{[9]}$ and 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine $[CH_2(Py)(3,5-Me_2Pz)]^{[9]}$ were prepared by published methods.

1.1 Synthesis of 2-(3-*tert*-butylpyrazol-1-ylmethyl)pyridine $[CH_2(Py)(3-Bu^tPz)]$

3-*tert*-Butylpyrazole (1.51 g, 12.2 mmol), chloro-

methylpyridine-HCl (2.20 g, 13.2 mmol), tetrabutylammonium bromide (0.3 g) and sodium hydroxide (4.0 g) were added to the mixed solvent of benzene (30 mL) and water (5 mL). The mixture was vigorously stirred and refluxed for 6 h. After cooling, the two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (30 mL \times 3). The organic phases were combined and dried over anhydrous magnesium sulfate. After evaporating the solvent, yellow oils were obtained, which were purified by column chromatography on silica using ethyl acetate/hexane (1:1, V/V) as eluent. The eluate was concentrated to dryness under a reduced pressure to give yellow oils. Yield: 2.25 g (86%). 1H NMR: δ 1.31 (s, 9H, $C(CH_3)_3$), 5.41 (s, 2H, CH_2), 6.14 (d, $J=2.4$ Hz, 1H, H^4 of pyrazole), 7.35 (d, $J=2.4$ Hz, 1H, H^5 of pyrazole), 6.82 (d, $J=7.8$ Hz, 1H), 7.14~7.17 (m, 1H), 7.56~7.60 (m, 1H), 8.53 (d, $J=1.8$ Hz, 1H) (C_5H_4N). ^{13}C NMR: δ 29.7 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 56.3 (CH_2), 101.5 (C^4 of pyrazole), 120.4, 121.4, 129.0, 135.9, 148.1, 156.5, 161.4 (C_5H_4N and C^3 as well as C^5 of pyrazole). HRMS (ESI, m/z): 238.1317 (Calcd. for $C_{13}H_{17}N_3Na$: 238.1315, $[M+Na]^+$, 100%).

1.2 Synthesis of $CH_2(Py)PzMo(CO)_4$ (1)

The solution of $Mo(CO)_6$ (1 mmol) and $CH_2(Py)Pz$

(1 mmol) dissolved in THF (40 mL) was irradiated with a 300 W high-pressure mercury lamp for *ca.* 8 h at room temperature. The solvent was removed under a reduced pressure, and the residue was purified by column chromatography on silica using ethyl acetate/hexane (2: 1, *V/V*) as eluent. The greenyellow eluate was again concentrated to dryness, the residue was recrystallized from CH_2Cl_2 /hexane to give greenyellow crystals. Yield: 43%. ^1H NMR (CD_3COCD_3): δ 5.58 (s, 2H, CH_2), 6.33 (t, $J=2.4$ Hz, 1H, H^4 of pyrazole), 7.36~7.40 (m, 1H), 7.73 (d, $J=5.4$ Hz, 1H), 7.90~7.96 (m, 1H), 8.94 (d, $J=7.5$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$), 7.78 (d, $J=1.8$ Hz, 1H), 8.00 (d, $J=2.4$ Hz, 1H) (H^3 and H^5 of pyrazole). IR $\nu(\text{C}\equiv\text{O})$: 2 006.8 (s), 1 906.2 (vs), 1 852.6 (vs), 1 813.0 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{MoN}_3\text{O}_4$ (%): C 42.53, H 2.47, N 11.44; found(%): C 42.33, H 2.53, N 11.32.

1.3 Synthesis of $\text{CH}_2(\text{Py})\text{PzW}(\text{CO})_4$ (2)

This compound was similarly obtained as for complex **1** by the reaction of $\text{CH}_2(\text{Py})\text{Pz}$ with $\text{W}(\text{CO})_6$. Yield: 52%. ^1H NMR (CD_3COCD_3): δ 5.62 (s, 2H, CH_2), 6.37 (t, $J=2.4$ Hz, 1H, H^4 of pyrazole), 7.37~7.41 (m, 1H), 7.79 (d, $J=7.5$ Hz, 1H), 7.95~8.01 (m, 1H), 9.08 (d, $J=5.7$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$), 7.88 (d, $J=2.1$ Hz, 1H), 8.06 (d, $J=2.1$ Hz, 1H) (H^3 and H^5 of pyrazole). IR $\nu(\text{C}\equiv\text{O})$: 2 000.5 (s), 1 893.6 (s), 1 845.1 (vs), 1 806.6 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_4\text{W}$ (%): C 34.31, H 1.99, N 9.23; found(%): C 34.53, H 2.39, N 9.54.

Complexes **1** and **2** have relatively low solubility in chlorinated solvents, and these complexes display moderately soluble in strong polar solvents, such as acetone.

1.4 Synthesis of $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{Mo}(\text{CO})_4$ (3)

This compound was similarly obtained as for complex **1** by the reaction of $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})$ with $\text{Mo}(\text{CO})_6$. Yield: 40%. ^1H NMR: δ 2.38, 2.46 (s, s, 3H, 3H, CH_3), 5.30 (s, 2H, CH_2), 5.95 (s, 1H, H^4 of pyrazole), 7.24~7.28 (m, 1H), 7.74 (d, $J=7.8$ Hz, 1H), 7.78~7.84 (m, 1H), 9.08 (d, $J=5.7$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$). ^{13}C NMR: δ 11.6, 15.6 (CH_3), 53.0 (CH_2), 107.1 (C^4 of pyrazole), 123.6, 124.9, 138.5, 140.5, 155.0, 152.6, 155.8 ($\text{C}_5\text{H}_4\text{N}$ as well as C^3 and C^5 of pyrazole), 206.1 (CO). Only one signal of carbonyl carbon was observed possibly due to the low signal intensity and the limited

solubility of **3**. IR $\nu(\text{C}\equiv\text{O})$: 2 011.2 (s), 1 905.4 (vs), 1 855.6 (vs), 1 824.2 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{MoN}_3\text{O}_4$ (%): C 45.58, H 3.32, N 10.63; found(%): C 45.50, H 3.35, N 10.21.

1.5 Synthesis of $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_4$ (4)

This compound was similarly obtained as for complex **1** by the reaction of $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})$ with $\text{W}(\text{CO})_6$. Yield: 54%. ^1H NMR: δ 2.32, 2.38 (s, s, 3H, 3H, CH_3), 5.45 (s, 2H, CH_2), 6.04 (s, 1H, H^4 of pyrazole), 7.26~7.38 (m, 1H), 7.87 (d, $J=7.6$ Hz, 1H), 7.79~7.96 (m, 1H), 9.04 (d, $J=5.4$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$). ^{13}C NMR: δ 11.7, 16.4 (CH_3), 54.8 (CH_2), 108.0 (C^4 of pyrazole), 125.6, 127.0, 140.7, 143.2, 153.2, 156.3, 156.9 ($\text{C}_5\text{H}_4\text{N}$ as well as C^3 and C^5 of pyrazole), 207.2 (CO). IR $\nu(\text{C}\equiv\text{O})$: 2 004.0 (s), 1 892.7 (vs), 1 861.4 (sh), 1 846.0 (vs), 1 819.0 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_4\text{W}$ (%): C 37.29, H 2.71, N 8.70; found(%): C 37.59, H 3.03, N 8.32.

1.6 Synthesis of $\text{CH}_2(\text{Py})(3\text{-BuPz})\text{Mo}(\text{CO})_4$ (5)

This compound was similarly obtained as for complex **1** by the reaction of $\text{CH}_2(\text{Py})(3\text{-BuPz})$ with $\text{Mo}(\text{CO})_6$. Yield: 43%. ^1H NMR: δ 1.47 (s, 9H, $\text{C}(\text{CH}_3)_3$), 5.53 (s, 2H, CH_2), 6.10 (d, $J=2.0$ Hz, 1H, H^4 of pyrazole), 7.74 (d, $J=2.0$ Hz, 1H, H^5 of pyrazole), 7.29 (d, $J=6.6$ Hz, 1H), 7.49 (d, $J=7.7$ Hz, 1H), 7.82 (t, $J=7.6$ Hz, 1H), 9.12 (d, $J=5.3$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$). IR $\nu(\text{C}\equiv\text{O})$: 2 015.2 (s), 1 871.9 (br, vs), 1 819.6 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{MoN}_3\text{O}_4$ (%): C 48.24, H 4.05, N 9.93; found(%): C 48.35, H 4.35, N 10.23.

1.7 Synthesis of $\text{CH}_2(\text{Py})(3\text{-BuPz})\text{W}(\text{CO})_4$ (6)

This compound was similarly obtained as for complex **1** by the reaction of $\text{CH}_2(\text{Py})(3\text{-BuPz})$ with $\text{W}(\text{CO})_6$. Yield: 48%. ^1H NMR: δ 1.56 (s, 9H, $\text{C}(\text{CH}_3)_3$), 5.50 (s, 2H, CH_2), 6.34 (d, $J=2.5$ Hz, 1H, H^4 of pyrazole), 7.60 (d, $J=2.5$ Hz, 1H, H^5 of pyrazole), 7.31 (d, $J=6.3$ Hz, 1H), 7.51 (d, $J=8.0$ Hz, 1H), 7.86 (dt, $J=1.2$ Hz, $J=7.8$ Hz, 1H), 9.25 (d, $J=5.0$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$). IR $\nu(\text{C}\equiv\text{O})$: 2 006.0 (s), 1 880.7 (br, vs), 1 830.7 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_4\text{W}$ (%): C 39.94, H 3.35, N 8.22; found(%): C 39.82, H 3.40, N 8.20.

1.8 Synthesis of $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{Mo}(\text{CO})_3(\text{Cl})\text{SnCl}_3$ (7)

SnCl_4 (0.4 mmol) was added by syringe to a stirring

solution of **3** (0.4 mmol) dissolved in 20 mL of CH_2Cl_2 . After stirring at room temperature for 2 h, the solution was concentrated to dryness in vacuo, and the residue was recrystallized from CH_2Cl_2 /hexane to yield orange-red crystals of **7**. Yield: 93%. ^1H NMR (CD_3COCd_3): δ 2.44, 2.48 (s, s, 3H, 3H, CH_3), 5.54 (s, 2H, CH_2), 6.10 (s, 1H, H^4 of pyrazole), 7.48~7.53 (m, 1H), 7.94 (d, $J=7.8$ Hz, 1H), 8.03~8.08 (m, 1H), 9.06 (d, $J=4.8$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$). IR $\nu(\text{C}\equiv\text{O})$: 2 021.8 (vs), 1 948.6 (sh), 1 924.7 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{Cl}_4\text{MoN}_3\text{O}_3\text{Sn}\cdot\text{CH}_2\text{Cl}_2$ (%): C 25.28, H 2.12, N 5.90; found (%): C 24.85, H 2.03, N 6.21.

1.9 Synthesis of $\text{CH}_2(\text{Py})(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_3(\text{Cl})\text{SnCl}_3$ (**8**)

This compound was similarly obtained as for complex **7** by the reaction of **4** with SnCl_4 . Red crystals, yield: 90%. ^1H NMR (CD_3COCd_3): δ 2.48, 2.56 (s, s, 3H, 3H, CH_3), 5.43 (d, $J=16.2$ Hz, 1H), 6.02 (d, $J=16.2$ Hz, 1H) (CH_2), 6.33 (s, 1H, H^4 of pyrazole), 7.79~7.83

(m, 1H), 8.14 (d, $J=7.2$ Hz, 1H), 8.25~8.30 (m, 1H), 8.83 (d, $J=5.7$ Hz, 1H) ($\text{C}_5\text{H}_4\text{N}$). IR $\nu(\text{C}\equiv\text{O})$: 2 023.4 (vs), 1 962.1 (s), 1 911.4 (vs) cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{Cl}_4\text{N}_3\text{O}_3\text{SnW}\cdot\text{CH}_2\text{Cl}_2$ (%): C 22.50, H 1.89, N 5.25; found (%): C 22.45, H 1.93, N 5.20.

1.10 Structure determination of complexes **6** and **8**

Crystals of **6** and **8** suitable for X-ray analyses were obtained by slow diffusion of hexane into their CH_2Cl_2 solution at 4 $^\circ\text{C}$. Intensity data were collected on a Bruker Apex II CCD diffractometer using the $\omega/2\theta$ scan technique, and a semi-empirical absorption correction was applied. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined with riding model position parameters. A summary of the fundamental crystal data for **6** and **8** is listed in Table 1.

CCDC: 820993, **6**; 820994, **8**.

Table 1 Crystallographic data and refinement parameters for complexes **6** and **8**

Complex	6	8 · CH_2Cl_2
Formula	$\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_4\text{W}$	$\text{C}_{15}\text{H}_{15}\text{Cl}_6\text{N}_3\text{O}_3\text{SnW}$
Formula weigh	511.19	800.54
Crystal size / mm	0.22×0.20×0.16	0.22×0.14×0.12
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.900 9(3)	0.872 9(2)
b / nm	0.942 8(3)	1.055 4(2)
c / nm	1.144 1(4)	1.480 0(3)
α / ($^\circ$)	82.432(4)	69.641(2)
β / ($^\circ$)	70.409(3)	84.412(2)
γ / ($^\circ$)	85.013(4)	72.937(2)
T / K	293(2)	293(2)
λ / nm	0.071 073	0.071 073
V / nm^3	0.906 6(5)	1.222 0(4)
D_c / ($\text{g}\cdot\text{cm}^{-3}$)	1.873	2.176
2θ range / ($^\circ$)	4.36~50.04	4.28~50.02
Absorption coefficient / mm^{-1}	6.396	6.402
Z	2	2
$F(000)$	492	752
Reflections collected	4 952	6 699
Independent reflections (R_{int})	3 164 (0.020 9)	4 272 (0.016 9)
Reflections observed with ($I>2\sigma(I)$)	2 849	3 679
No. of parameters	229	291
Residuals R , wR ($I>2\sigma(I)$)	0.022 4, 0.053 8	0.024 5, 0.055 0
Goodness-of-fit	0.991	1.007

2 Results and discussion

2.1 Characterization of complexes 1~6

The IR spectra of complexes **1**~**6** show three to four characteristic absorption peaks of metal carbonyl stretching bands in the range of 1 806~2 016 cm^{-1} , consistent with a typical *cis*-tetracarbonyl arrangement^[16]. The structure of complex **6** has been further confirmed by X-ray structural analyses. Selected bond distances and angles are listed in Table 2, and the crystal structure is presented in Fig.1. Although a bulky *tert*-butyl group is situated in the 3-position of pyrazole ring, 2-(3-*tert*-butylpyrazol-1-ylmethyl)pyridine still acts as a chelating ligand to the tungsten atom, giving a boat-conformational six-membered metallacycle, similar to those in group VIB metal carbonyl derivatives with bis(pyrazol-1-yl)methanes, such as in $\text{CH}_2(3,5\text{-Me}_2\text{-4-ClPz})_2\text{W}(\text{CO})_4$ ^[17] and $\text{Ph}_2(\text{Pr})\text{SnCH}(3,5\text{-Me}_2\text{Pz})_2\text{W}(\text{CO})_4$ ^[18]. The coordination geometry of the tungsten center is slightly distorted octahedral. The W-N_{pyrazolyl} bond distance is 0.232 8(3) nm, similar to the W-N_{pyridyl} bond distance (0.228 3(3) nm), and comparable to those reported in other octahedral tungsten(0) complexes with

pyrazolyl ligands, such as 0.223 6(4) nm in (3-Bu'PzH)W(CO)₅^[19], 0.226 4(4) nm in PhSCH₂(3,5-Me₂Pz)W(CO)₄^[20] and 0.228 9(8) nm as well as 0.226 0(8) nm in Ph₂(Pr)SnCH(3,5-Me₂Pz)₂W(CO)₄^[18]. It is worth noting that two *cis*-carbonyl groups in this complex considerably deviate from linearity with the W(1)-C(1)-O(1) angle of 171.7(4)° and the W(1)-C(4)-O(4) angle of

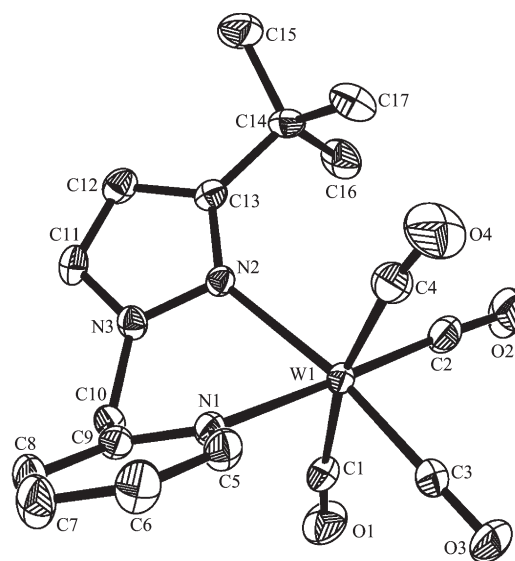


Fig.1 Molecular structure of complex **6** with thermal ellipsoids drawn at 30% probability level

Table 2 Selected bond distances (nm) and angles (°) for complexes **6** and **8**

Complex 6					
W(1)-N(1)	0.228 3(3)	W(1)-C(2)	0.194 3(5)	C(4)-O(4)	0.114 9(6)
W(1)-N(2)	0.232 8(3)	C(1)-O(1)	0.114 2(6)	N(3)-C(10)	0.145 6(5)
W(1)-C(1)	0.203 1(5)	C(2)-O(2)	0.117 7(6)		
W(1)-C(1)-O(1)	171.7(4)	N(1)-W(1)-N(2)	81.2(1)	C(1)-W(1)-N(1)	99.8(2)
W(1)-C(2)-O(2)	177.2(4)	N(3)-C(10)-C(9)	113.4(3)	C(3)-W(1)-N(2)	171.7(2)
W(1)-C(3)-O(3)	179.4(4)	C(3)-W(1)-N(1)	91.3(2)	C(2)-W(1)-N(2)	99.2(2)
W(1)-C(4)-O(4)	171.8(5)	C(2)-W(1)-N(1)	177.0(2)	C(4)-W(1)-N(2)	98.9(2)
C(1)-W(1)-C(4)	167.8(2)	C(4)-W(1)-N(1)	88.5(2)		
Complex 8					
W(1)-Sn(1)	0.274 09(5)	W(1)-Cl(4)	0.244 5(1)	Sn(1)-Cl(1)	0.235 5(1)
W(1)-N(1)	0.223 0(4)	Sn(1)-Cl(2)	0.234 0(1)	N(2)-C(9)	0.145 2(6)
W(1)-N(3)	0.227 8(4)	Sn(1)-Cl(3)	0.234 9(1)		
W(1)-C(1)-O(1)	172.8(4)	N(1)-W(1)-N(3)	79.4(1)	Cl(3)-Sn(1)-W(1)	116.45(4)
W(1)-C(2)-O(2)	175.8(4)	C(3)-W(1)-Sn(1)	116.7(1)	Cl(1)-Sn(1)-W(1)	120.01(4)
W(1)-C(3)-O(3)	178.8(5)	C(2)-W(1)-Sn(1)	71.1(1)	Cl(4)-W(1)-Sn(1)	139.37(3)
C(3)-W(1)-N(1)	169.1(2)	Cl(2)-Sn(1)-Cl(1)	98.85(6)	N(2)-C(9)-C(10)	112.1(4)
C(2)-W(1)-N(3)	163.2(2)	Cl(3)-Sn(1)-Cl(1)	99.96(5)		

171.8(5)°, suggesting the presence of steric repulsion between the ligand and these two carbonyls.

2.2 Characterization of complexes 7 and 8

The IR and NMR spectra of complexes **7** and **8** support the suggested structures. For example, three strong carbonyl stretching bands are observed in their IR spectra, consistent with the seven-coordinate complexes with tricarbonyl species. The crystal structure of complex **8** is presented in Fig.2. The fundamental molecular framework is similar to those in seven-coordinate carbonyl tungsten derivatives with pyrazolyl ligands, such as $\text{PhSCH}_2(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_3(\text{Cl})\text{SnCl}_3$ ^[20] and $\text{CH}_2(3,5\text{-Me}_2\text{-4-BrPz})_2\text{W}(\text{CO})_3(\text{Cl})\text{SnCl}_3(\text{A})$ ^[21]. A distorted capped-octahedral geometry with the SnCl_3 group in the unique capping position is observed in these complexes. The W-Sn bond distances in these complexes are also similar, such as 0.274 09(5) nm in complex **8** and 0.274 38(5) nm in complex A^[21]. The W-N_{pyridyl} bond distance is 0.227 8 (4) nm, similar to that in complex **6**. While the W-N_{pyrazolyl} bond distance (0.223 0(4) nm) is shorter than the corresponding bond distance in complex **6**, possibly owing to the small steric hindrance resulted by the methyl group on the 3-position of pyrazole ring in complex **8**, instead of the tert-butyl group in complex **6**, as well as the stronger Lewis acidity of the tungsten atom in complex **8** led by the electronegative chlorine and SnCl_3 groups. No chlorine bridge between the W-Sn bond in complex **8** is found, analogous to that in complex A. The chlorine

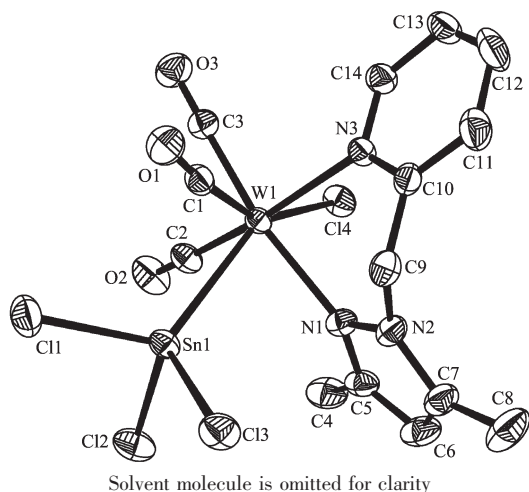


Fig.2 Molecular structure of complex **8** with thermal ellipsoids drawn at 30% probability level

bonded to the tungsten atom is trans to the SnCl_3 group with a Cl(4)-W(1)-Sn(1) angle of 139.37(3)°, slightly smaller than the corresponding angle in complex A (144.41(4)°)^[21]. The N-W-N bite angle is 79.4(1)°, very close to that in complex A (80.6(1)°) with bis(pyrazol-1-yl)methane.

2.3 Electrochemical properties of complexes 1~6

The cyclic voltammetric behavior of complexes **1~6** was investigated in their MeCN solutions with 0.1 mol · L⁻¹ (*n*-Bu)₄NPF₆ as supporting electrolyte, and with a scan rate of 100 mV · s⁻¹ at room temperature under argon atmosphere. The data reported here are related to those of the ferrocenium/ferrocene redox couple, and summarized in Table 3. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$. These complexes show similar electrochemical behavior. A quasi-reversible redox couple and one irreversible oxidative process are observed in these six complexes. The quasi-reversible redox couple is assigned for the M(0)/M(I) (M=Mo or W) process, while the irreversible oxidation should be relevant to the M(I)/M(II) process. The low stability of the bivalent species may be responsible for the irreversible oxidation. These results are remarkably different from those of analogous group VIB metal carbonyl derivatives containing bis(pyrazol-1-yl)methane^[17] or bis(1-methylimidazole-2-yl)methane^[22], while one reversible redox process is observed in the former^[17] and one irreversible oxidation is found in the latter^[22]. In addition, analogous $E_{1/2}$ values are found in complexes **1**, **3** and **5** as well as in **2**, **4** and **6**, indicating that the substituents of pyrazole ring hardly affect the quasi-reversible redox potential.

Table 3 Electrochemical data for complexes 1~6

Complex	1	2	3	4	5	6
E_{pa1} / mV	-138	-194	-124	-188	-139	-214
E_{pc1} / mV	-217	-277	-219	-299	-232	-284
$E_{1/2}$ / mV	-178	-236	-172	-244	-189	-249
E_{pa2} / mV	211	209	273	265	264	199

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