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桥头碳上氮杂芳基功能化的双吡唑甲烷与羰基钨反应

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摘要:研究了(氮甲基咪唑-2-基)双(3,5-二甲基吡唑)甲烷(L^1),2-吡啶基双(3,5-二甲基吡唑)甲烷(L^2)及 4-吡啶基双(3,5-二甲基吡唑)甲烷(L^3)与羰基钨的反应,合成了一系列以单齿,双齿及三齿氮配位的羰基金属衍生物 $LW(CO)_5$ (L=L^1 或 L^3),$LW(CO)_4$ (L=L^1, L^2 或 L^3)和 $LW(CO)_3$ (L=L^1 或 L^2)。核磁,红外及 X-射线单晶衍射分析表明这 3 种配体表现出了可变的配位方式。在 $LW(CO)_5$ 中,当配体为 L^1 时,其倾向于通过咪唑氮与金属配位,而为 L^3 则倾向于利用吡啶氮与金属作用;在 $LW(CO)_4$ 中,配体 L^1 表现为通过咪唑氮和吡唑氮原子配位的[N,N′]双齿配体,而 L^2 和 L^3 表现为通过吡唑氮原子配位的[N,N]双齿配体;在 $LW(CO)_3$ 中,L^1 和 L^2 起着[N,N,N′]三齿螯合配体的作用。

关键词:氮配体;双吡唑甲烷;咪唑;吡啶;钨
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Reaction of Tungsten Carbonyl with Bis(pyrazol-1-yl)methanes Functionalized by Azaaryl Groups

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Abstract: Reaction of $W(CO)_6$ with (*N*-methylimidazol-2-yl)bis(3,5-dimethylpyrazol-1-yl)methane (L^1), (pyridin-2-yl)bis(3,5-dimethylpyrazol-1-yl)methane (L^2) and (pyridin-4-yl)bis(3,5-dimethylpyrazol-1-yl)methane (L^3) yielded complexes $LW(CO)_5$ (L=L^1 or L^3), $LW(CO)_4$ (L=L^1, L^2 or L^3) and $LW(CO)_3$ (L=L^1 or L^2), respectively. NMR, IR and X-ray structural analyses indicated that these three ligands possessed variable coordination modes in these complexes. L^1 and L^3 acted as monodentate ligands through the imidazolyl nitrogen or the pyridyl nitrogen in $LW(CO)_5$. A N,N′-chelating bidentate ligand through the imidazolyl nitrogen and one pyrazolyl nitrogen was observed in $L^1W(CO)_4$, while L^2 and L^3 acted as N,N-chelating bidentate ligands through two pyrazolyl nitrogens in $L^2W(CO)_4$ and $L^3W(CO)_4$. A tridentate N,N,N′-chelating ligand through two pyrazolyl nitrogens and the imidazolyl or 2-pyridyl nitrogen was observed in $L^1W(CO)_3$ and $L^2W(CO)_3$. The different donor ability of these imidazolyl, pyridyl and pyrazolyl nitrogens possibly plays important roles for the structural diversity. CCDC: 1030402, **2**; 1030403, **4**; 1030404, **7**.

Key words: N ligand; bis(pyrazol-1-yl)methane; imidazole; pyridine; tungsten

As one of the most popular nitrogen-containing donor ligands, bis(pyrazol-1-yl)methane has been used extensively in bioinorganic, coordination chemistry and organometallic fields[1]. The modification of bis(pyrazol-1-yl)methane on the bridgehead carbon has drawn extensive attention in recent years, because the

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generated heteroscorpionate ligands show good donor properties and variable coordination behavior towards main group and transition metals[2-4]. For example, azaaryl functionalized bis(pyrazol-1-yl)methane on the methine carbon has been explored to prepare interesting metal supramolecular frameworks[5-8] as well as highly efficient catalysts or catalyst precursors[9-13]. Owing to the existence of the extra coordinate site, these azaaryl functionalized bis(pyrazol-1-yl)methanes can simultaneously supply hard donors (such as pyrazolyl nitrogen) and relatively soft donors (such as pyridyl nitrogen), which is further advantageous to adjust the coordination environments around the metal centers. Our previous investigations showed that functional bis(pyrazol-1-yl)methanes on the methine carbon atom displayed unusual reactivity[14-17]. For example, the reaction of aryl functionalized bis(pyrazol-1-yl)methanes with $W(CO)_5THF$ resulted in the cleavage of a C_{sp^3}-N bond to form novel pyrazole derivatives[16]. Reaction of bis(3,5-dimethylpyrazol-1-yl) methylthiolate with $Fe_3(CO)_{12}$ gave rise to the formation of unexpected (3,5-dimethylpyrazol-1-yl)dithioformate derivatives[15]. As part of our ongoing interest in functional bis(pyrazol-1-yl)methanes, herein we report the reaction of azaaryl functionalized bis(pyrazol-1-yl) methanes with tungsten carbonyl, which yielded a series of tungsten derivatives with mono-, bi- and tridentate ligands depending on different reaction conditions.

1 Experimental

All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled prior to use according to standard procedures. NMR (^1H and ^{13}C) were recorded on a Bruker 400 spectrometer using $CDCl_3$ as solvent unless otherwise noted, and the chemical shifts were reported with respect to the reference (internal $SiMe_4$ for ^1H and ^{13}C NMR). IR spectra were obtained as KBr pellets on a Nicolet 380 spectrometer. Elemental analyses were carried out on an Elementar Vairo EL analyzer. (*N*-Methylimidazol-2-yl)bis(3,5-dimethylpyrazol-1-yl)methane (L^1)[10-11], (pyridin-2-yl)bis(3,5-dimethylpyrazol-1-yl)methane (L^2)[10-11] and bis(3,5-dimethylpyrazol-1-yl)methanone[18] were prepared by the published methods.

1.1 Synthesis of (pyridin-4-yl)bis(3,5-dimethylpyrazol-1-yl)methane (L^3)

The mixture of bis (3,5-dimethylpyrazol-1-yl) methanone (2.20 g, 10 mmol), isonicotinaldehyde (0.95 mL, 10 mmol) and $CoCl_2\cdot 6H_2O$ (10 mg, 0.042 mmol) was stirred and heated at 50 ℃ for 2 h. After cooling to room temperature, CH_2Cl_2 (40 mL) was added to the reaction mixture. The CH_2Cl_2 solution was washed with water three times (3×30 mL), and dried over anhydrous $MgSO_4$. After removing of the solvent, the residue was recrystallized from CH_2Cl_2/hexane to give white crystals of L^3. Yield: 1.3 g (46%). ^1H NMR: δ 2.21 (s, 6H), 2.22 (s, 6H) (CH_3), 5.88 (s, 2H, H^4 of pyrazole), 6.88 (d, J=5.4 Hz, 2H), 8.60 (d, J=6.0 Hz, 2H) (C_5H_4N), 7.50 (s, 1H, C*H*). Anal. Calcd. for $C_{16}H_{19}N_5$ (%): C 68.30, H 6.81, N 24.89; Found(%): C 68.62, H 6.68, N 25.16.

1.2 Reaction of L^1 with $W(CO)_6$

A solution of $W(CO)_6$ (0.18 g, 0.5 mmol) and L^1 (0.14 g, 0.5 mmol) dissolved in THF (25 mL) was irradiated with a 300 W high-pressure Hg lamp for 10 h at room temperature. The solvent was removed *in vacuo*, and the residue was isolated by column chromatography on silica with ethyl acetate/hexane (1∶1, *V*/*V*) as the eluent firstly to give complex **1**. Then ethyl acetate was used as the eluent to give complex **2**. Recrystallization of complexes **1** and **2** from CH_2Cl_2/hexane afforded yellow crystals.

Data for **1**, yield: 30 mg (10%). ^1H NMR: δ 2.04 (s, 6H), 2.15 (s, 6H) (CH_3), 3.31 (s, 3H, NCH_3), 5.93 (s, 2H, H^4 of pyrazole), 6.86 (d, J=1.4 Hz, 1H), 7.27 (d, J=1.4 Hz, 1H) (protons of imidazole), 7.80 (s, 1H, C*H*). ^{13}C NMR: δ 10.4, 13.9 (CH_3), 35.1 (NCH_3), 69.6 (*C*H), 107.7 (C^4 of pyrazole), 124.3, 134.0, 134.5, 145.0, 149.0 (carbons of imidazole as well as C^3 and C^5 of pyrazole), 197.9 (4C), 201.6 (1C) (*C*O). IR ν(C≡O): 2 071 (m), 1 976 (sh), 1 909 (vs, br) cm^{-1}. Anal. Calcd. for $C_{20}H_{20}N_6O_5W$(%): C 39.49, H 3.31, N 13.82; Found(%): C 39.31, H 3.25, N 13.84.

Data for **2**, yield: 0.10 g (35%). ^1H NMR: δ 1.48 (s, 3H), 2.08 (s, 3H), 2.48 (s, 3H), 2.63 (s, 3H) (CH_3),

3.40 (s, 3H, NCH_3), 5.84 (s, 1H), 6.17 (s, 1H) (H^4 of pyrazole), 6.97 (s, 1H), 7.16 (s, 1H) (protons of imidazole), 7.40 (s, 1H, CH). ^{13}C NMR: δ 10.2, 12.4, 13.6, 17.8 (CH_3), 34.0 (NCH_3), 63.8 (CH), 109.2, 109.7 (C^4 of pyrazole), 122.5, 133.3, 140.1, 140.2, 144.1, 150.1, 156.9 (carbons of imidazole as well as C^3 and C^5 of pyrazole), 202.5, 203.3, 212.9, 213.1 (CO). IR ν(C≡O): 2 005 (s), 1 877 (vs), 1 840 (vs), 1 789 (vs) cm^{-1}. Anal. Calcd. for $C_{19}H_{20}N_6O_4W\cdot CH_2Cl_2$ (%): C 36.11, H 3.33, N 12.63; Found(%): C 35.82, H 3.31, N 12.44.

1.3　Reaction of L^1 with W(CO)$_5$THF

L^1 (0.14 g, 0.5 mmol) was added to the solution of W(CO)$_5$THF in THF, prepared *in situ* by irradiation of a solution of W(CO)$_6$ (0.18 g, 0.5 mmol) in THF (25 mL) for 8 h. The resulting reaction mixture was stirred and heated at reflux for 24 h. After cooling to room temperature, the yellow solids were filtered, and washed with acetone to give complex **3**. Yield: 0.15 g (54%). ^{1}H NMR (DMSO-d$_6$): δ 2.43 (s, 6H), 2.55 (s, 6H) (CH_3), 3.94 (s, 3H, NCH_3), 6.16 (s, 2H, H^4 of pyrazole), 7.19 (d, J=1.2 Hz, 1H), 7.31 (d, J=1.2 Hz, 1H) (protons of imidazole), 7.32 (s, 1H, CH). ^{13}C NMR (DMSO-d$_6$): δ 10.7, 15.4 (CH_3), 33.5 (NCH_3), 57.9 (CH), 106.9 (C^4 of pyrazole), 123.3, 130.6, 138.9, 141.5, 153.1 (carbons of imidazole as well as C^3 and C^5 of pyrazole), 223.3 (1C), 224.0 (2C) (CO). IR ν(C≡O): 1 895 (s), 1 749 (vs, br) cm^{-1}. Anal. Calcd. for $C_{18}H_{20}N_6O_3W$(%): C 39.15, H 3.65, N 15.22; Found(%): C 39.15, H 3.37, N 15.41.

Complex **3** was also obtained by heating **1** or **2** at reflux in THF in good yields (87% for **1** and 92% for **2**, respectively).

1.4　Reaction of L^2 with W(CO)$_6$

This reaction was carried out as above-mentioned reaction of L^1 with W(CO)$_6$, but L^1 was replaced by L^2. Complex **4** was obtained in 25% yield. ^{1}H NMR: δ 2.41 (s, 6H), 2.51 (s, 6H) (CH_3), 6.10 (s, 2H, H^4 of pyrazole), 6.28 (d, J=7.9 Hz, 1H), 7.21~7.23 (m, 1H), 7.61 (td, J=1.7 and 7.9 Hz, 1H), 8.51 (d, J=7.9 Hz, 1H) (protons of pyridyl), 7.19 (s, 1H, CH). ^{13}C NMR: δ 11.8, 17.3 (CH_3), 69.1 (CH), 108.1 (C^4 of pyrazole), 120.5, 124.6, 138.0, 142.8, 150.7, 155.8, 162.3 (carbons of pyridyl as well as C^3 and C^5 of pyrazole), 202.2, 203.5, 212.0 (2C) (CO). IR ν(C≡O): 2 004 (s), 1 878 (vs), 1 856 (vs), 1 813 (vs) cm^{-1}. Anal. Calcd. for $C_{20}H_{19}N_5O_4W$ (%): C 41.61, H 3.32, N 12.13; Found(%): C 41.86, H 3.48, N 12.54.

1.5　Heating 4 in refluxing THF

Complex **4** (50 mg, 0.087 mmol) was dissolved in THF (15 mL). The resulting solution was heated at reflux for 8 h. After cooling to room temperature, the red solids were filtered, and washed with CH_2Cl_2 to give complex **5**. Yield: 40 mg (87%). ^{1}H NMR (DMSO-d$_6$): δ 2.42 (s, 6H), 2.58 (s, 6H) (CH_3), 6.21 (s, 2H, H^4 of pyrazole), 7.50 (t, J=6.9 Hz, 1H), 8.13 (t, J=6.9 Hz, 1H), 8.47 (d, J=7.8 Hz, 1H), 9.01 (d, J=7.5 Hz, 1H) (protons of pyridyl), 7.74 (s, 1H, CH). ^{13}C NMR (DMSO-d$_6$): δ 10.8, 15.3 (CH_3), 66.7 (CH), 107.3 (C^4 of pyrazole), 125.6, 125.9, 139.9, 141.9, 151.2, 153.0, 155.5 (carbons of pyridyl as well as C^3 and C^5 of pyrazole), 202.7, 211.8 (2C) (CO). IR ν(C≡O): 1 889 (vs), 1 758 (vs, br) cm^{-1}. Anal. Calcd. for $C_{19}H_{19}N_5O_3W\cdot 0.5CH_2Cl_2$(%): C 39.58, H 3.41, N 11.84; Found(%): C 39.22, H 3.38, N 12.09.

1.6　Reaction of L^3 with W(CO)$_6$

This reaction was carried out as above-mentioned reaction of L^1 with W(CO)$_6$, but L^1 was replaced by L^3. When the mixture of ethyl acetate/hexane (2∶3, V/V) was firstly used as the eluent, complex **6** was obtained. Then acetone was used as the eluent to give complex **7**.

Data for **6**, yield: 22%. ^{1}H NMR: δ 2.21 (s, 12H, CH_3), 5.92 (s, 2H, H^4 of pyrazole), 6.85 (d, J=5.6 Hz, 2H), 8.78 (d, J=5.6 Hz, 2H) (protons of pyridyl), 7.48 (s, 1H, CH). ^{13}C NMR: δ 11.5, 13.6 (CH_3), 72.1 (CH), 107.7 (C^4 of pyrazole), 124.1, 141.0, 147.6, 149.3, 156.0 (carbons of pyridyl as well as C^3 and C^5 of pyrazole), 198.7 (4C), 202.3 (1C) (CO). IR ν(C≡O): 2 072 (m), 1 980 (s), 1 926 (sh), 1 903 (vs) cm^{-1}. Anal. Calcd. for $C_{21}H_{19}N_5O_5W$ (%): C 41.67, H 3.16, N 11.57; Found (%): C 41.50, H 3.32, N 11.58.

Data for **7**, yield: 48%. ^{1}H NMR (DMSO-d$_6$): δ 2.08 (s, 6H), 2.17 (s, 6H) (CH_3), 5.97 (s, 2H, H^4 of pyrazole), 7.07 (d, J=5.7 Hz, 2H), 8.98 (d, J=5.7 Hz, 2H) (protons of pyridyl), 7.86 (s, 1H, CH). ^{13}C NMR (DMSO-d$_6$): δ 10.9, 13.4 (CH_3), 69.9 (CH), 105.6 (C^4

of pyrazole), 124.8, 140.6, 147.3, 147.7, 156.2 (carbons of pyridyl as well as C^3 and C^5 of pyrazole), 198.4 (CO). IR ν(C≡O): 2 002 (m), 1 872 (vs), 1 847 (vs), 1 804 (vs) cm^{-1}. Anal. Calcd. for $C_{20}H_{19}N_5O_4W$(%): C 41.61, H 3.32, N 12.13; Found (%): C 41.34, H 3.21, N 11.79.

1.7 Reaction of L^3 with $W(CO)_5THF$

This reaction was carried out as above-mentioned reaction of L^1 with $W(CO)_5THF$, but L^1 was replaced by L^3. This reaction afforded complexes **6** in 19% yield and **7** in 34% yield, respectively.

1.8 X-ray crystallography

Yellow crystals of **2** and red crystals of **4** and **7** suitable for X-ray analysis were grown by slow diffusion of hexane into their CH_2Cl_2 solutions at −18 ℃. All intensity data were collected with a SCX-MINI CCD diffractometer for **2** and **7** as well as Rigaku Saturn CCD diffractometer for **4** using graphite monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm). Semi-empirical absorption corrections were applied using the Crystalclear program[19]. The structures were solved by direct methods and difference Fourier map using SHELXS of the SHELXTL package and refined with SHELXL[20] by full-matrix least-squares on F^2. Crystals of **2** and **4** contained one CH_2Cl_2 molecule. Crystals of **7** contained one water molecule. Furthermore, the hydrogen atoms of the water ligand in **7** could not be properly determined. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined with riding model position parameters. A summary of the fundamental crystal data for these complexes is listed in Table 1.

CCDC: 1030402, **2**; 1030403, **4**; 1030404, **7**.

2 Results and discussion

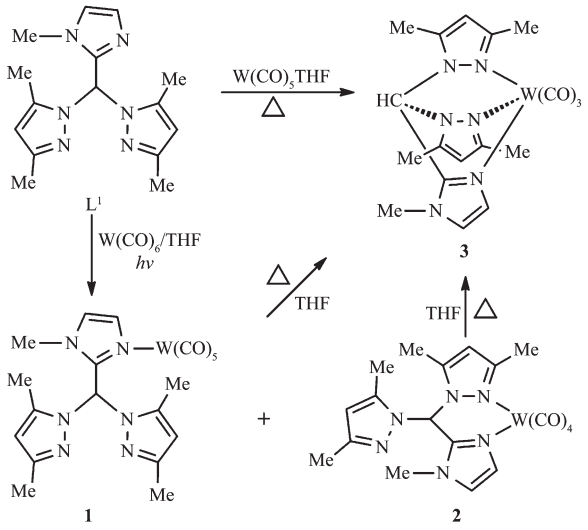
2.1 Reaction of (*N*-methylimidazol-2-yl)bis(3,5-dimethylpyrazol-1-yl)methane

(*N*-Methylimidazol-2-yl)bis(3,5-dimethylpyrazol-1-

Table 1 Crystallographic data and refinement parameters for complexes 2, 4 and 7

Complex	**2**·CH_2Cl_2	**4**·CH_2Cl_2	**7**·H_2O
Formula	$C_{20}H_{22}Cl_2N_6O_4W$	$C_{21}H_{21}Cl_2N_5O_4W$	$C_{20}H_{21}N_5O_5W$
Formula weight	665.18	662.18	595.25
Crystal size / mm	0.20×0.18×0.16	0.18×0.16×0.12	0.20×0.18×0.16
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$Fdd2$	$P2_1/c$
a / nm	0.927 8(2)	3.254 9(7)	0.951 1(2)
b / nm	1.000 8(2)	3.529 2(7)	1.671 6(3)
c / nm	1.500 0(3)	0.837 2(2)	1.623 8(3)
α / (°)	83.17(3)	90	90
β / (°)	89.77(3)	90	94.07(3)
γ / (°)	64.44(3)	90	90
V / nm^3	1.245 8(4)	9.617(3)	2.575 1(9)
Z	2	16	4
T / K	293(2)	113(2)	293(2)
D_c / (g·cm^{-3})	1.776	1.829	1.530
θ range / (°)	3.33~25.01	1.70~27.54	3.19~25.01
F(000)	650	5152	1152
μ / mm^{-1}	4.888	5.064	4.521
Number of reflections measured	10 905	16 949	21 780
Number of reflections observed (R_{int})	4 368 (0.043 2)	4 613 (0.036 2)	4 535 (0.115 1)
Number of reflections observed with ($I \geqslant 2\sigma(I)$)	3 954	4 439	3 049
Number of parameters	299	302	280
Residuals R_1, wR_2 ($I \geqslant 2\sigma(I)$)	0.038 0, 0.084 9	0.020 2, 0.042 1	0.079 1, 0.186 7
Goodness-of-fit	1.113	1.039	1.179

yl)methane (L^1) has been used as a chelating tridentate ligand in previous works[11]. Herein, we find that this ligand can act as a monodentate ligand through the imidazolyl nitrogen or a chelating bidentate ligand by the imidazolyl nitrogen and one pyrazolyl nitrogen atom. Reaction of L^1 with $W(CO)_6$ under the irradiation of high-pressure Hg lamp gave complexes **1** and **2** (Scheme 1), according to the results of their NMR and IR spectroscopy. In addition, these two complexes could be transformed to complex **3** when heated in refluxing THF. Complex **3** was also obtained by the direct reaction of L^1 with $W(CO)_5$THF under refluxing conditions.



Scheme 1　Reaction of (*N*-methylimidazol-2-yl)bis(3,5-dimethylpyrazol-1-yl)methane

Complexes **1**~**3** have been characterized by IR and NMR spectroscopy. They showed significantly different IR and NMR spectra. A $\nu(C\equiv O)$ band at 2 071 cm^{-1} corresponding to the A_{1eq} mode for the pseudo C_{4v} metal center in the $M(CO)_5$ fragment[21] was observed in the IR spectrum of **1**, implying that L^1 acted as a monodentate ligand in this complex. While complex **2** displayed four carbonyl absorption peaks in its IR spectrum, consistent with a typical cis-tetracarbonyl arrangement[22]. In addition, the IR spectrum of **3** matched those of the tricarbonyltungsten species. The NMR spectra of **1**~**3** also support the suggested structures. The ^{13}C NMR spectrum of **1** revealed two carbonyl carbon signals with *ca.* a 1∶4 intensity ratio, corresponding to a monosubstituted pentacarbonyl skeleton. Furthermore, its ^1H and ^{13}C NMR spectra disclosed two equivalent pyrazolyl rings, indicating that the donor atom was the imidazolyl nitrogen instead of the pyrazolyl nitrogen. In contrast, the ^{13}C NMR spectrum of **2** revealed four carbonyl carbon signals with the same intensity. Meanwhile, two inequivalent pyrazolyl rings were observed in its ^1H and ^{13}C NMR spectra. These results suggested that L^1 acted as a chelating bidentate ligand in **2** through the imidazolyl nitrogen and one pyrazolyl nitrogen. A chelating tridentate coordination mode of L^1 can be used to give explanation of the NMR spectra of **3**. For example, two carbonyl carbon signals with *ca.* a 1∶2 intensity ratio and two equivalent pyrazolyl signals were observed in its ^{13}C or ^1H NMR spectrum owing to the tridentate coordination mode of L^1.

The structure of **2** has been further confirmed by X-ray structural analyses, and is presented in Fig.1. The selected bond distances and angles are listed in Table 2. As above-mentioned by ^1H NMR, L^1 coordinates to the tungsten atom through the imidazolyl nitrogen and one pyrazolyl nitrogen atom, giving a six-membered metallacycle with a boat conformation. The uncoordinated pyrazolyl group occupies the axial position of the boat conformation, possibly avoiding the steric repulsion to the methyl groups of coordinated imidazolyl and pyrazolyl rings. Two *cis*-carbonyl groups are distorted with the angles W(1)-C(1)-O(1) of 170.7(6)° and W(1)-C(3)-O(3) of 170.5(8)°. The angle

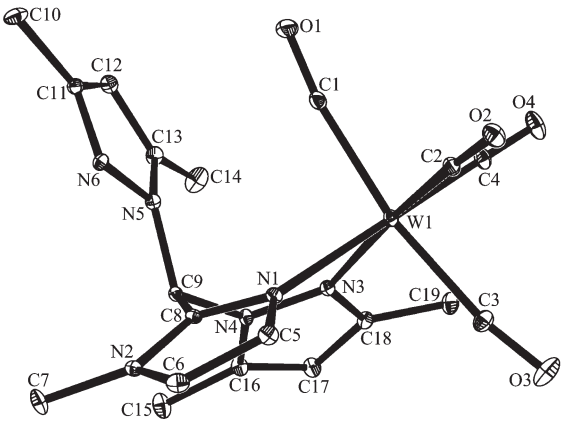


Fig.1　Molecular structure of **2** with 30% probability displacement ellipsoids

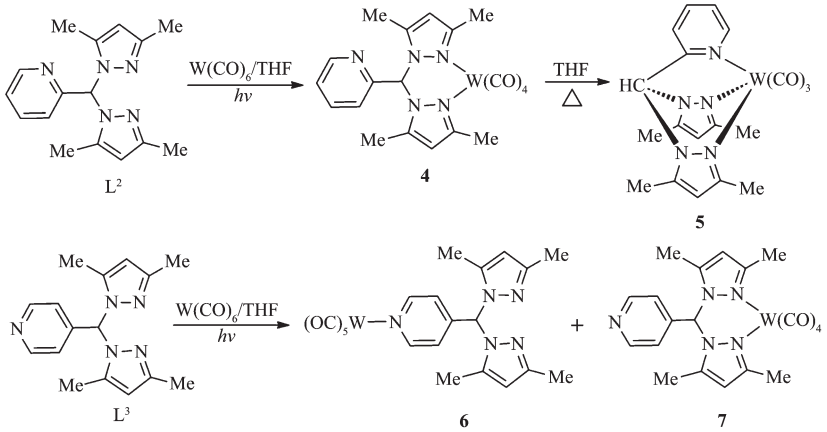
Table 2 Selected bond distances (nm) and angles (°) for complexes 2, 4 and 7

Complex **2**					
W(1)-N(1)	0.224 2(5)	W(1)-N(3)	0.230 3(5)	C(1)-O(1)	0.115 2(9)
W(1)-C(1)	0.204 5(8)	W(1)-C(3)	0.201 0(8)	C(3)-O(3)	0.115 4(9)
W(1)-C(1)-O(1)	170.7(6)	W(1)-C(2)-O(2)	177.3(6)	W(1)-C(3)-O(3)	170.5(8)
W(1)-C(4)-O(4)	178.6(6)	C(1)-W(1)-C(3)	169.8(3)	N(1)-W(1)-N(3)	79.4(2)
C(8)-C(9)-N(4)	111.7(5)	N(4)-C(9)-N(5)	111.6(5)		
Complex **4**					
W(1)-N(1)	0.224 7(3)	W(1)-N(4)	0.226 4(3)	C(2)-O(2)	0.115 5(5)
W(1)-C(2)	0.202 4(4)	W(1)-C(4)	0.203 4(4)	C(4)-O(4)	0.114 6(5)
W(1)-C(1)-O(1)	178.2(4)	W(1)-C(2)-O(2)	171.8(4)	W(1)-C(3)-O(3)	176.2(4)
W(1)-C(4)-O(4)	169.1(3)	C(2)-W(1)-C(4)	165.4(2)	N(1)-W(1)-N(4)	80.0(1)
C(15)-C(10)-N(3)	114.6(3)	N(2)-C(10)-N(3)	111.6(3)		
Complex **7**					
W(1)-N(3)	0.225 1(12)	W(1)-N(5)	0.227 4(12)	C(2)-O(2)	0.114(2)
W(1)-C(2)	0.203(2)	W(1)-C(4)	0.206(2)	C(4)-O(4)	0.111(2)
W(1)-C(1)-O(1)	176.8(14)	W(1)-C(2)-O(2)	172.6(19)	W(1)-C(3)-O(3)	179.0(15)
W(1)-C(4)-O(4)	167.9(15)	C(2)-W(1)-C(4)	166.8(7)	N(3)-W(1)-N(5)	80.5(4)
C(7)-C(10)-N(4)	114.8(12)	N(2)-C(10)-N(4)	113.1(12)		

C(1)-W(1)-C(3) of 169.8(3)° markedly deviates from linearity. These data reflect the presence of the large steric repulsion between these carbonyls with the ligand. The W-$N_{imidazolyl}$ bond distance is 0.224 2(5) nm, slightly shorter than the W-$N_{pyrazolyl}$ bond distance (0.230 3(5) nm), but comparable to those reported in other carbonyl tungsten derivatives with imidazolyl ligands[23-24].

2.2 Reaction of pyridylbis(3,5-dimethylpyrazol-1-yl)methanes

Irradiation of the solution of 2-pyridyl functionalized bis(pyrazol-1-yl)methane (L^2) and $W(CO)_6$ in THF using high-pressure Hg lamp gave only complex **4**, which could be transformed to complex **5** when heated in refluxing THF (Scheme 2). Similar treatment of 4-pyridyl analogs (L^3) and $W(CO)_6$ yielded complexes **6** and **7**. While **6** could not be converted to **7** even heated at high temperature. All these four complexes were fully characterized by IR and NMR spectroscopy, and the structures of **4** and **7** were unambiguously confirmed by X-ray crystallography.



Scheme 2 Reaction of pyridylbis(3,5-dimethylpyrazol-1-yl)methanes

The IR spectra of **4** and **7** were similar to that of **2**. They displayed analogous carbonyl carbon signals in their ^{13}C NMR spectra. Like **3**, complex **5** showed two strong carbonyl absorption bands in its IR spectrum, and two carbonyl carbon signals in its ^{13}C NMR spectrum. As anticipated, a ν_{CO} band assigned to the A_{1eq} mode for the pseudo C_{4v} metal center was observed in the IR spectrum of **6**. The corresponding carbonyl absorption occurred at 2 072 cm^{-1}, very close to the value in **1**. Moreover, complexes **1** and **6** showed very analogous chemical shifts of carbonyl carbon atoms in their ^{13}C NMR spectra. These results suggest that complexes **4**, **7** and **2**, **5** and **3**, **6** and **1** should possess similar carbonyl metal fragments. It is worth pointing out that a proton of the pyridyl group significantly shifted upfield (δ 6.28) in **4**, compared with that of the free L^2 (δ 6.92)[12]. A similar result was observed in **2**, in which one methyl proton signal appeared in the high field (δ 1.48). The upfield shift of these protons should be attributed to the shielding effect of one pyrazolyl ring, as disclosed by the X-ray crystal structural analyses of **2** and **4**. Fig.1 reveals that the methyl protons at 5-postion of the uncoordinated pyrazolyl ring locate over the plane of the coordinated pyrazolyl group. Fig.2 shows that the proton at 3-postion of the pyridyl group is situated over the N(2)-N(1)-C(6)-C(7)-C(8) pyrazolyl plane. This shielding phenomenon has found in other aryl functionalized bis(pyrazol-1-yl)methane derivatives[16].

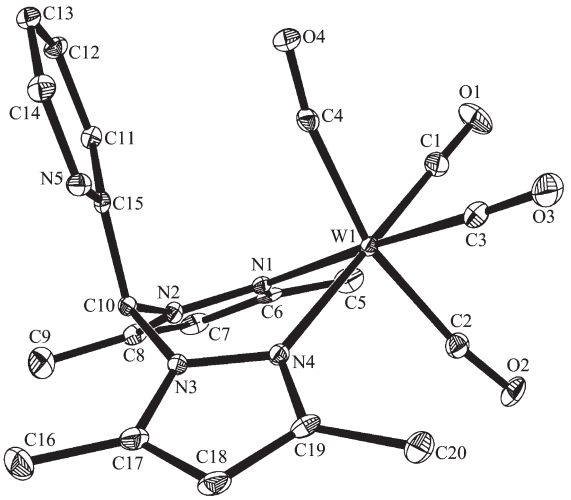


Fig.2　Molecular structure of **4** with 30% probability displacement ellipsoids

The molecular structures of **4** and **7** are shown in Figs.2 and 3, respectively. These two complexes possess a similar fundamental framework. For example, L^2 and L^3 coordinate to the tungsten atom in a bidentate chelating fashion, and the uncoordinated pyridyl group occupies the axial position of the boat conformation, like the uncoordinated pyrazolyl group in **2**. The crystal data reveal that complexes **4** and **7** share some analogous structural parameters, such as similar W-$N_{pyrazolyl}$ bond distances and N-W-N bite angles (see Table 2). These W-$N_{pyrazolyl}$ (0.224 7~0.227 4 nm) bond distances in **4** and **7** are comparable to those reported for carbonyl tungsten derivatives bearing N,N-bidentate chelating bis(pyrazol-1-yl)methane ligands, such as average 0.224 2 nm in (2-$MeOC_6H_4$)$CH(pz)_2W(CO)_4$ and 0.227 1 nm in (2-$MeOC_6H_4$)$CH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (pz=pyrazol-1-yl)[16]. Two *cis*-carbonyls in these two complexes deviate significantly from linearity. Moreover, the angle of W(1)-C(4)-O(4) in **7** (167.9(5)°) is smaller than the corresponding angles in **4** (169.1(3)°) and **2** (170.7(6)°). Additionally, the angle of C(2)-W(1)-C(4) in **4** (165.4(2)°) is slightly smaller than the corresponding angle in **7** (166.8 (7)°), and smaller than the angle of C(1)-W(1)-C(3) in **2** (169.8(3)°). These data reflect the presence of the larger steric repulsion between the ligands with two *cis*-carbonyls in **4** and **7** compared with **2**.

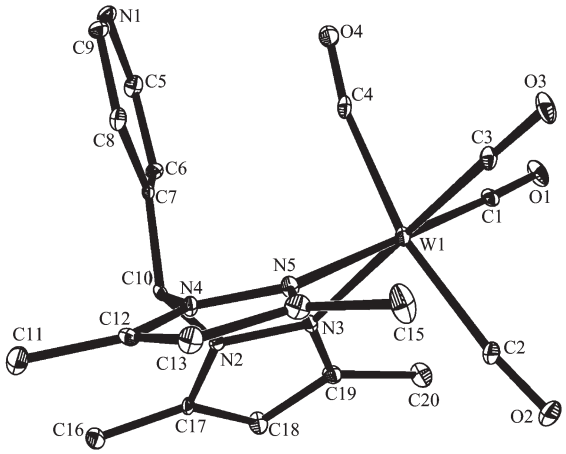


Fig.3　Molecular structure of **7** with 30% probability displacement ellipsoids

In summary, we have investigated the reaction of azaaryl functionalized bis(pyrazol-1-yl)methanes with

$W(CO)_6$, which gave rise to the formation of a series of new tungsten complexes with mono-, bi- and tridentate ligands. The different donor ability of imidazolyl, pyridyl and pyrazolyl nitrogen atoms as well as the controllable reaction conditions possibly plays important roles for the structural diversity of these derivatives.

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