

羟甲基功能化吡唑金属羰基化合物的合成及催化性质

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摘要: 研究了 3(5)-羟甲基-5(3)-甲基吡唑(L¹), 4-羟甲基吡唑(L²)及双(3-羟甲基-5-甲基吡唑)甲烷(L³)与羰基钨(钼)的反应,合成了一系列以单齿及双齿氮配位的羰基金属衍生物 LW(CO)₅ (L=L¹ 或 L²)和 L³M(CO)₄ (M=Mo 或 W)。通过核磁、红外及 X 射线单晶衍射分析,对这些化合物进行了详细的结构表征。结果表明,这些化合物往往通过 O-H...O, N-H...O 及 O-H...OC-M 等氢键作用,形成一维或二维金属有机超分子结构。并且依赖于配体中羟甲基所处的不同位置,这些金属有机超分子表现出明显不同的结构特征。初步的催化活性测试表明,这些新化合物在苯乙炔三聚反应中具有明显的催化活性。

关键词: 氮配体; 吡唑; 氢键; 羰基金属配合物; 催化活性

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Syntheses and Catalytic Properties of Metal Carbonyl Derivatives with Hydroxymethyl Functionalized Pyrazoles

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Abstract: Reaction of tungsten or molybdenum carbonyl with 3(5)-hydroxymethyl-5(3)-methylpyrazole (L¹), 4-hydroxymethylpyrazole (L²) and bis(3-hydroxymethyl-5-methylpyrazol-1-yl)methane (L³) yielded complexes LW(CO)₅ (L=L¹ or L²) and L³M(CO)₄ (M=Mo or W), respectively. These complexes have been fully characterized by NMR, IR and X-ray crystal structural analyses, indicating that they form 1D or 2D organometallic supramolecular architectures through O-H...O, N-H...O and O-H...OC-M hydrogen bonding interactions, and these structures are significantly affected by the relative position of the hydroxymethyl group on the pyrazole ring. In addition, these complexes show moderate catalytic activity for the cyclotrimerization reaction of phenylacetylene. CCDC: 1835473, **1**; 1835474, **2**; 1835475, **3**; 1835476, **6**.

Keywords: N ligand; pyrazole; hydrogen bond; metal carbonyl complex; catalysis

0 Introduction

It is well-known that hydrogen bonds play important roles in the self-assembly of metal complexes to form supramolecular architectures^[1-2]. Organometallic

building blocks can also aggregate into supramolecular structures through hydrogen-bonding interactions^[3-4]. Metal carbonyls as hydrogen bond acceptors in organometallic crystals engineering have been observed in several systems, in which these metal

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carbonyl derivatives show interesting one to three-dimensional supramolecular structures^[5-8]. On the other hand, derivatives of pyrazoles have been used extensively in bioinorganic, coordination chemistry and organometallic fields because of their versatile coordination behavior towards main group and transition metals^[9-11]. Among pyrazole derivatives, hydroxymethyl functionalized pyrazole is an excellent candidate for the construction of supramolecular architectures, since it not only has multiple coordination modes but also can form regular hydrogen bonding by functioning as both a hydrogen-bonding donor and acceptor^[12-13]. The group 6 metal carbonyl complexes are of great interest to scientists since they are widely applied in electron beam induced deposition technique as well as employed as catalysts in various organic synthesis^[14-15]. In this paper, we report the reaction of hydroxymethyl functionalized pyrazoles (L) with group 6 metal carbonyls, which yields a series of $\text{LW}(\text{CO})_5$ and $\text{LM}(\text{CO})_4$ ($\text{M}=\text{Mo}$ or W) derivatives with organometallic supramolecular structures through $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{OC}-\text{M}$ hydrogen-bonding interactions, and the preliminary catalytic activity of these corresponding complexes in the cyclotrimerization reaction of phenylacetylene.

1 Experimental

Solvents were dried and freshly distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of argon. NMR spectra were recorded on a Bruker 400 spectrometer using $\text{DMSO}-d_6$ as solvent, and the chemical shifts were reported with respect to the reference (internal SiMe_4 for ^1H and ^{13}C NMR spectra). IR spectra were recorded as KBr pellets on a Tensor 27 spectrometer. Elemental analyses were carried out on an Elementar Vario EL analyzer. Bis(3-hydroxymethyl-5-methylpyrazol-1-yl)methane was prepared by the published method^[16]. All the other chemicals were analytical reagents and used as received.

1.1 Syntheses of 1 and 2

3(5)-Hydroxymethyl-5(3)-methylpyrazole (0.112 g, 1 mmol) was added to a solution of $\text{W}(\text{CO})_5\text{THF}$ in

THF, prepared *in situ* by the irradiation of a solution of $\text{W}(\text{CO})_6$ (0.359 g, 1 mmol) in THF (60 mL) for 8 h. The mixture was stirred and heated at reflux for 4 h. After the reaction was completed, the solvent was removed under a reduced pressure, and the residue was isolated by column chromatography on silica using ethyl acetate/hexane (1:2, *V/V*) as the eluent to give **1** and **2** as yellow solids.

Complex **1**: Yield: 12%. ^1H NMR: δ 2.28 (s, 3H, CH_3), 4.46 (d, $J=5.6$ Hz, 2H, CH_2), 5.43 (t, $J=5.6$ Hz, 1H, OH), 6.20 (s, 1H, H^4 of pyrazole), 13.28 (s, 1H, NH). ^{13}C NMR: δ 16.4 (CH_3), 54.5 (CH_2), 105.6 (C^4 of pyrazole), 148.3, 153.3 (C^3 and C^5 of pyrazole), 198.2 (4 CO), 202.5 (CO). IR(cm^{-1}): $\nu(\text{OH})$ 3 208; $\nu(\text{NH})$ 3 150; $\nu(\text{CO})$ 2 073, 1 918 (br), 1 879. Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_6\text{W}(\%)$: C 27.55, H 1.85, N 6.42; Found(%): C 27.69, H 1.78, N 6.65.

Complex **2**: Yield: 33%. ^1H NMR: δ 2.29 (s, 3H, CH_3), 4.47 (s, 2H, CH_2), 5.45 (s, 1H, OH), 6.21 (s, 1H, H^4 of pyrazole), 13.29 (s, 1H, NH). ^{13}C NMR: δ 15.9 (CH_3), 54.0 (CH_2), 105.1 (C^4 of pyrazole), 147.8, 152.8 (C^3 and C^5 of pyrazole), 197.7 (4 CO), 202.1 (CO). IR(cm^{-1}): $\nu(\text{OH})$ 3 234; $\nu(\text{NH})$ 3 162; $\nu(\text{CO})$ 2 073, 1 984, 1 915, 1 847. Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_6\text{W}(\%)$: C 27.55, H 1.85, N 6.42; Found(%): C 27.62, H 1.94, N 6.29.

1.2 Synthesis of 3

The solution of 4-hydroxymethylpyrazole (49 mg, 0.5 mmol) and $\text{W}(\text{CO})_6$ (180 mg, 0.5 mmol) in THF (30 mL) was irradiated with a 300 W high-pressure mercury lamp for 8 h at room temperature. After the reaction was completed, the solvent was removed under a reduced pressure, and the residue was isolated by column chromatography on silica using ethyl acetate/hexane (1:1, *V/V*) as the eluent to give **3** as a yellow solid. Yield: 125 mg (60%). ^1H NMR: δ 4.37 (d, $J=5.3$ Hz, 2H, CH_2), 5.01 (t, $J=5.3$ Hz, 1H, OH), 7.82 (s, 1H) and 7.86 (s, 1H) (H^3 and H^5 of pyrazole), 13.64 (s, 1H, NH). The signals at 5.01 and 13.64 disappeared when D_2O was added. ^{13}C NMR: δ 54.0 (CH_2), 124.5 (C^4 of pyrazole), 131.1, 146.4 (C^3 and C^5 of pyrazole), 198.3 (4CO), 202.8 (CO). IR(cm^{-1}): $\nu(\text{OH})$ 3 182; $\nu(\text{NH})$ 3 137; $\nu(\text{CO})$ 2 074, 1 968(sh), 1 909, 1 859. Anal. Calcd. for $\text{C}_9\text{H}_6\text{N}_2\text{O}_6\text{W}(\%)$: C 25.62, H 1.43, N 6.64; Found(%):

C 25.28, H 1.25, N 6.38.

1.3 Synthesis of 4

Complex **4** was similarly obtained using 3,5-dimethyl-4-hydroxymethylpyrazole instead of 4-hydroxymethylpyrazole as above-mentioned synthesis of **3**. Yield: 57%. ^1H NMR: δ 2.23 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.25 (s, 2H, CH_2), 4.69 (s, br, 1H, OH), 12.93 (s, 1H, NH). ^{13}C NMR: δ 8.9 (CH_3), 14.0 (CH_3), 52.3 (CH_2), 117.8 (C^4 of pyrazole), 141.2, 151.9 (C^3 and C^5 of pyrazole), 197.7 (4 CO), 202.1 (CO). IR(cm^{-1}): $\nu(\text{OH})$ 3 199; $\nu(\text{NH})$ 3 159; $\nu(\text{CO})$ 2 072, 1 969 (sh), 1 908, 1 888. Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_6\text{W}$ (%): C 29.36, H 2.24, N 6.22; Found(%): C 29.31, H 2.31, N 6.24.

1.4 Synthesis of 5

Bis(3-hydroxymethyl-5-methylpyrazol-1-yl)methane (0.118 g, 0.5 mmol) was added to a solution of $\text{Mo}(\text{CO})_5\text{THF}$ in THF, prepared in situ by the irradiation of a solution of $\text{Mo}(\text{CO})_6$ (0.132 g, 0.5 mmol) in THF (60 mL) for 8 h. The mixture was stirred and heated at reflux for 4 h. After the reaction was completed, the solvent was removed under a reduced pressure, and the residue was purified by column chromatography on silica using acetone/hexane (2:3, V/V) as the eluent to give **5** as a yellow solid. Yield: 0.13 g (57%). ^1H NMR: δ 2.48 (s, 6H, CH_3), 4.67 (d, $J=5.2$ Hz, 4H, CH_2), 5.49 (t, $J=5.2$ Hz, 2H, OH), 6.17 (s, br, 1H, CH_2N), 6.30 (s, 2H, H^4 of pyrazole), 6.51 (s, br, 1H, CH_2N). ^{13}C NMR: δ 10.8 (CH_3), 57.1 (CH_2), 58.3 (CH_2), 105.5 (C^4 of pyrazole), 142.4, 157.9 (C^3 and C^5 of pyrazole), 220.1 (CO). IR(cm^{-1}): $\nu(\text{OH})$ 3 393; $\nu(\text{CO})$ 2 024, 1 921, 1 843. Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{MoN}_4\text{O}_6$ (%): C 40.55, H 3.63, N 12.61; Found(%): C 40.18, H 3.42, N 12.87.

1.5 Synthesis of 6

Complex **6** was similarly obtained using $\text{W}(\text{CO})_6$ instead of $\text{Mo}(\text{CO})_6$ as above-mentioned synthesis of **5**. Yield: 53%. ^1H NMR: δ 2.50 (s, 6H, CH_3), 4.63 (s, 2H, CH_2), 4.72 (s, 2H, CH_2), 5.56 (s, 2H, OH), 6.14 (d, $J=13.1$ Hz, 1H, CH_2N), 6.34 (s, 2H, H^4 of pyrazole), 6.55 (d, $J=13.1$ Hz, 1H, CH_2N). ^{13}C NMR: δ 11.4 (CH_3), 58.4 (CH_2), 59.6 (CH_2), 106.1 (C^4 of pyrazole), 143.0, 158.7 (C^3 and C^5 of pyrazole), 211.9 (CO). IR (cm^{-1}): $\nu(\text{OH})$ 3 393; $\nu(\text{CO})$ 2 016, 1 908, 1 840. Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_6\text{W}$ (%): C 33.86, H 3.03, N 10.53; Found(%):

C 33.92, H 3.25, N 10.37.

1.6 Catalyzed cyclotrimerization of phenylacetylene

Phenylacetylene (0.12 mL, 1 mmol) and complexes **1~6** ($x\%$, molar ratio) were charged in the reaction tube with 5 mL of toluene. After the reaction mixture was stirred at reflux for 9 h, the volatile materials were removed under reduced pressure. The residuals were purified by column chromatography on silica using CH_2Cl_2 /hexane (1:10, V/V) as the eluent to give the products, which were analyzed by ^1H NMR^[17].

1.7 Crystal structure determination

Green-yellow crystals of **1~3** suitable for X-ray analysis were grown by slow diffusion of hexane into their CH_2Cl_2 solutions at -18°C . While crystals of **6** were obtained through slow diffusion of hexane into the acetone solution. All intensity data were collected on a Rigaku Saturn CCD detector using Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at -160°C . Semi-empirical absorption corrections were applied using the Crystal-clear program^[18]. The O(6) atom in **3** was disordered over two sites, with the occupancy factor of 0.5. The complex **6** crystallized with one acetone and one water molecules in the asymmetric unit. The structures were solved by direct methods and difference Fourier map using SHELXS of the SHELXTL package and refined with SHELXL^[19] 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 these complexes is listed in Table 1.

CCDC: 1835473, **1**; 1835474, **2**; 1835475, **3**; 1835476, **6**.

2 Results and discussion

2.1 Syntheses of complexes 1~6

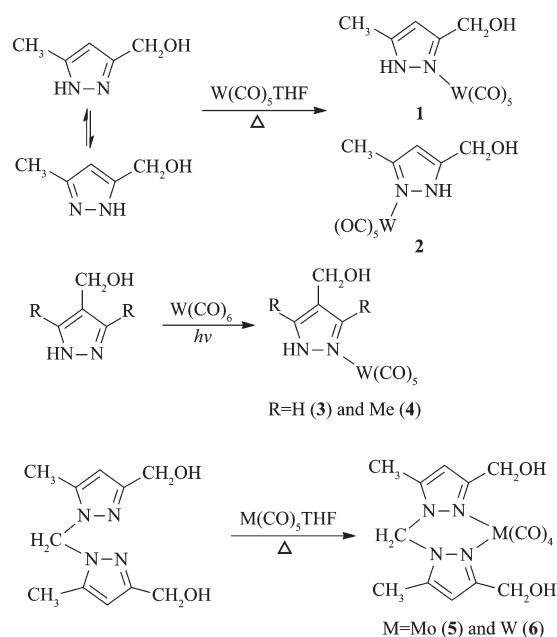
Reaction of 3(5)-hydroxymethyl-5(3)-methylpyrazole with $\text{W}(\text{CO})_5\text{THF}$ at refluxing THF or the direct photochemical reactions of 4-hydroxymethylpyrazoles with $\text{W}(\text{CO})_6$ at room temperature yielded complexes **1~4** (Scheme 1). Complexes **5** and **6** were also obtained through the similar reactions of bis(3-hydroxymethyl-

Table 1 Crystallographic data and refinement parameters for complexes 1~3 and 6

Complex	1	2	3	6·CH ₃ COCH ₃ ·H ₂ O
Formula	C ₁₀ H ₈ N ₂ O ₆ W	C ₁₀ H ₈ N ₂ O ₆ W	C ₉ H ₆ N ₂ O ₆ W	C ₁₈ H ₂₄ N ₄ O ₈ W
Formula weight	436.03	436.03	422.01	608.26
Crystal size / mm	0.20×0.18×0.12	0.20×0.18×0.12	0.20×0.18×0.12	0.20×0.18×0.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> / nm	0.705 16(16)	1.676 1(5)	0.702 15(16)	1.019 9(2)
<i>b</i> / nm	1.679 8(3)	0.900 9(2)	1.775 7(4)	1.051 6(2)
<i>c</i> / nm	1.094 9(3)	1.881 2(5)	0.991 7(2)	1.066 6(3)
α / (°)				88.411(15)
β / (°)	96.347(5)	111.968(4)	91.905(6)	87.754(14)
γ / (°)				78.571(15)
<i>V</i> / nm ³	1.288 9(5)	2.634 3(13)	1.235 8(5)	1.120 2(4)
<i>Z</i>	4	8	4	2
<i>D_c</i> / (g·cm ⁻³)	2.247	2.199	2.268	1.803
θ range / (°)	3.06~27.53	3.056~27.481	3.08~25.019	3.11~27.57
<i>F</i> (000)	816	1 632	784	596
μ / mm ⁻¹	8.986	8.793	9.368	5.206
Measured reflection	16 325	13 841	10 613	12 336
Unique reflection (<i>R_{int}</i>)	2 954 (0.031 5)	3 009 (0.025 6)	2 176 (0.035 5)	4 973 (0.023 4)
Observed reflection with [<i>I</i> ≥2σ(<i>I</i>)]	2 811	2 926	1 994	4 867
Parameter	178	181	182	292
GOF	1.088	1.471	1.216	1.065
Residuals <i>R</i> ₁ , <i>wR</i> ₂	0.012 2, 0.030 1	0.013 4, 0.041 6	0.032 0, 0.073 4	0.013 4, 0.034 0

5-methylpyrazol-1-yl)methane with M(CO)₅THF (M = Mo or W) in moderate yields. Complexes 1~6 have been characterized by spectroscopic methods. Complexes 1~4 displayed similar IR spectra. These four complexes showed two characteristic absorption peaks for the O-H (3 199~3 234 cm⁻¹) and N-H stretching bands (3 137~3 162 cm⁻¹). A ν(C≡O) band at *ca.* 2 073 cm⁻¹ corresponding to the A_{1eq} mode for the pseudo C_{4v} metal center in the M(CO)₅ fragment^[20] was observed in these four complexes, consistent with monodentate pyrazole complexes. The IR spectra of complexes 5 and 6 were different from those of 1~4. Four carbonyl absorption peaks in the range of 1 840~2 024 cm⁻¹ were observed for 5 and 6, matching a typical *cis*-tetracarbonyl arrangement^[21]. The NMR spectra of 1~6 also support the suggested structures. For example, the ¹³C NMR spectra of 1~4 showed two carbonyl carbon signals with *ca.* a 1:4 intensity ratio, corresponding to a monosubstituted pentacarbonyl species.

In addition, the protons of the methylene bridge of 5 and 6 displayed an AB system in their ¹H NMR



Scheme 1 Syntheses of complexes 1~6

spectra, indicating that the inversion of the boat conformation of six-membered metallacycle (crystal structure of **6**) was hindered possibly due to the repulsion among ligands.

2.2 Crystal structures of complexes **1**~**3** and **6**

The structures of complexes **1**~**3** and **6** were further confirmed by X-ray crystallography, and are shown in Fig.1~4, respectively. The selected bond distances and angles are listed in Table 2. Fig.1~3 show that hydroxymethylpyrazoles coordinate to the metal center in a monodentate fashion in **1**~**3**, causing them to possess a similar pentacarbonyl tungsten fragment, as shown by their NMR spectra. Complexes **1**~**3** also share some analogous structural parameters, such as similar W-N bond distance and N-W-C angle. The W-N distances in **1**~**3** (0.223 7~0.226 4 nm) are similar to those reported in other pentacarbonyl tungsten (0) complexes with azole ligands, such as 0.225 6(4) nm in $\text{CH}_2(3,5\text{-Me}_2\text{Pz})(\text{Bt-SnPh}_3)\text{W}(\text{CO})_5$ ^[22]. Fig.4 shows that bis(3-hydroxymethyl-5-methylpyrazol-1-yl)methane acts as a chelating $\kappa^2\text{-[N,N]}$ bidentate ligand to the tungsten atom in **6**, yielding a six-

membered metallacycle with a boat conformation. The W-N bond distances (0.226 4(2) and 0.226 9(2) nm) are similar to those in **1**~**3**, and comparable to those reported for other tetracarbonyl tungsten(0) derivatives with chelating bidentate pyrazolyl groups^[23]. Additionally, two *cis*-carbonyls (C(2)O(2) and C(5)O(5) in **1**, C(1)O(1) and C(4)O(4) in **2** and **3**, as well as C(1)O(1) and C(3)O(3) in **6**) are markedly distorted in these

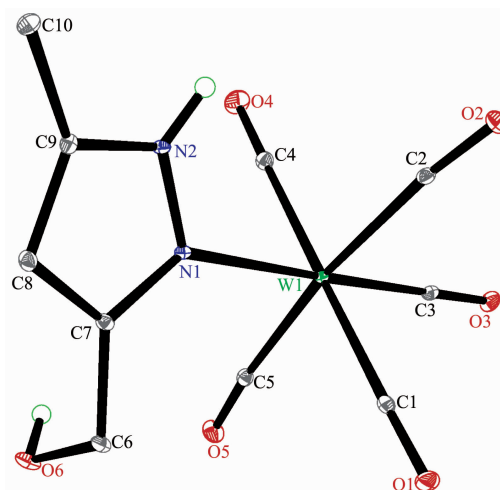


Fig.1 Molecular structure of **1** with 30% probability displacement ellipsoids

Table 2 Selected bond distances (nm) and angles (°) for complexes **1**~**3** and **6**

Complex 1					
W(1)-N(1)	0.226 4(2)	W(1)-C(1)	0.204 5(2)	W(1)-C(3)	0.196 1(2)
C(1)-O(1)	0.113 6(2)	C(3)-O(3)	0.116 1(2)	C(6)-O(6)	0.143 4(2)
W(1)-C(2)-O(2)	173.0(2)	W(1)-C(5)-O(5)	174.0(2)	C(2)-W(1)-C(5)	172.0(1)
Complex 2					
W(1)-N(1)	0.225 3(2)	W(1)-C(1)	0.2047(3)	W(1)-C(3)	0.196 1(3)
C(1)-O(1)	0.114 3(4)	C(3)-O(3)	0.116 1(4)	C(9)-O(6)	0.142 2(3)
W(1)-C(1)-O(1)	173.7(2)	W(1)-C(4)-O(4)	174.3(4)	C(1)-W(1)-C(4)	172.3(1)
Complex 3					
W(1)-N(1)	0.223 7(6)	W(1)-C(1)	0.202 8(8)	W(1)-C(3)	0.198 0(7)
C(1)-O(1)	0.113 0(10)	C(3)-O(3)	0.115 9(9)	C(9)-O(6)	0.147 1(15)
W(1)-C(1)-O(1)	176.0(7)	W(1)-C(4)-O(4)	175.6(7)	C(1)-W(1)-C(4)	174.6(3)
Complex 6					
W(1)-N(1)	0.226 4(2)	W(1)-N(4)	0.226 9(2)	C(1)-O(1)	0.114 3(2)
W(1)-C(1)	0.203 6(2)	W(1)-C(4)	0.195 5(2)	C(5)-O(5)	0.142 7(2)
W(1)-C(1)-O(1)	174.1(2)	W(1)-C(3)-O(3)	175.1(2)	C(1)-W(1)-C(3)	172.95(7)
N(1)-W(1)-N(4)	81.44(6)	N(1)-W(1)-C(4)	177.74(6)	N(2)-C(10)-N(3)	111.4(2)

four complexes, as evidenced by the corresponding nonlinear C-W-C and W-C-O angles (Table 2), indicating the presence of steric repulsion between the

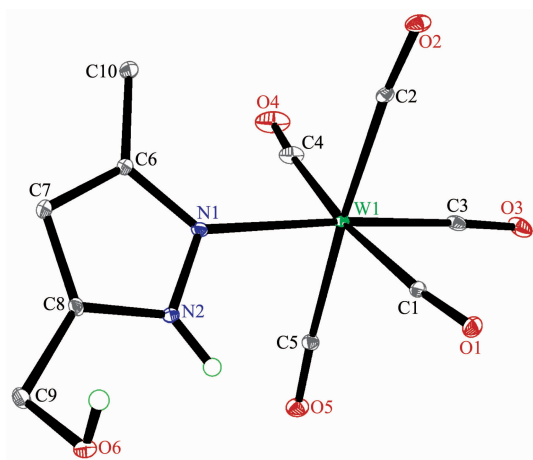


Fig.2 Molecular structure of **2** with 30% probability displacement ellipsoids

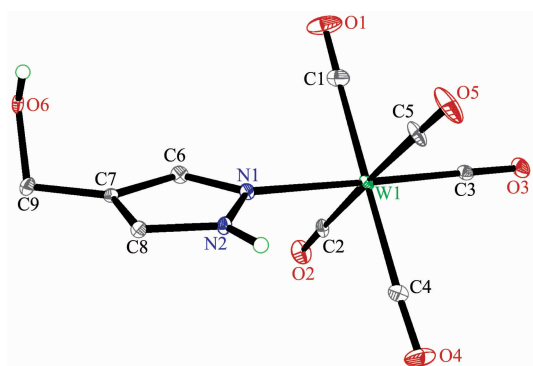


Fig.3 Molecular structure of **3** with 30% probability displacement ellipsoids

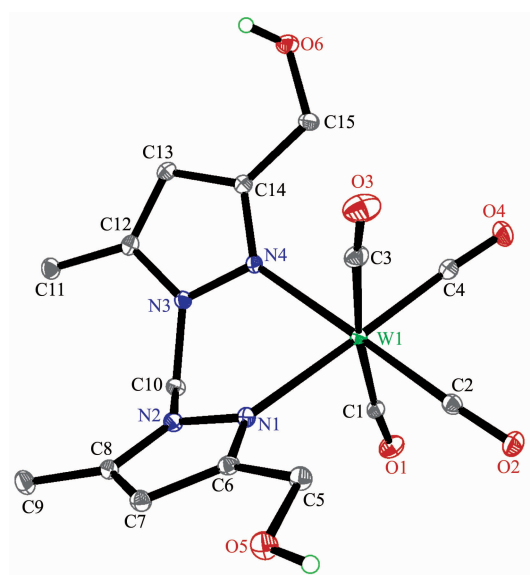
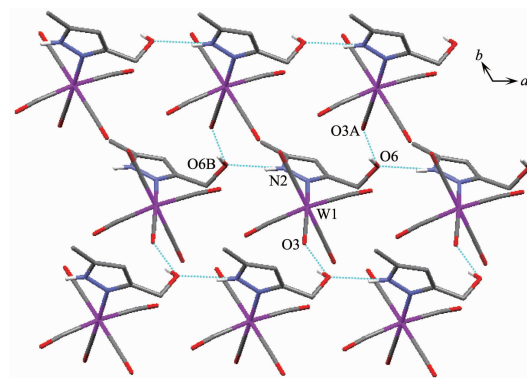


Fig.4 Molecular structure of **6** with 30% probability displacement ellipsoids

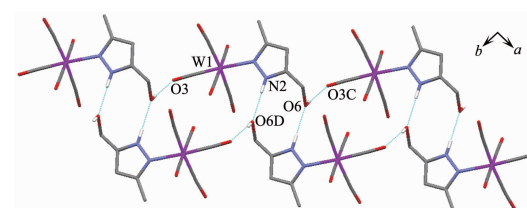
ligand and these carbonyls.

It is noteworthy that although complexes **1**~**3** have a similar molecular skeleton, they show significantly different supramolecular structures (Fig.5~7) owing to the different substitutional position of hydroxymethyl on the pyrazolyl ring. For example, Fig.5 shows that complex **1** aggregates into a 2D supramolecular network through O-H...O (carbonyl) and N-H...O(hydroxyl) hydrogen bonds, and Fig.6 illustrates that complex **2** only extends into a 1D supramolecular double chain. Moreover, Fig.7 shows that the metal carbonyls in **3** do not participate in the hydrogen bonding interactions, and this molecule is only linked into a one-dimensional chain via intermolecular N-H...O (hyd-



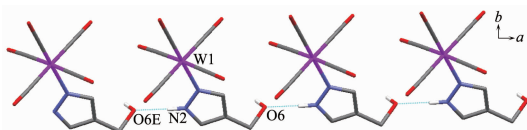
Hydrogen bond distances: O(6)...O(3A) 0.290 6(2) nm, N(2)...O(6B) 0.279 8(2) nm; Symmetry codes: A: $x+1/2, -y+1/2, z+1/2$; B: $x-1, y, z$

Fig.5 Two dimensional supramolecular structure of **1**



Hydrogen bond distances: O(6)...O(3C) 0.293 5(3) nm, N(2)...O(6D) 0.279 8(2) nm; Symmetry codes: C: $x+1/2, y-1/2, z$; D: $-x+2, -y+2, -z+1$

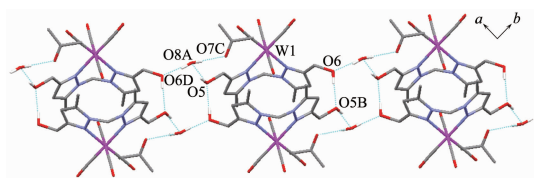
Fig.6 One dimensional supramolecular structure of **2**



Hydrogen bond distance: N(2)...O(6E) 0.270 6(2) nm; Symmetry codes: E: $x-1, y, z$

Fig.7 One dimensional supramolecular structure of **3**

roxyl) hydrogen bonds. In addition, Fig.8 shows that complex **6** forms a 1D supramolecular double chain with macrocyclic units through crystallization water molecule, and also no hydrogen bond is observed between the metal carbonyls with hydroxyl protons.



Hydrogen bond distances: O(5)···O(8A) 0.268 8(2) nm, O(6)···O(5B) 0.268 2(2) nm, O(8A)···O(7C) 0.275 4(2) nm, O(8A)···O(6D) 0.272 7(2) nm; Symmetry codes: A: $-x, -y+2, -z+1$; B: $-x+1, -y+2, -z$; C: $-x, -y+1, -z+1$; D: $-x+1, -y+1, -z+1$

Fig.8 One dimensional supramolecular structure of **6**·CH₃COCH₃·H₂O

2.3 Catalytic activity of complexes 1~6

The transition metal-catalyzed cyclotrimerization

Table 3 Catalytic activity for the cyclotrimerization of phenylacetylene

$$3\text{PhC}\equiv\text{CH} \xrightarrow{x\% (n/n) \text{ cat.}} \begin{array}{c} \text{Ph} \\ | \\ \text{C}_6\text{H}_2 \\ | \\ \text{Ph} \end{array} + \begin{array}{c} \text{Ph} \\ | \\ \text{C}_6\text{H}_2 \\ | \\ \text{Ph} \end{array}$$

A B

Entry	Cat.	$x / \%(n/n)$	Yield (A+B) / % ^a	Ratio of n_A/n_B ^b
1	1	15	63	1.4
2	2	15	66	1.4
3	3	5	43	1.5
4	3	15	63	1.5
5	3	20	62	1.5
6	4	15	56	1.5
7	5	15	53	1.5
8	6	15	55	1.5

^a Isolated yield; ^b Determined by ¹H NMR^[17].

3 Conclusions

In summary, a series of tungsten and molybdenum carbonyl derivatives with hydroxymethyl functionalized pyrazoles have been synthesized. These complexes show significantly different supramolecular structures owing to the different substitutional position of hydroxymethyl on the pyrazolyl ring. Preliminary catalytic studies prove that all these complexes exhibit moderate catalytic activity in the cyclotrimerization

reaction of alkynes has been widely used to prepare various polysubstituted benzene derivatives in recent years^[24]. Molybdenum carbonyl and its derivatives have exhibited efficient catalytic activity in the cyclotrimerization of alkynes^[25-26], but it seems that phenylacetylene tends to form polyphenylacetylene when tungsten carbonyl was used as the catalyst^[27]. Herein, our preliminary studies showed that all these molybdenum and tungsten carbonyl derivatives exhibited effective catalytic activity in the cyclotrimerization reaction of phenylacetylene (Table 3). Two isomers were obtained in moderate yields when 15% (n/n) of complex was used as the catalyst. 1,3,5-Trisubstituted benzene is the major product, similar to the result of the cyclotrimerization of phenylacetylene catalyzed by molybdenum carbonyl^[26]. The ratio of isomers needs to be further improved in future work.

reaction of phenylacetylene.

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