

Dinuclear Pentacarbonyl Tungsten Complex Bridged by Bis(3,5-dimethylpyrazol-1-yl)methane

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A new bis(pyrazol-1-yl)methane ligand, [Ph₂(HO)CCH(3,5-Me₂Pz)₂, Pz = pyrazole](1), with a bulky substituent on the methine carbon atom has been successfully synthesized by the reaction of bis(3,5-dimethylpyrazol-1-yl)methylithium with benzophenone. Treatment of this ligand with W(CO)₆ under UV-irradiation in THF at room temperature afforded a novel dinuclear complex CH₂(3,5-Me₂Pz)W(CO)₅(2) with loss of the Ph₂CO fragment, which was characterized by IR, ¹H NMR spectra and elemental analyses as well as the X-ray single crystal diffraction analysis. This compound crystallizes in the orthorhombic space group *Pbcn*, with *a* = 1.7690(3) nm, *b* = 1.4460(3) nm, *c* = 1.2994(2) nm, *Z* = 4, *V* = 3.3239(10) nm³, *D_c* = 1.775 g·cm⁻³, *μ* = 6.967 mm⁻¹, *F*(000) = 1672, *R*₁ = 0.0414 and *wR*₂ = 0.0988. Bis(3,5-dimethylpyrazol-1-yl)methane acts as a bridging bidentate ligand in this complex, which links two W(CO)₅ fragments. In addition, heating this complex under reflux in 1,2-dimethoxyethane (DME) gives the known chelated mononuclear complex CH₂(3,5-Me₂Pz)₂W(CO)₄(3).

Keywords bis(pyrazol-1-yl)methane, tungsten, X-ray crystal structure

Introduction

Poly(pyrazol-1-yl)alkanes, especially bis(pyrazol-1-yl)alkanes, have been one of popular polydentate nitrogen donor ligands since Trofimenko's first report¹ and Julia's later modification.² It has been found that the coordination behavior of these ligands can easily be adjusted by changing the electronic and steric characteristics of substituents on the pyrazole ring. Recent investigations have also shown that the central carbon atom of these ligands can be modified by the various functional groups to form versatile heteroscorpionate ligands, which usually have asymmetric N₂O,³ N₂S,⁴ N₃S⁵ or N₃O⁶ coordination environments. Our recent investigations exhibit that bis(pyrazol-1-yl)methanes with the substituents on the methine carbon have unusual reactivity,^{7,8} which encourages us to continue the investigation on the modification on the methine carbon of

bis(pyrazol-1-yl)methanes using other functional groups. In this paper, a new bis(pyrazol-1-yl)methane with a N₂O coordination environment and its reaction with W(CO)₆ to yield a novel bridged dinuclear carbonyl tungsten complex are reported.

Experimental

The reaction was carried out under an oxygen-free atmosphere. Solvents were dried by standard methods and distilled prior to use. ¹H NMR spectra were recorded on a Mercury 300 spectrometer using CDCl₃ as solvent unless otherwise noted, and chemical shifts were referenced to Me₄Si. IR spectral data were obtained from a Bio-Rad FTS 135 spectrometer in KBr pellets. Elemental analyses were carried out on a Perkin-Elmer 240 C analyser. Bis(3,5-dimethylpyrazol-1-yl)methane⁹ was prepared according to the reported method.

Preparation of 1

To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (1.22 g, 6 mmol) in THF (80 mL) was added a hexane solution of *n*-BuLi (6.1 mmol, 1.6 mol/L, 3.8 mL) at -78 °C, and the mixture was stirred for 1 h at that temperature. To the mixture was added slowly a solution of benzophenone (2.2 g, 12 mmol) in THF (20 mL) by syringe. The reaction mixture was stirred at -78 °C for 2 h, and allowed to slowly reach room temperature and stirred overnight. Then, the reaction was quenched with NH₄Cl (0.33 g, 6.2 mmol). The reaction mixture was filtered and the solvent was removed under a reduced pressure, and the residual solid was purified by column chromatography on silica using ethyl acetate/hexane as eluent. The eluent was concentrated to dryness under a reduced pressure to give 1.62 g of 1 [Ph₂(HO)CCH(3,5-Me₂Pz)₂, Pz = pyrazole] as a white solid. Yield 70%, m. p.

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188–190 °C. $^1\text{H NMR } \delta$: 2.01 (s, 6H), 2.02 (s, 6H, 3 or 5-CH₃), 5.67 (s, 2H, H⁴ of pyrazole), 6.93 (s, 1H, CH), 7.15–7.24 (m, 6H), 7.26–7.34 (m, 4H, C₆H₅), 7.97 (s, 1H, OH); $^1\text{H NMR (CDCl}_3 + \text{D}_2\text{O)}$ δ : 2.00 (s, 6H), 2.02 (s, 6H, 3 or 5-CH₃), 5.67 (s, 2H, H⁴ of pyrazole), 6.92 (s, 1H, CH), 7.13–7.17 (m, 6H), 7.22–7.31 (m, 4H, C₆H₅); IR ν : 3249.6 (br s, OH), 1565.8 (s, pyrazole ring) cm^{-1} ; MS (70 eV) m/z (%): 387 (22), 386 (M⁺, 10), 385 (100), 233 (M⁺ – 2Ph, 36), 182 (Ph₂CO⁺, 33). Anal. calcd for C₂₄H₂₆N₄O: C 74.58, H 6.78, N 14.50; found C 74.77, H 6.33, N 14.87.

Reaction of ligand **1** with W(CO)₆

The solution of W(CO)₆ (0.5 mmol) and ligand **1** (0.5 mmol) dissolved in THF (30 mL) was irradiated with a 300 W high-pressure mercury lamp for 24 h at room temperature. After the reaction was completed, the solvent was removed *in vacuo*, and the residual solid was purified by the column chromatography on alumina using ether/hexane as eluent. The green-yellow eluent was concentrated to dryness under a reduced pressure. The residual solid was recrystallized from CH₂Cl₂/hexane to give 0.2 g of green-yellow crystals, which were confirmed as CH₂(3,5-Me₂Pz)W(CO)₅ (**2**) by crystal X-ray diffraction analysis. Yield 54%; $^1\text{H NMR } \delta$: 1.71 (s, 6H), 2.52 (s, 6H, CH₃), 6.09 (s, 2H, H⁴ of pyrazole), 7.22 (s, 2H, CH₂); IR ν_{CO} : 2074.3 (m), 1986.7 (sh), 1973.3 (m), 1921.5 (vs), 1889.2 (vs) cm^{-1} . Anal. calcd for C₂₁H₁₆N₄O₁₀W₂·0.5C₄H₈O (THF): C 31.10, H 2.25, N 6.31; found C 30.88, H 2.22, N 6.79.

The reaction of Cr(CO)₆ or Mo(CO)₆ with ligand **1** was carried out as described above for W(CO)₆, but remarkable decomposition was observed during the reaction. When the solvent was removed *in vacuo*, the residual solid was extremely air-sensitive. So the products are difficult to purify, and no satisfactory result was obtained.

Heating complex **2** under reflux in 1,2-dimethoxyethane

The solution of complex **2** (0.13 g, 0.15 mmol) dissolved in 1,2-dimethoxyethane (DME) (20 mL) was heated at reflux for 4 h. After cooling to room temperature, the solvent was removed *in vacuo*, and the residual solid was purified by the column chromatography on silica using CH₂Cl₂/hexane as eluent. The green-yellow eluent was concentrated to dryness under a reduced pressure. The residual solid was recrystallized from CH₂Cl₂/hexane to give 0.04 g of green-yellow crystals of CH₂(3,5-Me₂Pz)₂W(CO)₄ (**3**). This complex was also obtained by heating bis(3,5-dimethylpyrazol-1-yl)methane with W(CO)₆ at reflux in DME¹⁰ or irradiating bis(3,5-dimethylpyrazol-1-yl)methane with W(CO)₆ in THF as described above for **2**.

Structure determination of complex **2**

Crystals of **2** suitable for X-ray diffraction analysis were obtained from a CH₂Cl₂/hexane solution at –10 °C. A single crystal with approximate dimensions of 0.25 mm × 0.20 mm × 0.20 mm was mounted in a glass capillary. Intensity data were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.071073$ nm) at room temperature using the $\omega/2\theta$ scan technique. The crystal structure belongs to orthorhombic, space group *Pbcn*, $a = 1.7690(3)$ nm, $b = 1.4460(3)$ nm, $c = 1.2994(2)$ nm, $Z = 4$, $V = 3.3239(10)$ nm³, $D_c = 1.775$ g · cm^{–3}, $\mu = 6.967$ mm^{–1}, $F(000) = 1672$. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . The non-hydrogen atoms were refined anisotropically to $R_1 = 0.0414$ and $wR_2 = 0.0988$ for 2936 observed reflections with $I > 2\sigma(I)$.

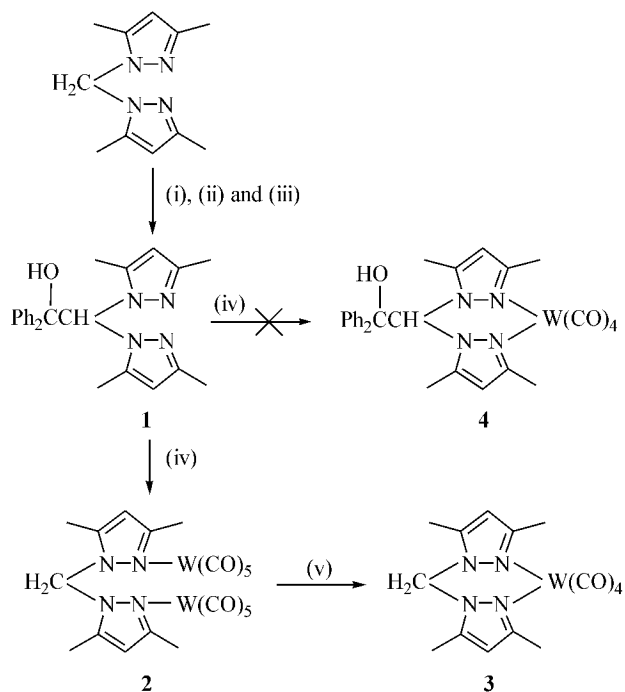
Results and discussion

Syntheses and properties of the ligand and complexes

Ligand **1** can be easily obtained by the reaction of bis(3,5-dimethylpyrazol-1-yl)methyl lithium with benzophenone as shown in Scheme 1. Its $^1\text{H NMR}$ spectrum showed that the proton signal of hydroxyl group appeared at δ 7.97 in CDCl₃, and this peak disappeared when D₂O was added. In general, bis(pyrazol-1-yl)alkane acts as a chelating bidentate ligand, and only in some examples it behaved as a bridging bidentate ligand.^{11,12} Our recent investigations showed that irradiation of bis(pyrazol-1-yl)methane with M(CO)₆ in THF gave (N–N)M(CO)₄ complexes [N–N represents bis(pyrazol-1-yl)methane, M = Cr, Mo or W],¹³ in which bis(pyrazol-1-yl)methane also acted as a chelating bidentate ligand. There was no report on group 6 metal carbonyl complexes containing the bridging bidentate bis(pyrazol-1-yl)alkanes. However, herein irradiation of ligand **1** and W(CO)₆ in THF solution at room temperature yielded the bridged dinuclear complex **2** with loss of the Ph₂CO fragment (Scheme 1), and no chelating complex **4** was obtained. This may be the results of the steric repulsion of the $\alpha(\text{OH})\text{Ph}_2$ group on the methine carbon with carbonyls and pyrazole rings in complex **4**, which comes from the boat conformation of the metallacyclic ring W–N–N–C–N–N in (N–N)M(CO)₄ complexes.^{7,13} At the same time, the steric congestion led by the $\alpha(\text{OH})\text{Ph}_2$ group maybe result in the inverse decomposition of ligand **1** during the reaction. The MS data of ligand **1** also show that it is easy to cleave the carbon-carbon bond between the $\alpha(\text{OH})\text{Ph}_2$ and CH₂(3,5-Me₂Pz)₂ fragments. In addition, heating complex **2** at reflux in DME gave the known chelated mononuclear complex **3**. The reaction of bis(3,5-dimethylpyrazol-1-yl)methane with

$W(CO)_6$ under reflux in DME¹⁰ or under UV-irradiation in THF also only gave complex **3**. The reaction of $Cr(CO)_6$ or $Mo(CO)_6$ with ligand **1** under UV-irradiation could also take place, but remarkable decomposition was observed during the reaction. Because the products were extremely air-sensitive, they are not easy to purify, and satisfactory analytical results were not obtained.

Scheme 1



Reagents and conditions: (i) *n*-BuLi, $-78\text{ }^\circ\text{C}$; (ii) Ph_2CO , $-78\text{ }^\circ\text{C}$ to r.t.; (iii) NH_4Cl ; (iv) $W(CO)_6/THF$, $h\nu$; (v) reflux in DME.

Complex **2** in solid was stable in air, but slightly sensitive to air in solution. Its spectroscopic data were consistent with its structure. No proton signals of the $C(OH)Ph_2$ unit were observed in its 1H NMR spectrum; while only one set of proton signals of bis(3,5-dimethylpyrazol-1-yl)methane appeared. Its IR spectrum was similar to those of monosubstituted $M(CO)_5L$ complexes ($L = \text{pyrazole}$),¹⁴ in which a ν_{CO} band was observed at *ca.* 2070 cm^{-1} corresponding to the A_{1eq} mode for the pseudo C_{4v} metal center in a metal pentacarbonyl moiety,¹⁵ but significantly different from those in the chelating complexes $(N-N)M(CO)_4$.¹³

Molecular structure of complex **2**

The structure of complex **2** has also been confirmed by crystal X-ray diffraction analysis. Selected bond distances and angles of complex **2** are shown in Table 1. The molecular structure is presented in Fig. 1, which clearly shows that bis(3,5-dimethylpyrazol-1-yl)methane acts as a bridging bidentate ligand, and no $C(OH)Ph_2$ structural unit is found in this complex. Two $W(CO)_5$ fragments are linked by the bridging ligand, and located in a mutually *cis*-position. Each tungsten atom is six-coordinated with a quasi-octahedral coordination geometry. The $W-N$ distance is $0.2318(8)\text{ nm}$, which is comparable to those found in other octahedral $W(0)$ complexes with pyrazole ligands [such as $0.2236(4)\text{ nm}$ in $3-Bu^tPzW(CO)_5$,¹⁶ $0.2204(8)\text{ nm}$ in $3-FcPzW(CO)_5$,¹⁴ average 0.2255 nm in $CH_2(3,5-Me_2-4-ClPz)_2W(CO)_4$,¹⁷ $0.2269(4)\text{ nm}$ in $Me_3SiCH(3,5-Me_2Pz)_2W(CO)_4$ ⁷ and 0.2275 nm in $(CH_2)_2(3,5-Me_2Pz)_2W(CO)_4$,¹⁸ respectively, $Pz = \text{pyrazole}$ and $Fc = \text{ferrocenyl}$].

Table 1 Selected bond distances (nm) and angles ($^\circ$) for complex **2**

$W(1)-\alpha(3)$	0.1987(13)	$W(1)-N(1)$	0.2318(8)
$W(1)-\alpha(2)$	0.2017(15)	$\alpha(1)-\alpha(1)$	0.1123(14)
$W(1)-\alpha(4)$	0.2045(14)	$\alpha(2)-\alpha(2)$	0.1176(15)
$W(1)-\alpha(1)$	0.2061(14)	$\alpha(3)-\alpha(3)$	0.1143(14)
$W(1)-\alpha(5)$	0.2071(13)	$\alpha(4)-\alpha(4)$	0.1138(15)
$N(2)-\alpha(11)$	0.1437(10)	$\alpha(5)-\alpha(5)$	0.1105(13)
$\alpha(3)-W(1)-\alpha(2)$	88.3(6)	$\alpha(1)-\alpha(1)-W(1)$	173.9(12)
$\alpha(4)-W(1)-\alpha(1)$	169.7(5)	$\alpha(2)-\alpha(2)-W(1)$	176.6(13)
$\alpha(3)-W(1)-\alpha(5)$	90.8(5)	$\alpha(3)-\alpha(3)-W(1)$	177.9(13)
$\alpha(2)-W(1)-\alpha(5)$	178.9(5)	$\alpha(4)-\alpha(4)-W(1)$	174.6(12)
$\alpha(4)-W(1)-\alpha(5)$	90.5(5)	$\alpha(5)-\alpha(5)-W(1)$	175.9(13)
$\alpha(1)-W(1)-\alpha(5)$	87.7(5)	$\alpha(7)-N(1)-N(2)$	103.8(8)
$\alpha(3)-W(1)-N(1)$	175.3(5)	$\alpha(7)-N(1)-W(1)$	128.6(7)
$\alpha(5)-W(1)-N(1)$	92.0(4)	$N(2)-N(1)-W(1)$	126.3(6)
$N(2)-\alpha(9)-\alpha(10)$	123.4(11)	$\alpha(9)-N(2)-\alpha(11)$	127.7(9)
$\alpha(8)-\alpha(9)-\alpha(10)$	129.8(10)	$N(1)-N(2)-\alpha(11)$	120.8(7)
$N(2)-\alpha(11)-N(2A)^a$	112.8(11)	$N(1)-\alpha(7)-\alpha(6)$	123.1(10)

^a $-x, y, -z + 1/2$.

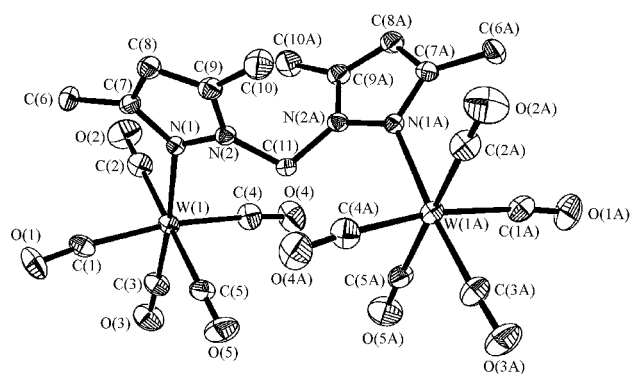


Fig. 1 Molecular structure of complex **2** (the thermal ellipsoids are drawn at the 30% probability level).

In conclusion, a new bis(pyrazol-1-yl)methane ligand **1** with a bulky substituent on the methine carbon atom has been successfully synthesized. Treatment of this ligand with $W(CO)_6$ under UV-irradiation gave a new dinuclear complex **2**, in which bis(pyrazol-1-yl)methane acts as a bridging bidentate ligand.

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