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Synthesis and reactivity of Group 6 metal carbonyl complexes containing bis(triazol-1-yl)methane: linkage coordination polymers

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Abstract

The reaction of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane, $CH_2(3,5\text{-}Me_2Tz)_2$, with $M(CO)_6$ (M = Cr, Mo or W) in refluxing DME produces $CH_2(3,5\text{-}Me_2Tz)_2M(CO)_4$ in moderate yield. The crystal structures determined by X-ray analysis show that bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane acts as a chelating bidentate ligand with two endodentate nitrogen atoms in these complexes. Reactions of complexes $CH_2(3,5\text{-}Me_2Tz)_2M(CO)_4$ (M = Mo or W) with R_2SnX_2 (R = Ph or Me; X = Cl or Br) in a 1:1 or 1:2 ratio, respectively, only yield 1:1 adducts. In these adducts, bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane may coordinate to tin atom through exodentate nitrogen atoms on the 4-position of triazole rings to form linkage coordination polymers. Possibly owing to weak donors of 4-position exonitrogen atoms on triazole rings to organotin acceptors, the dissociation of these adducts in solution could exist. Adduct of $CH_2(3,5\text{-}Me_2Tz)_2W(CO)_4\cdot SnPh_2Br_2$ absorbs one water molecule while crystals are growing and becomes the hydrolysis product $[SnPh_2Br_2(H_2O)]\cdot(CH_2(3,5\text{-}Me_2Tz)_2W(CO)_4)$, which is characterized by X-ray crystallography, indicating that tin atom is five coordinate with a trigonal bipyramid geometry, the water molecule coordinates to the tin atom, and is simultaneously connected to the exonitrogen atoms on the 4-position of triazole rings of two adjacent $CH_2(3,5\text{-}Me_2Tz)_2W(CO)_4$ units through hydrogen bonds to form linkage coordination polymers, in which two coordination modes are observed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Poly(triazol-1-yl)alkane; Group 6 metal carbonyl complex; Organotin(IV); X-ray crystal structure

1. Introduction

Poly(pyrazol-1-yl)borate has developed into one of the most versatile ligands in modern coordination chemistry [1,2]. The modification of this ligand through replacement of pyrazole rings by 1,2,4-triazole to form novel poly(triazol-1-yl)borate has also attracted considerable attention [3–11]. The replacement of pyrazole rings by tetrazole or benzotriazole to form poly(tetrazol-1-yl)borate [12] and poly(benzotriazol-1-yl)borate [13], respectively, has also been reported. Owing to the existence of more than one coordinate active nitrogen atom on triazole and tetrazole rings, the coordination modes of these novel ligands, which often form coordination polymers through the exodentate nitrogen donor atoms, are quite different from those of the parent poly(pyrazol-1-yl)borate ligands [1]. For example, three triazole rings in hydrotris(triazol-1-yl)borate ligand showed different coordination modes to the same kind of metal ion to form a 2-D coordination polymer [14]. In contrast, although similar substitutions of triazole or tetrazole for pyrazole in poly(pyrazol-1-yl)alkanes to form poly(triazol-1-yl) or poly(tetrazol-1-yl)alkanes have been reported [15–18], their coordination chemistry is noticeably underdeveloped [19,20]. Two recent reports show that bis(1,2,4-triazol-1-yl)alkanes coordinate with copper atoms through exonitrogen atoms on the triazole ring to yield 1-D or 2-D coordination polymers [21,22]. Recently, we investigated the coordination reactions between bis(1,2,4-triazol-1-yl)alkanes with organotin(IV) halides, and found that bis(1,2,4-tri-

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azol-1-yl)alkanes coordinate to tin atoms through exodentate nitrogen atoms on the 4-position of triazole rings to form linkage coordination polymers, which leads to a bridging instead of a general chelate coordination mode [23]. Herein, we report the synthesis of Group 6 metal carbonyl derivatives of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane and their reactions with diorganotin(IV) halides. This ligand chelates one Group 6 metal atom with two endodentate nitrogen atoms and also bridges two tin atoms through the exodentate nitrogen donors to form linkage coordination polymers.

2. Experimental

All reactions were carried out under an oxygen-free atmosphere. Solvents were dried by standard methods and distilled prior to use. NMR spectra (^{1}H, ^{13}C and ^{119}Sn) were recorded on Bruker AC-P-200 spectrometer, and the chemical shifts were reported in ppm with respect to the references (internal $SiMe_4$ for ^{1}H-NMR and ^{13}C-NMR spectra, external $SnMe_4$ for ^{119}Sn-NMR). IR spectral data were obtained from a Bio-Rad FTS 135 spectrometer in KBr pellets. Elemental analyses were carried out on a Perkin–Elmer 240C analyzer. Bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane [23] was prepared according to the literature method.

2.1. Reaction of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane with $M(CO)_6$ (M = Cr, Mo, W)

2.1.1. Preparation of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane tetracarbonyl chromium (1)

A solution of $Cr(CO)_6$ (1 mmol) and bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane (1 mmol) in DME (15 ml) was stirred and refluxed for 24 h under an Ar atmosphere. After cooling, the solvent was removed in vacuo to yield a dark-yellow solid. The residual solid was purified by a short column chromatography on alumina using acetone as eluent. The green–yellow elution was concentrated to dryness again under a reduced pressure to give a green–yellow solid, which was recrystallized from CH_2Cl_2–hexane to yield green–yellow crystals. Yield: 45%. ^{1}H-NMR ($CDCl_3$): δ 6.03 (s, br, 2H, CH_2), 2.60, 2.27 (s, s, 6H, 6H, CH_3). IR: $\nu_{CO} = 2009.0$ (s), 1896.5 (sh), 1875.0 (vs), 1829.5 (vs); $\nu_{triazolyl\ ring} = 1532.4$ (m), 1508.2 (m) cm^{-1}. Anal. Found: C, 42.30; H, 3.67; N, 22.31. Calc. for $C_{13}H_{14}CrN_6O_4$: C, 42.16; H, 3.78; N, 22.70%.

2.1.2. Preparation of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane tetracarbonyl molybdenum (2)

This compound was obtained similarly using $Mo(CO)_6$ and bis(3,5-dimethyl-1,2,4-triazol-1-yl)-methane as described above for **1**, but the reaction time was 4 h. Complex **2** was pale green–yellow crystals. Yield: 60%. ^{1}H-NMR (CD_3COCD_3): δ 6.77, 6.39 (s, s, br, br, 1H, 1H, CH_2), 2.68, 2.51 (s, s, 6H, 6H, CH_3). ^{13}C-NMR (CD_3COCD_3): δ 12.1, 15.4 (3- or 5-CH_3), 57.5 (CH_2), 156.2, 164.5 (C^3 or C^5 of triazole), 206.2, 221.0 (CO). IR: $\nu_{CO} = 2016.8$ (s), 1901.2 (vs), 1868.3 (vs), 1825.6 (vs); $\nu_{triazolyl\ ring} = 1532.7$ (m), 1504.8 (m) cm^{-1}. Anal. Found: C, 37.28; H, 3.27; N, 20.47. Calc. for $C_{13}H_{14}MoN_6O_4$: C, 37.68; H, 3.38; N, 20.29%.

2.1.3. Preparation of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane tetracarbonyl tungsten (3)

This compound was obtained similarly using $W(CO)_6$ and bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane as described above for **1**, but the reaction time was 20 h. Complex **3** was green–yellow crystals. Yield: 52%. ^{1}H-NMR ($CDCl_3$) δ : 6.39, 6.17 (d, d, $J = 12$ Hz, 1H, 1H, CH_2), 2.62 (s, 12H, CH_3). ^{13}C-NMR (CD_3COCD_3): δ 12.3, 15.9 (3- or 5-CH_3), 58.3 (CH_2), 156.2, 164.8 (C^3 or C^5 of triazole), 202.9, 212.1 (CO). IR: $\nu_{CO} = 2016.6$ (s), 1879.4 (vs), 1829.4 (vs), 1806.6 (vs); $\nu_{triazolyl\ ring} = 1532.1$ (m), 1498.8 (m) cm^{-1}. Anal. Found: C, 31.14; H, 2.79; N, 16.70. Calc. for $C_{13}H_{14}N_6O_4W$: C, 31.08; H, 2.79; N, 16.73%.

2.2. Reaction of complex of 2 or 3 with R_2SnX_2 (R = Ph or Me; X = Cl or Br)

All reactions were similar, a general procedure was described. To a stirred solution of complex **2** or **3** (0.2 mmol) in 15 ml CH_2Cl_2, the solution of R_2SnX_2 (0.2 mmol) in 5 ml CH_2Cl_2 was added. The reaction mixture was continuously stirred for 3 h at room temperature, then filtered off. The same volume petroleum ether (60–90 °C) was slowly added to the filter, which was placed at −15 °C to yield microcrystalline solids.

2.2.1. Preparation of complex 4

This compound was obtained by the reaction of complex **2** with Ph_2SnCl_2. Yield: 84%. ^{1}H-NMR ($CDCl_3$): δ 7.66, 7.53 (m, m, 4H, 6H, C_6H_5), 6.38, 6.17 (s, s, br, br, 1H, 1H, CH_2), 2.59, 2.58 (s, s, 6H, 6H, CH_3). IR: $\nu_{CO} = 2021.8$ (s), 1915.0 (vs), 1890.2 (vs), 1874.0 (vs); $\nu_{triazolyl\ ring} = 1533.4$ (m), 1506.5 (m) cm^{-1}. Anal. Found: C, 37.08; H, 3.23; N, 9.93. Calc. for $C_{25}H_{24}Cl_2MoN_6O_4Sn \cdot CH_2Cl_2$: C, 37.01; H, 3.08; N, 9.96%. The same product was obtained when complex **2** reacted with Ph_2SnCl_2 in a 1:2 ratio.

2.2.2. Preparation of complex 5

This compound was obtained by the reaction of complex **3** with Ph_2SnCl_2. Yield: 75%. ^{1}H-NMR ($CDCl_3$): δ 7.68, 7.53 (m, m, 4H, 6H, C_6H_5), 6.35, 6.23 (s, s, br, br, 1H, 1H, CH_2), 2.60, 2.59 (s, s, 6H, 6H, CH_3). ^{13}C-NMR (CD_3COCD_3): δ 12.3, 16.0 (3- or 5-CH_3), 58.4 (CH_2), 129.7, 131.3, 136.0, 143.5 (C_6H_5), 156.2, 164.9 (C^3 or C^5 of triazole), 206.3, 212.2 (CO). ^{119}Sn-NMR (CD_3COCD_3): δ −169.5. IR: $\nu_{CO} = 2016.1$ (s), 1911.0 (vs), 1881.0 (vs), 1867.0 (vs); $\nu_{\text{triazolyl ring}} =$ 1531.5 (m), 1507.2 (m) cm^{-1}. Anal. Found: C, 33.85; H, 3.05; N, 9.11. Calc. for $C_{25}H_{24}Cl_2N_6O_4SnW \cdot CH_2Cl_2$: C, 33.51; H, 2.79; N, 9.02%.

2.2.3. Preparation of complex **6**

This compound was obtained by the reaction of complex **2** with Ph_2SnBr_2. Yield: 76%. ^{1}H-NMR ($CDCl_3$): δ 7.66, 7.51 (m, m, 4H, 6H, C_6H_5), 6.38, 6.16 (s, s, br, br, 1H, 1H, CH_2), 2.59, 2.58 (s, s, 6H, 6H, CH_3). ^{13}C-NMR (CD_3COCD_3): δ 12.2, 15.4 (3- or 5-CH_3), 57.6 (CH_2), 129.8, 131.6, 135.7, 142.4 (C_6H_5), 156.3, 164.6 (C^3 or C^5 of triazole), 206.2, 221.0 (CO). ^{119}Sn-NMR (CD_3COCD_3): δ −180.2. IR: $\nu_{CO} = 2022.4$ (s), 1896.8 (vs), 1875.0 (vs), 1854.0 (vs); $\nu_{\text{triazolyl ring}} =$ 1533.4 (m), 1507.0 (m) cm^{-1}. Anal. Found: C, 33.39; H, 2.89; N, 8.77. Calc. for $C_{25}H_{24}Br_2MoN_6O_4Sn \cdot CH_2Cl_2$: C, 33.48; H, 2.79; N, 9.01%.

2.2.4. Preparation of complex **7**

This compound was obtained by the reaction of complex **3** with Ph_2SnBr_2. Yield: 64%. ^{1}H-NMR ($CDCl_3$): δ 7.65, 7.52 (m, m, 4H, 6H, C_6H_5), 6.35, 6.19 (d, d, 1H, 1H, $J = 13.6$ Hz, CH_2), 2.61 (s, 12H, CH_3). ^{13}C-NMR (CD_3COCD_3): δ 12.3, 16.0 (3- or 5-CH_3), 58.4 (CH_2), 129.8, 131.6, 135.7, 142.4 (C_6H_5), 156.3, 164.7 (C^3 or C^5 of triazole), 202.6, 212.2 (CO). ^{119}Sn-NMR (CD_3COCD_3): δ −171.9. IR: $\nu_{CO} = 2016.1$ (s), 1886.8 (sh), 1867.1 (vs), 1857.0 (sh); $\nu_{\text{triazolyl ring}} = 1533.4$ (w), 1505.9 (w) cm^{-1}. Anal. Found: C, 30.94; H, 2.26; N, 8.59. Calc. for $C_{25}H_{24}Br_2N_6O_4SnW \cdot 1/2CH_2Cl_2$: C, 31.30; H, 2.56; N, 8.59%.

2.2.5. Preparation of complex **8**

This compound was obtained by the reaction of complex **2** with Me_2SnCl_2. Yield: 60%. ^{1}H-NMR ($CDCl_3$): δ 6.37, 6.12 (s, s, br, br, 1H, 1H, CH_2), 2.60, 2.59 (s, s, 6H, 6H, CH_3), 1.18 (s, 6H, Sn–CH_3). IR: $\nu_{CO} = 2020.6$ (s), 1898.9 (vs), 1883.4 (vs), 1843.5 (vs); $\nu_{\text{triazolyl ring}} = 1534.3$ (w), 1510.4 (w) cm^{-1}. Anal. Found: C, 27.56; H, 3.60; N, 12.80. Calc. for $C_{15}H_{20}Cl_2MoN_6O_4Sn \cdot 1/2CH_2Cl_2$: C, 27.49; H, 3.10; N, 12.42%.

2.2.6. Preparation of complex **9**

This compound was obtained by the reaction of complex **3** with Me_2SnCl_2. Yield: 55%. ^{1}H-NMR ($CDCl_3$): δ 6.37, 6.18 (s, s, br, br, 1H, 1H, CH_2), 2.61 (s, 12H, CH_3), 1.19 (s, 6H, Sn–CH_3). IR: $\nu_{CO} = 2013.4$ (s), 1937.5 (vs), 1872.8 (vs), 1835.6 (vs); $\nu_{\text{triazolyl ring}} =$ 1532.2 (w), 1509.7 (m) cm^{-1}. Anal. Found: C, 23.97; H, 3.05; N, 11.24. Calc. for $C_{15}H_{20}Cl_2N_6O_4SnW \cdot 1/2CH_2Cl_2$: C, 24.33; H, 2.75; N, 10.99%.

2.3. Crystal structures determination

Crystals of complexes **2**, **3** and **7** suitable for X-ray analysis were grown from CH_2Cl_2–hexane at 4 °C. Complex **3** crystallized with one molecule CH_3OH. The crystals of complex **7** quickly eliminated the part incorporated solvents when taken out of the solvent phase. All intensity data were collected with an Enraf–Nonius CAD4 diffractometer for complex **2**, and Bruker SMART CCD diffractometer for complexes **3** and **7**, using graphite monochromated Mo–K_α 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 complexes **2**, **3** and **7** is listed in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

The reaction of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane with $M(CO)_6$ (M = Cr, Mo or W) in refluxing DME produced complexes **1**–**3** in moderate yield, according to Scheme 1.

The stability of complexes **1**–**3** was of the order W(0) > Mo(0) ~ Cr(0). The molybdenum and chromium complexes in solid were slightly sensitive to air at room temperature, but could be stored at low temperature under inert atmosphere for a long time. However, the tungsten complex in solid was stable in air. They were soluble in chlorinated solvents, acetone.

Reactions of complex of **2** or **3** with R_2SnX_2 (R = Ph or Me; X = Cl or Br) in a 1:1 or 1:2 ratio, respectively, only gave 1:1 adducts **4**–**9** in good yield according to the results of elemental analyses and ^{1}H-NMR data. These complexes were moderately soluble in chlorinated solvents, but once they precipitated out, it was difficult to redissolve them in these solvents. They were soluble in stronger polar solvents such as acetone, Me_2SO.

The IR spectra of complexes **1**–**3** showed four typical bands in the carbonyl-stretching region, as expected for *cis*-tetracarbonyl complexes. Two absorption peaks of heterocyclic ligand vibration were observed at ca. 1530 and 1500 cm^{-1}, respectively, and there was no significant shift upon coordination, compared with that of free ligand. The carbonyl absorption peaks in IR spectra of complexes **4**–**9** were similar to those of complexes **2** and **3**, indicating that the reactions of complexes **2** and **3** with R_2SnX_2 were possibly not related to metal molybdenum or tungsten center.

The ^{1}H-NMR spectra of complexes **1**–**9** indicated that the chemical shifts of protons for the ligands in complexes were similar to those of free ligands, only

Table 1
Crystal data for compounds **2**, **3** and **7**·H_2O

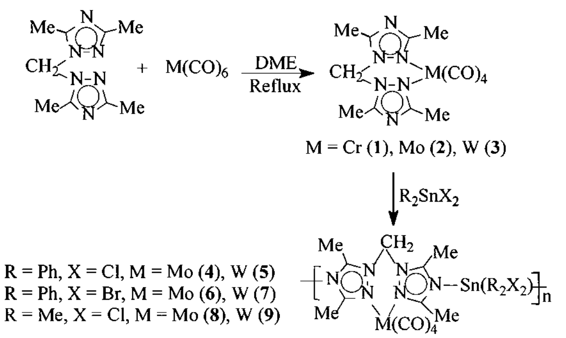
Compound	**2**	**3**·CH_3OH·$2H_2O$	**7**·H_2O·1/2CH_2Cl_2
Empirical formula	$C_{13}H_{14}MoN_6O_4$	$C_{14}H_{22}N_6O_7W$	$C_{26.50}H_{29}Br_2ClN_6O_5SnW$
Formula weight	414.23	570.21	973.92
Crystal size (mm)	0.25 × 0.30 × 0.30	0.30 × 0.20 × 0.10	0.25 × 0.20 × 0.20
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$C2$	$C2/c$
Unit cell dimensions			
a (Å)	10.207(2)	12.530(1)	18.92(1)
b (Å)	10.208(2)	19.023(1)	10.995(7)
c (Å)	16.693(3)	9.1230(8)	35.92(2)
β (°)	90.00	96.998(2)	104.17(1)
V (Å^3)	1739(1)	2158.3(3)	7245(7)
Z	4	4	8
T (K)	299	293	293
D_{calc} (Mg m^{-3})	1.582	1.730	1.786
F(000)	832	1080	3712
λ(Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.7628	5.396	6.107
Number of reflections measured	1742	4521	14478
Reflections observed	1659 ($I \geq 3\sigma(I)$)	3687 ($I \geq 2\sigma(I)$)	6327 ($I \geq 2\sigma(I)$)
Number of parameters	217	263	411
Residuals R, Rw	0.050, 0.052	0.029, 0.0664	0.0485, 0.0696

slightly shifted downfield compared with free ligands. But the protons of methylene group showed a typical AB system, which exhibited two sets of resonance in complexes **2**–**9**, and one broad singlet in complex **1** at room temperature. Obviously, the boat-to-boat inversion of the six-member metallacycle M–N–N–C–N–N (see Section 3.2) in solution is restricted, possibly owing to the steric hindrance. All the signals of the ^{13}C resonances of ligands in complexes **2** and **3** could be observed at room temperature, and two ^{13}C carbonyl signals were detected, as expected. The ^{13}C resonances of $M(CO)_4$ fragments and ligand in complexes **5**–**7** were very analogous to those in complexes **2** and **3**, and there was no remarkable difference, indicating that the $M(CO)_4$ fragments among these complexes could have similar structures. The ^{119}Sn-NMR signals of **5**, **6** and **7** in CD_3COCD_3 appeared at −169.5, −180.2 and −171.9 ppm, respectively, which were compared to those of organotin derivatives of poly(pyrazol-1-yl)alkanes or bis(triazol-1-yl)alkanes [23–25] and $SnPh_2X_2$ (−72.9 ppm for Br and −31.7 ppm for Cl) determined under the same conditions, indicating that extensive dissociation of these complexes in polar solution could also exist. This dissociation could also be found in other organotin derivatives containing poly(pyrazol-1-yl)alkanes and bis(triazol-1-yl)alkanes owing to weak interactions of ligands with organotin acceptors [23–27]. Above NMR data also show that bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane ligand in complexes **4**–**9** is not a good donor to organotin acceptors. Similar spectra of complexes **4**–**9** also indicate that bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane may have the same coordination mode in these organotin derivatives.

3.2. Crystal structures of complexes **2**, **3** *and* **7**·H_2O

In order to confirm the coordination mode of bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane in these complexes, the X-ray diffraction analyses of complexes **2**, **3** and **7**·H_2O were undertaken. The molecular structures of **2**, **3** and **7**·H_2O are shown in Figs. 1–3, respectively. Selected bond lengths and bond angles for **2**, **3** and **7**·H_2O are listed in Tables 2–4, respectively.

As shown in Fig. 1, bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane in complex **2** is coordinate to molybdenum atom by endodentate nitrogen atoms in a chelating metal coordination mode. The six-member Mo–N–N–C–N–N metallacycle adopts a distorted boat conformation, which is similar to those in CH_2(3,5-



Scheme 1.

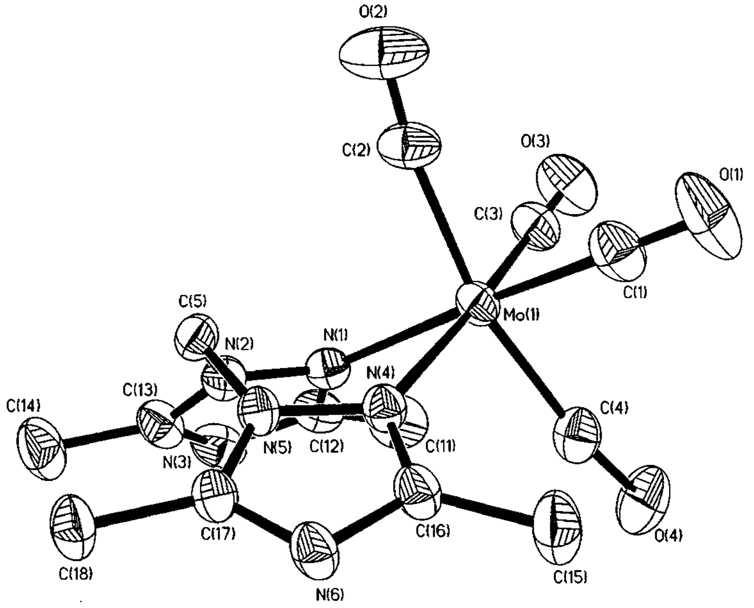


Fig. 1. The molecular structure of complex **2**.

$Me_2Pz)_2Mo(CO)_4$ [28] and $CH_2(3,5\text{-}Me_2\text{-}4\text{-}ClPz)_2W(CO)_4$ [29]. The molybdenum atom is six coordinate with a *quasi*-octahedral coordination geometry. The Mo(1)–N(1) and Mo(1)–N(4) bond lengths are 2.296(6) and 2.296(5) Å, respectively, which are compared to the Mo–N bond lengths (2.288(2), 2.286(2) Å) in $CH_2(3,5\text{-}Me_2Pz)_2Mo(CO)_4$ [28]. The angle ∠N(1)–Mo(1)–N(4) is 79.4(2)°, which is similar to the angle ∠N–Mo–N of 78.3(1)° in $CH_2(3,5\text{-}Me_2Pz)_2Mo(CO)_4$. The two *cis*-carbonyls C(2)O(2) and C(4)O(4) are repulsed by the ligand, with the result that they are away from the ligand. The angles ∠Mo(1)–C(2)–O(2) and ∠Mo(1)–C(4)–O(4) are 171.9(9) and 171.4(8)°, respectively, indicating that the two *cis*-carbonyls are distorted. However, the two *trans*-carbonyls are nearly linear with the angles ∠Mo(1)–C(1)–O(1) of 178.4(9)° and ∠Mo(1)–C(3)–O(3) of 179.8(7)°, which are quite different from those in $CH_2(3,5\text{-}Me_2Pz)_2Mo(CO)_4$ in which four carbonyls are distorted. The dihedral angle between two heterocyclic rings is 115.3°.

The molecular structure of complex **3** is shown in Fig. 2. The overall view of **3** is analogous to that of complex **2**, in which bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane acts as a chelating bidentate ligand. The W–N distances in complex **3** (2.27(1) and 2.26(1) Å) are similar to those in $CH_2(3,5\text{-}Me_2\text{-}4\text{-}ClPz)_2W(CO)_4$ (2.261(5) and 2.250(7) Å) [29]. The angles ∠N–M–N are also similar (80.3(2)° in complex **3**, 79.4(2)° in complex **2** and 79.4(2)° in $CH_2(3,5\text{-}Me_2\text{-}4\text{-}ClPz)_2W(CO)_4$, respectively). But, the angle ∠C(4)–W(1)–C(1) in complex **3** (175.2(3)°) is bigger than those in complex **2** (167.2(4)° and $CH_2(3,5\text{-}Me_2\text{-}4\text{-}ClPz)_2\text{-}W(CO)_4$ (169.0(3)°).

As a result of weak interaction between complexes **2** and **3** with diorganotin halide indicated by NMR, complexes **4**–**9** could be extensively dissociated in solution. When compound **7** crystallized, it absorbed one water molecule. As shown in Fig. 3, the water molecule coordinates to tin atoms and links Ph_2SnBr_2 unit with bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane ligand through hydrogen bonds to 4-position exonitrogen atoms on triazole rings, forming a linkage coordination polymer. There is no direct interaction between organotin unit and $W(CO)_4$ fragment. Bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane acts as a chelating bidentate ligand by two endodentate nitrogens in $W(CO)_4$ fragment and also bridges two tin atoms through the exodentate nitrogen donors to form linkage coordination polymers. The W–N distances in complex $\mathbf{7}\cdot H_2O$ (2.2305(7) and 2.286(7) Å) are slightly longer than those in complex **3**

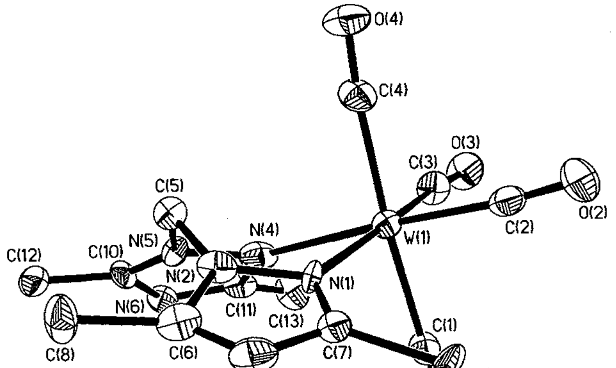


Fig. 2. The molecular structure of complex **3**.

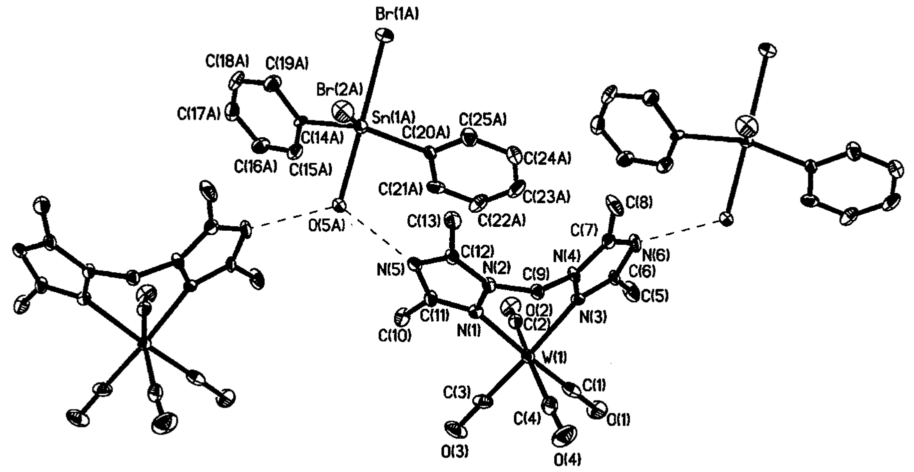


Fig. 3. The molecular structure of complex **7**·H_2O.

(2.27(1) and 2.26(1) Å), but the angles ∠N–M–N are similar (80.3(2)° in complex **3** and 80.0(3)° in complex **7**·H_2O, respectively). In addition, the angle ∠C(4)–W(1)–C(1) in complex **7**·H_2O (166.9(4)°) is remarkably smaller than that in complex **3** (175.2(3)°), and even smaller than that in complex **2** (167.2(4)°). Four carbonyls in complex **7**·H_2O are also different from those in complex **3**. Two *cis*-carbonyls are distorted while two *trans*-carbonyls are nearly linear, which are similar with those in complex **2**, but four carbonyls are distorted in complex **3**. The structure of Ph_2SnBr_2 unit in complex **7**·H_2O is analogous to that in $CH_2(3,5\text{-}Me_2Tz)_2SnPh_2Br_2{\cdot}H_2O$ [23]. Tin is five coordinate with a distorted trigonal bipyramid geometry. One bromine atom and one oxygen atom occupy the axial position, and the principal axis is almost linear with an O–Sn–Br angle of 178.9°. The Sn(1A)–O(5A) distance is 2.315(6) Å, and the hydrogen bonding O(5A)···N(5) distance is 2.821 Å.

In conclusion, bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane can act as a chelating bidentate ligand when coordinates to Group 6 metal carbonyl complexes. These derivatives also can coordinate to tin atoms through 4-position exonitrogen atoms on triazole rings to form linkage coordination polymers, in which two coordination modes are observed. In addition, 4-position exonitrogen atoms on triazole rings are weak donors to organotin acceptors.

Table 2
Selected bond length (Å) and angles (°) for **2**

Bond lengths			
Mo(1)–C(1)	1.946(9)	C(1)–O(1)	1.18(1)
Mo(1)–C(2)	2.052(8)	C(2)–O(2)	1.11(1)
Mo(1)–C(3)	1.949(8)	C(3)–O(3)	1.17(1)
Mo(1)–C(4)	2.029(8)	C(4)–O(4)	1.16(1)
Mo(1)–N(1)	2.296(6)	N(2)–C(5)	1.452(9)
Mo(1)–N(4)	2.296(5)	C(5)–N(5)	1.453(8)
Bond angles			
C(1)–Mo(1)–C(2)	84.1(4)	Mo(1)–N(4)–N(5)	121.1(4)
C(1)–Mo(1)–C(3)	88.3(4)	Mo(1)–N(4)–C(16)	135.8(4)
C(2)–Mo(1)–C(3)	86.3(3)	Mo(1)–C(3)–O(3)	179.8(7)
C(1)–Mo(1)–C(4)	84.5(4)	Mo(1)–C(4)–O(4)	171.4(8)
C(2)–Mo(1)–C(4)	167.2(4)	Mo(1)–N(1)–N(2)	121.6(4)
C(3)–Mo(1)–C(4)	87.4(3)	Mo(1)–N(1)–C(12)	134.3(5)
C(1)–Mo(1)–N(1)	176.1(3)	Mo(1)–C(1)–O(1)	178.4(9)
C(2)–Mo(1)–N(1)	97.4(3)	Mo(1)–C(2)–O(2)	171.9(9)
C(3)–Mo(1)–N(1)	95.4(3)	N(1)–Mo(1)–N(4)	79.4(2)
C(4)–Mo(1)–N(1)	94.3(3)	N(2)–C(5)–N(5)	110.1(5)
C(1)–Mo(1)–N(4)	97.0(3)	N(1)–N(2)–C(5)	119.5(5)
C(2)–Mo(1)–N(4)	93.0(3)	C(13)–N(2)–C(5)	130.0(6)
C(3)–Mo(1)–N(4)	174.6(3)	C(5)–N(5)–N(4)	119.3(5)
C(4)–Mo(1)–N(4)	94.3(3)	C(5)–N(5)–C(17)	130.8(5)

Table 3
Selected bond length (Å) and angles (°) for **3**

Bond lengths			
W(1)–C(3)	1.92(1)	C(1)–O(1)	1.14(1)
W(1)–C(2)	1.99(2)	C(2)–O(2)	1.17(3)
W(1)–C(4)	2.020(6)	C(3)–O(3)	1.17(2)
W(1)–C(1)	2.048(6)	C(4)–O(4)	1.137(7)
W(1)–N(4)	2.27(1)	C(5)–N(2)	1.31(1)
W(1)–N(1)	2.26(1)	C(5)–N(5)	1.58(1)
Bond angles			
C(3)–W(1)–C(2)	87.9(3)	O(1)–C(1)–W(1)	170(2)
C(3)–W(1)–C(4)	86.9(8)	O(2)–C(2)–W(1)	173.9(1)
C(2)–W(1)–C(4)	87.0(7)	O(3)–C(3)–W(1)	174.4(1)
C(3)–W(1)–C(1)	89.3(8)	O(4)–C(4)–W(1)	174.8(7)
C(2)–W(1)–C(1)	90.0(7)	N(2)–C(5)–N(5)	110.8(5)
C(4)–W(1)–C(1)	175.2(3)	C(7)–N(1)–W(1)	134.1(1)
C(3)–W(1)–N(4)	94.7(8)	N(2)–N(1)–W(1)	119.3(9)
C(2)–W(1)–N(4)	176.6(8)	N(5)–N(4)–W(1)	127.0(1)
C(4)–W(1)–N(4)	95.3(6)	C(11)–N(4)–W(1)	132.8(1)
C(1)–W(1)–N(4)	87.9(6)	N(4)–W(1)–N(1)	80.3(2)
C(3)–W(1)–N(1)	175.0(8)	C(4)–W(1)–N(1)	93.9(6)
C(2)–W(1)–N(1)	97.1(8)	C(1)–W(1)–N(1)	90.2(6)

Table 4
Selected bond lengths (Å) and angles (°) for **7**·H_2O

Bond lengths			
Sn(1A)–C(20A)	2.14(1)	O(1)–C(1)	1.19(1)
Sn(1A)–C(14A)	2.16(1)	O(2)–C(2)	1.15(1)
Sn(1A)–O(5A)	2.315(6)	O(3)–C(3)	1.18(1)
Sn(1A)–Br(2A)	2.495(1)	O(4)–C(4)	1.11(1)
Sn(1A)–Br(1A)	2.681(1)	W(1)–N(1)	2.305(7)
W(1)–C(3)	1.93(1)	W(1)–N(3)	2.286(7)
W(1)–C(1)	1.94(1)	N(2)–C(9)	1.43(1)
W(1)–C(2)	2.02(1)	N(4)–C(9)	1.46(1)
W(1)–C(4)	2.07(1)	O(5A)–N(5)	2.821
Bond angles			
C(20A)–Sn(1A)–C(14A)	132.6(4)	C(1)–W(1)–N(1)	177.1(4)
C(20A)–Sn(1A)–O(5A)	86.2(3)	C(2)–W(1)–N(1)	93.7(3)
C(14A)–Sn(1A)–O(5A)	85.9(3)	C(4)–W(1)–N(1)	99.2(3)
C(20A)–Sn(1A)–Br(2A)	113.8(3)	N(3)–W(1)–N(1)	80.0(3)
C(14A)–Sn(1A)–Br(2A)	112.6(3)	N(2)–C(9)–N(4)	112.8(7)
O(5A)–Sn(1A)–Br(2A)	88.2(1)	C(3)–W(1)–C(1)	86.8(4)
C(20A)–Sn(1A)–Br(1A)	94.1(3)	C(3)–W(1)–C(2)	88.9(4)
C(14A)–Sn(1A)–Br(1A)	93.1(2)	C(1)–W(1)–C(2)	84.4(4)
O(5A)–Sn(1A)–Br(1A)	178.9(1)	C(3)–W(1)–C(4)	87.4(5)
Br(2A)–Sn(1A)–Br(1A)	92.54(6)	O(1)–C(1)–W(1)	179.6(1)
C(1)–W(1)–C(4)	82.8(4)	O(2)–C(2)–W(1)	171.4(8)
C(2)–W(1)–C(4)	166.9(4)	O(3)–C(3)–W(1)	178.2(1)
C(3)–W(1)–N(3)	175.2(4)	O(4)–C(4)–W(1)	171.4(1)
C(1)–W(1)–N(3)	98.0(4)	C(11)–N(1)–W(1)	133.5(6)
C(2)–W(1)–N(3)	91.9(3)	N(2)–N(1)–W(1)	122.8(6)
C(4)–W(1)–N(3)	92.9(4)	N(1)–N(2)–C(9)	118.5(7)
C(3)–W(1)–N(1)	95.3(4)	C(6)–N(3)–W(1)	133.1(6)
C(7)–N(4)–C(9)	131.2(9)	N(4)–N(3)–W(1)	123.9(6)
N(3)–N(4)–C(9)	117.7(7)		

Symmetry code: A = x, $1+y$, z.

4. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles for complexes **2**, **3** and **7** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 166151–166153. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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