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Synthesis and crystal structures of Group 6 metal carbonyl complexes containing S-rich bis(pyrazol-1-yl)methane ligands

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Abstract

The reaction of 3(5)-methylthio-5(3)-phenylpyrazole with dibromomethane under phase-transfer catalytic conditions only affords a new ligand, bis(3-phenyl-5-methylthiopyrazol-1-yl)methane. However, the reaction of 3(5)-methylthio-5(3)-*p*-methoxyphenylpyrazole or 3(5)-methylthio-5(3)-*tert*-butylpyrazole with dibromomethane under the same conditions yields three isomers, respectively, indicating that the substituents significantly affect the steric and electronic properties of pyrazole ring during the formation of ligands. Treatment of these potential polydentate ligands with $M(CO)_6$ (M = Cr, Mo or W) under UV irradiation at room temperature affords (N–N)$M(CO)_4$ derivatives, in which some complexes contain asymmetric substituted bis(pyrazol-1-yl)methane ligands. The X-ray crystal structure analyses indicate that the sulfur atoms in these complexes do not take part in the coordination to the metal centers, and S-rich bis(pyrazol-1-yl)methanes actually act as bidentate chelating ligands by two nitrogen atoms. It is also interesting that in order to reduce the repulsion of methyl groups with carbonyls, the methyl groups in these complexes are oriented away from the metal centers.

Keywords: Bis(pyrazol-1-yl)methane; Group 6 metal carbonyl complexes; X-ray crystal structures

1. Introduction

Poly(pyrazol-1-yl)alkanes were first reported by Trofimenko in 1970 [1]. After that, and especially an improved synthetic method was developed by Elguero and coworkers [2], the coordination chemistry of these ligands has received increasing attention [3,4]. Recently, many main group [5] and transition metal [6] complexes containing poly(pyrazol-1-yl)alkanes have been synthesized and characterized, which display good physical and chemical properties. In order to meet the demand of rapid development in poly(pyrazol-1-yl)alkane chemistry, some new higher-yield and higher-purity synthetic methods for poly(pyrazol-1-yl)alkanes have also been explored [5b,7]. In addition, the heteroscorpionate ligands related to the poly(pyrazol-1-yl)methane have been of considerable interest in recent years owing to their important usage in biological enzyme models, which usually have the asymmetric N_2O [8,9], N_2S [10], N_3O [11] coordination environments. The heteroatom in these heteroscorpionate ligands usually lies in the bridged carbon. A recent study showed that poly(pyrazol-1-yl)alkanes containing phosphine groups in the pyrazole rings displayed variable coordination modes toward different metal centers [12], which encourages us to investigate the coordination modes of the poly(pyrazol-1-yl)alkanes containing more extensive donor atoms in the pyrazole rings. Furthermore, polythioether ligands are fascinating owing to their high affinity for many metals, some Group 6 metal carbonyl derivatives containing acyclic polythioether have also been prepared and exhibited unusual structures and properties [13]. In the present work we describe the preparation of S-rich bis(pyrazol-1-yl)methanes and their reactions with Group 6 metal carbonyl complexes.

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2. Experimental

All solvents were dried by standard methods and distilled prior to use. All reactions related to $M(CO)_6$ (M = Cr, Mo or W) were carried out under an Ar atmosphere. ^{1}H-NMR spectra were recorded in a Bruker AC-P-200 spectrometer, IR spectra data were obtained from a Nicolet FT-IR 170SX spectrometer in KBr pellets. Elemental analyses were carried out in a Perkin–Elmer 240C analyzer. 3(5)-Methylthio-5(3)-phenylpyrazole [14], 3(5)-methylthio-5(3)-*p*-methoxyphenylpyrazole [14] and 3(5)-methylthio-5(3)-*tert*-butylpyrazole [14,15] were prepared according to the literature methods.

2.1. Synthesis of bis(3-phenyl-5-methylthiopyrazol-1-yl)methane (1)

The mixture of 3(5)-methylthio-5(3)-phenylpyrazole (6.2 g, 32.5 mmol), CH_2Br_2 (1.14 ml, 16.25 mmol), NaOH (6 g) and *n*-Bu_4NBr (0.3 g) dissolved in the mixed solvent of H_2O (10 ml) and benzene (30 ml) was stirred and refluxed 48 h. After cooling to room temperature (r.t.), the organic layer was separated, and the water layer was extracted with CH_2Cl_2 (3 × 30 ml). The organic layers were combined and dried over anhydrous $MgSO_4$. After evaporating the solvent, the residue was recrystallized from benzene–hexane to yield 4.2 g (66%) of **1** as white crystals. ^{1}H-NMR ($CDCl_3$): δ 2.60 (s, 6H, CH_3), 6.61, 6.66 (s, s, 2H, 2H, CH_2 or H^4 of pyrazole), 7.34, 7.72 (m, m, 6H, 4H, C_6H_5). IR (cm^{-1}): $\nu_{pyrazole\ ring}$ 1526.3 (m). Anal. Calc. for $C_{21}H_{20}N_4S_2$: C, 64.29; H, 5.10; N, 14.29. Found: C, 63.96; H, 5.38; N, 14.21%.

2.2. Synthesis of (3-methylthio-5-p-methoxyphenyl-pyrazol-1-yl-3′-p-methoxyphenyl-5′-methylthiopyrazol-1-yl)methane (2), bis(3-methylthio-5-p-methoxyphenyl-pyrazol-1-yl)methane (3) and bis(3-p-methoxyphenyl-5-methylthiopyrazol-1-yl)methane (4)

3(5)-Methylthio-5(3)-*p*-methoxyphenylpyrazole (7.2 g, 32.5 mmol), CH_2Br_2 (1.14 ml, 16.25 mmol), NaOH (6 g) and *n*-Bu_4NBr (0.3 g) were added to the mixed solvent of H_2O (10 ml) and benzene (30 ml). The mixture was stirred and refluxed for 48 h. After cooling to r.t., the two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 ml). The organic layers were combined and dried over anhydrous $MgSO_4$. After evaporating the solvent, the residue was redissolved in CH_2Cl_2 and chromatographed through a short alumina column eluted with CH_2Cl_2. The eluent was concentrated to 5 ml, and then 10 ml hexane was slowly added to the mixture, a white solid was obtained, which was confirmed by ^{1}H-NMR to be the mixture of **2**–**4**. ^{1}H-NMR ($CDCl_3$): δ 2.48, 2.51 (s, s, CH_3S in **2**), 2.55, 2.59 (s, s, CH_3S in **3** or **4**), 3.79, 3.81 (s, s, CH_3O in **2**), 3.83, 3.85 (s, s, CH_3O in **3** or **4**), 5.96, 6.27 (s, s, H^4 of pyrazole in **3** or **4**), 6.14, 6.15 (s, s, H^4 of pyrazole in **2**), 6.58 (s, br, CH_2 in **2**, **3** and **4**), 6.86–6.96, 7.64–7.76 (m, m, C_6H_5 in **2**–**4**). The assignment of **2** is successful according to the splitting peaks and their relative intensity.

2.3. Synthesis of bis(3-methylthio-5-tert-butylpyrazol-1-yl)methane (5)

This ligand was prepared using 3(5)-methylthio-5(3)-*tert*-butylpyrazole (5.5 g, 32.5 mmol) and CH_2Br_2 (1.14 ml, 16.25 mmol) as described above for **2**. The eluent with CH_2Cl_2 was concentrated to 3 ml, and then 10 ml hexane was slowly added to the mixture, a white solid was obtained. The solid was filtered off, washed with hexane and dried in vacuo to give 0.87 g of **5**, which was confirmed by ^{1}H-NMR and X-ray diffraction. ^{1}H-NMR ($CDCl_3$):δ 1.39 (s, 18H, $C(CH_3)_3$), 2.41 (s, 6H, CH_3S), 5.96 (s, 2H, H^4 of pyrazole), 6.44 (s, 2H, CH_2). IR (cm^{-1}): $\nu_{pyrazole\ ring}$ 1518.3 (s). Anal. Calc. for $C_{17}H_{28}N_4S_2$: C, 57.95; H, 7.95; N, 15.91. Found: C, 57.73; H, 7.67; N, 15.82%. The mother liquor was concentrated to dryness to yield an oil, which was confirmed by ^{1}H-NMR to the mixture of bis(3-*tert*-butyl-5-methylthiopyrazol-1-yl)methane and (3-*tert*-butyl-5-methylthiopyrazol-1-yl-3′-methylthio-5′-*tert*-butylpyrazol-1-yl)methane.

2.4. Reaction of ligand 1 with $M(CO)_6$ (M = Cr or W)

2.4.1. Preparation of bis(3-phenyl-5-methylthiopyrazol-1-yl)methane tetracarbonyl chromium (6)

The solution of $Cr(CO)_6$ (1 mmol) and **1** (1 mmol) dissolved in THF (25 ml) was irradiated with a 400 W high-pressure mercury lamp for ca. 24 h at r.t. The solution became green–yellow. After the reaction completed, the solvent was removed under a reduced pressure, and the residual was purified by column chromatography on silica using CH_2Cl_2–hexane (V:V = 1:1) as eluent. The green–yellow eluent was again concentrated to dryness under a reduced pressure, the residual was recrystallized from CH_2Cl_2–hexane to give a green–yellow crystalline solid. Yield: 52%. ^{1}H-NMR ($CDCl_3$):δ 2.61 (s, 6H, CH_3S), 6.60, 6.66 (s, s, 2H, 2H, H^4 of pyrazole or CH_2), 7.35, 7.71 (m, m, 6H, 4H, C_6H_5). IR (cm^{-1}): ν_{CO} 2012.4 (s), 1894.3 (m), 1853.8 (s), 1819.4 (s); $\nu_{pyrazole\ ring}$ 1518.3 (m). Anal. Calc. for $C_{25}H_{20}CrN_4O_4S_2$: C, 53.96; H, 3.60; N, 10.07. Found: C, 53.63; H, 3.57; N, 10.32%.

2.4.2. Preparation of bis(3-phenyl-5-methylthiopyrazol-1-yl)methane tetracarbonyl tungsten (7)

This compound was obtained similarly using $W(CO)_6$ instead of $Cr(CO)_6$ as described above for **6**. Yield:

57%. ^{1}H-NMR ($CDCl_3$): δ 2.61 (s, 6H, CH_3S), 6.61, 6.66 (s, s, 2H, 2H, H^4 of pyrazole or CH_2), 7.31, 7.75 (m, m, 6H, 4H, C_6H_5). IR (cm^{-1}): ν_{CO} 2011.7 (s), 1908.6 (s), 1837.3 (s), 1821.2 (s); $\nu_{pyrazole\ ring}$ 1526.2 (m). Anal. Calc. for $C_{25}H_{20}N_4O_4S_2W$: C, 43.67; H, 2.91; N, 8.15. Found: C, 43.48; H, 3.19; N, 8.12%.

2.5. Reaction of the mixture of **2**–**4** with $M(CO)_6$ ($M = Cr$, Mo or W)

2.5.1. Preparation of (3-methylthio-5-p-methoxyphenyl-pyrazol-1-yl-3′-p-methoxy phenyl-5′-methylthiopyrazol-1-yl)methane tetracarbonylchromium (**8**) and bis(3-methylthio-5-p-methoxyphenylpyrazol-1-yl)-methane tetracarbonylchromium (**9**)

Compounds **8** and **9** were obtained by the reaction of the mixture of **2**–**4** with $Cr(CO)_6$ as described above for the reaction of **1** with $Cr(CO)_6$, which were isolated by column chromatography on silica using ether–hexane (V:V = 2:1) as eluent. Data for **8**: ^{1}H-NMR ($CDCl_3$): δ 2.55, 2.59 (s, s, 3H, 3H, CH_3S), 3.80, 3.85 (s, s, 3H, 3H, CH_3O), 6.28 (s, 2H, H^4 of pyrazole), 6.57 (s, br, 2H, CH_2), 6.89–7.03, 7.65–7.56 (m, m, 4H, 4H, C_6H_4). IR (cm^{-1}): ν_{CO} 2004.6 (m), 1877.8 (vs, br) and 1839.3 (s); $\nu_{pyrazole\ ring}$ 1576.1 (w). Anal. Calc. for $C_{27}H_{24}CrN_4O_6S_2$: C, 52.60; H, 3.90; N, 9.09. Found: C, 52.43; H, 3.59; N, 9.06%. Data for **9**: ^{1}H-NMR ($CDCl_3$): δ 2.50 (s, 6H, CH_3S), 3.80 (s, 6H, CH_3O), 6.14 (m, 4H, H^4 of pyrazole and CH_2), 6.74, 6.92 (m, m, 4H, 4H, C_6H_4). IR (cm^{-1}): ν_{CO} 2004.7 (m), 1878.2 (vs, br), 1839.2 (s); $\nu_{pyrazole\ ring}$ 1576.3 (w). Anal. Calc. for $C_{27}H_{24}CrN_4O_6S_2$: C, 52.60; H, 3.90; N, 9.09. Found: C, 52.54; H, 3.89; N, 9.36%. The product of the reaction of **4** with $Cr(CO)_6$ could not be obtained.

2.5.2. Preparation of (3-methylthio-5-p-methoxyphenyl-pyrazol-1-yl-3′-p-methoxy phenyl-5′-methylthiopyrazol-1-yl)methanetetracarbonylmolybdenum (**10**) and bis(3-methylthio-5-p-methoxyphenylpyrazol-1-yl)-methanetetracarbonylmolybdenum (**11**)

These compounds were obtained by the reaction of the mixture of **2**–**4** with $Mo(CO)_6$ as described above for the reaction of **1** with $Cr(CO)_6$, which were isolated by column chromatography on silica using CH_3CO_2Et–ether–hexane (V:V:V = 1:1:3) as eluent. Data for **10**: ^{1}H-NMR ($CDCl_3$): δ 2.50, 2.51 (s, s, 3H, 3H, CH_3S), 3.85, 3.87 (s, s, 3H, 3H, CH_3O), 6.21, 6.29 (s, s, 1H, 1H, H^4 of pyrazole), 6.61 (s, br, 2H, CH_2), 6.99–7.10, 7.28–7.50 (m, m, 4H, 4H, C_6H_4). IR (cm^{-1}): ν_{CO} 2012.1 (m), 1883.4 (s), 1864.1 (s), 1836.4 (s); $\nu_{pyrazole\ ring}$ 1577.1 (w). Anal. Calc. for $C_{27}H_{24}MoN_4O_6S_2$: C, 49.09; H, 3.64; N, 8.48. Found: C, 48.94; H, 3.93; N, 8.46%. Data for **11**: ^{1}H-NMR ($CDCl_3$): δ 2.48 (s, 6H, CH_3S), 3.81 (s, 6H, CH_3O), 6.13 (s, 2H, H^4 of pyrazole), 6.28 (dd, 2H, CH_2), 6.74, 6.93 (d, d, 4H, 4H, C_6H_4). IR (cm^{-1}): ν_{CO} 2012.3 (m), 1889.1 (s), 1870.3 (s), 1843.8 (s); $\nu_{pyrazole\ ring}$ 1576.0 (w). Anal. Calc. for $C_{27}H_{24}MoN_4O_6S_2$: C, 49.09; H, 3.64; N, 8.48. Found: C, 48.79; H, 3.75; N, 8.39%.

2.5.3. Preparation of (3-methylthio-5-p-methoxy-phenylpyrazol-1-yl-3′-p-methoxyphenyl-5′-methylthio-pyrzol-1-yl)methane tetracarbonyltungsten (**12**) and bis(3-methylthio-5-p-methoxyphenylpyrazol-1-yl)-methane tetracarbonyltungsten (**13**)

These compounds were obtained by the reaction of the mixture of **2**–**4** with $W(CO)_6$ as described above for the reaction of **1** with $Cr(CO)_6$, which were isolated by column chromatography on silica using ether–hexane (V:V = 2:1) as eluent. Data for **12**: ^{1}H-NMR ($CDCl_3$): δ 2.27, 2.48 (s, s, 3H, 3H, CH_3S), 3.85, 3.90 (s, s, 3H, 3H, CH_3O), 6.20, 6.29 (s, s, 1H, 1H, H^4 of pyrazole), 6.20, 6.50 (d, d, 2H, CH_2), 7.03–7.23, 7.35–7.49 (m, m, 4H, 4H, C_6H_4). IR (cm^{-1}): ν_{CO} 2000.0 (m), 1876.1 (s), 1854.2 (s), 1832.1 (s); $\nu_{pyrazole\ ring}$ = 1574.4 (w). Anal. Calc. for $C_{27}H_{24}N_4O_6S_2W$: C, 43.32; H, 3.21; N, 7.49. Found: C, 43.01; H, 3.28; N, 7.78%. Data for **13**: ^{1}H-NMR ($CDCl_3$): δ 2.51 (s, 6H, CH_3S), 3.63 (s, 6H, CH_3O), 6.17 (s, 2H, H^4 of pyrazole), 6.32 (m, 2H, CH_2), 6.77, 6.96 (d, d, 4H, 4H, C_6H_4). IR (cm^{-1}): ν_{CO} 2005.6 (m), 1889.4 (s), 1856.4 (s), 1825.6 (s); $\nu_{pyrazole\ ring}$ 1577.2 (w). Anal. Calc. for $C_{27}H_{24}N_4O_6S_2W$: C, 43.32; H, 3.21; N, 7.49. Found: C, 43.57; H, 3.51; N, 7.87%.

2.6. Reaction of ligand **5** with $M(CO)_6$ ($M = Cr$, Mo or W)

2.6.1. Preparation of bis(3-methylthio-5-tert-butylpyrazol-1-yl)methane tetracarbonylchromium (**14**)

This compound was obtained by the reaction of **5** with $Cr(CO)_6$ as described above for the reaction of **1** with $Cr(CO)_6$, which was isolated by column chromatography on silica using CH_2Cl_2–hexane (V:V = 1:1) as eluent. ^{1}H-NMR ($CDCl_3$): δ 1.48 (s, 18H, $C(CH_3)_3$), 2.56 (s, 6H, CH_3S), 6.09 (s, 2H, H^4 of pyrazole), 6.40 (s, br, 2H, CH_2). IR (cm^{-1}): ν_{CO} 2069.3 (m), 1988.1 (s), 1942.8 (vs, br); $\nu_{pyrazole\ ring}$ 1520.5 (s). Anal. Calc. for $C_{21}H_{28}CrN_4O_4S_2$: C, 48.84; H, 5.43; N, 10.85. Found: C, 48.65; H, 5.58; N, 10.56%.

2.6.2. Preparation of bis(3-methylthio-5-tert-butyl-pyrazol-1-yl)methane tetracarbonylmolybdenum (**15**)

This compound was obtained by the similar method as described above for **14** using $Mo(CO)_6$ instead of $Cr(CO)_6$. ^{1}H-NMR ($CDCl_3$): δ 1.47 (s, 18H, $C(CH_3)_3$), 2.46 (s, 6H, CH_3S), 6.02 (s, 2H, H^4 of pyrazole), 6.54 (s, 2H, CH_2). IR (cm^{-1}): ν_{CO} 2005.3 (m), 1879.2 (sh), 1863.7 (s), 1825.2 (s); $\nu_{pyrazole\ ring}$ 1511.2 (m). Anal. Calc. for $C_{21}H_{28}MoN_4O_4S_2$: C, 45.00; H, 5.00; N, 10.00. Found: C, 44.64; H, 5.27; N, 9.78%.

*2.6.3. Preparation of bis(3-methylthio-5-tert-butylpyrazol-1-yl)methane tetracarbonyltungsten (**16**)*

This compound was obtained by the similar method as described above for **14** using $W(CO)_6$ instead of $Cr(CO)_6$. ^{1}H-NMR ($CDCl_3$): δ 1.47 (s, 18H, $C(CH_3)_3$), 2.45 (s, 6H, CH_3S), 6.03 (s, 2H, H^4 of pyrazole), 6.56 (s, br, 2H, CH_2). IR (cm^{-1}): ν_{CO} 2000.1 (m), 1875.7 (s), 1864.1 (s), 1837.1 (s); $\nu_{pyrazole\ ring}$ 1525.0 (m). Anal. Calc. for $C_{21}H_{28}N_4O_4S_2W$: C, 38.89; H, 4.32; N, 8.64. Found: C, 38.77; H, 4.62; N, 8.56%.

2.7. Crystal structures determination

Crystals of **5**, **12**, **13** and **16** suitable for crystallographic investigation were grown from slow vaporization of a CH_2Cl_2–hexane solution at r.t., while crystals of **15** were obtained at -15 °C. Intensity data were collected in a Bruker SMART CCD diffractometer with graphite-monochromated Mo–K_α radiation ($\lambda =$ 0.71073 Å) using the ω–2θ scan technique. The structures were solved by direct methods 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 **5**, **12**, **13**, **15** and **16** is given in Table 1.

3. Results and discussion

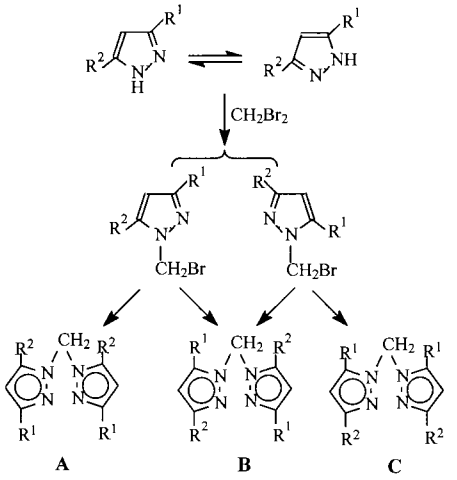
3.1. Synthesis of ligands

Because of the asymmetric substituted pyrazoles in the 3 and 5-positions existing in two tautomeric structures in solution, their reaction with alkylation agents such as methylene chloride or methylene bromide under phase-transfer catalytic conditions yields three isomers **A**–**C**, respectively (Scheme 1). The relative amount of isomeric bis(pyrazol-1-yl)methanes (**A**–**B**–**C**) significantly depends on the steric and electronic properties of the substituents of pyrazole ring. For instances, When R^1 was a *tert*-butyl group and R^2 was a hydrogen atom, only isomer **A** was obtained [5a], and R^1 was a 3-(2-pyridyl) group and R^2 still was a hydrogen atom, isomers **A** and **B** were formed [16]. In addition, R^1 was a methyl group and R^2 was a hydrogen atom, isomers **A**–**C** were simultaneously obtained [17].

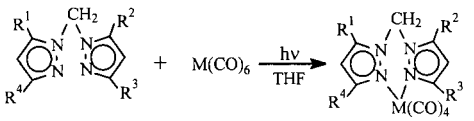
In the present work, we find that the reaction of 3(5)-methylthio-5(3)-phenylpyrazole with CH_2Br_2 under analogous conditions gives only isomer **A**, in which the larger steric hindrance of phenyl group than methylthio group plays the leading role. Its ^{1}H-NMR spectrum shows only one set of signal corresponding to ligand **1**. However, when one methoxyl group is linked to the 4-position of the phenyl group in pyrazole ring, the reaction of 3(5)-methylthio-5(3)-*p*-methoxyphenylpyrazole with CH_2Br_2 under the same conditions gives three isomers. It is quite obvious that the methoxyl group changes the electronic property of the phenyl group, and now the steric effect of the *p*-methoxyphenyl group is not the major factor affecting the relative amount of the three isomers. In addition, owing to the electron-donating methylthio group changing the electron-density on two nitrogen atoms of pyrazole, the steric hindrance of the *tert*-butyl group in 3(5)-methylthio-5(3)-*t*-

Table 1
Crystal data and structure refinement parameters for compounds **5**, **12**, **13**, **15** and **16**

Compound	**5**	**12**·0.5CH_2Cl_2	**13**	**15**	**16**
Empirical formula	$C_{17}H_{28}N_4S_2$	$C_{27.5}H_{25}ClN_4O_6S_2W$	$C_{27}H_{24}N_4O_6S_2W$	$C_{21}H_{28}MoN_4O_4S_2$	$C_{21}H_{28}N_4O_4S_2W$
Formula weight	352.55	790.94	748.47	560.54	648.44
Crystal size (mm)	$0.25\times0.20\times0.10$	$0.35\times0.20\times0.15$	$0.20\times0.05\times0.03$	$0.20\times0.15\times0.10$	$0.25\times0.30\times0.35$
Crystal class	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2(1)/c$	$P2(1)/m$	$P2(1)/n$	$P2(1)/n$
Unit cell parameters					
a (Å)	19.521(14)	10.67(2)	8.560(4)	9.96(3)	9.971(3)
b (Å)	9.617(7)	18.65(4)	15.150(7)	14.69(4)	14.863(5)
c (Å)	10.432(8)	15.35(3)	11.351(5)	17.04(5)	17.317(5)
β (°)	99.806(14)	98.52(4)	103.848(8)	96.80(5)	97.300(5)
V (Å)^3	1930(2)	3023(10)	1429.3(11)	2476(11)	2545.6(14)
Z	4	4	2	4	4
T (K)	293	293	293	293	298
Calculated density (Mg m^{-3})	1.213	1.738	1.739	1.498	1.692
$F(000)$	760	1556	736	1144	1280
μ (mm^{-1})	0.281	4.095	4.235	0.732	4.735
θ (°)	2.12–25.02	2.44–25.02	2.29–25.03	2.86–25.06	1.81–25.03
Number of reflections measured	3749	12 198	5859	9564	10 420
Number of reflections observed	1656	5289	2583	4143	4499
Number of parameters	107	388	196	290	289
Goodness-of-fit on F^2	0.944	0.927	1.075	1.011	0.984
R, $R_w[I>2\sigma(I)]$	0.0648, 0.1346	0.0378, 0.0707	0.0404, 0.0718	0.0773, 0.1649	0.0326, 0.0728



Scheme 1. **1**, **A**, R^1 = Ph, R^2 = MeS; **2**, **B**, R^1 = *p*-MeOPh, R^2 = MeS; **3**, **C**, R^1 = *p*-MeOPh, R^2 = MeS; **4**, **A**, R^1 = *p*-MeOPh, R^2 = MeS; **5**, **C**, $R^1 = C(CH_3)_3$, R^2 = MeS.



Scheme 2. $R^1 = R^2$ = MeS, $R^3 = R^4$ = Ph, M = Cr (**6**), W (**7**); $R^1 = R^3$ = MeS, $R^2 = R^4$ = *p*-MeOPh, M = Cr (**8**), Mo (**10**), W (**12**); $R^1 = R^2$ = *p*-MeOPh, $R^3 = R^4$ = MeS, M = Cr (**9**), Mo (**11**), W (**13**); $R^1 = R^2 = C(CH_3)_3$, $R^3 = R^4$ = MeS, M = Cr (**14**), Mo (**15**), W (**16**).

butylpyrazole cannot completely prevent the alkylation agent attacking the nitrogen atom adjacent to the *t*-butyl group, resulting that the reaction of 3(5)-methylthio-5(3)-*tert*-butylpyrazole with CH_2Br_2 under the same conditions also gives three isomers. It is difficult to isolate these isomers by the recrystallization or chromatographic methods. But bis(3-methylthio-5-*tert*-butylpyrazole)methane (**5**) has remarkably different solubility in hexane compared to the other two isomers, which can be easily obtained as the pure product by recrystallizing from hexane.

3.2. Complexes with Group 6 metal carbonyls

Irradiation of ligand **1** or **5** and $M(CO)_6$ (M = Cr, Mo or W) in THF solution at room temperature afforded complexes **6**–**7** and **14**–**16** in reasonable yield, according to Scheme 2. The product of the reaction of **1** with $Mo(CO)_6$ was not isolated owing to its poor stability. Irradiation of the mixture of **2**–**4** with $M(CO)_6$ also yielded the decarbonylation derivatives of $(N–N)M(CO)_4$ (N–N represents substituted bis(pyrazol-1-yl)methanes), which could be isolated by column chromatography on silica. But the products of the ligand **4** with $M(CO)_6$ could not be obtained, possibly owing to the low content of **4** in the mixture of isomers and the poor yields of substitution products led by the most steric hindrance on the coordinated nitrogen atom compared with **2** and **3**. In addition, the products of the reaction of bis(3-*tert*-butyl-5-methylthiopyrazol-1-yl)methane and (3-*tert*-butyl-5-methylthiopyrazol-1-yl-3′-methylthio-5′-*tert*-butylpyrazol-1-yl)methane with $M(CO)_6$ were also not isolated successfully owing to their very close solubility and R_f values. These new complexes were soluble in chlorinated solvents, CH_3CN and acetone. Molybdenum complexes were slightly air-sensitive in solution, but all complexes were stable to air in solid, and could be stored for several months at low temperature in air.

These new complexes have been characterized by elemental analysis, IR and ^{1}H-NMR spectra. They displayed the analogous IR spectra in solid, in which four bands in the carbonyl stretching region were observed, and these values of ν(CO) could also be compared with the reported for $(N–N)M(CO)_4$ complexes [6g], indicating a typical *cis*-tetracarbonyl arrangement. The ^{1}H-NMR spectra of **6**–**7**, **9**, **11** and **13**–**16** were similar to those of the corresponding ligands, displaying two equivalent pyrazole rings, while complexes **8**, **10** and **12** showed two asymmetric pyrazole rings in their ^{1}H-NMR spectra. In addition, the protons of methylene group of complexes **8**–**13** displayed an AB system at room temperature, which were also observed in other Group 6 metal carbonyl derivatives containing bis(pyrazol-1-yl)methane [6g]. These may be the results of the inversion of the boat conformation of six-membered metallacycle M–N–N–C–N–N (see Section 3.3) being slowed down due to the large substituents in the pyrazole rings.

3.3. The description of crystal structures

The crystal structures of complexes **12** and **13** determined by single-crystal X-ray diffraction are presented in Figs. 1 and 2, respectively. Selected distances and angles for complexes **12** and **13** are listed in Tables 2 and 3, respectively. Fig. 1 clearly indicates that two

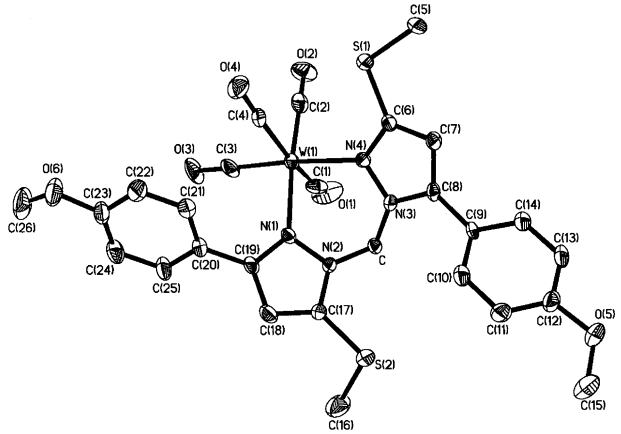


Fig. 1. The molecular structure of complex **12**.

p-methoxyphenyl groups in complex **12** lie in the 3 and 5′-positions of pyrazole rings, and bis(pyrazol-1-yl)methane is an asymmetric ligand. While in complex **13** (Fig. 2) bis(pyrzaol-1-yl)methane is symmetric, and two *p*-methoxyphenyl groups lie in the 5 and 5′-positions of pyrazole rings. The tungsten atoms in these two complexes are six-coordinate with a quasi-octahedral coordination geometry. Bis(pyrazol-1-yl)methane acts as a chelating bidentate ligand by two nitrogen atoms.

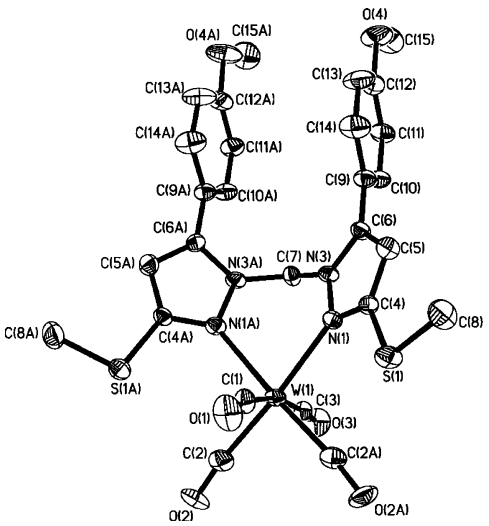


Fig. 2. The molecular structure of complex **13**.

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **12**

Bond lengths			
W(1)–C(3)	1.94(1)	N(2)–C	1.441(8)
W(1)–C(2)	1.96(1)	N(3)–C	1.435(8)
W(1)–C(1)	2.00(1)	O(1)–C(1)	1.15(1)
W(1)–C(4)	2.057(9)	O(2)–C(2)	1.141(1)
W(1)–N(4)	2.232(7)	O(3)–C(3)	1.172(9)
W(1)–N(1)	2.275(7)	O(4)–C(4)	1.134(8)
S(1)–C(6)	1.741(8)	O(5)–C(12)	1.369(9)
S(1)–C(5)	1.777(8)	O(5)–C(15)	1.39(1)
S(2)–C(17)	1.751(8)	O(6)–C(23)	1.371(9)
S(2)–C(16)	1.782(9)	O(6)–C(26)	1.39(1)
Bond angles			
C(3)–W(1)–C(2)	89.1(3)	C(19)–N(1)–W(1)	133.5(5)
C(3)–W(1)–C(1)	86.8(4)	N(2)–N(1)–W(1)	121.2(4)
C(2)–W(1)–C(1)	80.4(3)	N(4)–W(1)–N(1)	80.1(2)
C(3)–W(1)–C(4)	87.4(3)	C(6)–N(4)–W(1)	132.3(5)
C(2)–W(1)–C(4)	85.3(3)	N(3)–N(4)–W(1)	122.6(4)
C(1)–W(1)–C(4)	164.7(3)	N(2)–C–N(3)	111.7(6)
C(3)–W(1)–N(4)	173.4(3)	O(1)–C(1)–W(1)	167.8(8)
C(2)–W(1)–N(4)	97.1(3)	O(2)–C(2)–W(1)	176.2(7)
C(1)–W(1)–N(4)	96.1(3)	O(3)–C(3)–W(1)	178.4(8)
C(4)–W(1)–N(4)	91.2(2)	O(4)–C(4)–W(1)	169.0(7)
C(3)–W(1)–N(1)	93.9(3)	C(6)–S(1)–C(5)	99.9(4)
C(2)–W(1)–N(1)	174.5(3)	C(17)–S(2)–C(16)	100.6(4)
C(1)–W(1)–N(1)	95.1(3)	C(12)–O(5)–C(15)	117.9(8)
C(4)–W(1)–N(1)	99.4(3)	C(23)–O(6)–C(26)	117.6(8)

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **13**

Bond lengths			
W(1)–C(2)	2.003(8)	C(7)–N(3A)	1.416(7)
W(1)–C(2A)	2.003(8)	N(3)–C(7)	1.416(7)
W(1)–C(3)	2.04(1)	O(1)–C(1)	1.13(1)
W(1)–C(1)	2.05(1)	O(2)–C(2)	1.134(8)
W(1)–N(1)	2.292(6)	O(3)–C(3)	1.12(1)
S(1)–C(4)	1.760(6)	O(4)–C(12)	1.375(8)
S(1)–C(8)	1.744(8)	O(4)–C(15)	1.395(9)
Bond angles			
C(2)–W(1)–C(2A)	88.3(5)	C(2A)–W(1)–N(1)	95.9(3)
C(2)–W(1)–C(3)	85.5(3)	C(3)–W(1)–N(1)	96.1(2)
C(2A)–W(1)–C(3)	85.5(3)	C(1)–W(1)–N(1)	92.7(2)
C(2)–W(1)–C(1)	86.3(3)	N(1A)–W(1)–N(1)	79.8(3)
C(2A)–W(1)–C(1)	86.3(3)	C(4)–S(1)–C(8)	100.7(3)
C(3)–W(1)–C(1)	168.5(4)	C(4)–N(1)–W(1)	132.4(4)
C(2)–W(1)–N(1A)	95.9(3)	N(3)–N(1)–W(1)	120.7(4)
C(2A)–W(1)–N(1A)	175.6(3)	C(12)–O(4)–C(15)	117.5(7)
C(3)–W(1)–N(1A)	96.1(2)	O(1)–C(1)–W(1)	169.3(9)
C(1)–W(1)–N(1A)	92.7(2)	O(2)–C(2)–W(1)	173.8(7)
C(2)–W(1)–N(1)	175.6(3)	O(3)–C(3)–W(1)	173.8(9)
N(3A)–C(7)–N(3)	114.1(8)		

Symmetry transformations used to generate equivalent atoms: $A = x, -y+3/2, z$.

The average W–N distance is 2.2535(7) Å in **12**, and 2.292(6) Å in **13**, respectively, which is comparable to those found in other W(0) complexes with poly(pyrazol-1-yl)alkanes (such as average 2.255 Å in $CH_2(3,5\text{-}Me_2\text{-}4\text{-}ClPz)_2W(CO)_4$ [6g] and 2.275 Å in $(CH_2)_2(3,5\text{-}Me_2Pz)_2W(CO)_4$ [6h], respectively, Pz = pyrazole). The angles N–W–N and N–C–N in **12** (N(1)–W(1)–N(4) = 80.1(2)°, N(2)–C–N(3) = 111.7(6)°, respectively) are similar to those in **13** ($\angle$ N(1)–W(1)–N(1A) = 79.8(3)°, $\angle$ N(3)–C–N(3A) = 114.1(8)°. It is noteworthy that two *cis*-carbonyls C(1)O(1) and C(4)O(4) in **12** are significantly distorted with the angles W(1)–C(1)–O(1) of 167.8(8)° and W(1)–C(4)–O(4) of 169.0(7)°, while in **13** four carbonyls are distorted. The angle $\angle$ C(1)–W(1)–C(4) of 164.7(3)° in **12** is slightly smaller than the $\angle$ C(1)–W(1)–C(3) of 168.5(4)° in **13**, reflecting that the steric repulsion between the ligand and carbonyls in **12** and **13** is similar. It is also interesting that two phenyl planes in **13** are nearly parallel with the dihedral angle of 2.7°. The central distance of two phenyl planes is 4.134 Å, indicating that there is no $\pi-\pi$ interaction between them.

The molecular structure of ligand **5** is shown in Fig. 3, which clearly indicates that two bulky *tert*-butyl groups lie in the 5,5′-positions of pyrazole rings. Obviously, this ligand suffers from the biggest steric hindrance compared with the other two isomers during its formation, so its yield is low. In order to avoid the steric congestion, two bulky *tert*-butyl groups and two methylthio groups arrange in *trans*-position of the methylene carbon atom. But the conformation of this

ligand remarkably changes in complexes **15** and **16** to meet the requirements of bidentate binding, which are presented in Figs. 4 and 5, respectively.

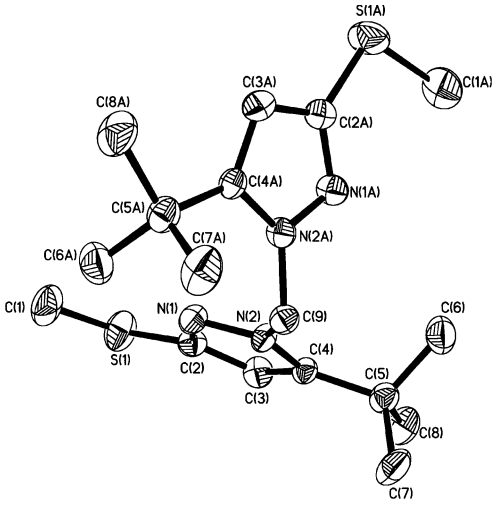


Fig. 3. The molecular structure of ligand **5**.

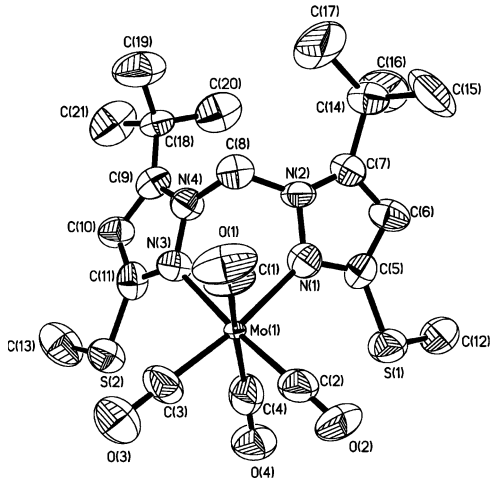


Fig. 4. The molecular structure of complex **15**.

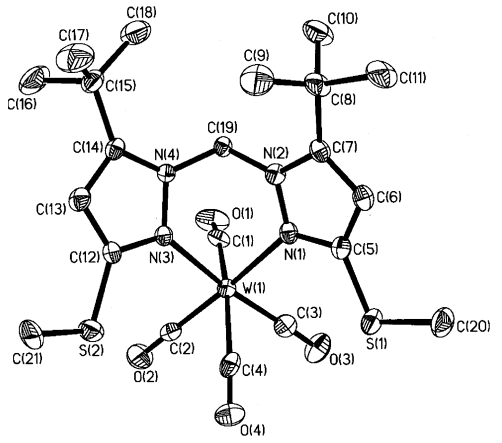


Fig. 5. The molecular structure of complex **16**.

Table 4
Selected bond lengths (Å) and bond angles (°) for complex **15**

Bond lengths			
Mo(1)–C(2)	1.90(2)	O(4)–C(4)	1.23(1)
Mo(1)–C(3)	1.91(1)	S(1)–C(12)	1.67(2)
Mo(1)–C(4)	1.94(2)	S(1)–C(5)	1.71(1)
Mo(1)–C(1)	2.06(1)	S(2)–C(11)	1.73(1)
Mo(1)–N(3)	2.23(1)	S(2)–C(13)	1.75(2)
Mo(1)–N(1)	2.25(1)	C(7)–C(14)	1.57(1)
N(2)–C(8)	1.43(1)	C(9)–C(18)	1.50 (1)
N(4)–C(8)	1.48(1)	O(2)–C(2)	1.18(1)
O(1)–C(1)	1.05(1)	O(3)–C(3)	1.19(1)
Bond angles			
C(2)–Mo(1)–C(3)	90.6(7)	O(1)–C(1)–Mo(1)	167.7(13)
C(2)–Mo(1)–C(4)	82.0(7)	O(2)–C(2)–Mo(1)	179.4(13)
C(3)–Mo(1)–C(4)	85.6(8)	O(3)–C(3)–Mo(1)	179.0(15)
C(2)–Mo(1)–C(1)	82.2(6)	O(4)–C(4)–Mo(1)	165.8(17)
C(3)–Mo(1)–C(1)	86.3(8)	N(2)–C(8)–N(4)	113.8(11)
C(4)–Mo(1)–C(1)	162.2(7)	C(16)–C(14)–C(15)	102(2)
C(2)–Mo(1)–N(3)	174.1(5)	C(16)–C(14)–C(17)	118.0(18)
C(3)–Mo(1)–N(3)	94.8(5)	C(15)–C(14)–C(17)	109(2)
C(4)–Mo(1)–N(3)	96.2(6)	C(7)–C(14)–C(17)	115.3(13)
C(1)–Mo(1)–N(3)	100.3(5)	C(21)–C(18)–C(20)	113.2(15)
C(2)–Mo(1)–N(1)	97.9(5)	C(9)–C(18)–C(20)	111.9(12)
C(3)–Mo(1)–N(1)	171.4(5)	C(21)–C(18)–C(19)	106.0(14)
C(4)–Mo(1)–N(1)	95.2(5)	C(20)–C(18)–C(19)	108.7(15)
C(1)–Mo(1)–N(1)	95.1(5)	C(11)–S(2)–C(13)	99.3(8)
N(3)–Mo(1)–N(1)	76.6(4)	C(12)–S(1)–C(5)	103.5(8)

The crystal structure of **15** (Fig. 4, Table 4) is similar to that of **16** (Fig. 5, Table 5). The average metal–N bond distances in **15** (2.244(1) Å) and **16** (2.2575(5) Å), respectively, are similar with those in **12** (2.2535(7) Å) and **13** (2.292(6) Å). The ∠N–M–N of 76.6(4)° in **15** is similar to that in **16** (76.06(19)°), but slightly smaller than those in **12** and **13** (80.1(2)° for **12** and 79.8(3)° for **13**, respectively). The ∠C(1)–W(1)–C(4) of 160.4(3)° in **16** is slightly smaller than the ∠C(1)–Mo(1)–C(4) of 162.2(7)° in **15**, but smaller than those in **12** and **13** (164.7(3)° for **12** and 168.5(4)° for **13**, respectively), indicating that the steric repulsion of the ligand and carbonyls in **15** and **16** may be more bigger than that in **12** and **13**. It is also noteworthy that two *cis*-carbonyls C(1)O(1) and C(4)O(4) in **15** and **16** are significantly distorted with the angles Mo(1)–C(1)–O(1) of 167.7(13)° and Mo(1)–C(4)–O(4) of 165.8(17)° for **15** and ∠W(1)–C(1)–O(1) of 168.6(7)° and ∠W(1)–C(4)–O(4) of 167.1(6)° for **16**, respectively, while the other two carbonyls in both **15** and **16** are nearly linear. In addition, some angles around *tert*-carbons of *tert*-butyl groups significantly depart from the values of sp^3 hybridized orbits possibly owing to the repulsion between two *tert*-butyl groups.

These complexes also have some analogous structural properties, such as the six-membered M–N–N–C–N–N metallacycle in each complex adopts a slightly distorted boat conformation. All sulfur atoms in complexes do not take part in the coordination to the metal centers. It is also interesting that in order to reduce the repul-

Table 5
Selected bond lengths (Å) and bond angles (°) for complex **16**

Bond lengths			
W(1)–C(2)	1.951(8)	C(1)–O(1)	1.133(8)
W(1)–C(3)	1.970(9)	C(2)–O(2)	1.166(8)
W(1)–C(1)	2.026(8)	C(3)–O(3)	1.160(8)
W(1)–C(4)	2.035(9)	C(4)–O(4)	1.141(9)
W(1)–N(1)	2.243(5)	C(7)–C(8)	1.52(1)
W(1)–N(3)	2.272(5)	C(14)–C(15)	1.52(1)
S(1)–C(5)	1.758(7)	S(2)–C(21)	1.785(7)
S(1)–C(20)	1.806(7)	N(2)–C(19)	1.459(8)
S(2)–C(12)	1.742(7)	N(4)–C(19)	1.465(8)
Bond angles			
C(2)–W(1)–C(3)	88.8(3)	O(1)–C(1)–W(1)	168.6(7)
C(2)–W(1)–C(1)	81.3(3)	O(2)–C(2)–W(1)	178.5(7)
C(3)–W(1)–C(1)	84.5(3)	O(3)–C(3)–W(1)	178.2(7)
C(2)–W(1)–C(4)	82.3(3)	O(4)–C(4)–W(1)	167.1(6)
C(3)–W(1)–C(4)	84.3(3)	C(7)–C(8)–C(10)	112.3(6)
C(1)–W(1)–C(4)	160.4(3)	C(10)–C(8)–C(9)	113.1(7)
C(2)–W(1)–N(1)	174.2(2)	C(7)–C(8)–C(11)	107.7(6)
C(3)–W(1)–N(1)	96.9(3)	C(10)–C(8)–C(11)	106.4(7)
C(1)–W(1)–N(1)	100.6(2)	C(17)–C(15)–C(18)	107.7(6)
C(4)–W(1)–N(1)	96.7(3)	C(14)–C(15)–C(18)	117.2(6)
C(2)–W(1)–N(3)	98.3(2)	C(17)–C(15)–C(16)	109.1(7)
C(3)–W(1)–N(3)	172.9(2)	C(18)–C(15)–C(16)	105.8(7)
C(1)–W(1)–N(3)	96.4(2)	N(2)–C(19)–N(4)	112.1(6)
C(4)–W(1)–N(3)	96.6(2)	C(5)–S(1)–C(20)	101.3(3)
N(1)–W(1)–N(3)	76.1(1)	C(12)–S(2)–C(21)	100.3(4)

sion of methyl groups with carbonyls, the methyl groups in these complexes are oriented away from the metal centers.

In conclusion, some S-rich bis(pyrazol-1-yl)methane ligands have been synthesized under phase-transfer catalytic conditions. The methylthio group significantly affects the steric and electronic properties of pyrazole ring during the formation of ligands. Treatment of these ligands with $M(CO)_6$ (M = Cr, Mo or W) under UV-irradiation yields a series of Group 6 metal carbonyl derivatives of S-rich bis(pyrazol-1-yl)methanes, in which some complexes contain asymmetric substituted bis(pyrazol-1-yl)methane ligands. The X-ray crystal structure analyses indicate that the sulfur atoms do not take part in the coordination to the metal centers, S-rich bis(pyrazol-1-yl)methanes actually act as bidentate chelating ligands by two nitrogen atoms.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 171643–171647 for compounds **16**, **13**, **12**, **15** and **5**, respectively. 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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