New multidentate heteroscorpionate ligands: N-Phenyl-2,2-bis(pyrazol-1-yl)thioacetamide and ethyl 2,2-bis(pyrazol-1-yl)dithioacetate as well as their derivatives

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Abstract

New multidentate heteroscorpionate ligands, N-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide PhHNCSCH(3,5-Me$_2$Pz)$_2$ (**1**), N-phenyl-2,2-bis(3,4,5-trimethylpyrazol-1-yl)thioacetamide PhHNCSCH(3,4,5-Me$_3$Pz)$_2$ (**2**), and ethyl 2,2-bis(3,5-dimethylpyrazol-1-yl)dithioacetate EtSCSCH(3,5-Me$_2$Pz)$_2$ (**8**), have been synthesized and their coordination chemistry studied. These heteroscorpionate ligands can act as monodentate, bidentate, or tridentate ligands, depending on the coordinate properties of different metals. Reaction of W(CO)$_6$ with **1** or **2** under UV irradiation yields monosubstituted carbonyl tungsten complexes W(CO)$_5$L (L = **1** or **2**), in which N-phenyl-2,2-bis(pyrazol-1-yl)thioacetamide acts as a monodentate ligand by the s-coordination to the tungsten atom. In addition, these monosubstituted tungsten complexes have also been obtained by heating ligand **1** or **2** with W(CO)$_5$THF in THF. While similar reaction of Fe(CO)$_5$ with **1**, **2**, or **8** under UV irradiation results in tricarbonyl iron complexes PhHNCSCH(3,5-Me$_2$Pz)$_2$Fe(CO)$_3$ (**5**), PhHNCSCH(3,4,5-Me$_3$Pz)$_2$Fe(CO)$_3$ (**6**), and EtSCSCH(3,5-Me$_2$Pz)$_2$Fe(CO)$_3$ (**9**), respectively, in which N-phenyl-2,2-bis(pyrazol-1-yl)thioacetamide or ethyl 2,2-bis(pyrazol-1-yl)dithioacetate acts as a bidentate ligand through one pyrazolyl nitrogen atom and the C=S π-bond in an η^2-C,S fashion side-on bonded to the iron atom to adopt a neutral bidentate κ^2-(π,N) coordination mode. Treatment of the lithium salt of **1** with Co(ClO$_4$)$_2$ · 6H$_2$O gives complex [PhNCSCH(3,5-Me$_2$Pz)$_2$]$_2$Co(ClO$_4$) with the oxidation of cobalt(II) to cobalt(III), in which N-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide acts as a tridentate monoanionic κ^3-(N,N,S) chelating ligand by two pyrazolyl nitrogen atoms and the sulfur atom of the enolized thiolate anion.
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Keywords: Bis(pyrazol-1-yl)methane; Heteroscorpionate ligand; Tungsten carbonyl; Iron carbonyl; Cobalt complex

1. Introduction

In recent years, poly(pyrazol-1-yl)alkane [1,2], especially bis(pyrazol-1-yl)methane [3], has been performing as one of the most popular nitrogen-containing donor ligands, and its coordination chemistry towards main group and transition metals has been extensively studied. Recently, the modification of bis(pyrazol-1-yl)methane by organic functional groups on the bridging carbon atom to form novel heteroscorpionate ligands has also drawn extensive atten-

tion [3–8]. These intriguing heteroscorpionate ligands usually have asymmetric N$_2$O, N$_2$S, N$_3$S, or N$_3$O coordination environments, which render them the potential to form novel complexes with various main group and transition metals. In addition, the modification of bis(pyrazol-1-yl)methanes by organometallic groups has also successfully broadened the scope of application of these novel ligands [9–11].

Our recent investigations on bis(pyrazol-1-yl)methane indicate that the modification of this ligand with organotin groups on the methine carbon atom can provide unusual reactivity [12,13]. For example, the reaction of triarylstannyl-bis(pyrazol-1-yl)methane with W(CO)$_5$THF results in

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oxidative addition of the Sn–C_{sp^3} bond to the tungsten(0) atom to yield novel four-membered metallacyclic complexes [12]. As part of our ongoing interest in functionalized bis(pyrazol-1-yl)methane ligands, we continue our investigation of the modification of bis(pyrazol-1-yl)methane by introducing heteroatoms on the methine carbon to form novel heteroscorpionate ligands. Herein we report the modification of bis(pyrazol-1-yl)methane by phenyl isothiocyanate and CS_2 on the bridging carbon atom to yield N-phenyl-2,2-bis(pyrazol-1-yl)thioacetamide and bis(pyrazol-1-yl)dithioacetate, which have the attractive character of being able to act as a monodentate, bidentate, or tridentate ligand, depending on different metal atoms. Very recently, the modification of bis(pyrazol-1-yl)methane by enantiopure isocyanate and isothiocyanate fragments has been reported [14,15].

2. Results and discussion

### 2.1. Synthesis of bis(pyrazol-1-yl)thioacetamide

The modification of bis(pyrazol-1-yl)methane by phenyl isothiocyanate on the methine carbon is easily carried out. Treatment of the bis(pyrazol-1-yl)methide anion [16], prepared in situ by the reaction of bis(pyrazol-1-yl)methane with n-BuLi, with phenyl isothiocyanate, and subsequently with water gives ligands 1 and 2 in reasonable yields, as shown in Scheme 1, which have been characterized by NMR. The proton signal of CH group in 1 (7.16 ppm) and 2 (7.13 ppm), respectively, markedly shifts to lower field than that of the methylene group in bis(3,5-dimethylpyrazol-1-yl)methane (5.94 ppm), possibly due to the deshielding effect by the C=S bond. In addition, the ^{13}C NMR signal of C=S occurs at 188.03 ppm for 1 and 189.63 ppm for 2, respectively. These two new multidetate ligands are expected to exhibit intriguing coordination

chemistry owing to the existence of both sulfur and nitrogen atoms, which have different electron-donating ability.

2.2. Reaction of bis(pyrazol-1-yl)thioacetamide with $W(CO)_6$

Upon irradiation of the solution of ligand 1 or 2 and $W(CO)_6$ in THF at room temperature, or treatment of ligand 1 or 2 with $W(CO)_5$THF in refluxing THF, complexes 3 and 4 are obtained (Scheme 1), which are characterized by NMR, IR spectra, and elemental analyses. The IR spectra of complexes 3 and 4 show a pattern of ν_{CO} bands that is consistent with the $W(CO)_5$ fragment, such as a ν_{CO} band observed at ca. 2071 cm^{-1}, corresponding to the A_{1eq} mode for the pseudo C_{4v} metal center in a metal pentacarbonyl moiety [17–19]. The ^{13}C NMR spectrum of 3 also supports the proposed structure, which clearly shows two signals of the carbonyl carbon atoms with ca. a 1:4 intensity ratio.

The structure of complex 3 has also been confirmed by crystal X-ray diffraction analysis, and presented in Fig. 1, which clearly manifests that N-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide acts as a monodentate ligand by the sulfur atom only, and the pyrazolyl nitrogen atoms do not take part in the coordination to the metal. The tungsten atom is six-coordinate with a slightly distorted octahedral coordination geometry. The W–S (2.578(1) Å) and C=S (1.675(3) Å) distances are comparable to those in other thiocarbonyl W(0) complexes (such as 2.5687(9) Å for W–S and 1.708(4) Å for C=S in $W(CO)_5$-(DTTT), DTTT = 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione) [19]. An intramolecular hydrogen bonding interaction has been observed between the N(5)–H group and the N(2) atom. The hydrogen bond N(5)–H⋯N(2) distance is 2.765(4) Å, and the angle of ∠N–H⋯N is 143.30(5)°. It is noteworthy that one carbonyl C(3)O(3) is
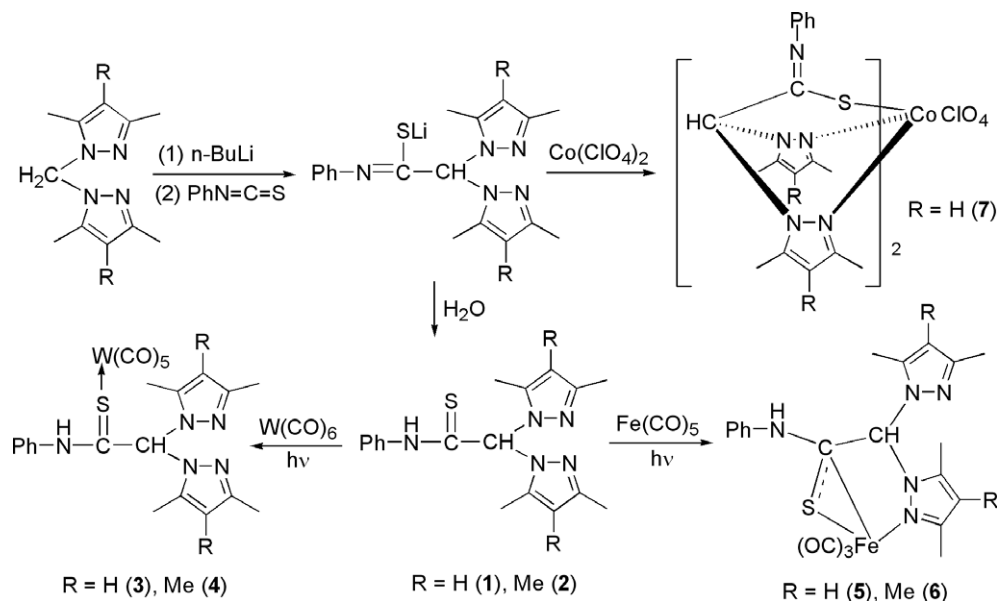
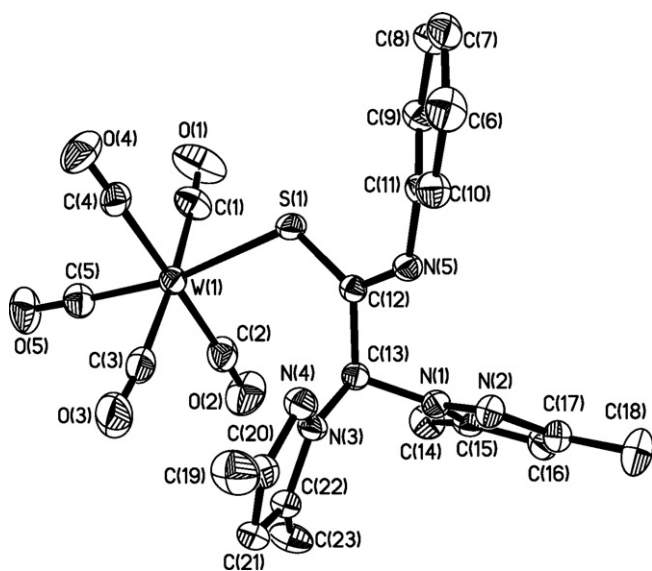Scheme 1. Syntheses of ligands 1 and 2 as well as their related reactions.

Fig. 1. The molecular structure of complex **3**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–S(1) 2.578(1), W(1)–C(2) 2.028(4), W(1)–C(5) 1.968(4), S(1)–C(12) 1.675(3), O(1)–C(1) 1.139(5), O(5)–C(5) 1.153(4), N(1)–C(13) 1.463(3), N(3)–C(13) 1.450(4), N(5)–C(12) 1.317(3), N(5)–C(11) 1.427(3), N(5)···N(2) 2.765(4); C(5)–W(1)–C(2) 88.9(1), C(1)–W(1)–C(3) 174.5(1), C(2)–W(1)–C(4) 177.3(1), C(5)–W(1)–S(1) 169.0(1), C(2)–W(1)–S(1) 101.2(1), C(12)–S(1)–W(1) 119.4(1), O(3)–C(3)–W(1) 173.3(3), O(1)–C(1)–W(1) 175.5(3), O(4)–C(4)–W(1) 179.1(3), N(5)–C(12)–C(13) 114.5(2), N(5)–C(12)–S(1) 124.0(2), C(13)–C(12)–S(1) 121.5(2), N(3)–C(13)–N(1) 111.4(2), N(3)–C(13)–C(12) 110.2(2), N(5)–H···N(2) 143.30(5).

significantly distorted with the angle of ∠W(1)–C(3)–O(3) of 173.3(3)°, indicating the presence of the steric repulsion between the ligand and carbonyl.

2.3. Reaction of bis(pyrazol-1-yl)thioacetamide with Fe(CO)₅

Upon irradiation of ligands **1** and **2** with Fe(CO)₅ under the similar experimental conditions to those for **1** and **2** with W(CO)₆, novel complexes **5** and **6** are yielded, which are air-stable in the solid state and even their solution can be manipulated in air without notable decomposition. Their proton signals of the CH groups (6.44 ppm in **5** and 6.43 ppm in **6**, respectively) are considerably shifted to higher field than those (7.13–7.16 ppm) in free ligands **1** and **2** as well as complexes **3** and **4**. Furthermore, their proton signals of the NH groups (5.15 ppm in **5** and 5.05 ppm in **6**, respectively) are also markedly upfield shifted, compared with those in free ligands **1** and **2** (12.47 ppm), possibly due to the disappearance of the hydrogen bonds in complexes.

It is known that thioamide has variable coordination modes depending on different metals. For example, it can act as a monodentate ligand by the sulfur atom [19–21], as in complex **3**, as well as a chelating bidentate ligand by both sulfur and nitrogen atoms [22]. Although iron(0) carbonyl complexes of thiocarbamoyls [23,24] or thioa-

mides [25,26] have been reported in literatures, neutral thioamides bonded to the iron(0) atom by the C=S π-bond in an η²-C,S fashion are still rare [26]. Herein, complex **5** provides an interesting case. Such coordination mode is consistent with the results of NMR spectra. For example, two sets of ¹H and ¹³C NMR signals corresponding to two inequivalent pyrazolyl ligands have been observed in complexes **5** and **6**. In addition, the ¹³C NMR signals of the thiocarbonyl groups in these two complexes are also markedly shifted to higher field, compared with those in free ligands and complexes **3** and **4**.

The molecular structure of complex **5** has been confirmed by crystal X-ray diffraction analysis as shown in Fig. 2. Selected bond distances and angles are listed in Table 1. As seen in Fig. 2, *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide acts as a neutral bidentate κ²-(π,N) ligand through only one pyrazolyl nitrogen atom and the C=S π-bond, which is side-on bonded to the iron atom in an η²-C,S fashion. The iron atom has a distorted trigonal bipyramidal coordination geometry with one carbon atom and one nitrogen atom occupying the axial positions. The axial angle of ∠C(1)–Fe(1)–N(4) is 171.71(9)°. The Fe–S (2.275(6) Å) and Fe–C(10) (2.015(2) Å) distances are comparable to those in π bonded thio ester derivatives of iron(0) carbonyl complexes (such as 2.2810(9) Å for Fe–S and 1.987(3) Å for Fe–C in [HC(S)OEt]₂Fe₂(CO)₆) [27]. The C=S (1.757(2) Å) and C(S)–N (1.428(3) Å) bond distances are longer than those in **3** (1.675(3) Å for C=S and 1.317(3) Å for C(S)–N, respectively), indicating that the π coordination to the iron atom weakens the double bond character of the C=S.

2.4. Synthesis of cobalt complex

The reaction of PhNCS(Li)CH(3,5-Me₂Pz)₂ with Co(ClO₄)₂ · 6H₂O in CH₃OH solution yields Co(III) complex **7**. Its IR spectrum displays the characteristic strong and
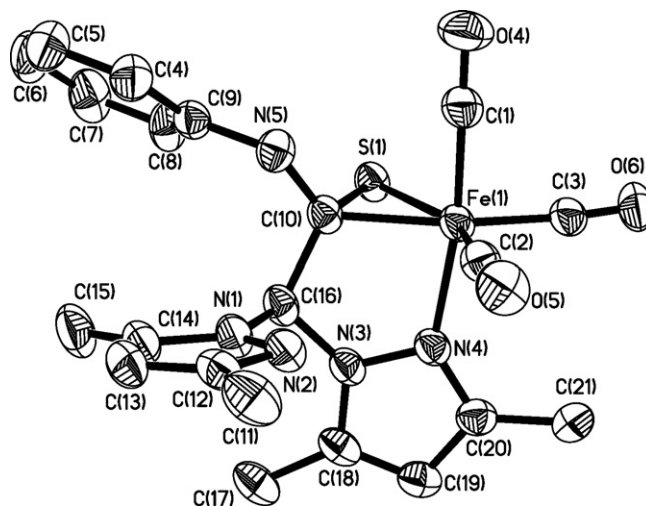

Fig. 2. The molecular structure of complex **5**. The thermal ellipsoids are drawn at the 30% probability level.

Table 1
Selected bond distances (Å) and angles (°) for complexes **5** and **9**

Complex **5**		Complex **9**			
Fe(1)–C(1)	1.775(3)	Fe(1)–C(1)	1.807(4)	Fe(2)–C(4)	1.804(4)
Fe(1)–C(2)	1.800(3)	Fe(1)–C(2)	1.824(4)	Fe(2)–C(5)	1.830(4)
Fe(1)–C(3)	1.825(3)	Fe(1)–C(3)	1.763(4)	Fe(2)–C(6)	1.758(4)
Fe(1)–C(10)	2.015(2)	Fe(1)–C(7)	2.042(3)	Fe(2)–C(19)	2.032(3)
Fe(1)–N(4)	1.997(1)	Fe(1)–N(1)	1.988(2)	Fe(2)–N(5)	1.988(2)
Fe(1)–S(1)	2.2775(6)	Fe(1)–S(1)	2.2806(9)	Fe(2)–S(3)	2.2855(9)
N(5)–C(10)	1.428(3)	N(2)–C(8)	1.446(4)	N(6)–C(20)	1.447(3)
N(5)–C(9)	1.394(3)	N(3)–C(8)	1.455(3)	N(7)–C(20)	1.445(3)
N(3)–C(16)	1.447(3)	C(7)–C(8)	1.533(4)	C(19)–C(20)	1.533(4)
N(1)–C(16)	1.453(3)	C(7)–S(1)	1.740(3)	C(19)–S(3)	1.754(3)
C(10)–S(1)	1.757(2)	C(7)–S(2)	1.805(3)	C(19)–S(4)	1.786(3)
C(1)–Fe(1)–C(3)	89.9(1)	C(1)–Fe(1)–C(3)	89.7(1)	C(4)–Fe(2)–C(6)	91.3(2)
C(2)–Fe(1)–C(3)	100.0(1)	C(2)–Fe(1)–C(3)	90.2(1)	C(5)–Fe(2)–C(6)	87.3(1)
C(1)–Fe(1)–N(4)	171.71(9)	C(3)–Fe(1)–N(1)	173.3(1)	C(6)–Fe(2)–N(5)	174.5(1)
C(2)–Fe(1)–N(4)	88.91(9)	C(1)–Fe(1)–N(1)	91.0(1)	C(4)–Fe(2)–N(5)	91.4(1)
C(1)–Fe(1)–C(10)	90.1(1)	C(3)–Fe(1)–C(7)	91.5(1)	C(6)–Fe(2)–C(19)	92.7(1)
C(3)–Fe(1)–C(10)	153.75(9)	C(2)–Fe(1)–C(7)	152.3(1)	C(5)–Fe(2)–C(19)	155.5(1)
N(4)–Fe(1)–C(10)	81.70(8)	N(1)–Fe(1)–C(7)	81.9(1)	N(5)–Fe(2)–C(19)	81.9(1)
C(2)–Fe(1)–S(1)	153.96(8)	C(1)–Fe(1)–S(1)	152.0(1)	C(4)–Fe(2)–S(3)	152.0(1)
C(3)–Fe(1)–S(1)	105.99(7)	C(2)–Fe(1)–S(1)	105.5(1)	C(5)–Fe(2)–S(3)	108.1(1)
C(10)–Fe(1)–S(1)	47.83(6)	C(7)–Fe(1)–S(1)	47.07(8)	C(19)–Fe(2)–S(3)	47.49(8)
C(10)–S(1)–Fe(1)	58.22(7)	C(7)–S(1)–Fe(1)	59.24(9)	C(19)–S(3)–Fe(2)	58.66(9)
O(4)–C(1)–Fe(1)	179.1(2)	O(1)–C(1)–Fe(1)	174.3(3)	O(4)–C(4)–Fe(2)	175.9(3)
O(5)–C(2)–Fe(1)	175.9(2)	O(2)–C(2)–Fe(1)	175.5(3)	O(5)–C(5)–Fe(2)	173.2(3)
O(6)–C(3)–Fe(1)	174.9(2)	O(3)–C(3)–Fe(1)	178.9(4)	O(6)–C(6)–Fe(2)	177.4(4)
N(3)–C(16)–N(1)	110.3(1)	N(2)–C(8)–N(3)	109.3(2)	N(7)–C(20)–N(6)	109.2(2)
N(3)–C(16)–C(10)	107.98(1)	C(8)–C(7)–S(1)	114.2(2)	C(20)–C(19)–S(3)	114.5(2)
N(5)–C(10)–C(16)	113.8(1)	S(1)–C(7)–S(2)	122.4(1)	S(3)–C(19)–S(4)	119.3(1)
N(5)–C(10)–S(1)	119.4(1)	C(8)–C(7)–S(2)	111.3(1)	C(20)–C(19)–S(4)	113.5(2)
N(5)–C(10)–Fe(1)	117.7(1)	S(2)–C(7)–Fe(1)	119.4(1)	S(4)–C(19)–Fe(2)	118.7(1)
C(16)–C(10)–Fe(1)	112.5(1)	C(8)–C(7)–Fe(1)	110.8(1)	C(20)–C(19)–Fe(2)	111.7(1)
S(1)–C(10)–Fe(1)	73.95(8)	S(1)–C(7)–Fe(1)	73.7(1)	S(3)–C(19)–Fe(2)	73.9(1)

broad band at 3423.1 cm^{-1} of O–H stretching vibration, originating from the water in the lattice. The strong peak at 1562.1 cm^{-1} is attributed to the C=N stretching vibration. In addition, the strong peak near 1090 cm^{-1} indicates the presence of typical non-coordinate perchlorate ion [28]. The molecular structure of complex **7** has been confirmed by crystal X-ray diffraction analysis, and the structure of its cation is presented in Fig. 3. In this complex, the cobalt atom is octahedrally coordinated by four pyrazolyl nitrogen atoms and two sulfur atoms, and *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide acts as a tridentate monoanionic κ^3-(N,N,S) chelating ligand. Two sulfur atoms lie in a *cis*-position with the bite angle of ∠S–Co–S (89.2(1)°). The average Co–S (2.262 (1) Å) and Co–N (1.970(4) Å) distances are comparable to those in related octahedral cobalt(III) complexes [29–32]. The N(5)–C(7) (1.287(6) Å) and N(10)–C(25) (1.263(6) Å) distances are considerably shorter than the N(5)–C(6) (1.433(7) Å) and N(10)–C(24) (1.423(7)Å) distances, but similar to the C=N distance of the –C(S$^-$)=N– fragment in complexes [Cp(CH$_3$)C=N–N=C(S)C$_4$H$_3$O]W(CO)$_3$SnCl$_2$ (1.298(6) Å) and [Cp(CH$_3$)C=N–N=C(S)C$_4$H$_3$S]Mo(CO)$_3$SnCl$_2$ (1.286(8) Å) [33], indicating the C=N double bond character of these two bonds.

2.5. Synthesis of ethyl 2,2-bis(3,5-dimethylpyrazol-1-yl)-dithioacetate and its reaction with Fe(CO)$_5$

Ethyl 2,2-bis(3,5-dimethylpyrazol-1-yl)dithioacetate (**8**) can be easily obtained by the reaction of 2,2-bis(3,5-dimethylpyrazol-1-yl)dithioacetate anion [34] with ethyl iodide (Scheme 2). Treatment of this ligand with Fe(CO)$_5$ under UV irradiation gives complex **9**, which has been characterized by NMR. The proton signal of CH group in **9** (6.22 ppm) is considerably shifted to higher field than that in free ligand **8** (7.07 ppm), but similar with those in complexes **5** (6.44 ppm) and **6** (6.43 ppm), respectively. In addition, two sets of ^{1}H and ^{13}C NMR signals corresponding to two inequivalent pyrazolyl ligands have been observed in complex **9**. These results are consistent with the κ^2-(π,N) coordination mode of ligand **8** in this complex.

The structure of complex **9** has also been confirmed by crystal X-ray diffraction analysis, which consists of two crystallography independent molecules. The two molecules are essentially the same, only slightly different in bond distances and angles. One of them is presented in Fig. 4, and selected bond distances and angles are listed in Table 1. Similar with *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide ligand in complex **7**, ethyl
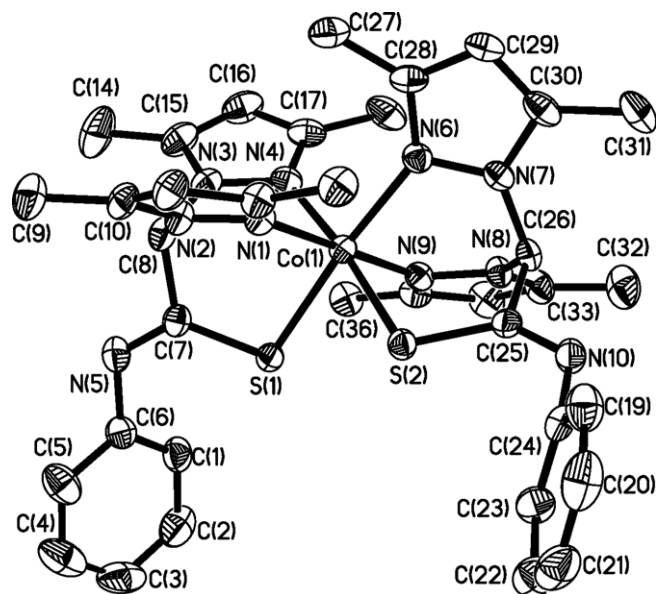
Fig. 3. Crystal structure of the complex cation of **7**. The thermal ellipsoids are drawn at the 30% probability level. The anion and uncoordinated water molecule have been omitted for clarity. Selected bond distances (Å) and angles (°): Co(1)–N(1) 1.952(4), Co(1)–N(4) 1.976(4), Co(1)–N(6) 2.002(4), Co(1)–N(9) 1.951(4), Co(1)–S(1) 2.259(1), Co(1)–S(2) 2.264(1), S(1)–C(7) 1.712(5), N(2)–C(8) 1.430(6), N(3)–C(8) 1.437(6), N(5)–C(6) 1.433(7), N(5)–C(7) 1.287(6), N(7)–C(26) 1.448(6), N(8)–C(26) 1.428(6), N(10)–C(24) 1.423(7), N(10)–C(25) 1.263(6); N(1)–Co(1)–N(9) 179.7(1), N(1)–Co(1)–N(4) 87.9(1), N(4)–Co(1)–N(6) 91.7(1), N(1)–Co(1)–S(1) 89.2(1), N(1)–Co(1)–S(2) 91.4(1), N(4)–Co(1)–S(2) 173.8(1), S(1)–Co(1)–S(2) 79.59(5), C(7)–S(1)–Co(1) 104.1(1), N(2)–C(8)–N(3) 111.4(4), N(8)–C(26)–N(7) 111.0(4), C(25)–N(10)–C(24) 119.9(4), C(7)–N(5)–C(6) 120.5(4), N(10)–C(25)–S(2) 129.9(4), C(26)–C(25)–S(2) 116.0(3), N(5)–C(7)–C(8) 113.9(4), N(5)–C(7)–S(1) 130.1(4).

Scheme 2. Synthesis of ligand **8** and its reaction with Fe(CO)$_5$.

2,2-bis(3,5-dimethylpyrazol-1-yl)dithioacetate also acts as a neutral bidentate κ^2-(π,N) ligand through only one pyrazolyl nitrogen atom and the C=S π-bond, which is side-on bonded to the iron atom in an η^2-C,S fashion. The axial angle of $\angle$C(3)–Fe(1)–N(1) (173.3(1)°) is slightly bigger than the corresponding angle of $\angle$C(1)–Fe(1)–N(4)
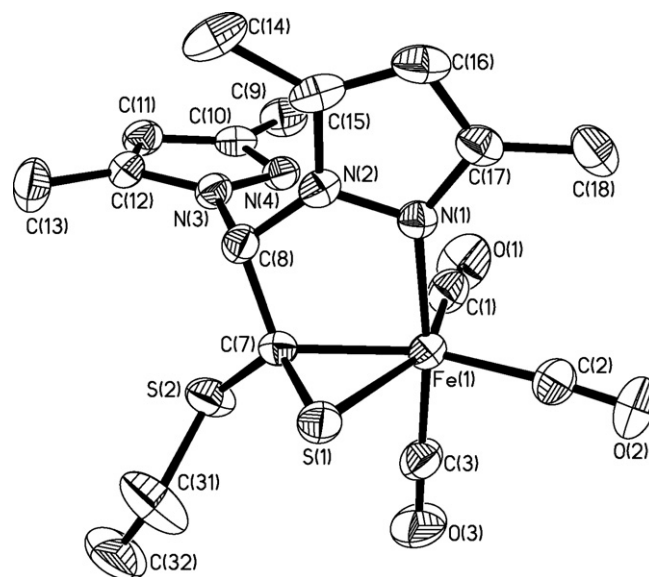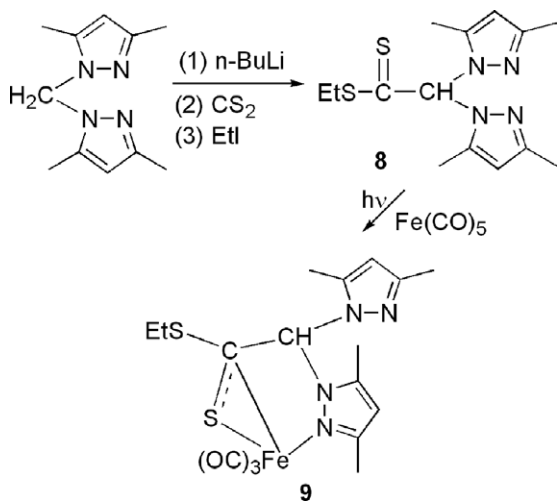

Fig. 4. The molecular structure of complex **9**. The thermal ellipsoids are drawn at the 30% probability level.

(171.71(9)°) in complex **7**. In addition, the C=S (C(7)–S(1) 1.740(3) Å) is comparable to that in complex **7** (1.757(2) Å), but still slightly longer than that in complex **3** (1.675(3) Å). Other structural parameters, such as the Fe–S distances (2.2806(9) Å in complex **9** and 2.275(6) Å in complex **7**) and Fe–C distances (Fe(1)–C(7) 2.042(3) Å in complex **9**) and Fe–C(10) (2.015(2) Å in complex **7**), are very similar in complexes **9** and **7**.

In summary, new heteroscorpionate ligands, *N*-phenyl-2,2-bis(pyrazol-1-yl)thioacetamides and ethyl 2,2-bis(pyrazol-1-yl)dithioacetate, have been successfully prepared. *N*-phenyl-2,2-bis(pyrazol-1-yl)thioacetamides can coordinate in three different ways, as monodentate ligand by the sulfur atom to carbonyl tungsten complexes, as neutral κ^2-(π,N) bidentate ligand by one pyrazolyl nitrogen atom and the C=S π-bond to carbonyl iron complexes, and as tridentate monoanionic κ^3-(N,N,S) chelating ligand by two pyrazolyl nitrogen atoms and the sulfur atom to cobalt(III) complexes. Ethyl 2,2-bis(pyrazol-1-yl)dithioacetate also acts as a neutral κ^2-(π,N) bidentate ligand when reacts with carbonyl iron.

3. Experimental

Solvents were dried by standard methods and distilled prior to use. All reactions were carried out under an argon atmosphere using standard Schlenk and Cannula techniques. NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker AV300 spectrometer, and the chemical shifts were reported in ppm with respect to reference standards (internal SiMe$_4$ for ^{1}H NMR and ^{13}C NMR spectra) using CDCl$_3$ as solvent unless otherwise noted. IR spectral data were obtained from a Bruker Equinox55 spectrometer in KBr pellets or Nujol mulls. Elemental analyses were carried out on an Elementar Vairo EL analyzer. Melting

points were reported with a X-4 digital melting-point apparatus and were uncorrected.

3.1. Preparation of PhHNCSCH(3,5-Me₂Pz)₂ (1)

To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (0.408 g, 2 mmol) in THF (30 ml) was added a hexane solution of *n*-BuLi (2 M, 1.0 ml) at $-70\,^{\circ}C$, and the mixture was stirred for 1 h at that temperature. To the mixture was added phenyl isothiocyanate (0.24 ml, 2 mmol). The reaction mixture was stirred at $-70\,^{\circ}C$ for 1 h, and allowed to slowly reach room temperature and stirred overnight. The solvent was removed under a reduced pressure, and the residual solid was washed with hexane and dried *in vacuo* to yield PhNCS(Li)CH(3,5-Me₂Pz)₂ as a slightly yellow solid. After water (1 ml) was added to this solid, CH₂Cl₂ (20 ml) was used to extract this solid. The extracted solution was passed through a short silica column to give a yellow solution. After the solvent was removed, PhHNCSCH(3,5-Me₂Pz)₂ (**1**) (0.44 g) was obtained as a yellow solid. Yield: 65%, mp 102–104 °C. ^{1}H NMR: δ 12.47 (br, s, 1H, N*H*), 7.87, 7.42, 7.28 (d, t, t, 2H, 2H, 1H, C₆*H*₅), 7.16 (s, 1H, C*H*), 5.91 (s, 2H, *H*⁴ of pyrazole ring), 2.45, 2.27 (s, s, 6H, 6H, C*H*₃). ^{1}H NMR (CDCl₃ + D₂O): δ 7.88, 7.41, 7.27 (d, t, t, 2H, 2H, 1H, C₆*H*₅), 7.17 (s, 1H, C*H*), 5.88 (s, 2H, *H*⁴ of pyrazole ring), 2.43, 2.25 (s, s, 6H, 6H, C*H*₃). ^{13}C NMR: δ 188.03 (*C*=S), 148.86, 139.68 (3- or 5-position carbon of pyrazole ring), 137.46, 127.82, 125.94, 121.88 (*C*₆H₅), 106.08 (4-position carbon of pyrazole ring), 74.00 (*C*H), 12.84, 10.40 (3- or 5-*C*H₃). Anal. Calc. for C₁₈H₂₁N₅S: C, 63.69; H, 6.24; N, 20.63. Found: C, 63.35; H, 6.21; N, 20.18%.

3.2. Preparation of PhHNCSCH(3,4,5-Me₃Pz)₂ (2)

This ligand was obtained as a yellow solid in a similar method using bis(3,4,5-trimethylpyrazol-1-yl)methane instead of bis(3,5-dimethylpyrazol-1-yl)methane as described above for **1**. Yield: 60%, mp 140–142 °C. ^{1}H NMR: δ 12.47 (br, s, 1H, N*H*), 7.84, 7.40, 7.26 (d, t, t, 2H, 2H, 1H, C₆*H*₅), 7.13 (s, 1H, C*H*), 2.34, 2.18, 1.88 (s, s, s, 6H, 6H, 6H, C*H*₃). ^{13}C NMR: δ 189.63 (*C*=S), 149.06, 138.63 (3- or 5-position carbon of pyrazole ring), 137.12, 128.83, 126.88, 122.93 (*C*₆H₅), 113.25 (4-position carbon of pyrazole ring), 76.80 (*C*H), 12.30, 9.95, 8.09 (3-, 4-, or 5-*C*H₃). Anal. Calc. for C₂₀H₂₅N₅S: C, 65.36; H, 6.86; N, 19.06. Found: C, 65.67; H, 6.51; N, 19.53%.

3.3. Reaction of 1 and 2 with W(CO)₆ and Fe(CO)₅

Since all reactions were run similarly, a general procedure was described. The solution of W(CO)₆ or Fe(CO)₅ (0.3 mmol) and ligand **1** or **2** (0.3 mmol) dissolved in THF (30 ml) was irradiated with a 300 W high-pressure mercury lamp for 10 h at room temperature. After the reaction completed, the solvent was removed *in vacuo*, and the residual was purified by column chromatography on silica

using CH₂Cl₂/hexane (v/v = 1:1) as eluent. The red or yellow eluent was concentrated to dryness under vacuum, and the residual was recrystallized from CH₂Cl₂/hexane to give complexes **3–6**.

3.3.1. PhHNCSCH(3,5-Me₂Pz)₂W(CO)₅ (3)

This complex was obtained by the reaction of W(CO)₆ with ligand **1** as a orange-red crystal. Yield: 82%. In addition, this complex has also been obtained by the reaction of ligand **1** with W(CO)₅ THF in THF under reflux for 1 h. ^{1}H NMR: δ 12.01 (br, s, 1H, N*H*), 7.65, 7.48, 7.35 (d, t, m, 2H, 2H, 2H, C₆*H*₅ and C*H*), 5.95 (s, 2H, *H*⁴ of pyrazole ring), 2.32, 2.21 (s, s, 6H, 6H, C*H*₃). ^{13}C NMR: δ 206.62, 197.12 (*C*O), 188.99 (*C*=S), 150.73, 141.05 (3- or 5-position carbon of pyrazole ring), 137.13, 129.43, 128.40, 123.65 (*C*₆H₅), 108.10 (4-position carbon of pyrazole ring), 74.59 (*C*H), 13.74, 11.04 (3- or 5-*C*H₃). IR (KBr, cm⁻¹): ν_{NH} = 3198.2 (w); ν_{CO} = 2071.6 (m), 1981.4 (m), 1950.3 (vs), 1924.7 (vs), 1884.6 (vs). (Nujol, cm⁻¹): ν_{NH} = 3185 (w); ν_{CO} = 2071.6 (m), 1982.1 (m), 1951.0 (vs), 1912.1 (vs), 1883.2 (vs). Anal. Calc. for C₂₃H₂₁N₅O₅SW: C, 41.64; H, 3.19; N, 10.56. Found: C, 41.58; H, 3.05; N, 10.66%.

3.3.2. PhHNCSCH(3,4,5-Me₃Pz)₂W(CO)₅ (4)

This complex was obtained by the reaction of W(CO)₆ with ligand **2** as a red crystal. Yield: 80%. ^{1}H NMR: δ 12.04 (br, s, 1H, N*H*), 7.65, 7.49–7.33 (d, m, 2H, 4H, C₆*H*₅ and C*H*), 2.24, 2.15, 1.90 (s, s, s, 6H, 6H, 6H, C*H*₃). ^{13}C NMR: δ 197.18 (*C*O), 189.09 (*C*=S), 149.89, 140.05 (3- or 5-position carbon of pyrazole ring), 137.29, 129.36, 128.83, 123.65 (*C*₆H₅), 114.45 (4-position carbon of pyrazole ring), 74.80 (*C*H), 12.28, 9.65, 8.01 (3-, 4-, or 5-*C*H₃). IR (Nujol, cm⁻¹): ν_{NH} = 3185 (w); ν_{CO} = 2071.4 (m), 1984.9 (m), 1948.6 (vs), 1913.3 (vs), 1877.8 (vs). Anal. Calc. for C₂₅H₂₅N₅O₅SW: C, 43.43; H, 3.64; N, 10.13. Found: C, 43.05; H, 3.70; N, 10.16%.

3.3.3. PhHNCSCH(3,5-Me₂Pz)₂Fe(CO)₃ (5)

This complex was obtained by the reaction of Fe(CO)₅ with ligand **1** as a yellow crystal. Yield: 70%. ^{1}H NMR: δ 7.16, 6.96, 6.74 (t, d, t, 2H, 2H, 1H, C₆*H*₅), 6.44 (s, 1H, C*H*), 5.74, 5.64 (s, s, 1H, 1H, *H*⁴ of pyrazole ring), 5.15 (s, 1H, N*H*, which disappeared when D₂O was added), 2.38, 2.19, 1.97, 1.60 (s, s, s, s, 3H, 3H, 3H, 3H, C*H*₃). ^{13}C NMR: δ 209.15, 208.74, 206.49 (*C*O), 151.40, 149.89, 142.67, 141.12 (3- or 5-position carbon of pyrazole ring), 148.31, 129.11, 118.84, 114.84 (*C*₆H₅), 108.89, 105.21 (4-position carbon of pyrazole ring), 90.14 (*C*=S), 73.29 (*C*H), 15.70, 13.80, 11.73, 9.82 (3- or 5-*C*H₃). IR (KBr, cm⁻¹): ν_{CO} = 2064.8 (vs), 2010.8 (s), 2003.4 (s), 1993.0 (vs), 1976.1 (vs). Anal. Calc. for C₂₁H₂₁FeN₅O₃S: C, 52.62; H, 4.42; N, 14.61. Found: C, 52.39; H, 4.86; N, 15.06%.

3.3.4. PhHNCSCH(3,4,5-Me₃Pz)₂Fe(CO)₃ (6)

This complex was obtained by the reaction of Fe(CO)₅ with ligand **2** as a yellow crystal. Yield: 68%. ^{1}H NMR: δ 7.17, 6.94, 6.73 (t, d, t, 2H, 2H, 1H, C₆*H*₅), 6.43 (s, 1H,

C*H*), 5.05 (s, 1H, N*H*), 2.32, 2.16, 1.91, 1.77, 1.75, 1.50 (s, s, s, s, s, s, 3H, 3H, 3H, 3H, 3H, 3H, C*H₃*). ¹³C NMR: δ 209.06, 208.71, 206.47 (*C*O), 150.01, 148.80, 139.61, 137.71 (3- or 5-position carbon of pyrazole ring), 148.34, 129.34, 119.07, 114.69 (*C₆H₅*), 112.93, 111.30 (4-position carbon of pyrazole ring), 90.25 (*C*=S), 73.66 (*C*H), 13.79, 12.13, 10.08, 8.37, 8.33, 7.80 (3-, 4-, or 5-*C*H₃). IR (KBr, cm⁻¹): ν_{CO} = 2064.6 (vs), 2010.9 (s), 2003.2 (s), 1993.2 (vs), 1976.2 (vs). Anal. Calc. for $C_{23}H_{25}FeN_5O_3S$: C, 54.44; H, 4.97; N, 13.80. Found: C, 54.16; H, 4.96; N, 13.37%.

3.4. Preparation of [PhNCSCH(3,5-Me₂Pz)₂]₂Co(ClO₄) · H₂O (7 · H₂O)

A methanol (5 ml) solution of PhNCS(Li)CH(3,5-Me₂Pz)₂ (345 mg, 1 mmol) was slowly placed over the same solution (5 ml) of Co(ClO₄)₂ · 6H₂O (183.5 mg, 0.5 mmol) in air. After several days, brown crystals were formed, which were filtered off and dried *in vacuo* to give 0.13 g (30%) of complex **7 · H₂O**. IR (KBr, cm⁻¹): ν_{OH} = 3423.1 (br, s); $\nu_{C=N}$ = 1562.1 (vs), ν_{ClO_4} = 1090.5 (vs). Anal. Calc for $C_{36}H_{40}ClCoN_{10}O_4S_2 · H_2O$: C, 50.65; H, 4.69; N, 16.42. Found: C, 50.30; H, 4.99; N, 16.38%.

3.5. Preparation of CH₃CH₂SCSCH(3,5-Me₂Pz)₂ (8)

To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (0.408 g, 2 mmol) in THF (30 ml) was added a hexane solution of *n*-BuLi (2 M, 1.0 ml) at −70 °C, and the mixture was stirred for 1 h at that temperature. To the mixture

was added carbon disulfide (0.12 ml, 2 mmol). The reaction mixture was stirred at −70 °C for 1 h, and allowed to slowly reach room temperature and stirred continuously for 2 h. Then, ethyl iodide (0.16 ml, 2 mmol) was added and the mixture was stirred for 8 h at room temperature. The solvent was removed under a reduced pressure, and the residual solid was dissolved in CH₂Cl₂ (10 ml). The solution was passed through a short silica column to give a red solution. After the solvent was removed again, the residual solid was washed with hexane to give 0.26 g of **8** as orange-yellow crystals. Yield: 40%, mp 103–105 °C. ¹H NMR: δ 7.07 (s, 1H, C*H*), 5.82 (s, 2H, *H⁴* of pyrazole ring), 3.17 (q, 2H, CH₃C*H₂*), 2.22, 2.18 (s, s, 6H, 6H, C*H₃*), 1.26 (t, 3H, C*H₃*CH₂). ¹³C NMR: δ 226.14 (*C*=S), 149.18, 141.82 (3- or 5-position carbon of pyrazole ring), 107.38 (4-position carbon of pyrazole ring), 81.90 (*C*H), 31.70 (CH₃*C*H₂), 13.90 (*C*H₃CH₂), 12.09, 11.86 (3- or 5-*C*H₃). Anal. Calc. for $C_{14}H_{20}N_4S_2$: C, 54.51; H, 6.54; N, 18.16. Found: C, 54.26; H, 6.72; N, 18.05%.

3.6. Reaction of ligand 8 with Fe(CO)₅

This reaction was carried out similarly as described above for the reaction of ligand **1** or **2** with Fe(CO)₅. After the reaction completed, the solvent was removed *in vacuo*, and the residual was purified by column chromatography on silica using CH₂Cl₂/hexane (v/v = 1:1) as eluent. The red eluent was concentrated to dryness under vacuum, and the residual was recrystallized from CH₂Cl₂/hexane to give EtSCSCH(3,5-Me₂Pz)₂Fe(CO)₃ (**9**) as a red crystal. Yield: 65%. ¹H NMR: 6.22 (s, 1H, C*H*), 5.84, 5.72 (s, s, 1H,

Table 2
Crystallographic data and refinement parameters for complexes **3**, **5**, **7**, and **9**

Complex	3	5	7 · H₂O	9
Formula	$C_{23}H_{21}N_5O_5SW$	$C_{21}H_{21}FeN_5O_3S$	$C_{36}H_{42}ClCoN_{10}O_5S_2$	$C_{34}H_{40}Fe_2N_8O_6S_4$
Formula weight	663.36	479.34	853.30	896.68
Crystal size (mm)	0.28 × 0.22 × 0.20	0.28 × 0.24 × 0.22	0.22 × 0.18 × 0.16	0.22 × 0.18 × 0.16
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
Cell parameters				
a (Å)	18.339(13)	13.504(1)	14.085(5)	11.871(1)
b (Å)	10.936(8)	14.773(1)	16.327(6)	11.886(1)
c (Å)	13.592(9)	12.286(1)	17.722(7)	14.950(2)
α (°)	90	90	90	96.487(2)
β (°)	108.521(8)	110.637(1)	90	91.105(2)
γ (°)	90	90	90	91.230(2)
V (Å)³	2585(3)	2293.7(4)	4075(3)	2094.9(6)
Z	4	4	4	2
T (K)	293(2)	293(2)	293(2)	293(2)
D_{calc} (g cm⁻³)	1.705	1.388	1.391	1.421
2θ Range (°)	4.40–50.06	4.24–50.06	3.4–50.06	4.16–50.06
$F(0\,0\,0)$	1296	992	1776	928
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm⁻¹)	4.592	0.780	0.643	0.943
Number of reflections measured	13500	12266	22180	11482
Number of reflections observed [R_{int}]	4548 [0.0256]	4055 [0.0186]	7193 [0.0485]	7305 [0.0186]
Number of parameters	321	284	511	496
Goodness-of-fit	1.015	1.046	1.048	1.040
Residuals R, Rw [$I > 2\sigma(I)$]	0.020, 0.048	0.032, 0.083	0.047, 0.120	0.0389, 0.0981

1H, H^4 of pyrazole ring), 2.56 (m, 5H, CH_3 and CH_2CH_3), 2.36, 2.10, 1.90 (s, s, s, 3H, 3H, 3H, CH_3), 1.08 (t, 3H, CH_2CH_3). ^{13}C NMR: δ 208.93, 208.63, 206.68 (CO), 151.24, 148.70, 142.55, 140.05 (3- or 5-position carbon of pyrazole ring), 108.84, 105.62 (4-position carbon of pyrazole ring), 82.85 (CH), 32.34 (CH$_3C$H$_2$), 15.74 (CH$_3C$H$_2$), 14.21, 13.72, 11.71, 11.54 (3- or 5-CH$_3$). The carbon of thiocarbonyl group was not observed possibly owing to low solubility and low sensitivity of carbonyl carbon. IR (KBr, cm^{-1}): v_{CO} = 2069.0 (vs), 2003.7 (vs), 1990.4 (vs). Anal. Calc. for $C_{17}H_{20}FeN_4O_3S_2$: C, 45.54; H, 4.50; N, 12.50. Found: C, 45.51; H, 4.62; N, 12.76%.

3.7. X-ray crystallography

Crystals of complexes **3**, **5**, and **9** suitable for X-ray analysis were obtained by slow evaporating their CH$_2$Cl$_2$/hexane solutions at 4 °C, while crystals of complex **7** were obtained by slowly placing the solution of PhNCS(Li)-CH(3,5-Me$_2$Pz)$_2$ in CH$_3$OH over the solution of Co(ClO$_4$)$_2$ · 6H$_2$O in the same solvent. Complex **7** had water of crystallization, which was disordered. The site occupation factor of this disordered oxygen atom was adjusted (0.5) to give reasonable thermal parameters. Intensity data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) using the $\omega/2\theta$ scan technique, and a semi-empirical absorption correction was applied for all complexes. 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 **3**, **5**, **7**, and **9** is listed in Table 2.

Acknowledgements

Appendix A. Supplementary material

CCDC 619075, 619076, 619077 and 626511 contain the supplementary crystallographic data for **3**, **5**, **7** and **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.030.

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