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Synthesis of bis(pyrazol-1-yl)methanes with organogermyl and organosilyl groups on the methine carbon and their reaction with $W(CO)_5(THF)$. X-ray crystal structures of $Ph_3GeCHPz_2W(CO)_4$ and $Me_3SiCHPz_2W(CO)_4$ (Pz = 3,5-dimethylpyrazole)

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Abstract

A series of new bis(pyrazol-1-yl)methane ligands with organogermyl and organosilyl groups on the methine carbon, $MCHPz_2$ ($M = Ph_3Ge$, $PhMe_2Si$, $^iPr_3Si$ or Me_3Si; Pz = 3,5-dimethylpyrazole or 3,4,5-trimethylpyrazole), have been prepared by the reaction of bis(pyrazol-1-yl)methyllithium with triphenylgermanium bromide and organosilyl chloride. Treatment of these ligands with $W(CO)_5(THF)$ in refluxing THF resulted in new heterobimetallic complexes $MCHPz_2W(CO)_4$ as major products, accompanied by partial decomposition of ligands to yield a certain amount of $PzW(CO)_5$ as by-products. These new ligands and complexes have been characterized by ^{1}H-NMR, IR and elemental analysis. The molecular structures of complexes $Ph_3GeCHPz_2W(CO)_4$ and $Me_3SiCHPz_2W(CO)_4$ (Pz = 3,5-dimethylpyrazole) have been determined by X-ray structure analysis, indicating that bis(pyrazol-1-yl)methanes act as chelating bidentate ligands in these complexes, and organometallic groups lie in the axial position of the methine carbon. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bis(pyrazol-1-yl)methane; Tungsten; Silicon; Germanium; X-ray crystal structures

1. Introduction

Poly(pyrazol-1-yl)alkanes have been one of popular polydentate nitrogen donor ligands since Trofimenko's first report [1] and especially Julia's later modification [2]. The coordination behavior of poly(pyrazol-1-yl)alkanes towards main group and transition metal has been extensively investigated [3–5]. A number of main group [6] and transition metal [7] complexes containing poly(pyrazol-1-yl)alkanes have been synthesized and characterized in recent years. In order to meet the rapid development of poly(pyrazol-1-yl)alkanes chemistry, some new higher-yield and higher-purity synthetic methods for poly(pyrazol-1-yl)alkanes have been explored [6c,8]. It has been found that the coordination behavior of poly(pyrazol-1-yl)alkanes can easily be adjusted by changing the electronic and steric characteristics of substituents on the 3-, 4- or 5-positions of the pyrazole ring. Recent investigations show that the bridging carbon atom can also be modified by the organic functional groups to form novel heteroscorpionate ligands, which usually have asymmetric N_2O [9], N_2S [10], N_3S [11] or N_3O [12] coordination environments. Moreover, replacement of the bridging atom by the silicon atom to form poly(pyrazol-1-yl)silanes has also been reported [13]. However, the modification of poly(pyrazol-1-yl)alkanes by organometallic groups on the bridging carbon atom is rare [14].

We have recently described the synthesis of new poly(pyrazol-1-yl)alkanes modified by introduction of organotin groups on the bridging carbon atom and their reaction with $W(CO)_5(THF)$ [15], displaying that such poly(pyrazol-1-yl)alkanes have unusual reactivity owing to the introduction of the organometallic groups. Now we continue our investigation of the modification of poly(pyrazol-1-yl)alkanes by introducing organometal-

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lic groups on the methine carbon. In the present work, we report the synthesis of new poly(pyrazol-1-yl)alkanes modified by organogermyl and organosilyl groups on the bridging carbon atom, and their reactions with $W(CO)_5(THF)$ to yield new heterobimetallic complexes.

2. Experimental

All reactions were carried out under an oxygen-free atmosphere. Solvents were dried by standard methods and distilled prior to use. ^1H-NMR spectra were recorded on a Bruker AC-P-200 spectrometer using $CDCl_3$ as solvent unless otherwise noted. IR spectral data were obtained from a Bio-Rad FTS 135 spectrometer in KBr pellets or liquid films. Melting points (m.p.) were determined on a PHMK (Germany) melting point apparatus and were uncorrected. Elemental analyses were carried out on a Perkin–Elmer 240C analyser.

*2.1. Synthesis of ligands **1–5***

2.1.1. Preparation of triphenylgermyl-bis(3,5-dimethylpyrazol-1-yl)methane $Ph_3GeCH(3,5\text{-}Me_2Pz)_2$ (1)

To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (2 mmol) in THF (40 ml) was added a hexane solution of *n*-BuLi (2 M, 1.0 ml) at −78 °C, and the mixture was stirred for 1 h at that temperature. To the mixture was added a solution of triphenylgermanium bromide (2 mmol) in THF (10 ml). The reaction mixture was stirred at −78 °C for 2 h, and allowed to slowly reach room temperature (r.t.) and stirred overnight. The solvent was removed under a reduced pressure, and the residual solid was recrystallized from hexane to yield white crystals of **1**. Yield: 48%, m.p. 114–116 °C. ^1H-NMR: δ 1.81, 2.11 (s, s, 6H, 6H, 3 or 5-CH_3), 5.71 (s, 2H, H^4 of pyrazole), 6.74 (s, 1H, C*H*), 7.30 (m, 15H, C_6H_5). IR: $\nu_{\text{pyrazole ring}} = 1559.4$ (s) cm^{-1}. Anal. Calc. for $C_{29}H_{30}GeN_4$: C, 68.64; H, 5.92; N, 11.05. Found: C, 68.77; H, 6.33; N, 10.87%.

2.1.2. Preparation of phenyldimethylsilyl-bis(3,5-dimethylpyrazol-1-yl)methane $PhMe_2SiCH(3,5\text{-}Me_2Pz)_2$ (2)

This ligand was obtained similarly using $PhMe_2SiCl$ instead of Ph_3GeBr as described above for **1**. Yield: 51%, m.p. 84–86 °C. ^1H-NMR: δ 0.57 (s, 6H, $Si(CH_3)_2Ph$), 1.72, 2.18 (s, s, 6H, 6H, 3 or 5-CH_3), 5.69 (s, 2H, H^4 of pyrazole), 6.04 (s, 1H, C*H*), 7.28 (m, 5H, C_6H_5). IR: $\nu_{\text{pyrazole ring}} = 1554.4$ (s) cm^{-1}. Anal. Calc. for $C_{19}H_{26}N_4Si$: C, 67.46; H, 7.69; N, 16.57. Found: C, 67.19; H, 7.46; N, 16.75%.

2.1.3. Preparation of triisopropylsilyl-bis(3,5-dimethylpyrazol-1-yl)methane $^iPr_3SiCH(3,5\text{-}Me_2Pz)_2$ (3)

This ligand was obtained similarly using $^iPr_3SiCl$ instead of Ph_3GeBr as described above for **1**. Yield: 46%, m.p. 39–41 °C. ^1H-NMR: δ 1.02 (d, 18H, $Si(CH(CH_3)_2)_3$), 1.45 (m, 3H, $Si(CH(CH_3)_2)_3$), 2.01, 2.15 (s, s, 6H, 6H, 3 or 5-CH_3), 5.73 (s, 2H, H^4 of pyrazole), 6.23 (s, 1H, C*H*). IR: $\nu_{\text{pyrazole ring}} = 1558.1$ (s) cm^{-1}. Anal. Calc. for $C_{20}H_{36}N_4Si$: C, 66.67; H, 10.00; N, 15.56. Found: C, 66.91; H, 9.89; N, 15.79%.

2.1.4. Preparation of trimethylsilyl-bis(3,5-dimethylpyrazol-1-yl)methane $Me_3SiCH(3,5\text{-}Me_2Pz)_2$ (4)

To a solution of bis(3,5-dimethylpyrazol-1-yl)methane (2 mmol) in THF (40 ml) was added a hexane solution of *n*-BuLi (2 M, 1.0 ml) at −78 °C, and the mixture was stirred for 1 h at that temperature. To the mixture was added a solution of trimethylsilyl chloride (2 mmol) in THF (10 ml). The reaction mixture was stirred at −78 °C for 2 h, and allowed to slowly reach r.t. and stirred overnight. The solvent was removed under a reduced pressure, and the residual oil was extracted with hot hexane (40 ml) and then filtered off. The filter was concentrated to ca. 4 ml and cooled to −15 °C to yield a white solid, which was confirmed to be 3,5-dimethylpyrazole by ^1H-NMR. The filter was concentrated to dryness to give an oil, which was confirmed to be ligand **4** by ^1H-NMR. Yield: 42%. ^1H-NMR: δ 0.20 (s, 9H, $Si(CH_3)_3$), 1.94, 2.16 (s, s, 6H, 6H, 3 or 5-CH_3), 5.74 (s, 2H, H^4 of pyrazole), 5.91 (s, 1H, C*H*). IR: $\nu_{\text{pyrazole ring}} = 1555.6$ (s) cm^{-1}. Anal. Calc. for $C_{14}H_{24}N_4Si$: C, 60.87; H, 8.70; N, 20.29. Found: C, 60.98; H, 8.55; N, 19.95%.

2.1.5. Preparation of trimethylsilyl-bis(3,4,5-trimethylpyrazol-1-yl)methane $Me_3SiCH(3,4,5\text{-}Me_3Pz)_2$ (5)

This ligand was obtained similarly using bis(3,4,5-trimethylpyrazol-1-yl)methane instead of bis(3,5-dimethylpyrazol-1-yl)methane as described above for **4** as an oil. With the exception of **5**, a certain amount of 3,4,5-trimethylpyrazole have been obtained. Yield: 39%. ^1H-NMR: δ 0.17 (s, 9H, $Si(CH_3)_3$), 1.80, 1.86, 2.19 (s, s, s, 6H, 6H, 6H, 3, 4 or 5-CH_3), 5.91 (s, 1H, C*H*). IR: $\nu_{\text{pyrazole ring}} = 1586.7$ (s) cm^{-1}. Anal. Calc. for $C_{16}H_{28}N_4Si$: C, 63.16; H, 9.21; N, 18.42. Found: C, 62.97; H, 9.27; N, 18.52%.

*2.2. Reaction of ligands **1–5** with $W(CO)_5(THF)$*

Since all reactions were run similarly, a general procedure was described. Ligands (0.5 mmol) were added to the solution of $W(CO)_5(THF)$ in THF, prepared in situ by the irradiation of the solution of

$W(CO)_6$ (0.5 mmol) in THF (20 ml) for 8 h, was the mixture and refluxed under stirring for 2 h. After the reaction completed, the solvent was removed under a reduced pressure, and the residual solid was purified by column chromatography on alumina using CH_2Cl_2–hexane as eluent. The eluent was concentrated to dryness under a reduced pressure, and the residual solid was recrystallized from CH_2Cl_2–hexane to give green–yellow crystals.

2.2.1. Preparation of $Ph_3GeCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (**6**)

This compound was obtained by the reaction of ligand **1** with $W(CO)_5(THF)$. Yield: 43%. ^{1}H-NMR: δ 1.90, 2.57 (s, s, 6H, 6H, 3 or 5-CH_3), 6.02 (s, 2H, H^4 of pyrazole), 6.91 (s, 1H, C*H*), 7.34(m, 15H, C_6H_5). IR: $\nu_{CO} = 1999.5$ (s), 1874.0 (vs), 1855.7 (vs), 1827.0 (s); $\nu_{\text{pyrazole ring}} = 1559.6$ (m) cm^{-1}. Anal. Calc. For $C_{33}H_{30}GeN_4O_4W$: C, 49.32; H, 3.74; N, 6.97. Found: C, 49.48; H, 3.79; N, 7.01%.

2.2.2. Preparation of $PhMe_2SiCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (**7**)

This compound was obtained by the reaction of ligand **2** with $W(CO)_5(THF)$. Yield: 36%. ^{1}H-NMR: δ 0.48 (s, 6H, $Si(CH_3)_2Ph$), 2.06, 2.55 (s, s, 6H, 6H, 3 or 5-CH_3), 5.98 (s, 2H, H^4 of pyrazole), 6.11 (s, 1H, C*H*), 7.44 (m, 5H, C_6H_5). IR: $\nu_{CO} = 2000.8$ (s), 1875.2 (vs), 1854.1 (vs), 1814.8 (vs); $\nu_{\text{pyrazole ring}} = 1558.2$ (m) cm^{-1}. Anal. Calc. For $C_{23}H_{26}N_4O_4SiW$: C, 43.53; H, 4.10; N, 8.83. Found: C, 43.65; H, 4.32; N, 8.70%.

2.2.3. Preparation of $^iPr_3SiCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (**8**)

This compound was obtained by the reaction of ligand **3** with $W(CO)_5(THF)$. Yield: 25%. ^{1}H-NMR: δ 0.97 (d, 18H, $Si(CH(CH_3)_2)_3$), 1.60 (m, 3H, $Si(CH(CH_3)_2)_3$), 2.38, 2.53 (s, s, 6H, 6H, 3 or 5-CH_3), 5.96 (s, 2H, H^4 of pyrazole), 6.20 (s, 1H, C*H*). IR: $\nu_{CO} = 1998.1$ (s), 1881.4 (s), 1858.3 (vs), 1823.3 (vs); $\nu_{\text{pyrazole ring}} = 1558.1$ (m) cm$^{-1.}$ Anal. Calc. For $C_{24}H_{36}N_4O_4SiW$: C, 43.90; H, 5.49; N, 8.54. Found: C, 43.89; H, 5.51; N, 8.73%. Some $W(CO)_5L$ (L = 3,5-dimethylpyrazole) derivatives were also isolated with the exception of the heterobimetallic complex **8**.

2.2.4. Preparation of $Me_3SiCH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (**9**)

This compound was obtained by the reaction of ligand **4** with $W(CO)_5(THF)$. Yield: 32%. ^{1}H-NMR: δ 0.15 (s, 9H, $Si(CH_3)_3$), 2.35, 2.55 (s, s, 6H, 6H, 3 or 5-CH_3), 6.01 (s, 2H, H^4 of pyrazole), 6.13 (s, 1H, C*H*). IR: $\nu_{CO} = 1997.5$ (s), 1855.2 (vs, br), 1829.9 (vs); $\nu_{\text{pyrazole ring}} = 1559.5$ (m) cm^{-1} Anal. Calc. For $C_{18}H_{24}N_4O_4SiW$: C, 37.76; H, 4.20; N, 9.79. Found: C, 38.11; H, 4.33; N, 9.91%.

2.2.5. Preparation of $Me_3SiCH(3,4,5\text{-}Me_3Pz)_2W(CO)_4$ (**10**)

This compound was obtained by the reaction of ligand **5** with $W(CO)_5(THF)$. Yield: 23%. ^{1}H-NMR: δ 0.19 (s, 9H, $Si(CH_3)_3$), 1.95, 2.28, 2.50 (s, s, s, 6H, 6H, 6H, 3, 4 or 5-CH_3), 6.21 (s, 1H, C*H*). IR: $\nu_{CO} =$ 2002.5(s), 1973.7 (vs), 1856.1 (vs), 1810.1 (vs); $\nu_{\text{pyrazole ring}} = 1578.3$ (m) cm^{-1} Anal. Calc. For $C_{20}H_{28}N_4O_4SiW$: C, 40.00; H, 4.67; N, 9.33. Found: C, 39.89; H, 4.59; N, 9.45%.

2.3. Crystal structure determination

Crystals of complexes **6** and **9** suitable for X-ray analysis were grown from CH_2Cl_2–hexane at 4 °C. Intensity data were collected on 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 complexes **6** and **9** is listed in Table 1.

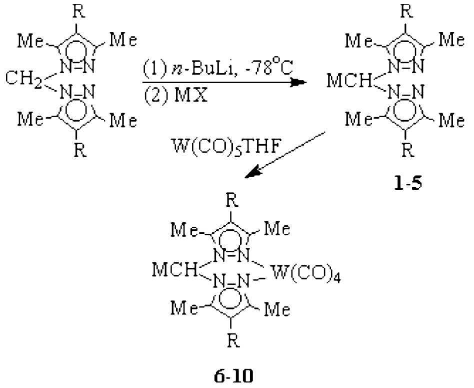
3. Results and discussion

3.1. Synthesis of ligands and complexes

Ligands **1**–**5** can easily be obtained as a solid or an oil by the reaction of bis(pyrazol-1-yl)methyllithium with triphenylgermanium bromide or organosilyl chloride as shown in Scheme 1. During the preparation of ligands **4**

Table 1
Crystallographic data for complexes **6** and **9**

Complex	$6 \cdot 2H_2O$	**9**
Formula	$C_{33}H_{30}GeN_4O_4W \cdot 2H_2O$	$C_{18}H_{24}N_4O_4SiW$
Formula weight	839.08	572.35
Crystal size (mm)	0.25 × 0.15 × 0.10	0.15 × 0.20 × 0.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	16.805(5)	9.149(3)
b (Å)	13.759(4)	18.644(5)
c (Å)	17.108(5)	13.695(4)
β (°)	114.457(5)	106.381(5)
V (Å^3)	3600.5(17)	2241.3(11)
$D_{\text{calc.}}$ (g cm^{-3})	1.548	1.696
Absorption coefficient (mm^{-1})	4.072	5.236
Z	4	4
$F(000)$	1656	1120
Reflections collected	14 699	9227
Independent reflections	6311	3951
Number of parameters	428	253
R, R_w [$I > 2\sigma(I)$]	0.0528, 0.1001	0.0307, 0.0567
Goodness-of-fit on F^2	0.903	0.982



Scheme 1. R=H, M=Ph$_3$Ge (**1**) and (**6**); R=H, M=PhMe$_2$Si (**2**) and (**7**); R=H, M=^{i}Pr$_3$Si (**3**) and (**8**); R=H, M=Me$_3$Si (**4**) and (**9**); R=Me, M=Me$_3$Si (**5**) and (**10**).

and **5**, some substituted pyrazoles from the decomposition of bis(pyrazol-1-yl)methane have also been isolated.

When these ligands were treated with W(CO)$_5$(THF) under the same experimental conditions as the reaction of Ph$_3$SnCHPz$_2$ with W(CO)$_5$(THF) [15], only heterobimetallic complexes **6**–**10** were isolated. The analogous oxidative addition reaction of the Ge–C or Si–C bond to W(0) center did not take place, which may be related to the lower reactivity of the Ge–C and Si–C bonds, compared with the Sn–C bond [16]. In addition, the analogous oxidative addition products of the Ge–C and Si–C bonds to W(0) center are possibly unstable owing to the lower stability of the W–Ge and W–Si bonds, compared with the W–Sn bond [17], as well as the interior strain of the oxidative addition products. It is also noted that the reaction of ligands **3**–**5** with W(CO)$_5$(THF) gave some W(CO)$_5$L (L = substituted pyrazole) complexes with the exception of the heterobimetallic complexes. These pyrazole derivatives should be the results of the reaction of W(CO)$_5$(THF) with pyrazoles from the decomposition of ligands. Complexes **6**–**10** in solid were stable in air, but they, especially complexes **7** and **10**, were sensitive to air in solution. All complexes were insoluble in alkanes and ether, but soluble in chlorinated solvents and acetone.

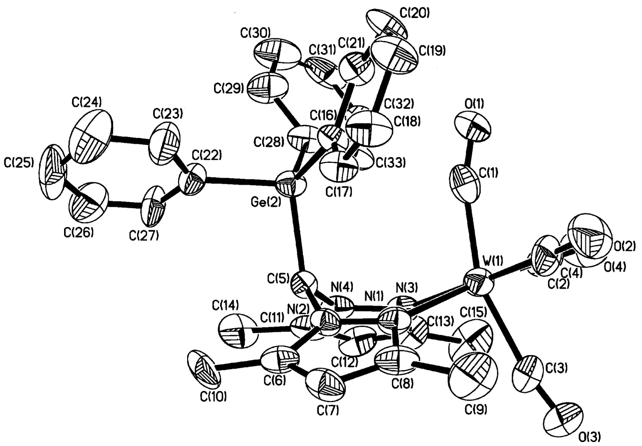


Fig. 1. The molecular structure of complex **6**. The thermal ellipsoids are drawn at the 30% probability level.

Spectroscopy investigation has been taken to characterize these complexes. Their IR spectra were similar, 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 (N–N represents substituted bis(pyrazol-1-yl)methane) [18], indicating a typical *cis*-tetracarbonyl arrangement. Their ^{1}H-NMR spectra showed the expected proton signals, and were similar to those of the corresponding free ligands, being only slightly shifted downfield. In addition, two equivalents pyrazole rings were also observed.

3.2. The description of crystal structures

The crystal structure of complex **6** determined by X-ray structure analyses is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. Ligand **1** acts as a chelating bidentate ligand in this complex. In addition, the triphenylgermyl group on the methine carbon lies in the axial position so as to reduce the steric repulsion with the methyl groups on the five-position of pyrazole rings. The metallacyclic ring W–N–N–C–N–N adopts a boat conformation, similar to that reported in CH$_2$(3,5-Me$_2$-4-ClPz)$_2$W(CO)$_4$ [18] and CH$_2$(3-MeS-5-Bu^{t}Pz)$_2$W(CO)$_4$ [19]. The central metal of W is six-coordinate with a quasi-octahedral coordination geometry. The average W–N distance is 2.25 Å, which is comparable to the corresponding values found in other W(0) complexes with poly(azol-1-yl)alkanes or poly(pyrazol-1-yl)silane (such as average 2.255 Å in CH$_2$(3,5-Me$_2$-4-ClPz)$_2$W(CO)$_4$ [18], 2.2575(5) Å in CH$_2$(3-MeS-

Table 2
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths			
W(1)–C(1)	1.976(16)	N(2)–C(5)	1.433(12)
W(1)–C(3)	2.034(15)	C(5)–N(4)	1.442(12)
W(1)–N(1)	2.247(9)	C(1)–O(1)	1.185(14)
W(1)–N(3)	2.253(11)	C(3)–O(3)	1.134(13)
Ge(2)–C(28)	1.957(11)	Ge(2)–C(5)	2.031(10)
Bond angles			
C(4)–W(1)–C(1)	79.3(5)	C(16)–Ge(2)–C(28)	113.2(5)
C(2)–W(1)–C(1)	82.9(6)	C(22)–Ge(2)–C(28)	105.8(6)
C(2)–W(1)–C(3)	85.0(6)	C(16)–Ge(2)–C(5)	116.8(4)
C(1)–W(1)–C(3)	160.0(5)	C(22)–Ge(2)–C(5)	100.7(5)
C(4)–W(1)–N(1)	174.6(5)	C(28)–Ge(2)–C(5)	112.3(5)
C(2)–W(1)–N(1)	97.1(5)	O(1)–C(1)–W(1)	163.9(11)
C(1)–W(1)–N(1)	105.6(4)	O(2)–C(2)–W(1)	177.8(13)
C(3)–W(1)–N(1)	91.7(5)	O(3)–C(3)–W(1)	168.5(14)
C(2)–W(1)–N(3)	176.9(5)	O(4) C(4)-W(1)	178.9(12)
C(1)–W(1)–N(3)	96.4(4)	N(2)–C(5)–N(4)	111.1(8)
C(3)–W(1)–N(3)	96.5(5)	N(2)–C(5)–Ge(2)	114.2(7)
N(1)–W(1)–N(3)	80.2(4)	N(4)–C(5)–Ge(2)	120.4(7)

5-Bu^{t}Pz)$_2$W(CO)$_4$ [19], 2.284 Å in MeSi(3,5-Me$_2$Pz)$_3$W(CO)$_3$ [13a] and 2.265 Å in CH$_2$(3,5-Me$_2$Tz)$_2$W(CO)$_4$ [20], Pz = pyrazole and Tz = 1,2,4-triazole, respectively). The angle ∠N–W–N is 80.2(4)°, which is similar to that in CH$_2$(3,5-Me$_2$-4-ClPz)$_2$W(CO)$_4$ (79.4(2)°) [18], but slightly larger than that in CH$_2$(3-MeS-5-Bu^{t}Pz)$_2$W(CO)$_4$ (76.1(1)°) [19]. Moreover, the angle ∠C(1)–W(1)–C(3) of 160.0(5)° in **6** is also similar to that in CH$_2$(3-MeS-5-Bu^{t}Pz)$_2$W(CO)$_4$ (160.4(3)°), but smaller than that in CH$_2$(3,5-Me$_2$-4-ClPz)$_2$W(CO)$_4$ (169.0(3)°), indicating that the steric repulsion of the ligand with carbonyls in **6** and CH$_2$(3-MeS-5-Bu^{t}Pz)$_2$W(CO)$_4$ may be more bigger than that in CH$_2$(3,5-Me$_2$-4-ClPz)$_2$W(CO)$_4$. Two *cis*-carbonyl groups in **6** are markedly distorted with the angles ∠W(1)–C(1)–O(1) of 163.9(11)° and ∠W(1)–C(3)–O(3) of 168.5(14)°, owing to the steric repulsion between the ligand with two *cis*-carbonyls. It is also noteworthy that some angles around the Ge(2) and C(5) atoms (such as the angles ∠C(22)–Ge(2)–C(5) of 100.7(5)° and ∠N(4)–C(5)–Ge(2) of 120.4(7)°) significantly deviate from the tetrahedral geometry of the sp^3-hybridized Ge(2) and C(5) atoms, possibly owing to the repulsion among phenyl groups or between phenyl groups with pyrazole rings.

The crystal structure of complex **9** determined by X-ray structure analyses is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. The overall view of **9** is analogous to that of complex **6**. Ligand **4** also acts as a chelating bidentate ligand, and the trimethylsilyl group on the methine carbon lies in the axial position. The metallacyclic ring W–N–N–C–N–N adopts a boat conformation, similar to that in complex **6**. The average W–N bond distance is 2.269(4) Å, which is also compared with that in complex **6** (2.25 Å). However, some remarkable structural difference exists between complexes **9** and **6** owing to the smaller steric hindrance of trimethylsilyl group in complex **9** than that of triphenylgermyl group in complex **6**. The angle ∠C(15)–W(1)–C(13) of 162.4(2)° in complex **9**, which is slightly larger than the corresponding one in complex **6** (∠C(1)–W(1)–C(3), 160.0(5)°). Two *cis*-carbonyl groups in complex **9** are still distorted, but the angles ∠W(1)–C(15)–O(4) of 166.8(5)° and ∠W(1)–C(13)–O(2) of 169.8(5)° in complex **9** are larger than the corresponding angles in complex 6 (163.9(11)° and 168.5(14)°, respectively). In addition, some angles around the Si(1) and C(6) atoms (such as the angles ∠C(18)–Si(1)–C(16) of 118.4(3)° and ∠N(1)–C(6)–Si(1) of 118.1(4)°) still significantly deviate from the tetrahedral geometry of the *sp^3* hybridized Si(1) and C(6) atoms owing to the steric repulsion between trimethylsilyl group with pyrazole rings.

Table 3
Selected bond lengths (Å) and angles (°) for **9**

Bond lengths			
W(1)–C(15)	2.008(7)	O(3)–C(14)	1.163(7)
W(1)–C(13)	2.022(6)	O(4)–C(15)	1.155(6)
W(1)–N(4)	2.268(4)	O(1)–C(12)	1.156(7)
W(1)–N(2)	2.270(4)	O(2)–C(13)	1.149(6)
Si(1)–C(16)	1.857(6)	N(3)–C(6)	1.456(7)
Si(1)–C(6)	1.947(5)	N(1)–C(6)	1.445(6)
Bond angles			
C(14)–W(1)–C(15)	79.9(3)	N(3)–N(4)–W(1)	124.4(3)
C(14)–W(1)–C(13)	84.1(3)	N(1)–C(6)–N(3)	111.6(4)
C(15)–W(1)–C(13)	162.4(2)	N(1)–C(6)–Si(1)	118.1(4)
C(14)–W(1)–N(4)	177.1(2)	N(3)–C(6)–Si(1)	116.8(4)
C(15)–W(1)–N(4)	103.0(2)	N(2)–N(1)–C(2)	110.4(4)
C(14)–W(1)–N(2)	98.4(2)	N(2)–N(1)–C(6)	122.9(4)
C(12)–W(1)–N(2)	173.6(2)	C(2)–N(1)–C(6)	126.7(4)
C(15)–W(1)–N(2)	96.5(2)	C(4)–N(2)–N(1)	105.7(4)
N(4)–W(1)–N(2)	80.55(15)	O(1)–C(12)–W(1)	177.4(6)
C(18)–Si(1)–C(16)	118.4(3)	O(2)–C(13)–W(1)	169.8(5)
C(17)–Si(1)–C(16)	107.3(3)	O(3)–C(14)–W(1)	177.2(6)
C(17)–Si(1)–C(6)	104.1(3)	O(4)–C(15)–W(1)	166.8(5)

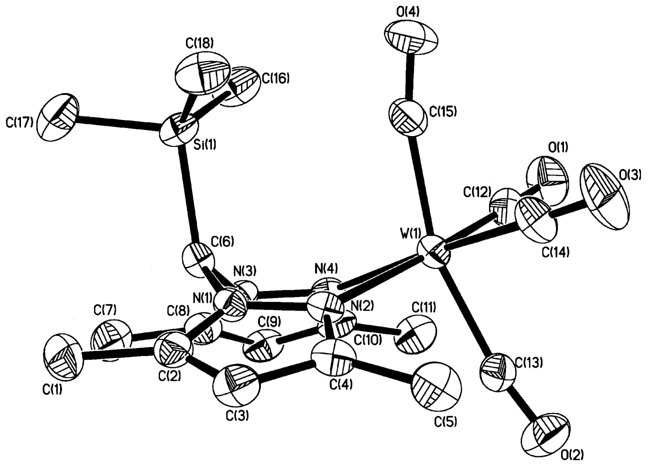


Fig. 2. The molecular structure of complex **9**. The thermal ellipsoids are drawn at the 30% probability level.

In conclusion, the modification of bis(pyrazol-1-yl)methane by substitution of organogermyl or organosilyl groups on the methine carbon atom was successfully carried out. The reactions of these ligands with W(CO)$_5$(THF) result in a series of new heterobimetallic complexes, which are confirmed by X-ray structure analyses, indicating that bis(pyrazol-1-yl)methanes act as chelating bidentate ligands in these complexes, and organometallic groups lie in the axial position of the methine carbon.

4. Supplementary information

Crystallographic data (CIF files) for the structures of complexes **6** and **9** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no.181934 for **6** and CCDC no.181935 for **9**, 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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References

[1] S. Trofimenko, J. Am. Chem. Soc. 70 (1970) 5118.
[2] S. Julia, J.M. Del Mazo, L. Avila, J. Elguero, Org. Prep. Proceed. Int. 16 (1984) 299.
[3] S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115.
[4] P.K. Byers, A.J. Canty, R.T. Honeyman, Adv. Organomet. Chem. 34 (1992) 1.
[5] L.F. Tang, Z.H. Wang, J.T. Wang, Youji Huaxue 19 (1999) 442.
[6] Selected recent examples:
(a) D.L. Reger, C.A. Little, M.D. Smith, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, I.A. Guzei, Inorg. Chem. 41 (2001) 19;
(b) D.L. Reger, J.E. Collins, W.A. Flomer, A.L. Rheingold, C. Incarvito, L.A. Guzei, Polyhedron 20 (2001) 2491;
(c) L.F. Tang, Z.H. Wang, W.L. Jia, Y.M. Xu, J.T. Wang, Polyhedron 19 (2000) 381;
(d) C. Pettinari, M. Pellei, A. Cingolani, D. Martini, A. Drozdov, S. Troyanov, W. Panzeri, A. Mele, Inorg. Chem. 38 (2001) 5777;
(e) D.L. Reger, J.E. Collins, M.A. Mattews, A.L. Rheingold, L.M. Liable-Sands, I.A. Guzei, Inorg. Chem. 36 (1997) 6266;
(f) D.L. Reger, J.E. Collins, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, Inorg. Chem. 36 (1997) 345.
[7] Selected recent examples:
(a) B. Binotti, G. Bellachioma, G. Cardaci, A. Macchioni, C. Zuccaccia, E. Foresti, P. Sabatino, Organometallics 21 (2002) 346;
(b) S.C. Lawrence, M.E.G. Skinner, J.C. Green, P. Mountford, Chem. Commun. (2001) 705;
(c) L.D. Field, B.A. Messerle, L. Soler, I.E. Buys, T.W. Hambley, J. Chem. Soc. Dalton Trans. (2001) 1959;
(d) L. Zhang, L.F. Tang, Z.H. Wang, M. Du, M. Julve, F. Lloret, J.T. Wang, Inorg. Chem. 40 (2001) 3619;
(e) N. Arroyo, F. Gómez-de la Torre, F.A. Jalón, B.R. Manzano, B. Moreno-Lara, A.M. Rodríguez, J. Organomet. Chem. 603 (2000) 174;
(f) S. Tsuji, D.C. Swenson, R.F. Jordan, Organometallics 18 (1999) 4758;
(g) D.L. Reger, J.E. Collins, A.L. Rheingold, L.M. Liable-Sands, Inorg. Chem. 38 (1999) 3235;
(h) D.L. Reger, J.E. Collins, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, Organometallics 16 (1997) 349;
(i) I.K. Dhawan, M.A. Bruck, B. Sching, C. Grittini, J.H. Enmark, Inorg. Chem. 34 (1995) 3801.
[8] (a) D.L. Reger, T.C. Grattan, K.J. Brown, C.A. Little, J.J.S. Lamba, A.L. Rheingold, R.D. Sommer, J. Organomet. Chem. 607 (2000) 120;
(b) D.L. Reger, J.E. Collins, D.L. Jameson, R.K. Castellano, Inorg. Synth. 32 (1998) 63;
(c) C. Titze, J. Hermann, H. Vahrenkamp, Chem. Ber. 128 (1995) 1095.
[9] (a) B.S. Hammes, C.J. Carrano, Inorg. Chem. 38 (1999) 3562;
(b) T.C. Higgs, C.J. Carrano, Inorg. Chem. 36 (1997) 291;
(c) A. Otero, J. Fernández-Baeza, J. Tejeda, A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, A. Lara-Sánchez, M. Fernández-López, J. Chem. Soc. Dalton Trans. (2000) 2367;
(d) A. Otero, J. Fernández-Baeza, A. Antiñolo, F. Carrillo-Hermosilla, J. Tejeda, E. Díez-Barra, A. Lara-Sanchez, L. Sanchez-Barba, I. López-Solera, M.R. Ribeiro, J.M. Campos, Organometallics 20 (2001) 2428;
(e) A. Beck, B. Weibert, N. Burzlaff, Eur. J. Inorg. Chem. (2001) 521;
(f) N. Burzlaff, I. Hegelmann, B. Weibert, J. Organomet. Chem. 626 (2001) 16.
[10] (a) B.S. Hammes, C.J. Carrano, Inorg. Chem. 40 (2001) 919;
(b) B.S. Hammes, C.J. Carrano, Chem. Commun. (2000) 1635;
(c) T. Astley, M.A. Hitchman, B.W. Skelton, A.H. White, Aust. J. Chem. 50 (1997) 145;
(d) R. Alsfasser, H. Vahrenkamp, Inorg. Chim. Acta 209 (1993) 19;
(e) A.J. Canty, R.J. Honeyman, J. Organomet. Chem. 387 (1990) 247.
[11] M. Müller, E. Lork, R. Mews, Angew. Chem. Int. Ed. 40 (2001) 1247.
[12] W. Kläui, M. Berghahn, G. Rheinwald, H. Lang, Angew. Chem. Int. Ed. 39 (2000) 2464.
[13] (a) E.E. Pullen, D. Rabinovich, C.D. Incarvito, T.E. Concolino, A.L. Rheingold, Inorg. Chem. 39 (2000) 1561;
(b) L.M. Richburg, J.A. Farouq, C.D. Incarvito, A.L. Rheingold, D. Rabinovich, Polyhedron 19 (2000) 1815;
(c) R.T. Stibrany, S. Knapp, J.A. Potenza, H.J. Schugar, Inorg. Chem. 38 (1999) 132.
[14] (a) A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, J. Fernández-Baeza, M. Fernández-López, A. Lara-Sánchez, A. Moreno, A. Otero, A.M. Rodriguez, J. Tejeda, J. Chem. Soc. Dalton Trans. (1998) 3737;
(b) E. Díez-Barra, A. De la Hoz, A. Sánchez-Migallón, J. Tejeda, J. Chem. Soc Perkin Trans. 1 (1993) 1079;
(c) A.R. Katritzky, A.E. Abdel-Rahman, D.E. Leahy, O.A. Schwarz, Tetrahedron 39 (1983) 4133.
[15] L.F. Tang, W.L. Jia, D.T. Song, Z.H. Wang, J.F. Chai, J.T. Wang, Organometallics 21 (2002) 445.
[16] A.G. MacDiarmid, Organometallic Compounds of the Group IV Elements, Dekker, New York, 1968.
[17] G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry, vol. 6, Pergamon, Oxford, 1982, p. 1062.
[18] L.F. Tang, Z.H. Wang, Y.M. Xu, J.T. Wang, H.G. Wang, X.K. Yao, Polyhedron 18 (1999) 2383.
[19] L.F. Tang, W.L. Jia, Z.H. Wang, J.T. Wang, J. Organomet. Chem. 649 (2002) 152.
[20] L.F. Tang, Z.H. Wang, J.F. Chai, X.B. Leng, J.T. Wang, H.G. Wang, J. Organomet. Chem. 642 (2002) 179.