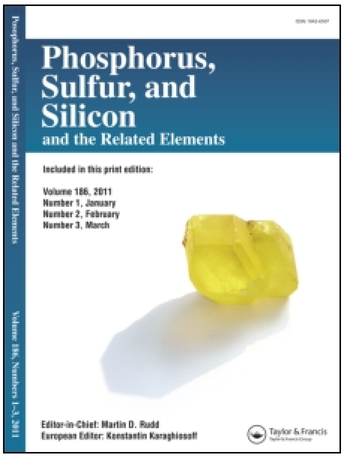

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ORGANOBISMUTH HOMOCYCLES $(RBi)_n$ AND HETEROCYCLES $(RBiS)_2$

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*The homocycles $(RBi)_n$ $(n = 3–5)$ react with $MeC_5H_4Mn(CO)_2(thf)$ (thf = tetrahydrofuran) or $Fe_2(CO)_9$ to give $Bi_2[Mn(CO)_2MeC_5H_4]_3$ (**1**) or $Bi_2Fe_3(CO)_9$ (**3**). Reaction of R_4Bi_2 $(R = Me_3SiCH_2)$ with $Fe_2(CO)_9$ in toluene gives $R_2Bi_2Fe_2(CO)_8$ (**4**) and $R_4Bi_2Fe(CO)_4$ (**5**). The heterocycles $(RBiS)_2$(R = 2-$(Me_2NCH_2)C_6H_4$ (**6**), 2, 6-$(Me_2NCH_2)_2C_6H_4$ (**7**) are formed by reaction of the corresponding dihalides $RBiCl_2$ with Na_2S. The reaction of $(RBiS)_2$(R = 2-$(Me_2NCH_2)C_6H_4$) with $W(CO)_5(thf)$ leads to $(RBiS)_2[W(CO)_5]_2$ (**8**).*

Keywords: Bismuth; heterocycles; sulfur; transition metal complexes

Organobismuth homocycles $(RBi)_n$ are known for $R = (Me_3Si)_2CH$,[1] n = 3, 4; $R = (Me_3Si)_3Si$, $(Me_3C)_3Si$,[2,3] n = 4; $R = Me_3SiCH_2$[4], Me_3CCH_2,[5] n = 3, 5; and R = 2-$(Me_2NCH_2)C_6H_4$, n = 3, 4.[6] A common feature of the majority of bismuth ring systems is the participation in ring-ring equilibria with preference in solution for trimers rather than tetramers ($R = (Me_3Si)_2CH$,[1] 2-$(Me_2NCH_2)C_6H_4$[6]) or pentamers ($R = Me_3SiCH_2$,[4] Me_3CCH_2[5]). Reactions of bismuth homocycles $(RBi)_n$ with $W(CO)_5(thf)$ lead to dibismuthene complexes, $(RBi)_2\{W(CO)_5\}_2$ and $(RBi)_2W(CO)_5$ ($R = Me_3CCH_2$, Me_3SiCH_2)[4,5] or to $RBi[W(CO)_5]_2$ (R = 2-$(Me_2NCH_2)C_6H_4$)[6] a complex with the bismuthinidene ligand.

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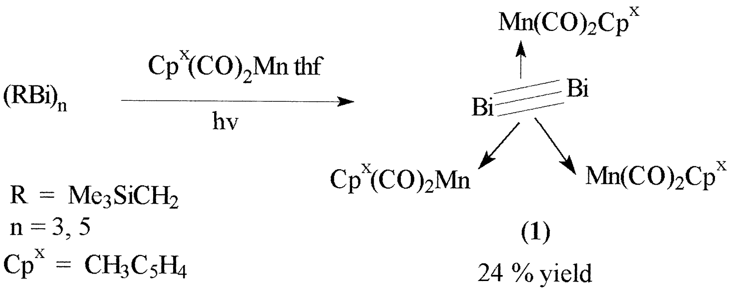
An example for an organobismuth heterocycle $(RBiE)_n$, E = chalcogen with a known structure is $(RBiO)_2$ R = $\{2,4\text{-}[(Me_3Si)_2CH]_2\text{-}6\text{-}(Me_3Si)_3C\}\text{-}C_6H_2$.[11] We report here on reactions of monocycles, $(RBi)_n$ and a dibismuthine, $(R_2Bi)_2$ with transition metal carbonyl complexes, and on the formation and coordination chemistry of two novel bismuth heterocycles $(RBiS)_2$(R = $2\text{-}(Me_2NCH_2)C_6H_4$, $2,6\text{-}(Me_2NCH_2)_2C_6H_4$).

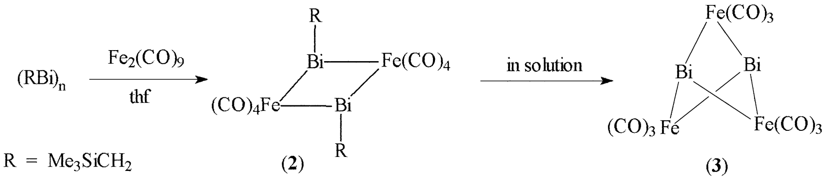
RESULTS AND DISCUSSION

Irradiation of a thf solution of $(Me_3SiCH_2Bi)_n$, n = 3, 5 and $MeC_5H_4Mn(CO)_2(thf)$ (1:1 molar ratio) for 10 min with an UV-lamp (TQ 150 Mercury lamp) leads to substitution of the alkyl substituents and formation of the dibismuth complex $Bi_2[Mn(CO)_2MeC_5H_4]_3$(**1**) (Eq. 1). Removal of the solvent and extraction with petroleum ether gave dark brown crystals of **1** in 24% yield. The identity of **1** was proved by NMR-spectroscopy and by x-ray diffraction, through measurement of the unit cell. **1** was prepared before by Huttner et al. from $\{[Cp^xMn(CO)_2]_2H\}^-$ and $BiCl_3$.[8]



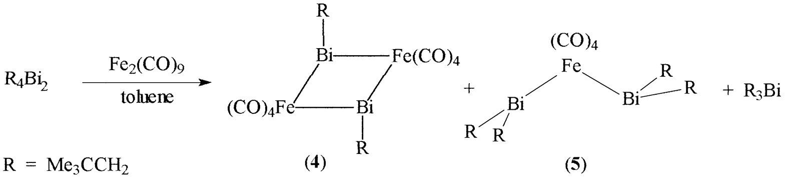
(1)

The reaction of $(RBi)_n$ (n = 3–5, R = Me_3SiCH_2) with $Fe_2(CO)_9$ (5:1 molar ratio) in toluene at 0°C for 2.5 h gives the dark red heterocycle $[RBiFe(CO)_4]_2$ (**2**, 45% yield) which further reacts with removal of the alkyl groups and formation of $Bi_2Fe_3(CO)_9$ (**3**) (Eq. 2). **2** was characterized by ^{1}H-NMR and mass spectra. The identity of **3** was proven by a x-ray structure analysis at −100°C and comparison with reported data.[9]



(2)

The reaction of R_4Bi_2 ($R = Me_3CCH_2$) with $Fe_2(CO)_9$ (1:1 molar ratio) in toluene at 25°C for 24 h, gives a mixture of the dark red heterocycle $[RBiFe(CO)_4]_2$ (**4**, 48% yield) and $R_4Bi_2Fe(CO)_4$ (**5**, 32% yield) (Eq. 3). **4** and **5** were characterized by ^1H- and ^{13}C-NMR spectra, mass spectra and x-ray diffraction. Known analogues of **4** are *cyclo*-$[RBiFe(CO)_4]_2$ (R = Me,[12] Ph,[9] i-Bu[13]).



(3)

Crystals of **4** and **5** were obtained by fractionated crystallization from toluene. The molecular structures of **4** and **5** are shown in Figure 1. **4** exhibits a central planar Bi_2Fe_2 core where the alkyl groups are in *trans*-positions. **5** consists of two R_2Bi fragments coordinated to $Fe(CO)_4$.

The heterocycles $(RBiS)_2$ [R = 2-$(Me_2NCH_2)C_6H_4$ (**6**), 50.2% yield; R = 2, 6-$(Me_2NCH_2)_2C_6H_3$ (**7**) 80%] are formed by reactions of 2,6-$(Me_2NCH_2)_2C_6H_3BiCl_2$[10] or 2-$(Me_2NCH_2)C_6H_4BiCl_2$ with Na_2S in CH_3CN or with Na_2S in liquid NH_3. The novel heterocycles

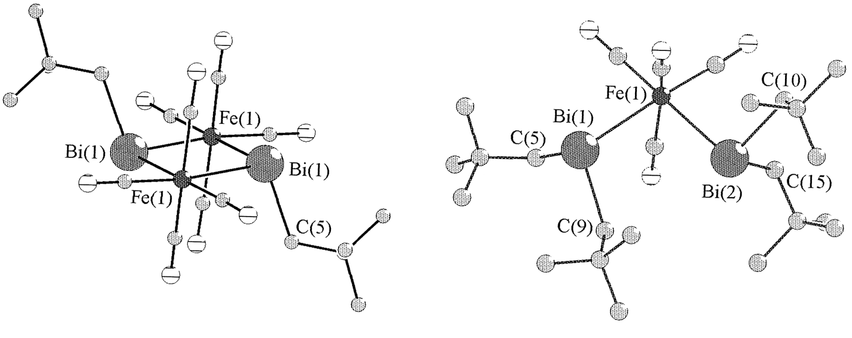


FIGURE 1 Structures of **4** (left) and **5** (right). Selected bond lengths (Å) and angles (°): (**4**): Bi(1)—C(5) 2.316(16), Bi(1)—Fe(1) 2.792(3), Fe(1)—C(2) 1.753(18); C(5)—Bi(1)—Fe(1) 1.045(5), C(5)—Bi(1)—Fe(1′) 1.017(5), Fe(1)—Bi(1)—Fe(1′) 96.90(6), C(3)—Fe(1)—Bi(1′) 78.8(5), C(4)—Fe(1)—Bi(1′) 84.3(5), Bi(1)—Fe(1)—Bi(1′) 83.10(6). (**5**): Bi(1)—Fe(1) 2.8001(17), Bi(2)—Fe(1) 2.7328(16), Bi(1)—C(10) 2.234(9), Bi(1)—C(5) 2.289(9), Bi(2)—C(20) 2.236(9), Bi(2)—C(15) 2.303(10); C(10)—Bi(1)—C(5) 91.8(3), C(10)—Bi(1)—Fe(1) 105.1(3), C(5)—Bi(1)—Fe(1) 96.5(2), C(20)—Bi(2)—C(15) 95.1(3), C(20)—Bi(2)—Fe(1) 94.2(3), C(15)—Bi(2)—Fe(1) 100.3(3), Bi(2)—Fe(1)—Bi(1) 91.32(5).

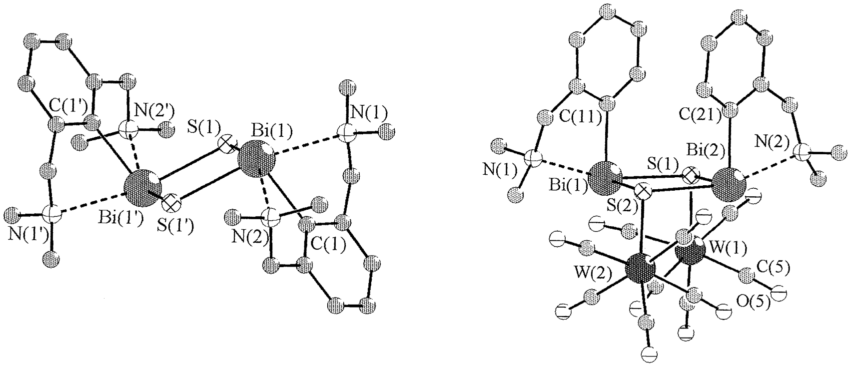


FIGURE 2 Structures of **7** (left) and **8** (right). Selected bond lengths (Å) and angles (°): **7**, Bi(1)—S(1) 2.578(4) Bi(1)—S(1′) 2.577(3), Bi(1)—N(1) 2.834(6) Bi(1)—N(2) 2.851(5). **8**, Bi(1)—N(1) 2.523(13), Bi(2)—N(2) 2.575(13), Bi(1)—S(2) 2.559(4), Bi(1)—S(1) 2.747(4), Bi(2)—S(1) 2.561(4), Bi(2)—S(2) 2.758(4), W(1)—S(1) 2.599(3), W(2)—S(2) 2.586(3).

are stable in air, soluble in chloroform and toluene. They were characterized by NMR and MS methods. The reaction of **6** with $W(CO)_5$thf in thf gives the red complex $(RBiS)_2[W(CO)_5]_2$ [R = 2-$(Me_2NCH_2)C_6H_4$) (**8**), 44% yield]. The crystal structures of **7** and **8**·C_6H_6 were determined by x-ray diffraction (Figure 2). The structures feature planar Bi_2S_2 rings with the aryl groups in *trans* (**7**) or *cis* (**8**) positions. All amino groups are coordinated to the Bi centers.

In **8**·C_6H_6 the $W(CO)_5$ fragments are coordinated to the S atoms The benzene molecules occupy the free space between molecules of **8** showing no interactions with neighboring groups.

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