

Low-Valent Organobismuth Compounds with Intramolecular Coordination: *cyclo*-R₃Bi₃, *cyclo*-R₄Bi₄, RBi[W(CO)₅]₂, and R₄Bi₂ [R = 2-(Me₂NCH₂)C₆H₄]

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The cyclobismuthanes R_nBi_n [R = 2-(Me₂NCH₂)C₆H₄; n = 3 (**1a**), 4 (**1b**)] have been synthesised by reduction of RBiCl₂ with Na in liquid NH₃ or by reaction of R₂BiCl with LiAlH₄ in Et₂O. The reaction of **1a/b** with W(CO)₅·THF afforded the bismuthinidene complex RBi[W(CO)₅]₂ (**2**). R₂BiCl reacts with Mg in THF to give the dibismuthane R₄Bi₂ (**3**). Single-

crystal X-ray structure analyses of **1b**, **2**, and **3** reveal intramolecular coordination of the pendant CH₂NMe₂ groups to the bismuth atom.

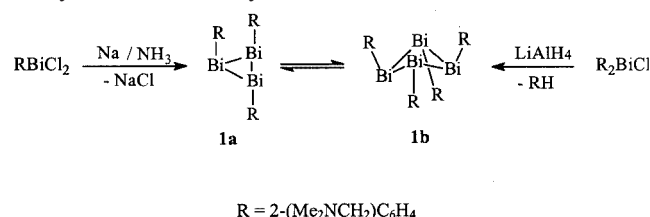
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Introduction

Relativistic effects^[1] are expected to favour the lower oxidation states of bismuth and to stabilize singlet bismuthinidenes RBi. Known examples of Bi^I derivatives^[2] are the dibismuthenes RBi=BiR [R = 2,4,6-[(Me₃Si)₂CH]₃-C₆H₂,^[3,4] 2,6-(Me₃C₆H₂)₂C₆H₃,^[5] *cyclo*-R_nBi_n oligomers [n = 3, 4; R = (Me₃Si)₂CH,^[6] (Me₃Si)₃Si,^[7] and n = 5; R = Me₃SiCH₂,^[8]], and a complex of R₂Bi₂ (R = Me₃SiCH₂), i.e. [(RBi=BiR){W(CO)₅}]₂.^[8] Monomeric bismuthinidenes have not been isolated, but RBi groups have been incorporated into *cyclo*-[RBiFe(CO)₄]₂ (R = Me,^[9] Ph,^[10] *i*Bu^[11]). The oxidation state of bismuth in these complexes is, however, ambiguous. Bismuth(II) compounds are known as dibismuthanes R₄Bi₂.^[12–16] All low-valent organobismuth compounds tend to decompose with formation of elemental Bi and R₃Bi, unless protected by bulky groups or stabilized by complexation. Usually, monodentate alkyl or aryl ligands are used for steric protection. We expected additional stabilization with substituents containing a pendant donor group available for internal coordination at Bi. Examples of compounds with internal coordination at Bi^{III} are the 2-(dimethylaminomethyl)phenyl derivatives R₂BiCl,^[17] RBiI₂,^[17] or R₃Bi^[18] [R = 2-(Me₂NCH₂)C₆H₄]. We report here on arylbismuth(I) and -bismuth(II) compounds with internal nitrogen coordination of the 2-(Me₂NCH₂)C₆H₄ ligand.

Results and Discussion

Both the reduction of RBiCl₂ with Na in liquid ammonia at –70 °C and the reaction of R₂BiCl with LiAlH₄ in Et₂O resulted in isolation of a black-green product (49 and 65% yield, respectively), which was identified as *cyclo*-R_nBi_n (**1**) by elemental analysis. A possible intermediate for the latter reaction is R₂BiH, which gives **1** by elimination of RH (Scheme 1). Three- (**1a**) and four-membered (**1b**) R_nBi_n rings were identified by NMR spectroscopy in solution, whereas the crystals of **1** consist of the four-membered ring **1b**, the structure of which was established by a single-crystal X-ray diffraction study.



Scheme 1

Crystals of **1b** are stable for a long time at room temperature under argon. Solutions of **1** in hydrocarbon solvents are more sensitive, however, and in sealed tubes at 25 °C the R_nBi_n rings decompose after several hours to R₄Bi₂ (**2**) and metallic bismuth. At –28 °C, however, they are stable for weeks. The colour of the crystals is dark green, while solutions in hydrocarbon solvents are dark red. Variable-temperature and concentration-dependent ¹H NMR spectra in C₆D₅CD₃ enable the rings **1a** and **1b** to be easily distinguished. Two sets of signals (1:2 intensity ratio) for the 2-(dimethylaminomethyl)phenyl group could be assigned to the *cyclo*-trimer **1a** in the *cis-trans* configuration. For the tetramer **1b** only one set of signals was observed, corre-

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sponding to the *all-trans* configuration with equivalent substituents. Each set consists of two singlets, for the CH_3 and the CH_2 protons respectively, and a group of signals for the spin system of the aromatic protons. The ^1H NMR spectroscopic data suggest rapid reversible dissociation of the pendant CH_2NMe_2 arm in solution.

The relative concentration of **1a** and **1b** in solution depends on the temperature and the absolute concentration of the ring systems. Lower temperatures and higher concentrations favour the four-membered ring **1b** at the expense of the three-membered ring **1a**. Similar solution equilibria following the principle of Le Chatelier were also reported for *cyclo*- $[(\text{Me}_3\text{Si})_2\text{CH}]_n\text{Bi}_n$ ($n = 3, 4$)^[6] and *cyclo*- $(\text{Me}_3\text{SiCH}_2)_n\text{Bi}_n$ ($n = 3, 5$).^[8] In contrast to the *cyclo*- $(\text{Me}_3\text{SiCH}_2)_n\text{Bi}_n$ system, where the equilibrium between the trimer and the pentamer is frozen at -15°C , the equilibrium between **1a** and **1b** occurs even at -45°C . The equilibrium constant $K = [\mathbf{1a}]^4/[\mathbf{1b}]^3$ is 36 ± 5 mol/L at 0°C .

Additional signals for species containing equivalent R groups were observed at high dilution and high temperature. These signals can be assigned to $[\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4]\text{Bi}$ or $[\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4]_2\text{Bi}_2$.

Single crystals of **1b** suitable for X-ray diffraction studies were obtained by cooling a petroleum ether solution of a mixture of the rings to -28°C . The molecular structure is depicted in Figure 1. The structure consists of a folded four-membered bismuth ring with the $\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4$ substituents in the *all-trans* configuration, consistent with the NMR spectroscopic data in solution. The Bi–Bi dihedral angles are 107.9 and 109.4° , respectively. The Bi–Bi bond lengths [$3.0095(16)$ – $3.0221(16)$ Å] compare well with the analogous values found in $[(\text{Me}_3\text{Si})_2\text{CH}]_4\text{Bi}_4$ [$2.970(5)$ – $3.044(2)$ Å]^[6] and $[(\text{Me}_3\text{Si})_3\text{Si}]_4\text{Bi}_4$ [$3.013(1)$ – $3.028(1)$ Å].^[7] The Bi–C bonds [$2.24(3)$ – $2.30(3)$ Å] are shorter than the corresponding bonds in $[(\text{Me}_3\text{Si})_2\text{CH}]_4\text{Bi}_4$ [$2.33(2)$ – $2.39(2)$ Å].^[6] The $\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4$ groups act as bidentate chelating ligands with weak N→Bi intramolecular interactions [$2.97(3)$ – $3.05(2)$ Å] *trans* to a Bi–Bi bond. The N–Bi distances lie between the sum of the covalent (2.2 Å) and van der Waals radii (3.7 Å) of N and Bi. Comparable interactions were observed in $[\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4]_3\text{Bi}$ [Bi–N $3.04(2)$ – $3.11(3)$ Å]^[17] and $[\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4]_2\text{BiCl}$ [Bi–N $2.570(5)$, $3.047(5)$ Å].^[18] The orientation of the aryl groups leads to a propeller-like arrangement. The geometry about the bismuth atoms is distorted pseudo-trigonal-bipyramidal with one of the neighbouring bismuth atoms and the nitrogen atom in axial positions [Bi–Bi–N $158.7(6)$ – $163.5(5)^\circ$]. The second bismuth atom, the *ipso*-carbon atom and the lone pair of electrons are in equatorial positions. The Bi–Bi–Bi angles [$76.79(4)$ – $79.51(4)^\circ$] are similar to those found in *cyclo*- $[(\text{Me}_3\text{Si})_2\text{CH}]_4\text{Bi}_4$ [$78.97(8)$ – $79.93(6)^\circ$].^[6] The transannular Bi⋯Bi distances in **1b** [$3.753(1)$, $3.857(1)$ Å] and *cyclo*- $[(\text{Me}_3\text{Si})_2\text{CH}]_4\text{Bi}_4$ ^[6] [3.834 , 3.859 Å] are also similar.

Coordination of the bismuthinidene $[\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4]\text{Bi}$ was achieved by treatment of the **1a/1b** mixture with $\text{W(CO)}_5\cdot\text{THF}$ in at 0°C affording the complex $\text{RBi[W(CO)}_5]_2$ (**2**) [Equation (1)].

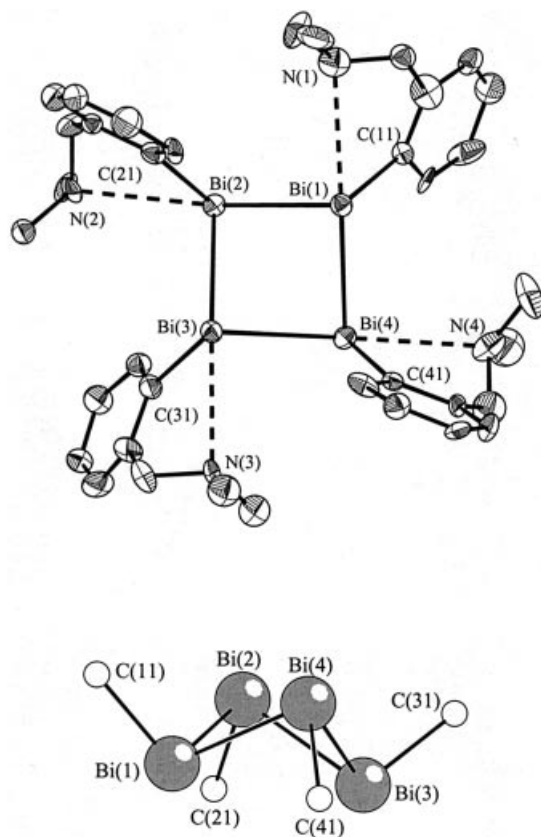
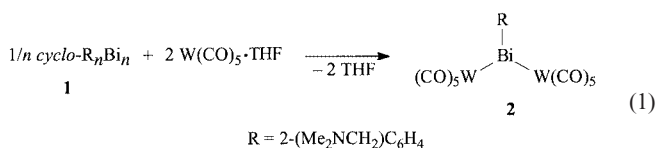


Figure 1. Structure of **1b** in the crystal; the ellipsoids represent 40% probability; selected bond lengths [Å] and angles [$^\circ$]: Bi(1)–Bi(2) $3.0095(16)$, Bi(1)–Bi(4) $3.0206(16)$, Bi(2)–Bi(3) $3.0187(15)$, Bi(3)–Bi(4) $3.0221(16)$, Bi(1)–C(11) $2.24(3)$, Bi(2)–C(21) $2.30(3)$, Bi(3)–C(31) $2.28(3)$, Bi(4)–C(41) $2.28(3)$; Bi(2)–Bi(1)–Bi(4) $79.51(4)$, Bi(1)–Bi(2)–Bi(3) $77.01(4)$, Bi(2)–Bi(3)–Bi(4) $79.34(4)$, Bi(1)–Bi(4)–Bi(3) $76.79(4)$, Bi(2)–Bi(1)–C(11) $99.4(7)$, Bi(4)–Bi(1)–C(11) $98.6(7)$, Bi(1)–Bi(2)–C(21) $97.7(7)$, Bi(3)–Bi(2)–C(21) $93.2(7)$, Bi(2)–Bi(3)–C(31) $96.7(8)$, Bi(4)–Bi(3)–C(31) $101.7(7)$, Bi(1)–Bi(4)–C(41) $92.3(6)$, Bi(3)–Bi(4)–C(41) $94.4(7)$



Red-orange crystals of **2** were obtained from a red toluene solution at -28°C . The ^1H NMR spectrum of **2** shows the expected two singlets for the CH_3 and CH_2 groups, respectively, and the signals for the aryl protons. In the CI mass spectrum, the molecular ion peak of **2** was observed as the one with highest mass. The molecular structure of this bismuthinidene complex with intramolecular base coordination is depicted in Figure 2.

The $[\text{2-(Me}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_4]\text{Bi}$ group bridges two pentacarbonyltungsten fragments. The bismuth atom is tetra-coordinate in an irregular trigonal-pyramidal environment. The Bi–W bond lengths [$2.8248(8)$ and $2.8362(8)$ Å] are similar to the values observed in $[\text{Ph}_3\text{BiW(CO)}_5]$ [$2.8294(5)$ Å],^[19] $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ph}_2\text{Bi}\{\text{W(CO)}_5\}_2]$ [$2.891(2)$, $2.997(3)$ Å]^[20] and $[(\text{Bi}_2)\text{W}_2(\text{CO})_8][\text{MeBiW(CO)}_5]$ [$2.851(2)$ – $3.001(3)$ Å].^[21]

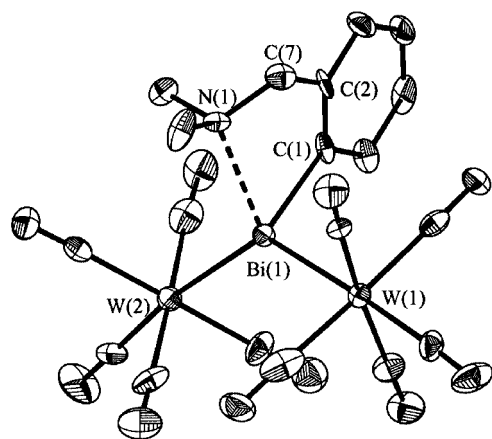
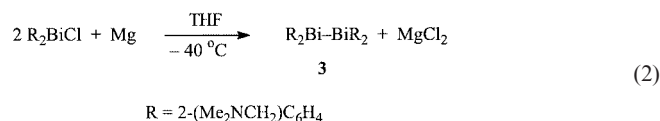


Figure 2. Structure of **2** in the crystal; the ellipsoids represent 40% probability; selected distances [Å] and angles [°]: Bi(1)–C(1) 2.22.3(16), Bi(1)–N(1) 2.435(12), Bi(1)–W(2) 2.8248(8), Bi(1)–W(1) 2.8362(8); C(1)–Bi(1)–N(1) 73.7(5), C(1)–Bi(1)–W(2) 108.8(3), N(1)–Bi(1)–W(2) 111.7(3), C(1)–Bi(1)–W(1) 105.7(3), N(1)–Bi(1)–W(1) 109.2(3), W(2)–Bi(1)–W(1) 132.13(3)

The intramolecular N–Bi distance [2.435(12) Å] in **2** is shorter than in R_2BiCl [2.570(5) Å]^[18] or $RBiI_2$ [2.503(6) Å]^[18] [$R = 2-(Me_2NCH_2)C_6H_4$]. The W_2BiC framework of the $Bi(C,N)W_2$ core is almost planar (the sum of angles around Bi is 346.53°), with the Bi atom situated only 0.5 Å above the W_2C plane. Compound **2** can be described as a complex of an RBi ligand with two sp^2 -orbitals containing lone pairs of electrons and an empty p-orbital at the bismuth atom. The filled orbitals are involved in the dative bonds to the tungsten atoms and the empty p-orbital accepts electron density from the amine group and the tungsten atoms. The structure is certainly also influenced by the constraints imposed by the five-membered chelate ring.

Analogous base-stabilized bismuthinidene complexes with donation of two lone pairs of electrons to two 16-electron complex fragments are unknown. Closely related compounds are the dinuclear complexes with phosphinidene, arsinidene, or stibinidene ligands, which have been studied by Huttner et al. They found that the tendency to form adducts with Lewis bases is considerably stronger for the heavier group-15 element ligands.^[22] The formation of **2** does not prove unambiguously the presence of a monomeric bismuthinidene in the reaction solution. Alternatively, the reaction of the rings **1a** or **1b** with $W(CO)_5 \cdot THF$ followed by splitting of the Bi–Bi bond might lead to **2**. It is remarkable that the analogous reaction of $cyclo-(Me_3SiCH_2)_nBi_n$ with $W(CO)_5 \cdot THF$, carried out under very similar conditions, gave the dibismuthene complex $[(RBi=BiR)\{W(CO)_5\}_2]$ ($R = Me_3SiCH_2$) instead of a bismuthinidene complex.^[8]

The dibismuthane R_4Bi_2 (**3**) was synthesised by reduction of $[2-(Me_2NCH_2)C_6H_4]_2BiCl$ with Mg in THF at $-40^\circ C$ [Equation (2)] and was isolated in 78% yield as a dark red hydrocarbon-soluble solid. Solutions of **3** are air-sensitive, but under an inert gas they are stable at room temperature for a long time ($\tau_{1/2} = 14$ d). Crystals of **3** are stable in air for several hours.



The 1H NMR spectrum of **3** shows one singlet for the methyl groups and an AB spin system for the CH_2 groups, indicating that all substituents are equivalent in solution. Variation of the temperature between $+20$ and $-60^\circ C$ does not result in significant changes in the 1H NMR spectrum. The EI mass spectrum of **3** displays a peak for the R_2Bi^+ fragment at highest mass. Single crystals of **3** were obtained from diethyl ether at $-28^\circ C$ and the structure was determined by a single-crystal X-ray diffraction study. The molecular structure is depicted in Figure 3. Compound **3** is a dibismuthane exhibiting an antiperiplanar (*trans*) conformation [$\varphi = lp-Bi-Bi-lp$ 132.18(1)°; lp = assumed position of the lone pair of electrons], which brings two organic groups on different metal atoms in an almost eclipsed position relative to each other [$C(31)-Bi(2)-Bi(1)-C(11)$ 35.2(2)°]. This behaviour contrasts with the ideal *trans* conformation found in other dibismuthanes, $R_2Bi-BiR_2$ [$R = Ph$: $\varphi = 180.00(5)$;^[14] $R = Me_3Si$: $\varphi = 180.00(3)$ ^[15]]. Intramolecular N–Bi coordination occurs through three of the four nitrogen atoms, the pendant arm carrying the N(1) atom being twisted far from the Bi(1) atom.

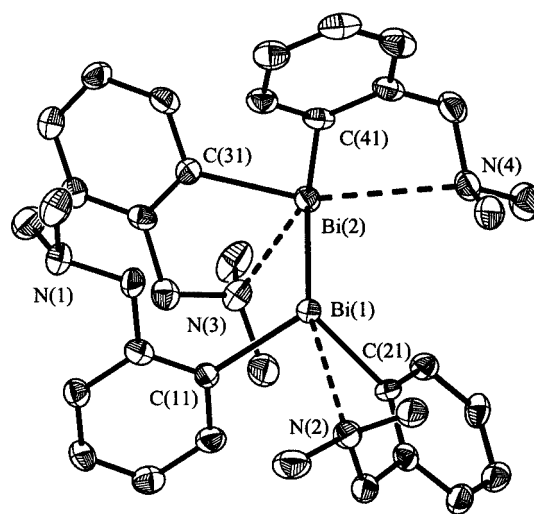


Figure 3. Structure of **3** in the crystal; the ellipsoids represent 40% probability; selected distances [Å] and angles [°]: Bi(1)–Bi(2) 3.0657(5), Bi(1)–C(11) 2.272(5), Bi(1)–C(21) 2.295(6), Bi(1)–N(2) 2.952(5), Bi(2)–C(31) 2.287(5), Bi(2)–C(41) 2.317(5), Bi(2)–N(3) 3.027(4), Bi(2)–N(4) 3.170(4); C(11)–Bi(1)–C(21) 96.29(19), C(11)–Bi(1)–N(2) 85.15(16), C(21)–Bi(1)–N(2) 67.39(18), C(11)–Bi(1)–Bi(2) 101.20(13), C(21)–Bi(1)–Bi(2) 96.04(15), N(2)–Bi(1)–Bi(2) 162.97(10), C(31)–Bi(2)–C(41) 94.3(2), C(31)–Bi(2)–N(3) 66.54(17), C(41)–Bi(2)–N(3) 159.83(18), C(31)–Bi(2)–Bi(1) 106.33(15), C(41)–Bi(2)–Bi(1) 81.77(14), N(3)–Bi(2)–Bi(1) 97.24(10), C(31)–Bi(2)–N(4) 159.31(17), C(41)–Bi(2)–N(4) 65.72(17), N(3)–Bi(2)–N(4) 133.92(13), Bi(1)–Bi(2)–N(4) 77.10(9)

This results in a wide range of Bi–Bi–C angles [81.77(14)–106.33(14)°] and different overall coordination geometries at the metal atoms. Bi(1) is in a distorted pseudo-trigonal-bipyramidal environment similar to that of the bismuth atoms in **1b**, with N(2) and Bi(2) in axial positions [N(2)–Bi(1)–Bi(2) 162.97(10)°].

The coordination geometry around Bi(2) is distorted tetragonal-pyramidal, with Bi(1) in the apical position and a C₂N₂ basal plane. The Bi–N distances [2.952(5), 3.027(4), and 3.170(4) Å] in the molecule of **3** are similar to the corresponding Bi–N bond lengths in **1b** [2.97(3)–3.05(2) Å], while the Bi–Bi distance in **3** [3.0657(5) Å] corresponds to a normal single bond as found in **1b** [3.0095(16)–3.0221(16) Å] or Ph₄Bi₂ [2.990(2) Å].^[14] The Bi–Bi–C angles in **3** lie in the range between 81.77(14) and 106.33(15)°.

Conclusions

The present results show that the use of the 2-(dimethylaminomethyl)phenyl group stabilizes di- and *cyclo*-bismuthanes through intramolecular coordination of the pendant CH₂NMe₂ arm. The stabilizing effect is, however, not sufficient to allow the isolation of the monomeric 8-electron

bismuthinidene species, RBi. This moiety was trapped by formation of a complex with pentacarbonyltungsten.

Experimental Section

General Comments: Syntheses were carried out under argon using dried solvents freshly distilled under argon. NMR spectra were recorded with a Bruker DPX 200 instrument. Mass spectra were recorded with a Finnigan MAT 8222 instrument and IR spectra with an FT-IR SPEKTRUM 1000. Compounds with the formulae [2-(Me₂NCH₂)C₆H₄]_nBiCl_{3–n} were prepared according to the literature method.^[17] The crystal structure measurement and refinement data for **1b**, **2**, and **3** are given in Table 1. Data for **1b** and **2** were collected with a Siemens P4 four-circle diffractometer. Data for **3** were collected with a STOE IPDS diffractometer. In both cases a graphite monochromator was used to produce a wavelength (Mo-K_α) of 0.71073 Å. The crystals were attached with Kel-F oil to a glass fibre and cooled under a nitrogen stream at 173 K. The structures were solved by direct methods (full-matrix least squares on *F*²). All non-hydrogen atoms were refined with anisotropic thermal parameters. Structure solutions and refinements were carried out using the SHELX-97 software package.^[23] Diagrams were created using the Diamond program by Crystal Impact GbR.^[24] CCDC-195483 (**1b**), -195484 (**2**), and -195482 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html

Table 1. Data for the X-ray structure determinations of **1b**, **2**, and **3**

	1b	2	3
Empirical formula	C ₃₆ H ₄₈ Bi ₄ N ₄	C ₁₉ H ₁₂ BiNO ₁₀ W ₂	C ₃₆ H ₄₈ Bi ₂ N ₄
Formula mass	1372.70	990.98	954.74
Colour	dark green	orange	red
Temp. [K]	173(2)	173(2)	173(2)
Crystal size [mm]	0.40 × 0.30 × 0.30	0.25 × 0.10 × 0.05	0.5 × 0.4 × 0.3
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	11.589(3)	9.8730(10)	19.759(4)
<i>b</i> [Å]	14.460(4)	10.2640(10)	11.045(2)
<i>c</i> [Å]	23.807(4)	12.1440(10)	16.315(3)
α [°]	90	81.25	90
β [°]	90	82.83	90.12(3)
γ [°]	90	84.72	90
<i>Z</i>	4	2	4
<i>d</i> _{calcd.} [g cm ^{–3}]	2.285	2.735	1.781
μ [mm ^{–1}]	17.618	16.880	9.900
<i>F</i> (000)	2496	888	1832
θ range [°]	2.22–27.51°	2.54–27.49	2.11–25.89
Index ranges	–15 ≤ <i>h</i> ≤ 9, –18 ≤ <i>k</i> ≤ 18, –10 ≤ <i>l</i> ≤ 30	–12 ≤ <i>h</i> ≤ 1, –13 ≤ <i>k</i> ≤ 13, –15 ≤ <i>l</i> ≤ 15	–24 ≤ <i>h</i> ≤ 24, –13 ≤ <i>k</i> ≤ 13, –19 ≤ <i>l</i> ≤ 19
No. of measured data	6237	6579	48837
No. of unique data [<i>R</i> (int)]	5889 [<i>R</i> (int) = 0.0270]	5521 [<i>R</i> (int) = 0.0399]	6873 [<i>R</i> (int) = 0.1091]
Data/restraints/parameters	5889/108/408	5521/0/303	6873/0/390
Absorption correction	empirical (SHELXA)	empirical (SHELXA)	empirical (SHELXA)
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0657	0.0571	0.0277
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.1161	0.1107	0.0440
<i>R</i> 1 (all data)	0.1238	0.1023	0.0553
<i>wR</i> 2 (all data)	0.1374	0.1279	0.0474
Goodness-of-fit on <i>F</i> ²	1.018	1.006	0.824
Residual density [e·Å ^{–3}]	1.854, –1.818	2.320, –2.006	0.548, –0.766

[or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of [2-(Me₂NCH₂)C₆H₄]_nBi_n (*n* = 3 (1a**), 4 (**1b**)).** **Procedure 1:** Na (1.0 g, 44.4 mmol) was dissolved in liquid ammonia (ca. 150 mL) and [2-(Me₂NCH₂)C₆H₄]₂BiCl₂ (9.0 g, 21.7 mmol) was added. The reaction mixture was stirred for 9 h and the liquid ammonia evaporated. The remaining black residue was extracted with petroleum ether (250 mL). After filtration, the petroleum ether was evaporated leaving a black-green solid (3.7 g, 49.5%). Compound **1b** [m.p. 53 °C (dec.)] separated as dark-green crystals from petroleum ether at -28 °C after a few weeks. ¹H NMR (200 MHz, 25 °C, C₆D₅CD₃, TMS): R₃Bi₃ (**1a**): δ = 2.29 (s, 12 H, *cis*-CH₃), 2.34 (s, 6 H, *trans*-CH₃), 3.38 (s, 4 H, *cis*-CH₂), 3.34 (s, 2 H, *trans*-CH₂), 6.42–6.99 (m, 9 H, 3–5-H), 7.57 (dd, ³J_{H,H} = 7.4, ⁴J_{H,H} = 1.3, 2 H, *cis*-6-H), 7.87 (dd, ³J_{H,H} = 7.4, ⁴J_{H,H} = 1.3, 1 H, *trans*-6-H); R₄Bi₄ (**1b**): δ = 1.91 (s, 24 H, CH₃), 3.43 (s, 8 H, CH₂), 6.68–6.99 (m, 12 H, 3–5-H), 8.93 (d, ³J_{H,H} = 6.2, 4 H, 6-H). C₃₆H₄₈Bi₄N₄ (1372.70): calcd. C 31.50, H 3.52; found C 31.39, H 3.42. **Procedure 2:** LiAlH₄ (0.4 g, 10.7 mmol) was added with stirring to a solution of [2-(Me₂NCH₂)C₆H₄]₂BiCl (5.0 g, 9.7 mmol) in Et₂O (90 mL) at -78 °C. The reaction mixture was then warmed slowly to -30 °C. At -30 °C the solution was filtered through a precooled glass frit. The dark red filtrate was concentrated in vacuo at -30 °C leaving dark green crystals of **1b** (2.2 g, 65.9%). The identity of the product was established by ¹H NMR and X-ray diffraction (determination of the unit cell parameters).

Synthesis of [{2-(Me₂NCH₂)C₆H₄]₂Bi{W(CO)₅}] (2**):** A solution of [W(CO)₅THF] (2.3 g, 5.8 mmol) in THF (100 mL) was added to **1** (1.0 g, 0.7 mmol) in THF (40 mL) at 0 °C and the mixture was stirred for 3 h at 0 °C. After removal of the solvent in vacuo, the residue was extracted with toluene (100 mL) and then filtered through a glass frit covered with kieselguhr. The clear filtrate was concentrated and cooled to -28 °C to give orange-red crystals of **2** (1.6 g, 57.6%) (m.p. 82–85 °C). ¹H NMR (200 MHz, 25 °C, C₆D₆, TMS): δ = 1.99 (s, 6 H, CH₃), 3.07 (s, 2 H, CH₂), 6.88–7.21 (m, 3 H, 3–5-H), 7.58 (dd, ³J_{H,H} = 7.2, 1 H, 6-H) ppm. ¹³C NMR (50 MHz, 25 °C, C₆D₆, TMS): δ = 49.85 (s, CH₃), 72.73 (s, CH₂), 131.59 (s, C-4), 134.96 (s, C-3), 143.48 (s, C-5), 163.74 (s, C-6), 198.07 (s, CO_{eq}), 200.89 (s, CO_{ax}) ppm. IR (nujol): ν̃ = 2072, 2054, 1940, 1908 cm⁻¹ (C=O). MS (EI, 70 eV): *m/z* (%) = 990 (5) [M⁺], 822 (2) [M⁺ - 6 CO], 794 (3) [M⁺ - 7 CO], 766 (2) [M⁺ - 8 CO], 583 (10) [RW(CO)₂], 343 (60) [RBi⁺], 134 (76) [R⁺], 58 (100) [Me₂NCH₂]. C₁₉H₁₂BiO₁₀W₂ (990.98): calcd. C 23.03, H 1.22; found C 22.79, H 1.23.

Synthesis of [2-(Me₂NCH₂)C₆H₄]₂Bi₂ (3**):** A solution of [2-(Me₂NCH₂)C₆H₄]₂BiCl (7.0 g, 13.8 mmol) in THF (70 mL) was added dropwise at -40 °C to Mg (0.5 g, 21.4 mmol) activated with 1,2-dibromoethane (0.5 mL). The reaction mixture was stirred for 3 h and then the temperature was raised to 0 °C. The solvent was removed in vacuo leaving a dark red solid. After extraction with petroleum ether (150 mL) and filtration, the solvent was evaporated to dryness and the residue dissolved in Et₂O (20 mL). Cooling to -28 °C gave **3** (4.9 g, 78.3%) as red crystals (m.p. 69–79 °C). ¹H

NMR (200 MHz, 25 °C, C₆D₆, TMS): δ = 1.93 (s, 6 H, CH₃), AB spin system with δ_A = 3.14 and δ_B = 3.32 (²J_{H,H} = 12.8, 2 H, CH₂), 6.99 (ddd, ³J_{H,H} = 7.1, ⁴J_{H,H} = 1.5, 1 H, 4-H), 7.13 (ddd, ³J_{H,H} = 7.4, ⁴J_{H,H} = 1.5, 5-H), 7.24 (dd, ³J_{H,H} = 7.4, ⁴J_{H,H} = 1.2, 1 H, 3-H), 8.67 (dd, ³J_{H,H} = 7.1, ⁴J_{H,H} = 1.5, 1 H, 6-H) ppm. ¹³C NMR (50 MHz, 25 °C, C₆D₆, TMS): δ = 45.12 (s, CH₃), 69.13 (s, CH₂), 126.75 (s, C-4), 129.75 (s, C-3), 129.99 (s, C-5), 145.46 (s, C-6), 146.31 (s, C-1), 151.73 (s, C-2) ppm. MS (EI, 70 eV): *m/z* (%) = 477 (100) [R₂Bi⁺], 342 (8) [RBi⁺], 134 (50) [R⁺]. C₃₆H₄₈Bi₂N₄ (954.74): calcd. C 45.29, H 5.07; found C 45.10, H 5.05.

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