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Trapping of the *N,C,N*-chelated organobismuth(I) compound, [2,6-$(Me_2NCH_2)_2C_6H_3$]Bi, by its coordination toward selected transition metal fragments

Iva Vránová, Tereza Dušková, Milan Erben, Roman Jambor, Aleš Růžička, Libor Dostál*

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10, Pardubice, Czech Republic

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ABSTRACT

The *in situ* reduction of the *N,C,N*-chelated bismuth(III) chloride ($ArBiCl_2$) (where Ar = 2,6-$(Me_2NCH_2)_2C_6H_3$) with 2 equivalents of K[B(*s*-Bu)$_3$H] produced an unstable bismuth(I) compound ArBi (**1**) that was trapped by its coordination toward suitable transition metal fragments. Using this strategy a set of complexes with Group 6 metal carbonyls was obtained, i.e. [ArBiM(CO)$_5$] (**1-M**; where M = Cr, Mo, W). The treatment of **1** with [$Fe_2(CO)_9$] provided the expected complex [ArBiFe(CO)$_4$] (**1-Fe**) along with [ArBi(Fe(CO)$_4$)$_2$] (**1-Fe$_2$**) as a minor by-product. By contrast, the reaction of **1** with the dinuclear complex [$Co_2(CO)_8$] furnished ionic complex [(ArBi)$_2$Co(CO)$_3$][Co(CO)$_4$] (**1-Co**). All compounds were characterized using ^1H and $^{13}C\{^1H\}$ NMR, IR and Raman spectroscopy. Molecular structures of **1-Cr**, **1-Fe**, **1-Fe$_2$** and **1-Co** were determined by the help of single-crystal X-ray diffraction analysis.

1. Introduction

The investigation of so-called low-valent (or subvalent) heavier main group element compounds represents a continuously and quickly developing area of inorganic and organometallic chemistry [1–8]. By contrast to a significant progress among the compounds containing elements of the Group 13 [9,10] and 14 [11–15], the Group 15 compounds with the central atom in the formal oxidation state + I is somewhat less studied area [16–19]. This situation is especially striking in the case of the heaviest stable element bismuth, where, besides various oligomeric or cluster compounds, only limited number of compounds with the bismuth atom in the oxidation state + I has been successfully characterized. The first bismuth(I) compound, reported by Tokitoh [20] more than 20 years ago, is the sterically shielded dibismuthene [2,4,6-{$(Me_3Si)_2CH$}$_3$ C_6H_2]Bi=Bi[C_6H_2{$CH(SiMe_3)_2$}-2,4,6], that was shortly after followed by Power's dibismuthenes (2,6-$Ar_2C_6H_3$)Bi=Bi($C_6H_3Ar_2$-2,6) (where Ar = 2,4,6-$Me_3C_6H_2$ or 2,6-*i*-$Pr_2C_6H_3$) [21]. For a long time, these compounds remained the only examples and their reactivity was quite rarely studied [22–24]. This family has been enriched by the isolation of the ferrocenyl-decorated dibismuthene (2,5-Ar_2-Fc) Bi=Bi($FcAr_2$-2,5) (where Ar = 3,5-*t*-$Bu_2C_6H_3$) again by Tokitoh [25,26] and the boryl dibismuthene by Jones [27] [(DAB)B]Bi=Bi [B(DAB)] (where DAB = 1,3-bis(2,6-di-isopropylphenyl)-1,3-dihydro-2H-1,3,2-diazaborol-2-yl). Recently, interesting double bonded bismuth(I) compounds with Bi-Ga, i.e. [{CH(C(Me)NDipp)$_2$} (OTf)Ga]Bi=Bi[Ga(OTf){(NDippC(Me))$_2$CH}] [28,29], or Bi-P bonds, i.e. [(*t*-$BuPh_2Si)_2$P]Bi=Bi[P($SiPh_2$*t*-Bu)$_2$] [30], have been reported as well. Noteworthy, unique persistent radical bismuth compounds have also been isolated and characterized [31,32].

Nevertheless, above mentioned compounds represent mainly doubly bonded species, while monomeric bismuthinidenes remained elusive. Only in 2010 and later on, we demonstrated that the utilization of bis(ketimino)- or bis(aldimino)- *(N),C,N*-chelating ligands (i.e. 2,6-(R'N=CR)$_2C_6H_3$, where R = H or Me, R' = *t*-Bu, Dipp, 2,6-$Me_2C_6H_3$ etc. or 2-(DippN = CH)-4,6-*t*-$Bu_2C_6H_2$) even allowed the stabilization of monomeric bismuth(I) species, that may be regarded as thermodynamically stabilized bismuthinidenes although their structure is perturbed by the presence of the nitrogen donors [33,34]. By contrast, the application of a more flexible *N,C,N*-chelating ligand backbone (i.e. 2,6-$(Me_2NCH_2)_2C_6H_3$, denoted as Ar hereafter) did not allowed the isolation of stable

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* Corresponding author.
E-mail address: libor.dostal@upce.cz (L. Dostál).

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Table 1
Crystallographic Data for studied compounds.

	1-Cr	1-Fe	1-Fe_2	1-Co
chemical formula	$C_{17}H_{19}BiCrN_2O_5$	$C_{16}H_{19}BiFeN_2O_4$ 0.5(C_7H_8)	$C_{20}H_{19}BiFe_2N_2O_8$	$C_{27}H_{38}Bi_2CoN_4O_3$ C_4CoO_4 (C_6H_{14})
Cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	*P-1*	$P2_1/c$	$P2_1/c$
a[Å]	6.5110(4)	9.3811(6)	8.9470(6)	10.0880(10)
b[Å]	16.8101(12)	10.4770(3)	13.9240(11)	12.9550(13)
c[Å]	17.890(2)	11.9150(7)	19.4331(17)	31.016(2)
α[°]	90	106.084(4)	90	90
β[°]	90	103.228(5)	104.308(7)	103.335(7)
γ[°]	90	102.747(3)	90	90
Z	4	2	4	4
$\mu[mm^{-1}]$	9.558	9.141	8.751	9.775
D_x [$Mg\ m^{-3}$]	2.009	1.955	2.084	2.022
Crys tsize [mm]	0.30 × 0.13 × 0.12	0.44 × 0.23 × 0.10	0.59 × 0.27 × 0.12	0.32 × 0.10 × 0.07
Θ range, [deg]	1–27.5	1–27.5	1.82–27.5	1–27.5
T_{min}, T_{max}	0.250, 0.417	0.121, 0.505	0.075, 0.410	0.247, 0.597
no. of reflns measd	13 618	19 649	36 243	24 921
no. ofunique reflns, R_{int}	4282, 0.033	4763, 0.028	5320, 0.054	8531, 0.083
no. of obsd reflns [$I>2\sigma(I)$]	3743	4492	4549	5363
no. of params	235	217	298	415
S all data	1.137	1.095	1.200	1.070
final R indices [$I>2\sigma(I)$]	0.029	0.020	0.030	0.060
wR2 indices (all data)	0.063	0.046	0.078	0.097
Δρ, max., min. [e $Å^{-3}$]	1.614, −2.076	0.634, −1.203	2.909, −2.719	1.735, −1.119

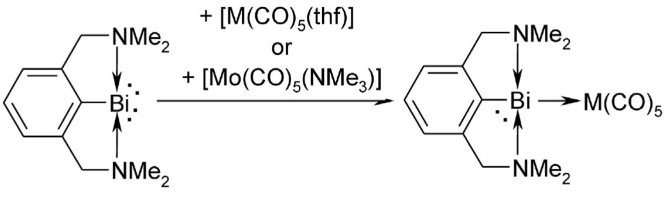
Definitions: $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$ for all data.

bismuth(I) compound ArBi (**1**), although the same ligand was shown to be sufficient for the stabilization of analogous organodibismuthane [35] and organoantimony(I) compounds [36]. Thus, the existence of **1** had to be indirectly confirmed by its *in situ* oxidation with various dichalcogenides [37,38]. Nevertheless, Breunig et al. shoved that the monomeric *C,N*-chelated organobismuth(I) compound [2-(Me_2NCH_2)C_6H_4]Bi can be stabilized by its coordination toward two $W(CO)_5$ fragments [39]. Recently, we have also proven that the stable bismuthinidene [2,6-(*t*-BuN = CH)$_2C_6H_3$]Bi (denoted as Ar'Bi hereafter) is useful ligand for selected transition metals [40–42].

With this in mind, we were curious if the bismuthinidene **1** could be stabilized with a transition metal fragment and thereby also enrich the family of available bismuth(I) donor-based ligands. Therefore, we report herein on the reactivity of *in situ* prepared **1** with selected transition metal complexes.

2. Results and discussion

As described earlier, the reduction of the *N,C,N*-chelated bismuth(III) chloride $ArBiCl_2$ [43] with 2 equivalents of K[B(*s*-Bu)$_3$H] in thf produced an intensively violet coloured solution that could be used at low temperature as a source of the bismuth(I) compound ArBi (**1**) in the reaction with a variety of dichalcogenides [37,38]. Using the same synthetic protocol, a thf solution of **1** reacted with Group 6 complexes [$M(CO)_5$(thf)] (where M = Cr or W) and [$Mo(CO)_5(NMe_3)$] [44] to form bismuth complexes [ArBiM$(CO)_5$] **1-M** (where M = Cr, Mo, W) (Scheme 1). All compounds were isolated as orange to red solids in good yields (69–75%). All complexes are well soluble in thf and aromatic solvents, but show only very limited solubility in hexane. The ^1H NMR spectra revealed an AX pattern for the CH_2N moiety in each case at $\delta(^1H)$ 2.75 and 3.93 ppm ($^2J_{H,H}$ = 14.6 Hz, M = Cr), 3.04 and 3.82 ppm ($^2J_{H,H}$ = 14.4 Hz, M = Mo) and 2.96 and 3.80 ppm ($^2J_{H,H}$ = 14.5 Hz, M = W), while non-equivalent methyl groups of the N*Me*$_2$ moieties showed two singlets ($\delta(^1H)$ 2.28 and 2.31 ppm for Cr, 2.40 and 2.45 ppm for Mo and 2.35 and 2.39 ppm for W). Similarly, an expected set of signals for the Ar ligand was detected in the $^{13}C\{^1H\}$ NMR spectra i.e. three signals for *C*H_2N and non-equivalent N*Me*$_2$ groups along with four signals in the aromatic region (see the Experimental Section and Supplementary Information). Furthermore, the presence of $M(CO)_5$ fragments was corroborated by the observation of two signals for *C*O groups being located either in equatorial or axial positions, i.e. $\delta(^{13}C)$ 222.4 (eq.), 220.2 (ax.) ppm (M = Cr), 212.5 (eq.), 215.5 (ax.) (M = Mo) ppm and 203.5 (eq., $^1J_{W,C}$ = 124 Hz) and 203.0 (ax., $^1J_{W,C}$ = 167 Hz) ppm (M = W).



(**1**) (**1-M**)

M = Cr, Mo, W

Scheme 1. Synthesis of Group 6 complexes **1-M** (where M = Cr, Mo, W).

The IR and Raman spectra of **1-M** complexes show bands in the region 2055–1865 cm^{-1} due to terminal carbonyl functions. The presence of a medium band corresponding to IR forbidden B_1 mode (1945 ± 7 cm^{-1}) together with broadening of the E band witnesses for a significant perturbation of an ideal C_{4v} symmetry of the $M(CO)_5$ moiety. The observed ν_{CO} frequencies in studied compounds **1-M** are only slightly lower than those reported for analogous complexes [Ar'BiM$(CO)_5$] (Ar' = 2,6-(*t*-BuN = CH)$_2C_6H_3$) [41] indicating their comparable electron donor properties.

Compound **1-Cr** crystallizes in orthorhombic $P2_12_12_1$ space group and its molecular structure is shown in Fig. 1 (see also Table 1). The ArBi unit is coordinated to the Cr(1) atom in a side on manner (*cf.* bonding angle C(1)-Bi(1)-Cr(1) 104.06(16)°) being consistent with the involvement of mainly p-type lone pair of the bismuth atom in this dative bond, although this values is remarkably wider than in [Ar'BiCr$(CO)_5$] (*cf. av.* value 97°) [40–42]. The Bi(1)-Cr(1) bond length (2.7565(12) Å) is slightly shorter than in [Ar'BiCr$(CO)_5$] (*av.* for two independent molecules 2.8047 Å) [41].