

Reactions of Terphenylbismuth Dihalides with $\text{KSi}(\text{SiMe}_3)_3$, $\text{K}_2\text{Si}_2(\text{SiMe}_3)_4$ and $\text{Na}_2[\text{Fe}(\text{CO})_4]$: Reduction vs. Metathesis

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The reactions of terphenylbismuth dihalides with various reducing agents were investigated. Attempted metathesis of $\text{Ar}'\text{BiCl}_2$ [$\text{Ar}' = 2,6-(2,6\text{-iPr}_2\text{-C}_6\text{H}_3)_2\text{-C}_6\text{H}_3$] with one equivalent of $\text{KSi}(\text{SiMe}_3)_3$ gave the 1,2-dichlorodibismuthane $\text{Ar}'(\text{Cl})\text{Bi}-\text{Bi}(\text{Cl})\text{Ar}'$ (**1**) in 40 % yield. The reaction of $\text{Ar}'\text{BiCl}_2$ (**1**) with the dianionic salt $\text{K}_2\text{Si}_2(\text{SiMe}_3)_4$ yielded the dibismuthene $\text{Ar}'\text{Bi}=\text{BiAr}'$ (**2**) in 72 %. The terphenylbismuth dihalides ArBiCl_2 [$\text{Ar} = 2,6-(2,6\text{-iPr}_2\text{-C}_6\text{H}_3)_2\text{-C}_6\text{H}_3$ (Ar'), $2,6-(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)_2\text{-C}_6\text{H}_3$ ($\text{Ar}^\#$)] were treated with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ in THF to afford the iron dibismuthene complexes

$[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}'_2)]$ (**3**) and $[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}^\#_2)]$ (**4**) in modest yields (25 and 15 % respectively). The compounds **1–4** were characterized by X-ray crystallography and by spectroscopic methods (^1H and ^{13}C NMR, IR, and UV/Vis spectroscopy). The results show that reduction of the bismuth center is strongly preferred over salt metathesis chemistry due to the reducing power of the silanide and ferrate salts and the strength of the $\text{Bi}=\text{Bi}$ bond.

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Introduction

The discovery of the first stable diphosphene, $\text{Mes}^*\text{P}=\text{PMes}^*$ ($\text{Mes}^* = 2,4,6\text{-iBu}_3\text{-C}_6\text{H}_2$), by Yoshifuji and co-workers in 1981 was a landmark achievement which was rapidly followed by extensive reactivity and spectroscopic studies of diphosphenes and their heavier congeners.^[2–5] Numerous transition metal complexes of diphosphenes with unsupported phosphorus – phosphorus double bonds such as $[\{\text{Fe}(\text{CO})_4\}\text{-trans-(P}_2\text{R}_2)]$ ($\text{R} =$ bulky organic group)^[7] are known and these complexes illustrate the versatility of diphosphenes as ligands.^[6–9] In contrast, $\text{Bi}=\text{Bi}$ double bonds were only experimentally authenticated in 1997 when Tokitoh and co-workers reported the synthesis of the aryl dibismuthene $\text{TbtBi}=\text{BiTbt}$ ($\text{Tbt} = \text{C}_6\text{H}_2\text{-2,4,6-}\{\text{CH}(\text{SiMe}_3)_2\}_3$).^[10] Soon after, other dibismuthenes featuring the related aryl substituents $\text{Ar}^\# = 2,6-(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)_2\text{-C}_6\text{H}_3$ or $\text{Ar}^* = 2,6-(2,4,6\text{-iPr}_3\text{-C}_6\text{H}_2)_2\text{-C}_6\text{H}_3$, were reported.^[11] At present, stable examples of dibismuthenes, either as complexed or uncomplexed entities, remain extremely rare^[11–14] while compounds with a double bond between bismuth and another *p*-block element are limited to $\text{Mes}^*\text{P}=\text{BiTbt}$ ^[15] and $\text{TbtSb}=\text{BiTbt}$.^[16]

Bulky terphenyl ligands such as $\text{Ar}^\#$ and Ar^* ^[17] have proven very useful in the stabilization of new types of metal–metal multiple bonds^[18] and have enabled the prepa-

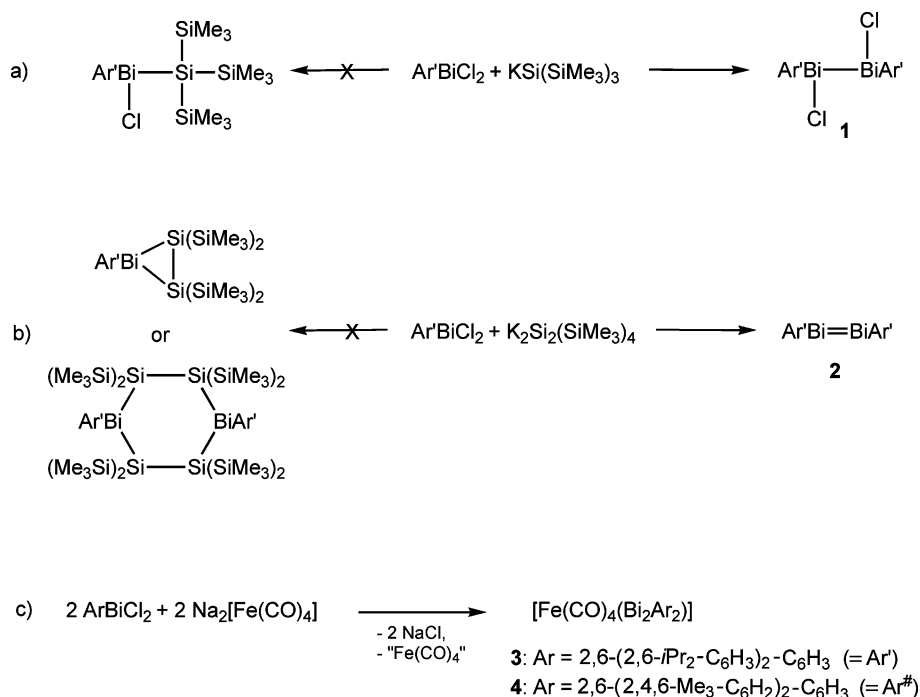
ration of a homologous series of stable, heavier dipnictenes $\text{RE}=\text{ER}$ ($\text{E} = \text{P, As, Sb and Bi}$).^[11] Herein, we report our attempts to exploit the beneficial properties of these ligands for the preparation of novel bismuth–silicon and bismuth–iron compounds that exhibit new bonding motifs. These investigations have yielded novel $\text{Bi}-\text{Bi}$ bonded products via the reduction of the terphenylbismuth dichloride starting material. Thus, the reaction of $\text{Ar}'\text{BiCl}_2$ [$\text{Ar}' = 2,6-(2,6\text{-iPr}_2\text{-C}_6\text{H}_3)_2\text{-C}_6\text{H}_3$] with $\text{KSi}(\text{SiMe}_3)_3$ and $\text{K}_2\text{Si}_2(\text{SiMe}_3)_4$ led not to silylbismuth species but to the dibismuthane $\text{Ar}'(\text{Cl})\text{Bi}-\text{Bi}(\text{Cl})\text{Ar}'$ (**1**) and the new dibismuthene $\text{Ar}'\text{Bi}=\text{BiAr}'$ (**2**), respectively. Reactions of ArBiCl_2 ($\text{Ar} = \text{Ar}'$ and $\text{Ar}^\#$) with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ yielded the first iron–dibismuthene complexes $[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}'_2)]$ (**3**) and $[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}^\#_2)]$ (**4**).

Results and Discussion

Syntheses and Structures of $\text{Ar}'(\text{Cl})\text{BiBi}(\text{Cl})\text{Ar}'$ (**1**) and $\text{Ar}'\text{Bi}=\text{BiAr}'$ (**2**)

In order to access the hypothetical silylbismuth compound $\text{Ar}'\text{BiCl}(\text{Si}\{\text{SiMe}_3\}_3)$, a possible precursor for a $\text{Bi}=\text{Si}$ double bond, we attempted the reaction of the sterically encumbered arylbismuth dichloride $\text{Ar}'\text{BiCl}_2$ with the bulky silanide $\text{KSi}(\text{SiMe}_3)_3$ ^[19] (Scheme 1, a). However, in place of the intended salt metathesis reaction, we observed a redox process which led to the formation of the singly bonded dibismuthane $\text{Ar}'(\text{Cl})\text{BiBi}(\text{Cl})\text{Ar}'$ (**1**). In a similar manner, the reaction of $\text{Ar}'\text{BiCl}_2$ with the disilane-1,2-diide $\text{K}_2\text{Si}_2(\text{SiMe}_3)_4$ ^[20] was carried out with the aim of producing

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Scheme 1.

unusual cyclic compounds such as *cyclo*-(BiAr'₂Si₂{SiMe₃})₄ or *cyclo*-(BiAr'₂Si₂{SiMe₃})₄.^[21] However, as seen for the reaction of KSi(SiMe₃)₃, the reduction of Ar'BCl₂ with K₂Si₂(SiMe₃)₄ transpired to give the dibismuthene Ar'Bi=BiAr' (**2**) in a 72% yield (Scheme 1, b). Analysis of the mother liquors from the above reactions further supported the presence of redox chemistry. For example the synthesis of **1** resulted in concomitant synthesis of (Me₃Si)₃SiSi(SiMe₃)₃. During the synthesis of **2** oxidation of K₂Si₂(SiMe₃)₄ occurred to afford the unstable intermediate (Me₃Si)₂SiSi(SiMe₃)₂ which is readily dimerized to give *cyclo*-(Si(SiMe₃)₂)₄ as verified by ²⁹Si NMR spectroscopy. Our present report thus underlines the potential of alkali metal silanides as benign and easily separable reducing agents towards substituted bismuth halides. However, in reactions with pure bismuth halides reduction may not occur and Linti and Köstler have observed that the cyclotetrabismuthane *cyclo*-(Bi₄{SiMe₃})₄ featuring Bi-Si bonds can be synthesized from BiBr₃ and 3 equiv. of Li(THF)₃(Si{SiMe₃})₃.^[22]

The compounds **1** and **2** were characterized by X-ray crystallography, ¹H and ¹³C NMR and UV/Vis spectroscopy. The solid-state molecular structure of **1** (Figure 1, Table 1) shows a mixed-substituted dibismuthane with a Bi-Bi single bond length of 3.0232(4) Å. The aryl and chlorine substituents adopt strictly *trans* arrangements which are dictated by a crystallographic center of symmetry located at the midpoint of the Bi-Bi vector. While the structure of a heteroleptic dibismuthane such as **1** with two different substituents on Bi has to the best of our knowledge not been reported (nor, in fact, has an example of an antimony analogue), a number of homoleptic compounds R₂BiBiR₂ have been structurally characterized and display Bi-Bi dis-

tances ranging from 2.983(8) to 3.2092(8) Å.^[12,23,24] The Bi-Bi bond length in **1** is thus in the expected range. Similar to other dibismuthanes^[12,23] **1** displays a strictly *anti*-periplanar conformation. The terphenyl ligands Ar' are almost co-planar (C2-C1-Bi1-Bi1a torsion angle: -175°), leading to the close approach of the flanking 2,6-*i*Pr₂-C₆H₃ substituents to a neighboring bismuth atom. Bismuth-arene π-interactions have been observed previously,^[25] nonetheless, the long Bi1-centroid distance of 3.283 Å indicates that, if such an interaction is present in **1**, it is rather weak and is probably of relatively minor structural significance. The steric effect of the large terphenyl ligands is apparent in the bond angles around Bi1: while the two bond angles

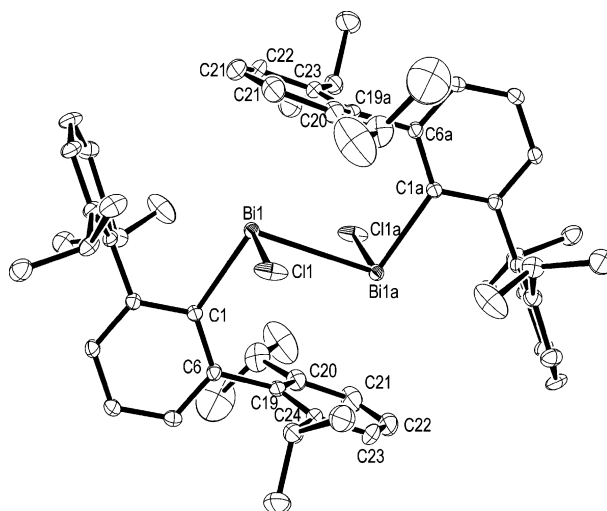


Figure 1. Structure of Ar'(Cl)Bi-Bi(Cl)Ar' (**1**) in the solid state (30% ellipsoid level, H-atoms are not shown for clarity).

Table 1. Selected bond lengths [Å] and angles [°] of **1–4**.

	1	2		3	4
Bi(1)–Bi(1a)	3.0232(4)	2.8560(3)	Bi(1)–Bi(2)	2.9432(2)	2.9294(2)
Bi(1)–C(1)	2.297(5)	2.327(2)	Bi(1)–C(<i>ipso</i>)	2.337(2)	2.313(3)
C(1)–Bi(1)–Bi(1a)	103.8(2)	105.44(6)	Bi(2)–C(<i>ipso</i>)	2.344(2)	2.302(3)
C(2)–C(1)–Bi(1)–Bi(1a)	–175.0	180.0	Bi(1)–Bi(2)–C(<i>ipso</i>)	106.73(6)	102.37(7)
Bi(1)–Cl1	2.566(2)		Bi(2)–Bi(1)–C(<i>ipso</i>)	105.30(6)	101.50(7)
Cl(1)–Bi(1)–Bi(1a)	84.62(5)		C(<i>ipso</i>)–Bi(1)–Bi(2)–C(<i>ipso</i>)	161.68	165.11
C(1)–Bi(1)–Cl(1)	88.9(2)		Bi(1)–Fe(1)	2.8033(4)	2.8248(5)
			Bi(2)–Fe(1)	2.8105(4)	2.8058(5)
			av. Fe–C	1.805(3)	1.805(3)
			av. C–O	1.140(3)	1.142(4)
			Bi(1)–Bi(2)–Fe(1)	58.262(8)	58.968(9)
			Bi(2)–Bi(1)–Fe(1)	58.500(8)	58.33(1)
			Bi(1)–Fe(1)–Bi(2)	63.238(8)	62.70(2)
			C(<i>ipso</i>)–Bi(1)–Fe(1)	102.18(6)	102.24(7)
			C(<i>ipso</i>)–Bi(1)–Fe(1)	100.16(6)	102.68(7)

involving the chlorine atom are slightly narrower than 90°, the C1–Bi1–Bi1a angle of 103.5(2)° is widened due to the large size of the Ar' substituent.

The solid-state structure of **2** (Figure 2, Table 1) resembles the only two other structurally characterized uncomplexed dibismuthenes in that it has a trans-bent core structure.^[10,11,26] The molecule resides on a crystallographic centre of symmetry and displays a strictly *anti*-periplanar, *trans*-bent geometry of the C–Bi–Bi–C core. The Bi–Bi bond length of 2.8560(3) Å is significantly (5.5%) shorter than the Bi–Bi distance in Ar'(Cl)Bi–Bi(Cl)Ar' (**1**) which is consistent with the presence of double bond character. However, this distance is slightly longer than the values found in the related compounds TbtBi=BiTbt [2.8206(8) Å, Tbt = 2,4,6-{CH(SiMe₃)₂}₃–C₆H₂^[10]] and Ar[#]Bi=BiAr[#] [2.833(2) Å].^[11] This small difference may be a consequence of the higher steric repulsion between the much larger Ar' ligands in **2**. The increased crowding may also cause the quite wide Bi1a–Bi1–C1 angle of 105.44(6)° observed for **2**, which may be compared to the corresponding angles within Ar[#]Bi=BiAr[#] and TbtBi=BiTbt which are 92.5(4) and

100.5(7)° respectively. The Bi–Bi distance in **2** also exceeds the 2.8377(7) Å^[4] found in the unsubstituted dianion [Bi₂]^{2–} where a relatively short Bi–Bi double-bonded distance is observed in spite of the electronic repulsion.^[27] Interestingly, the conformation of **2** also differed from that observed in the previously synthesized dibismuthenes; thus in Ar[#]Bi=BiAr[#] and TbtBi=BiTbt, the central aryl rings are nearly perpendicular to the Bi–Bi bond axis, whereas the central aryl rings in **2** are approximately coplanar (Bi1a–Bi1–C1–C2 –8.9°). As in **1**, weak contacts were observed between Bi and the flanking aryl rings of the Ar' substituent (Bi1–centroid: 3.328 Å).

The ¹H NMR spectra of **1** and **2** are in agreement with the centrosymmetric structures observed in the solid state and indicate the presence of magnetically equivalent 2,6-*i*Pr₂–C₆H₃ substituents with diastereotopic methyl groups. The UV/Vis spectrum of **2** spectrum displays a maximum absorption at 526 nm which corresponds well to the absorptions at 505 nm and 518 nm observed previously for the related π–π* transitions in the diaryl dibismuthenes Ar[#]Bi=BiAr[#] and Ar^{*}Bi=BiAr^{*}.^[11]

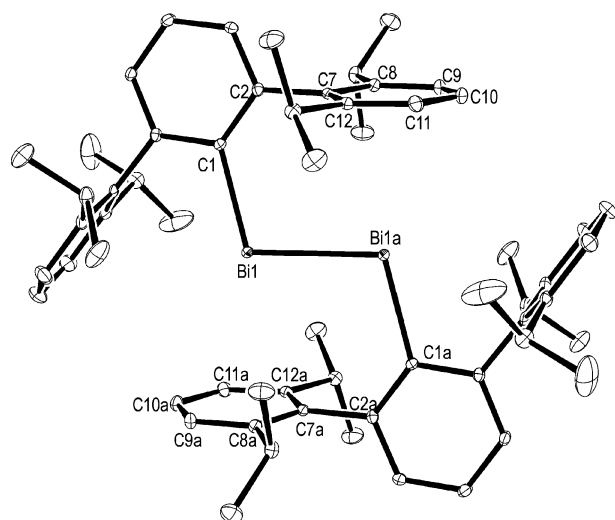


Figure 2. Solid-state structure of Ar'Bi=BiAr' (**2**) (30% ellipsoid level, H-atoms are not shown for clarity).

Syntheses and Structures of [Fe(CO)₄(Bi₂Ar'₂)] (**3**) and [Fe(CO)₄(Bi₂Ar[#]₂)] (**4**)

Cassidy and Whitmire have reported that the dinuclear complex [Fe(CO)₄(BiPh)₂] is formed from the reaction of Collman's reagent, Na₂[Fe(CO)₄], with two equiv. of Ph₂BiCl or one equiv. of PhBiBr₂, respectively.^[28] In order to investigate the steric effects of a very bulky aryl substituent on such a transformation we reacted Na₂[Fe(CO)₄]^[29] and ArBiCl₂ (Ar = Ar' and Ar[#], Scheme 1, c) and obtained the complexes **3** and **4** as dark-red, crystalline solids in modest yields (15% and 25%). Both compounds were characterized by NMR, UV/Vis and IR spectroscopy. Interestingly, compounds **3** and **4** appear to be air-stable as solids for several days, although significant quantities of ArBi=BiAr (Ar = Ar' or Ar[#], respectively) were observed in the ¹H NMR spectra after storing C₆D₆ solutions of **3** and **4** at room temperature for several weeks. X-ray crystallographic studies revealed very similar structures for both compounds

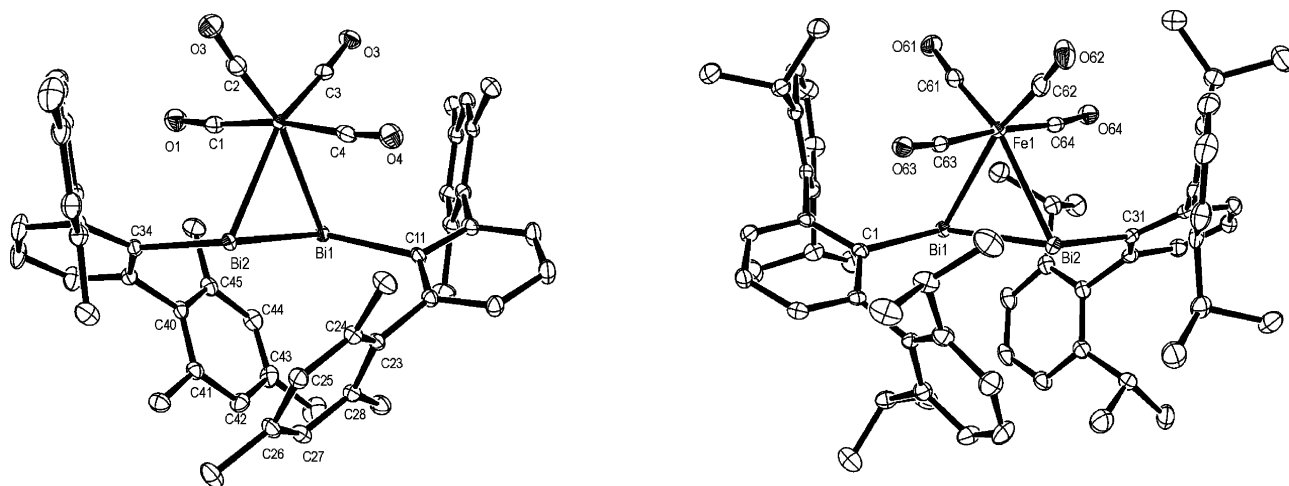


Figure 3. Solid-state molecular structure of $[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}^\#_2)]$ (**3**) (left image) and $[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}'_2)]$ (**4**) (right image, H-atoms are not shown for clarity, thermal ellipsoids at the 30% probability level, toluene solvent molecules not shown).

which contain $\text{ArBi}=\text{BiAr}$ dibismuthene units in a *trans* arrangement coordinated to an $\text{Fe}(\text{CO})_4$ moiety in a symmetrical η^2 -fashion (Figure 3, Table 1). The structures resemble that of the distibene complex $[\text{Fe}(\text{CO})_4(\text{Sb}_2\text{R}_2)]$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$), which was prepared by a similar route to **3** and **4** and has an $\text{Sb}-\text{Sb}$ bond length of $2.774(1) \text{ \AA}$.^[30] The dibismuthenes in **3** and **4** are bound “face-on” to the $\text{Fe}(\text{CO})_4$ moiety which produces an out of plane bending of the terphenyl substituents as reflected in the $\text{C}(\textit{ipso})-\text{Bi}(1)-\text{Bi}(2)-\text{C}(\textit{ipso})$ torsion angles of 161.68 and 165.11° respectively.^[5] In contrast, related diphosphene complexes generally have the $\text{RP}=\text{PR}$ unit bound in an *end-on* fashion to the metal carbonyl fragment in related diphosphene complexes.^[4–7]

Although the $\text{Bi}-\text{Bi}$ bonds of $2.9432(2)$ and $2.9294(2) \text{ \AA}$ in **3** and **4** are significantly longer than the $2.8560(3) \text{ \AA}$ observed in the free ligand $\text{Ar}'\text{Bi}=\text{BiAr}'$ (**2**, vide infra) and the related dibismuthenes $\text{ArBi}=\text{BiAr}$ ($\text{Ar} = 2,4,6\text{-}\{\text{CH}(\text{SiMe}_3)_2\}_3\text{-C}_6\text{H}_2$, $2.8206(8) \text{ \AA}$; $\text{Ar} = \text{Ar}^\#$, $2.833(2) \text{ \AA}$),^[10,11] the values are nonetheless shorter than single bond lengths typically observed for $\text{Bi}-\text{Bi}$ single bonds.^[1] In addition, they are notably shorter than those in the related complexes, $[\{\text{W}(\text{CO})_5\}_2\{\text{Bi}_2(\text{CH}_2\text{SiMe}_3)_2\}]$ [$\text{Bi}-\text{Bi}$ $3.0024(7) \text{ \AA}$],^[13a] $[\{\text{W}(\text{CO})_5\}_2\text{Bi}_2\{\text{CH}_2\text{tBu}\}_2]$ [$\text{Bi}-\text{Bi}$ $2.9979(7) \text{ \AA}$],^[13b] and $[\text{Cp}_2\text{Zr}(\text{Bi}_2\text{Ar}^\#_2)]$ [$\text{Bi}-\text{Bi}$ $3.1442(7) \text{ \AA}$],^[14] although they are longer than that in the complex $[\{\text{W}(\text{CO})_5\}(\text{Bi}_2\{\text{CH}_2\text{SiMe}_3\}_2)]$ [$\text{Bi}-\text{Bi}$ $2.8769(5) \text{ \AA}$].^[13a] This is consistent with theoretical investigations which have shown that some double bond character of the $\text{Bi}-\text{Bi}$ bond is preserved in the latter compound, although not in the zirconocene complex which features a much longer $\text{Bi}-\text{Bi}$ bond length.^[14] In view of the significantly larger inter-ligand repulsions in **3** and **4** compared to $[\text{W}(\text{CO})_5\{\text{Bi}_2(\text{CH}_2\text{SiMe}_3)_2\}_2]$, it seems likely that the $\text{Bi}-\text{Bi}$ bonds in **3** and **4** also retain some π -character.

The $\text{Bi}-\text{Fe}$ bond lengths in **3** and **4** range from $2.8033(4)$ to $2.8248(5) \text{ \AA}$. These values are similar to those in the complexes $[\{\text{Fe}(\text{CO})_4\}_2(\text{BiPh}_2)_2]$ and $[\text{Fe}(\text{CO})_4(\text{BiPh})_2]$ [$2.823(2)$ and $2.779(2) \text{ \AA}$, respectively],^[28] although they are at the

longer end of the range observed in other $\text{Bi}-\text{Fe}$ clusters containing iron carbonyl fragments.^[31] Finally, it should be noted that the different steric demand of the flanking aryl rings has only a very minor effect on the overall structures of **3** and **4**. In **3**, the $\text{Bi}-\text{Bi}$ and $\text{Bi}-\text{C}$ bonds are slightly longer and the $\text{Bi}-\text{Bi}-\text{C}$ angles are marginally wider which is in accord with larger bulk of the aryl substituents. However, although the $\text{Bi}(1)-\text{Bi}(2)-\text{C}(\textit{ipso})$ angle in **3** ($106.73(6)^\circ$) is similar to the corresponding angle ($105.44(6)^\circ$) in uncomplexed **2**, the angle in **4** ($102.37(7)^\circ$) is ca. 10° wider than that in $\text{Ar}^\#\text{Bi}=\text{BiAr}^\#$.

The composition of **3** and **4** was confirmed by spectroscopic methods. Three bands were detected in the characteristic region for the CO stretching vibration in the IR spectrum. In the ^1H and ^{13}C NMR spectra in C_6D_6 four inequivalent environments were observed for the *ortho*-Me and *i*Pr groups respectively, suggesting hindered rotation about the $\text{Bi}-\text{C}(\textit{ipso})$ bonds as well as the $\text{C}-\text{C}$ bonds connecting the aryl rings of the terphenyl ligands.^[32] The observation of only one signal for the carbonyl groups in the ^{13}C NMR spectrum may indicate fluxional behavior of the carbonyl ligands in solution.

Conclusions

Reactions of ArBiCl_2 ($\text{Ar} = \text{Ar}^\#, \text{Ar}'$) with $\text{KSi}(\text{SiMe}_3)_3$, $\text{K}_2\text{Si}_2(\text{SiMe}_3)_4$ and $\text{Na}_2[\text{Fe}(\text{CO})_4]$ have been studied as possible routes to novel silicon and iron compounds containing BiAr units. In all cases, the formation of $\text{Bi}-\text{Bi}$ bonded products was observed instead of simple salt metathesis due to a combination of the reducing power of the anionic silicon and iron reagents, and the stability of the $\text{Bi}-\text{Bi}$ bonds. The dibismuthane $\text{Ar}'(\text{Cl})\text{BiBi}(\text{Cl})\text{Ar}'$ (**1**) was isolated from the reaction of $\text{Ar}'\text{BiCl}_2$ with $\text{KSi}(\text{SiMe}_3)_3$ while the reaction of $\text{Ar}'\text{BiCl}_2$ with $\text{K}_2\text{Si}_2(\text{SiMe}_3)_4$ yielded the corresponding dibismuthene $\text{Ar}'\text{Bi}=\text{BiAr}'$ (**2**). Interestingly, the related distibane $\text{Ar}^*(\text{Cl})\text{SbSb}(\text{Cl})\text{Ar}^{*111}$ could only be obtained as a mixture with

$\text{Ar}^*\text{Sb}=\text{SbAr}^*$ [$\text{Ar}^* = 2,6-(2,4,6\text{-iPr}_3\text{-C}_6\text{H}_2)_2\text{-C}_6\text{H}_3$] from the reduction of Ar^*SbCl_2 with KC_8 . Dipnictanes such as $\text{Ar}(\text{Cl})\text{E}-\text{E}(\text{Cl})\text{Ar}$, may thus be viewed as likely intermediates in the formation of dipnictenes $\text{ArE}=\text{EAR}$ ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{and Bi}$).

The reaction of ArBiCl_2 ($\text{Ar} = \text{Ar}^\#, \text{Ar}'$) with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ afforded the iron-capped dibismuthene complexes $[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}'_2)]$ (**3**) and $[\text{Fe}(\text{CO})_4(\text{Bi}_2\text{Ar}^\#_2)]$ (**4**) in which the $\text{Fe}(\text{CO})_4$ moiety is coordinated to the Bi–Bi array in a symmetrical face-on (η^2) fashion. This coordination mode is generally observed for dibismuthenes $\text{RBi}=\text{BiR}$ while, in contrast, related diphosphenes exhibit more varied coordination behavior in the presence of transition metals.^[5–7]

Experimental Section

General Methods: All manipulations were carried out with the use of modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All solvents were dried by the method of Grubbs^[33] and degassed three times (freeze–pump–thaw) prior to use. $\text{Ar}^\#\text{BiCl}_2$,^[11] $\text{KSi}(\text{SiMe}_3)_3$,^[19] and $\text{K}_2\{\text{Si}_2(\text{SiMe}_3)_4\}$ ^[20] were prepared according to literature procedures. ^1H NMR spectra were recorded on Varian 300 and 600 MHz instruments and referenced to the residual protio benzene in the C_6D_6 or to the Me signal of the toluene solvent.

Data Collection and Structural Refinement of 1–4: Crystals of sufficient quality for X-ray crystallography were removed from a Schlenk tube under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil.^[34] A suitable crystal was selected, attached to a glass fiber, and quickly placed under a low-temperature nitrogen stream. Data were recorded by using either a Bruker SMART 1000 CCD (for **1** and **2**) and a Bruker APEXII

CCD system (for **3** and **4**). Absorption corrections were performed using SADABS.^[35,36] The structures were solved with direct methods and the non-hydrogen atoms were refined anisotropically (except for disordered parts of the molecules, full-matrix least-squares on F^2).^[38,39] The structure of **3** contained one toluene molecule in the unit cell which was disordered over an inversion center and refined as a rigid group using the AFIX instruction. The structure of **4** also displayed a disordered toluene molecule. The affected carbon and hydrogen atoms were refined over split positions with isotropic atomic displacement parameters. DFIX instructions were used to restrain the C–C distance in the disordered of methyl group of the toluene molecule and EADP to constrain their thermal displacement parameters. Further crystallographic details are given in Table 2.

CCDC-675732 (for **1**), -675733 (for **2**), -675734 (for **3**), and -675735 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$\text{Ar}'\text{BiCl}_2$: A solution of 6.07 g (15.0 mmol) of $\text{Ar}'\text{Li}$ dissolved in 25 mL of toluene was added dropwise with stirring to a cold (-80°C) slurry of 5.68 g (18.0 mmol) of BiCl_3 in 25 mL of toluene. After the addition was complete, the reaction mixture was kept at this temperature for an additional 2 h. The reaction was subsequently warmed to room temperature and stirring was continued for further 12 h. The reaction mixture was filtered through a filter-tipped cannula, concentrated in vacuo to a volume of 10 mL and storage at -20°C for 48 h yielded $\text{Ar}'\text{BiCl}_2$ as pale brown, almost colorless crystals. Yield 5.03 g (49%); m.p. 148°C . ^1H NMR (C_6D_6 , $+25^\circ\text{C}$, 300.08 MHz): $\delta = 0.95$ (d, $^3J_{\text{H-H}} = 6.6$ Hz, 12 H, CH_3), 1.26 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 12 H, CH_3), 2.88 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 4 H, CH), 7.10 (d, $^3J_{\text{H-H}} = 5.1$ Hz, 2 H, *m*-H), 7.20 (t, $^3J_{\text{H-H}} = 4.5$ Hz, 2 H, *p*-H), 7.67 (d, $^3J_{\text{H-H}} = 4.5$ Hz, 4 H, *m*-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , $+25^\circ\text{C}$, 75.45 MHz): $\delta = 23.2, 25.9, 30.9, 122.7, 123.4, 127.9, 130.0, 136.5, 148.1, 148.4, 182.1$ ppm.

Table 2. Crystallographic data for **1–4**.

	1	2	3	4
Formula	$\text{C}_{60}\text{H}_{74}\text{Bi}_2\text{Cl}_2$	$\text{C}_{60}\text{H}_{74}\text{Bi}_2\text{Cl}_2$	$\text{C}_{52}\text{H}_{50}\text{Bi}_2\text{O}_4\text{Fe}\cdot 0.5\text{C}_7\text{H}_8$	$\text{C}_{64}\text{H}_{74}\text{Bi}_2\text{O}_4\text{Fe}\cdot 1.5\text{C}_7\text{H}_8$
<i>M</i>	1284.05	1213.15	1258.80	1519.24
<i>T</i> [K]	90(2)	90(2)	90(2)	90(2)
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/n$	$Pccn$	$P\bar{1}$	$C2/c$
<i>a</i> [Å]	13.3721(6)	20.612(2)	11.3868(8)	46.289(2)
<i>b</i> [Å]	14.4248(6)	15.757(2)	11.5796(8)	13.8362(5)
<i>c</i> [Å]	14.0513(6)	16.175(2)	19.395(2)	21.2717(8)
α [°]	90	90	102.610(1)	90
β [°]	95.0270(10)	90	92.643(1)	105.985(1)
γ [°]	90	90	106.044(1)	90
<i>V</i> [Å ³]	2699.9(2)	5253.5(7)	2382.9(3)	13097.1(8)
<i>Z</i>	2	4	2	8
Crystal size [cm]	$0.30 \times 0.10 \times 0.05$	$0.50 \times 0.48 \times 0.13$	$0.40 \times 0.10 \times 0.04$	$0.15 \times 0.10 \times 0.05$
ρ_{calcd} [Mg m ^{−3}]	1.579	1.534	1.754	1.541
<i>F</i> (000)	1268	2400	1222	6056
$\mu(\text{Mo-K}\alpha)$ [cm ^{−1}]	6.644	6.726	7.712	5.628
<i>hkl</i> range	−18/18, −20/20, 19/19	−28/29, −22/22, 22/22	−17/17, −17/17, 29/29	−60/60, −17/17, 27/27
$2\theta_{\text{max}}$ [°]	60.04	60.00	66.28	55.00
Reflections collected/unique	14150/7875	57741/7664	41717/17308	71067/15007
<i>R</i> (int)	0.0386	0.0501	0.0326	0.0374
Data/restraints/parameters	7875/0/297	7664/0/288	17308/0/551	15007/2/723
Goodness of fit on F^2	1.111	1.052	1.071	1.025
<i>R1/wR2</i> [$I > 2\sigma(I)$]	0.0393/0.1028	0.0254/0.0573	0.0284/0.0739	0.0211/0.0475
<i>R1/wR2</i> (all data)	0.0566/0.1137	0.0332/0.0601	0.0366/0.0779	0.0273/0.0490
Largest diff. peak/hole [e Å ^{−3}]	3.521/−1.168	2.515/−1.477	2.763/−2.875	1.175/−0.999

Ar₂Bi₂Cl₂ (1): To a cooled (0 °C) solution of 0.75 g (1.11 mmol) of Ar[#]BiCl₂ in 10 mL of toluene, was added dropwise a solution of 0.320 g (1.11 mmol) KSi(SiMe₃)₃ in 10 mL of toluene. This resulted in an immediate color change from colorless to deep purple. After concentration to about 5 mL and storage at room temperature for 48 h, **1** was obtained as colorless needles of suitable quality for X-ray crystallography. Yield 0.280 g (40%); m.p. >129 °C (decomp.). ¹H NMR (C₆D₆, +25 °C, 300.08 MHz): δ = 1.02 (d, ³J_{H-H} = 6.8 Hz, 12 H, CH₃), 1.31 (d, ³J_{H-H} = 6.8 Hz, 12 H, CH₃), 2.88 (sept, ³J_{H-H} = 6.8 Hz, 4 H, CH), 7.03 (d, ³J_{H-H} = 3.6 Hz, 4 H, *m*-H), 7.06 (t, ³J_{H-H} = 4.2 Hz, 2 H, *p*-H), 7.20 (t, ³J_{H-H} = 4.2 Hz, 2 H, *p*-H), 7.68 (d, ³J_{H-H} = 3.6 Hz, 4 H, *m*-H) ppm. ¹³C NMR (C₆D₆, +25 °C, 75.45 MHz): δ = 23.2, 25.9, 31.1, 122.8, 123.4, 128.5, 130.0, 136.6, 147.7, 148.3 ppm; C (*ipso*) of the Ar[#] ligand not observed. UV/Vis (hexanes): λ_{max} (ε/L mol⁻¹ cm⁻¹) = 325 (shoulder), 542 nm (3100).

Ar₂Bi₂ (2): To a solution of 0.67 g (0.95 mmol) of Ar[#]BiCl₂ in 15 mL of toluene, precooled to -80 °C, was added a solution of 0.943 g (1.00 mmol) of 1,2-dipotassio-1,1,2,2-tetrakis(trimethylsilyl)disilane dissolved in 20 mL of toluene. The reaction mixture and was kept at this temperature for 2 h whereupon the reaction mixture adopted a purple color that intensified upon subsequent warming to room temperature. Stirring was continued for 12 h and the dark purple solution was then concentrated in vacuo to ca. 15 mL and filtered using a filter tipped cannula. The volume of the filtrate was reduced to ca. 7 mL and storage at ca. -20 °C yielded dark purple, almost black crystals of **2** of suitable quality for X-ray crystallography. Yield 0.390 g (72%); m.p. 156–158 °C. UV/Vis (hexanes): λ_{max} (ε/L mol⁻¹ cm⁻¹) = 308 (shoulder), 356 (shoulder), 526 nm (2900). ¹H NMR (C₆D₆, +25 °C, 300.08 MHz): δ = 0.99 (d, *J* = 6.6 Hz, 12 H, CH₃), 1.16 (d, ³J_{H-H} = 6.6 Hz, 12 H, CH₃), 2.72 (sept, ³J_{H-H} = 6.6 Hz, 4 H, CH), 7.04 (d, ³J_{H-H} = 7.8 Hz, 4 H, *m*-H), 7.08 (t, ³J_{H-H} = 7.2 Hz, 2 H, *m*-H), 7.11 (t, ³J_{H-H} = 7.2 Hz, 2 H, *p*-H), 7.23 (d, ³J_{H-H} = 7.8 Hz, 4 H, *m*-H) ppm. ¹³C{¹H} NMR (C₆D₆, +25 °C, 75.45 MHz): δ = 24.30, 26.37, 31.05, 122.70, 123.69, 129.36, 140.91, 145.0, 146.69, 147.23, 154.32 ppm.

[Fe(CO)₄(Bi₂Ar[#]₂)] (3): A solution of Ar[#]BiCl₂ (1.0 g, 1.5 mmol) in ca. 30 mL of THF was added to a suspension of Na₂[Fe(CO)₄] (0.32 g, 1.5 mmol) in ca. 15 mL of THF at -78 °C. An orange suspension formed immediately and the mixture was warmed to room temperature over several hours, then stirred overnight. The solvent was removed, the dark residue was extracted with toluene (60 mL) and the mixture was filtered. The deep-red filtrate was concentrated to ca. 8 mL and storage of this solution at ambient temperature for two days gave deep-red crystals of **3** which were isolated. After drying in the vacuum for ca. 1 h the compound still contains one equiv. of toluene per molecule of **3**. Yield 0.28 g (25%); m.p. 246–248 °C. ¹H NMR (C₆D₆, +25 °C, 300.08 MHz): δ = 0.94–1.11 (overlapping m, 30 H, CH₃), 1.27 (d, CH₃, *J* = 6.9 Hz, 6 H, CH₃), 1.39 (d, *J* = 6.9 Hz, 6 H, CH₃), 1.62 (d, *J* = 6.9 Hz, 6 H, CH₃), 2.11 (s, 3 H, CH₃ of C₇H₈), 2.53 (sept, *J* = 6.9 Hz, 2 H, CH), 2.83 (sept, *J* = 6.9 Hz, 2 H, CH), 2.94 (sept, *J* = 6.9 Hz, 2 H, CH), 3.42 (sept, *J* = 6.9 Hz, 2 H, CH), 6.97–7.35 (overlapping m, 22 H, aromatic CH) ppm. ¹³C{¹H} NMR (C₆D₆, +25 °C, 75.45 MHz): δ = 21.43 (s, CH₃ of C₇H₈), 23.22 (s, CH₃ of *i*Pr), 24.14 (s, CH₃ of *i*Pr), 25.42 (s, CH₃ of *i*Pr), 25.63 (s, CH₃ of *i*Pr), 26.02 (s, CH₃ of *i*Pr), 26.13 (s, CH₃ of *i*Pr), 27.24 (s, CH₃ of *i*Pr), 28.06 (s, CH₃ of *i*Pr), 29.96 (s, CH of *i*Pr), 30.15 (s, CH of *i*Pr), 31.09 (s, CH of *i*Pr), 33.37 (s, CH of *i*Pr), 122.85 (s, Ar[#]), 124.23 (s, Ar[#]), 124.63 (s, Ar[#]), 125.29 (s, Ar[#]), 125.72 (s, C₇H₈), 126.77 (s, Ar[#]), 127.76 (s, Ar[#]), 127.94 (s, C₇H₈), 128.60 (s, C₇H₈), 128.81 (s, Ar[#]), 129.31 (s, Ar[#]), 129.36 (s, Ar[#]), 129.58 (s, Ar[#]), 129.91 (s, Ar[#]), 137.92 (s, C₇H₈),

142.99 (s, Ar[#]), 145.22 (s, Ar[#]), 145.33 (s, Ar[#]), 146.97 (s, Ar[#]), 147.20 (s, Ar[#]), 147.40 (s, Ar[#]), 148.51 (s, Ar[#]), 151.22 (s, Ar[#]), 154.35 (s, Ar[#]), 210.50 (s, Fe(CO)₄) ppm. IR (Nujol): ν̃ = 2046 (s), 1991 (w), 1977 (vs) cm⁻¹. UV/Vis (hexanes): λ_{max} (ε/L mol⁻¹ cm⁻¹) = 524 nm (740).

[Fe(CO)₄(Bi₂Ar[#]₂)] (4): This compound was prepared by an analogous procedure to **3** using Ar[#]BiCl₂ (0.9 g, 1.5 mmol) and Na₂[Fe(CO)₄] (0.32 g, 1.5 mmol). C₅₂H₅₀Bi₂FeO₄·0.5C₇H₈ (1212.22). Yield 0.14 g (15%) of a red-brown, crystalline solid. Deep-red crystals of **4** were obtained by recrystallization of the compound from toluene and storage of the saturated solution at -7 °C for several days; m.p. 215 °C (decomp.). ¹H NMR (C₆D₆, +25 °C, 300.08 MHz): δ = 1.84 (s, 6 H, *o*-CH₃ of Ar[#]), 2.04 (s, 6 H, *o*-CH₃ of Ar[#]), 2.07 (s, 6 H, *o*-CH₃ of Ar[#]), 2.11 (s, 5 H, 1 CH₃ of C₇H₈), 2.17 (s, 6 H, *o*-CH₃ of Ar[#]), 2.37 (s, 6 H, *p*-CH₃ of Ar[#]), 2.43 (s, 6 H, *p*-CH₃ of Ar[#]), 6.80–7.00 (overlapping m, 16 H, aromatic CH). ¹³C{¹H} NMR (C₆D₆, +25 °C, 75.45 MHz): δ = 21.04 (s, CH₃ of C₇H₈), 21.92 (s, *o*-CH₃ of Ar[#]), 21.29 (s, *o*-CH₃ of Ar[#]), 21.32 (s, *o*-CH₃ of Ar[#]), 21.48 (s, *o*-CH₃ of Ar[#]), 23.14 (s, *p*-CH₃ of Ar[#]), 23.50 (s, *o*-CH₃ of Ar[#]), 125.74 (s, C₇H₈), 127.22 (s, Ar[#]), 127.93 (s, C₇H₈), 128.59 (s, C₇H₈), 128.83 (s, Ar[#]), 129.36 (s, Ar[#]), 129.44 (s, Ar[#]), 130.12 (s, Ar[#]), 135.77 (s, Ar[#]), 136.15 (s, Ar[#]), 136.31 (s, Ar[#]), 136.74 (s, Ar[#]), 137.25 (s, Ar[#]), 137.53 (s, C₇H₈), 143.36 (s, Ar[#]), 145.67 (s, Ar[#]), 151.50 (s, Ar[#]), 152.09 (s, Ar[#]), 206.58 (s, Fe(CO)₄) ppm. IR (Nujol): ν̃ = 2044 (s), 1989 (m), 1983 (s), 1966 (s) cm⁻¹. UV/Vis (thf): λ_{max} (ε/L mol⁻¹ cm⁻¹) = 572 nm (580).

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