Isolation of a Bismuth Chloride−Iron Carbonyl Adduct: Synthesis and Structural Characterization of $[PhCH_2NMe_3]_2[Bi_2Cl_4(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}]$

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The reaction of bismuth(III) chloride with $[PhCH_2NMe_3]_2[Fe(CO)_4]$ at a ratio of 2:1 in acetonitrile yields the iron carbonyl−bismuth chloride adduct $[PhCH_2NMe_3]_2[Bi_2Cl_4(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}]$ cleanly in high yield. The complex consists of two $BiCl_3$ groups bridged by an $[Fe(CO)_4]^{2-}$ unit. Two chloride ligands are shared between the Bi atoms, producing square-pyramidal coordination at bismuth and octahedral coordination at the iron center. The production of this complex represents the synthesis of a stable adduct of a highly nucleophilic metal carbonyl anion with a strongly Lewis acidic main group halide. The compound $C_{24}H_{32}N_2O_4Bi_2Cl_6Fe$ crystallizes in the orthorhombic space group *Pba*2 (No. 32) with cell parameters $a = 14.624(3)$ Å, $b = 17.010(3)$ Å, $c = 7.1990(10)$ Å, $V = 1790.8(5)$ Å^3, and $Z = 2$.

Introduction

Complexes and clusters between transition metal (M) carbonyls and group 15 main group (E) elements have been the subject of intensive study in recent years, with a wide variety of compounds having new and interesting structures and properties being produced.[1] These compounds range in size from very small molecules[2−5] to very large clusters with structures closely resembling close-packed arrays of metal atoms one would expect to see in a solid-state compound.[6−8] However, relatively few such compounds have been produced which preserve intact main group−halide bonds.[9−16] Here we report the synthesis, isolation, and characterization of a novel bismuth chloride−iron carbonyl complex, $[PhCH_2NMe_3]_2[Bi_2Cl_4(\mu\text{-}Cl_2)\{\mu\text{-}Fe(CO)_4\}]$ (**1**). To our knowledge, **1** represents the first transition metal−group 15 element complex in which a simple adduct of a highly nucleophilic metal carbonyl anion with a group 15 halide has been structurally characterized.

The anion $[Fe(CO)_4]^{2-}$ is known in particular for its high reactivity in nucleophilic substitution reactions and has even been referred to as a "supernucleophile".[17] In a wide variety of reactions of both inorganic and organic substrates, it readily displaces halide ions. The $[Fe(CO)_4]^{2-}$ anion is also strongly reducing and undergoes facile electron transfer reactions. Thus these properties would lead one to expect either (1) nucleophilic attack of the iron carbonyl anion on the bismuth centers with displacement of the chloride ligands from bismuth or (2) reduction of the bismuth halide.[9−16,18] Bismuth centers, on the other hand, are often highly Lewis acidic, as has been demonstrated with numerous conventional coordination complexes as well as in a variety of organometalated bismuth halides. The latter have been studied extensively by Norman and co-workers.[18] The Lewis acidity of the bismuth center thus opposes the displacement of halide ions.

Experimental Section

General Considerations. All reactions were performed under an inert atmosphere of nitrogen or argon using standard Schlenk/vacuum line techniques. Diethyl ether and tetrahydrofuran were dried by distillation from CaH_2 followed by distillation from Na/benzophenone ketyl. Acetonitrile and dichloromethane were distilled from CaH_2 prior to use. Water used to wash the product was deoxygenated by sparging with argon for 30 min prior to use. Infrared spectra were obtained with a Perkin-Elmer Model 1640 FTIR instrument, and ^1H (250.13 MHz) and $^{13}C\{^1H\}$ (62.90 MHz) NMR spectra were measured on a Bruker AC 250 spectrometer in the solvent noted. Analyses for carbon monoxide content were performed by digestion of the compound with $[PyH]Br_3$ in degassed CH_2Cl_2 at 75 °C in a vacuum flask, followed by quantitation of the liberated CO using a Toepler pump. Collman's reagent, $Na_2[Fe(CO)_4]\cdot{}^3/_2C_4H_8O_2$, was prepared by the literature method.[19] $BiCl_3$ was purified by overnight reflux in $SOCl_2$ followed by removal of the volatile components *in vacuo*. $[PhCH_2NMe_3]Cl$ and

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Table 1. Crystal Data and Structure Refinement Parameters for **1**

empirical formula	$C_{24}H_{32}Bi_2Cl_6FeN_2O_4$
fw	1099.03
temp	223(2) K
radiation	Mo Kα ($\lambda = 0.71069$ Å)
system [space group]	orthorhombic [*Pba*2 (No. 32)]
unit cell dimensions	$a = 14.562(3)$ Å
	$b = 17.062(3)$ Å
	$c = 7.2210(10)$ Å
	$V = 1794.1(5)$ Å^3
Z	2
ρ_{calc}	2.034 Mg/m^3
μ	10.660 mm
final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0521$, $_wR_2 = 0.1257$
R indices (all data)^a	$R_1 = 0.0873$, $_wR_2 = 0.1514$
flack param [extinction coeff]	0.27(2) [0.0008(4)]
largest diff peak and hole	0.873 and 0.858 e Å^{-3}

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $_wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

methyldichlorophosphine were used as received from Janssen Chimica and Strem Chemicals, respectively.

Synthesis of $[PhCH_2NMe_3]_2[Bi_2Cl_6\{\mu\text{-}Fe(CO)_4\}]$, 1. Method 1. A 0.589 g (3.17 mmol) sample of $[PhCH_2NMe_3]Cl$ was added to a solution of 0.549 g (1.59 mmol) of $Na_2Fe(CO)_4\cdot 1.5$(dioxane) in 60 mL of MeCN. The mixture was stirred for 1.5 h and filtered. In a separate flask, 1.00 g (3.17 mmol) $BiCl_3$ was dissolved in 80 mL of MeCN. The iron carbonyl solution was added dropwise to this solution via a dropping funnel over a period of 1 h. The resulting orange solution was filtered and the solvent removed *in vacuo*. The solid was washed with deoxygenated water, dichloromethane, and tetrahydrofuran and then dried under vacuum. The solid was extracted with 100 mL of MeCN, the extract was filtered, and 500 mL of diethyl ether was added to effect precipitation. The solvent was filtered off and the bright orange solid dried *in vacuo*, giving analytically pure **1** (yield 1.43 g, 82%). The compound may be crystallized by vapor-phase diffusion of diethyl ether with a concentrated MeCN solution of **1** at −10 °C. IR (ν_{CO} in cm^{-1}, MeCN): 2084 (ms), 2025 (vs). ^1H NMR (250.13 MHz, CD_3CN, 295 K): δ 7.55, 7.52, 7.49 (m, 5H, C_6H_5), 4.34 (s, 2H, CH_2), 2.95 (s, 9H, $N(CH_3)_3$). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_3CN, 295 K): δ 210.0, 186.7 (s, CO), 134.3, 131.7, 130.2, 128.5 (s, C_6H_5), 71.3 (s, CH_2), 54.5 (t, $N(CH_3)_3$). Anal. Calcd for **1**: 0.84 mmol of CO. Found: 0.83 mmol of CO. **1** is soluble in MeCN, slightly soluble in Me_2CO, but insoluble in CH_2Cl_2, THF, toluene, Et_2O, and hexanes.

Method 2. A 50 mL portion of MeCN was added to a 100 mL Schlenk flask containing $[PhCH_2NMe_3]_2$[**I**] (0.500 g, 0.290 mmol). A 3.0 equiv amount of $MePCl_2$ (0.87 mmol, 0.10 g, 0.08 mL) was then added by syringe to the solution. The solution turned a deeper red color and was allowed to stir for approximately 10 h, during which it became dark green/orange. The solution was filtered through diatomaceous earth and the solvent removed under vacuum. The dark oil was washed with several 50 mL portions of Et_2O, and the solid remaining was placed in a Soxhlet extraction thimble and extracted with additional Et_2O for a few hours to remove the residual phosphine byproducts. The solid was extracted with a few 20 mL portions of THF, and the dark green filtrates were combined. The remaining solid was extracted with MeCN and the orange solution filtered. The MeCN was removed *in vacuo* and the material worked up as described above. Yield: 0.117 g, 18% (based on Bi). The green compound, $[PhCH_2NMe_3][(\mu\text{-}H)Fe_2(CO)_6Bi_2(\mu\text{-}Cl)_2]$, which will be described elsewhere, forms exclusively in the reaction with precisely 2.0 equiv of $MePCl_2$. **1** forms at its expense in greater quantity as more of the phosphine reagent is added.

X-ray Structure Determination of 1. A summary of data collection parameters for compound **1** is found in Table 1. The data were acquired using a Rigaku AFC5S four-circle automated diffractometer (Rigaku CONTROL Automatic Data Collection Series, Molecular Structure Corp., The Woodlands, TX) using graphite-monochromated Mo Kα radiation (0.7107 Å). The crystal was mounted on a glass fiber with Epoxy cement, and data were collected with ω scans at 4°/min. Three standard reflections were monitored for decay every 150 reflections throughout data collection. An absorption correction from azimuthal (ψ) scans was applied to the data. The programs used in solving the structure were part of the Siemens Analytical X-Ray Instruments data reduction and refinement package SHELXTL PC,[20] and refinement of the structure was performed using the data refinement program package SHELXL-93.[21]

Large dark crystals of **1** were obtained by the procedure described above. A columnar crystal (0.3 × 0.3 × 0.5 mm^3) was used for data collection, with the primitive unit cell determined from 25 random reflections and shown to be orthorhombic. Data were collected for $\pm h,\pm k,\pm l$, ranging from $h = -16$ to $+16$, $k = -19$ to $+19$, and $l = -8$ to $+8$ with $\theta_{max} = 23.98°$. The acentric space group *Pba*2 (No. 32) was determined after resolving an orientational disorder problem which caused it to be pseudocentrosymmetric. The structure was solved by direct methods using the program XS, part of the SHELXTL-PC package, to locate the Bi and Fe atoms and subsequent least-squares difference maps and Fourier syntheses using SHELXL-93 to find the remaining non-hydrogen atoms. The hydrogen atom positions of the counterion were calculated using the HFIX routine and were treated via a riding model tied to the carbon atom to which they are associated. All non-hydrogen atoms were refined anisotropically, with the exception of the carbonyl ligands and three carbon atoms of the counterion. Upon refinement, three large residual peaks were located in the vicinity of the cluster which were finally recognized as the metal atoms of a second orientation of the anion. Two orientations of the anion were thus refined, with the occupancies tied to a free variable such that their sum was 1. The disordered components lie 180° inverted with respect to each other as shown in Figure 2. The terminal chloride ligands are common to both orientations. Given this disorder in the acentric space group setting, a new crystal was carefully chosen and examined for the possibility of a doubled or tripled axis. Prolonged exposures in taking axial photographs revealed no X-ray intensities in the intermediate locations, so that the original disorder model was chosen as the correct solution. The data were corrected for absorption (ψ scans), and a secondary extinction coefficient was calculated. Decay was insignificant, so no correction for this was made. The structure was refined as a twin, with a refined Flack parameter of 0.27(2). The largest peak in the final difference map was 0.873 e/Å^3.

Computational Details. Calculations were carried out within the standard extended Hückel formalism[22] using the modified Wolfsberg−Helmholz formula[23] and with the CACAO package developed by Proserpio and Mealli.[24] Standard atomic parameters were assumed for H, C, and O.[25] Parameters for Bi[26] and Fe[27] were taken from the literature. It has been confirmed that a reasonable variation of these parameters do not modify significantly the qualitative conclusions of this study. An idealized geometry of C_2 symmetry was used for the calculations. The assumed bond distances were taken from averaged experimental values (Å): Fe−Bi = 2.70; Fe−C = 1.83; C−O = 1.09; $Bi-Cl_{terminal} = 2.62$; $Bi-Cl_{bridge1} = 2.90$; $Bi-Cl_{bridge2} = 2.94$. The different bridging distances were used to reflect the asymmetry in the experimentally determined structure, in which the bridging chlorine ligands are unequally shared between the bismuth centers.

Results and Discussion

Structure of $[PhCH_2NMe_3]_2[Bi_2Cl_6\{\mu\text{-}Fe(CO)_4\}]$, 1. The reaction of 2 equiv of bismuth(III) chloride with $[PhCH_2NMe_3]_2[Fe(CO)_4]$ produces **1** cleanly. It may be isolated in 82% yield as a bright orange solid. The compound is unstable in solution

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Table 2. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**[a]

	x	*y*	*z*	*U*(eq)	% occ
Bi(1)	1117.1(5)	54286(4)	34347(13)	33.4(3)	69.1(2)
Fe(1)	0	5000	6233(7)	35(1)	34.6(2)
Cl(1)	2585(2)	4813(2)	4858(8)	55(1)	100.0
Cl(2)	540(4)	4006(4)	1553(11)	43(2)	69.1(2)
Cl(3)	1472(3)	6827(2)	4856(8)	64(1)	100.0
C(11)	50(2)	4019(10)	6010(30)	32(7)	69.1(2)
O(11)	799(13)	3436(9)	6070(30)	68(5)	69.1(2)
C(12)	844(13)	5369(12)	7910(20)	33(6)	69.1(2)
O(12)	1435(11)	5525(9)	8770(30)	58(5)	69.1(2)
Bi(1′)	1121(2)	5425(1)	6271(3)	47(1)	30.9(2)
Fe(1′)	0	5000	3520(30)	45(2)	15.5(2)
Cl(2′)	535(9)	4011(7)	8410(40)	59(4)	30.9(2)
C(11′)	510(30)	4018(14)	3740(80)	36(12)	30.9(2)
O(11′)	830(20)	3441(13)	3630(80)	62(11)	30.9(2)
C(12′)	790(40)	5390(40)	1780(80)	60(20)	30.9(2)
O(12′)	1350(30)	5610(30)	930(60)	50(20)	30.9(2)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) for **1**[a]

Bi(1)−Fe(1)	2.695(4)	Bi(1′)−Fe(1)	2.673(13)
Bi(1)−Cl(1)	2.594(4)	Bi(1′)−Cl(1)	2.584(5)
Bi(1)−Cl(2)	2.905(6)	Bi(1′)−Cl(2′)	2.99(2)
Bi(1)−Cl(2a)	2.932(6)	Bi(1′)−Cl(2′a)	3.02(2)
Bi(1)−Cl(3)	2.648(4)	Bi(1′)−Cl(3)	2.651(5)
Bi(1)−Bi(1a)	3.567(2)	Bi(1′)−Bi(1′a)	3.573(5)
Fe(1)−C(11)	1.83(2)	Fe(1′)−C(11′)	1.84(2)
Fe(1)−C(12)	1.84(2)	Fe(1′)−C(12′)	1.83(2)
Cl(2)−Bi(1a)	2.943(10)	Cl(2′)−Bi(1′a)	3.02(2)
C(11)−O(11)	1.09(2)	C(11′)−O(11′)	1.09(2)
C(12)−O(12)	1.09(2)	C(12′)−O(12′)	1.08(2)

[a] Symmetry transformation used to generate equivalent atoms: (a) $-x, -y + 1, z$.

Table 4. Selected Bond Angles (deg) for **1**[a]

Fe(1)−Bi(1)−Bi(1a)	48.56(7)	Cl(1)−Bi(1′)−Cl(3)	93.1(2)
Bi(1)−Fe(1)−Bi(1a)	82.9(2)	Cl(1)−Bi(1′)−Cl(2′)	96.5(3)
Bi(1)−Cl(2)−Bi(1a)	75.3(2)	Cl(1)−Bi(1′)−Cl(2′a)	171.6(5)
Fe(1)−Bi(1)−Cl(2a)	86.6(2)	Cl(1)−Bi(1′)−Bi(1′a)	126.1(1)
Cl(1)−Bi(1)−Fe(1)	95.2(1)	Cl(1)−Bi(1′)−Fe(1′)	95.8(2)
Cl(1)−Bi(1)−Bi(1a)	125.83(9)	Cl(2′)−Bi(1′)−Cl(2′a)	76.5(6)
Cl(1)−Bi(1)−Cl(2)	94.9(2)	Cl(2′)−Bi(1′)−Cl(3)	169.3(5)
Cl(1)−Bi(1)−Cl(2a)	174.2(2)	Cl(2′)−Bi(1′)−Bi(1′a)	53.9(3)
Cl(1)−Bi(1)−Cl(3)	92.9(2)	Cl(2′)−Bi(1′)−Fe(1′)	89.5(5)
Cl(2)−Bi(1)−Fe(1)	87.1(2)	Cl(3)−Bi(1′)−Cl(2′a)	93.6(3)
Cl(2)−Bi(1)−Bi(1a)	52.7(1)	Cl(3)−Bi(1′)−Bi(1′a)	122.8(1)
Cl(2)−Bi(1)−Cl(2a)	79.6(2)	Cl(3)−Bi(1′)−Fe(1′)	94.3(2)
Cl(2)−Bi(1)−Cl(3)	172.0(2)	Cl(2′a)−Bi(1′)−Bi(1′a)	51.3(3)
Cl(2A)−Bi(1)−Bi(1a)	52.0(1)	Fe(1′)−Bi(1′)−Bi(1′a)	48.1(3)
Cl(3)−Bi(1)−Fe(1)	94.1(1)	Fe(1′)−Bi(1′)−Cl(2′a)	88.8(5)
Cl(3)−Bi(1)−Bi(1a)	123.2(1)	Bi(1′)−Fe(1′)−Bi(1′a)	83.9(5)
Cl(3)−Bi(1)−Cl(2a)	92.5(2)	Bi(1′)−Cl(2′)−Bi(1′a)	73.0(4)

[a] Symmetry transformation used to generate equivalent atoms: (a) $-x, -y + 1, z$.

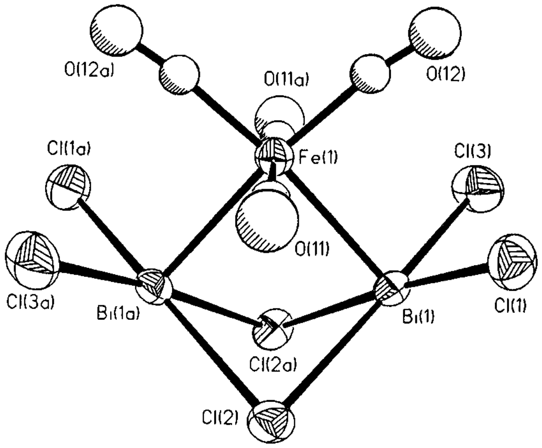

Figure 1. Thermal ellipsoid plot of the anion in the major component of the structure of **1** showing 50% probability ellipsoids and the atom-labeling scheme.

but can be recrystallized. Carbon monoxide analysis of the compound gave results consistent with the formula derived from the crystal structure determination. ^{1}H and ^{13}C NMR spectra of the complex showed resonances for the cation in the expected regions, while the ^{13}C resonances of the carbonyl ligands showed two equal-intensity carbon sites at room temperature ($\delta = 210.0$, 186.7). The carbonyl resonances were somewhat broad, which presumably is due primarily to slow exchange of the carbonyl ligands in the two environments relative to the time scale of the experiment. The signal at 186.7 ppm is at unusually low field for an iron carbonyl complex, especially an anionic one, and most likely represents that of the CO's *trans* to Bi. This is consistent with a substantial *trans* influence induced by the electronegative Bi−Cl fragments. It is noteworthy that the adduct **1** is stable to water, since $BiCl_3$ itself is highly moisture sensitive, readily forming BiOCl.

The solid-state structure of this complex, as determined by single-crystal X-ray diffraction, consists of a discrete $[Bi_2Cl_4(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}]^{2-}$ ion sitting about a crystallographic C_2 axis which passes through Fe(1) and the midpoint between the two bismuth atoms. Selected atomic coordinates, bond distances, and bond angles are given in Tables 2−4, respectively. There is one unique $[PhCH_2NMe_3]^+$ counterion, giving an overall ratio of two cations per anion. The complex anion has a structure consisting of two square-pyramidally coordinated bismuth atoms and one octahedrally coordinated iron atom. The iron atom occupies the apical positions of both Bi atoms, as required by the symmetry of the molecule. The anion is disordered in the solid state, with two orientations occupying the same location but rotated by 180° relative to one another. The occupancies of the orientations were refined to approximately 67% and 33%. The fact that the orientations were present in an almost exactly $^{2}/_{3}$ to $^{1}/_{3}$ ratio indicated the possibility of an axis being too short. Therefore, tests for the presence of weak zones were performed both by using a software routine in the diffractometer control system and by taking photographic images. Both of these methods failed to locate any weak-zone reflections. A thermal ellipsoid plot of the major component of the structure of **1** is shown in Figure 1. Figure 2 gives a plot of both components together, in order to show the relationship between the two molecules. The ensuing discussion will concentrate only on the major component of the molecule.

Both the bridging and terminal Cl−Bi−Fe angles (87.6(2)° average and 94.4(2)° average, respectively) are very close to the expected angle of 90° for square-pyramidal coordination, but the Bi(1)−Fe(1) bond leans slightly toward the bridging Cl ligands. A similar distortion is seen in the Cl−Bi−Cl angles in the basal plane of the square-pyramid, with the Cl(2)−Bi(1)−Cl(2a) angle (79.2(4)°) being significantly smaller and the Cl(1)−Bi(1)−Cl(3) angle (92.5(3)°) slightly larger than ideal. These effects are most likely caused by the restraints imposed by the bridging nature of the Fe atom and the Cl(2) ligands. The square-pyramidal coordination geometry at bismuth is consistent with a stereochemically active lone pair of electrons *trans* to the Bi−Fe bond and is common to a number of simple inorganic Bi coordination complexes, such as $[Bi_2Cl_8]^{2-}$ (**2**).[28]

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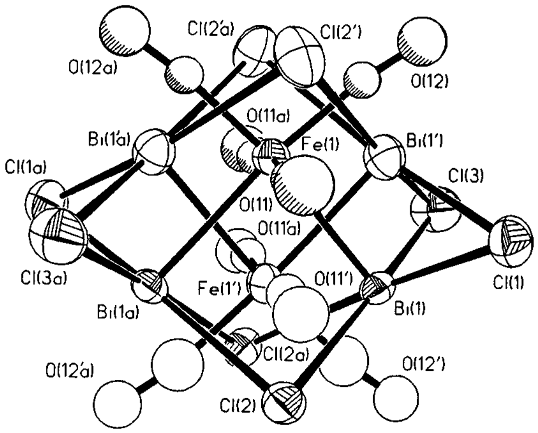
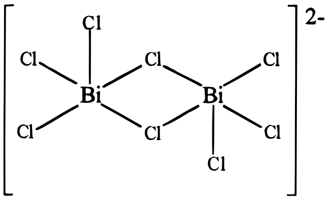
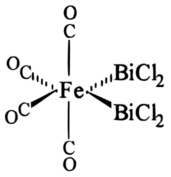


Figure 2. Thermal ellipsoid plot of both anionic components of the structure of **1** showing 50% probability ellipsoids and the atom-labeling scheme. Shaded isotropic spheres and thermal ellipsoids represent the major component, and unshaded atoms belong to the minor component. Cl(1), Cl(3), and their symmetry counterparts are shared between the two orientations.



(2)



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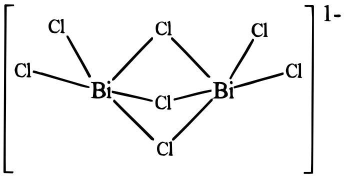

(5)

The square-pyramidal coordination geometry about bismuth in **2** is very regular, with mean Cl−Bi−Cl angles of 89.9°, but the geometry in **1** is distorted by the bridging configuration of the iron carbonyl fragment. Compound **1** may be viewed as a bis(chloride ion) adduct of the hypothetical molecule $[Fe(CO)_4(BiCl_2)_2]$ (**3**), analogous to $Fe(CO)_4\{BiPh_2\}_2$ (**4**).[29] Alternatively, one may view the molecule as one in which the $[Fe(CO)_4]^{2-}$ ion serves as a pseudohalide donor ligand by replacing a μ-Cl^- ion in the hypothetical ion $[Bi_2Cl_4(\mu\text{-}Cl)_3]^-$ (**5**). Such adduct formation is reminiscent of metal basicity studies which showed the ability of electron-deficient group 13 trihalides to complex to the metal center in electron-rich transition metal carbonyl complexes.[30] The donor−acceptor complexes $[CpM(CO)_3BiCl_3]^-$ (M = Mo, W) have been reported but were not characterized in detail due to experimental difficulties.[31]

The angles about the Fe atom conform closely to those expected for an octahedrally coordinated metal center, except the angles C(12)−Fe(1)−C(12a) (106(2)°) and C(12)−Fe(1)−Bi(1a) and C(12a)−Fe(1)−Bi(1) (86.0(11)°). Tilting of the carbonyl ligands toward the main group atoms in transition metal−main group element complexes is commonly observed and has been rationalized as involving back-bonding interactions of the M−E σ-bonds with the π^* CO molecular orbitals.[32] The most similar molecule available for comparison to **1** is $Fe(CO)_4\{BiPh_2\}_2$ (**4**),[29] in which the octahedral Fe atom is coordinated by two *cis* $BiPh_2$ functions, but **4** does not show the distortion of the C−Fe−C angle observed in **1**. In addition, the Bi−Fe−Bi angle for **4** (90.39(6)°) conforms to that expected for octahedral coordination, as opposed to 82.3(2)° in **1**. The origins of the differences in the angles may be ascribed to the restrictions imposed by the bridging chlorides.

The Bi−Cl bond parameters show some interesting effects. The $Bi-Cl_{terminal}$ bonds average 2.639(9) Å, which is within the normal range,[33] but the distances to the bridging chloride ligands (2.922(10) Å average) are considerably longer. While other $Bi-Cl_{bridge}$ distances may be found in this range,[34] most are only slightly longer than $Bi-Cl_{terminal}$ distances. In general, if the bridging chloride ion has such a long distance to one metal, the other distance is considerably shorter. In the present case, the two bridging chloride atoms are shared almost equally between the two bismuth atoms. The fact that the Bi−(μ-Cl) bonds in **1** are much longer than one would expect, even considering the equal sharing of the ligands, may be due to the presence of a third bridging group. The Bi−Fe distance of 2.694(5) Å is normal[3,12−15,35] and actually somewhat shorter than that found in **4**, where the steric demand of the Ph groups may cause lengthening of the Fe−Bi bonds.

Preliminary studies by infrared spectroscopy using As and Sb halides suggest similar reactivity patterns for those compounds. These products decrease in stability toward the lighter element, so that it has not yet proven possible to isolate pure samples of those compounds. The reaction between $[PhCH_2NMe_3]_2[Fe(CO)_4]$ and 2 equiv of BiF_3 was attempted to determine if the iron anion could be used to solubilize BiF_3, but a mixture of $[HFe(CO)_4]^-$ and $[Bi\{Fe(CO)_4\}_4]^{3-}$ resulted, along with an insoluble residue which lacked ν(CO) bands in its IR spectrum. Substituting Bi(O-*t*-Bu)$_3$ for BiF_3 produced a similar result, with the only detectable carbonyl-containing product being $[HFe(CO)_4]^-$.

Calculations. In order to gain some insight into the bonding in the $[Fe(CO)_4Bi_2Cl_6]^{2-}$ anion, we carried out extended Hückel (EH) calculations on this compound. The idealized model considerered in the calculations is an averaged structure of the $[Fe(CO)_4Bi_2Cl_6]^{2-}$ anion, having overall C_2 symmetry, but with

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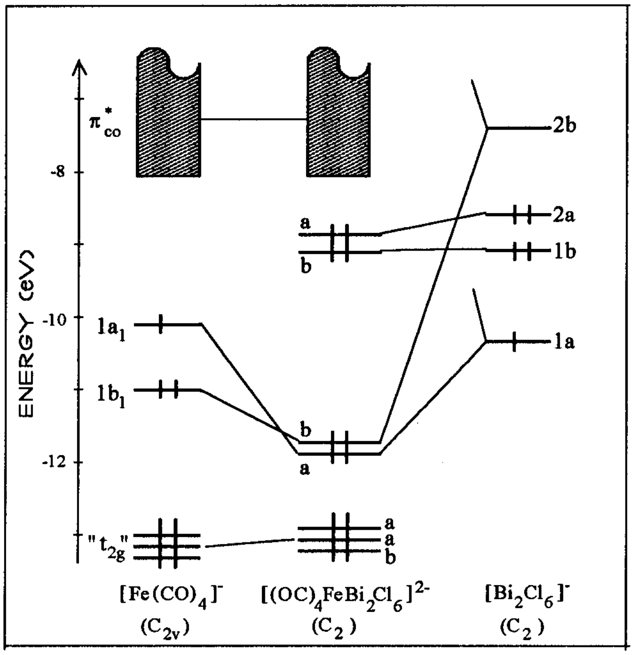

Figure 3. MO diagram for **1** based on the interaction of the $[Fe(CO)_4]^-$ (left) and $[Bi_2Cl_6]^-$ (right) fragments.

the $Fe(CO)_4Bi_2(Cl_{term})_2$ moiety having $C2_v$ symmetry. The (OC)−Fe−(CO) and Cl_{term}−Bi−Cl_{term} bond angles were set to the idealized value of 90°, while the experimental Bi−Fe−Bi angle was used (83°). It has been confirmed that reasonable geometrical variations in this $Fe(CO)_4Bi_2(Cl_{term})_2$ fragment do not significantly change the results of the calculations. The bridging chloride ions (Cl_{br}) have been placed in such a way that they lie in the plane of the $Bi(Cl_{term})_2$ groups, with the Bi−Cl_{br} distances equal to 2.90 and 2.94 Å, respectively. For this distorted square-planar coordination of the bismuth atoms, the Cl_{br}−Bi−Cl_{br} angle is equal to 71°, a value close to the experimental one (78°). The overall computed data obtained with this idealized model are very much the same as those obtained for the experimental structures, which will not be discussed here.

Figure 3 shows the MO diagram of the $[Fe(CO)_4Bi_2Cl_6]^{2-}$ anion, based on the interaction between the $Fe(CO)_4$ and Bi_2Cl_6 fragments. The frontier-orbital set of the $Fe(CO)_4$ unit is well-known.[27] It is composed of two hybrid orbitals pointing toward the Bi atoms, namely $1b_1$ and $1a_1$ (plotted in Figure 4) lying above a set of three d-type levels which do not interact significantly with the Bi atoms, giving rise to the nonbonding "t_{2g}" set of the octahedrally coordinated Fe atom in $[Fe(CO)_4Bi_2Cl_6]^{2-}$.

The Bi_2Cl_6 fragment has four frontier orbitals which are plotted in Figure 4. These four levels can be derived as resulting from the interaction of the frontier orbitals of two Bi atoms in an approximate square-planar environment. Each square-planar Bi atom bears two frontier orbitals of *z* (i.e. perpendicular to the square plane) and s dominant character, with some Cl antibonding admixture. In the Bi_2Cl_6 fragment, interaction between the two coupled square-planar units causes s/*z* hybridization on each Bi atom, giving rise to the in-phase and out-of-phase combinations of two types of Bi sp_z hybrids, namely 1a, 1b, 2a, and 2b (Figure 4). Only the combinations of the hybrids which point toward the Fe atom (1a and 2b) interact strongly with the metallic fragment. The 1b and 2a levels interact to a lesser extent and generate the nonbonding orbitals associated with the Bi lone pairs.

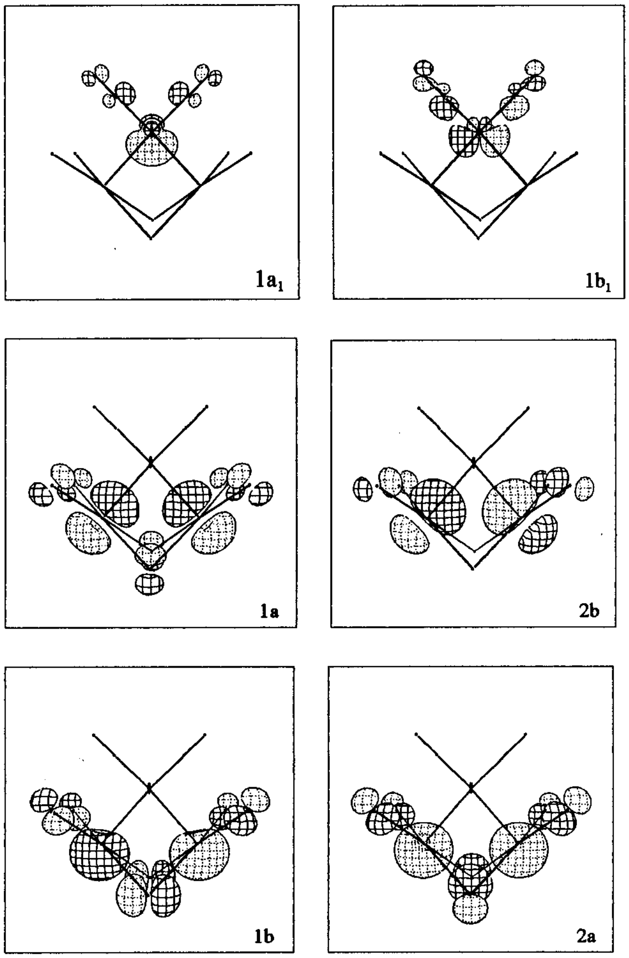

Figure 4. CACAO4.0 plots of major fragment frontier orbitals for **1**: (top) $[Fe(CO)_4]^-$ (contribution of the CO ligand situated in front of the picture omitted for clarity); (middle, bottom) $[Bi_2Cl_6]^-$.

It follows that the two Bi−Fe bonds result principally from the interaction of the $Fe(CO)_4$ $1b_1$ orbital with the 2b orbital of Bi_2Cl_6 and from the metallic $1a_1$ level with the 1a combination of Bi_2Cl_6. As long as the Cl character of the Bi_2Cl_6 frontier orbitals is not considered, the bismuth−iron interactions can be described within a localized 2-electron/2-center scheme. After interaction, the populations in the $1a_1$ and $1b_1$ frontier orbitals of $Fe(CO)_4$ are 0.93 and 1.39, respectively. The overall populations of the frontier orbitals are 3.04 for the 1a + 2a orbitals of Bi_2Cl_6 and 2.56 for the 1b + 2b orbitals. Subtracting 2 electrons for the Bi lone pairs from these values, 1.04 and 0.56 electrons remain in the a and b sets, respectively, of the Bi_2Cl_6 fragment involved in the bonding with iron. Thus, one Fe−Bi bonding pair can be formally considered as originating from the $1b_1$ metal orbital, while the other one can be considered as formally being provided equally by both the metal $1a_1$ and Bi_2Cl_6 2b orbitals. This would correspond to an oxidation state of −1 for Fe and +2.5 for Bi. The calculated net charges of Fe and Bi (−0.87 and +1.13) are consistent with these oxidation states, taking into account the various charge tranfers associated with the different covalent interactions. In the isolated $[Fe(CO)_4]^-$ and $(Bi_2Cl_6)^-$ fragments, the Fe and Bi net charges are −1.04 and +1.12, respectively. These values indicate that the overall $[(CO)_4Fe]^- \rightarrow [Bi_2Cl_6]^-$ donation is largely delocalized on the chlorine atoms, due to the significant halogen character of the frontier orbitals of Bi_2Cl_6 (Figure 4). This delocalization is related to the hypervalent character of bismuth.

The calculated Bi−Cl_{br} overlap populations (0.037 and 0.029) are small, as compared to those of Bi−Cl_{term} (0.330 and 0.309).

This difference in the Bi–Cl bond strength is probably overestimated by the EH method. Although significant, the computed HOMO/LUMO gap (0.80 eV) is not very large, due to the high energy of the Bi lone pairs. We think that these are artifacts related to the overestimation of the antibonding Bi–Cl_{br} character of the Bi lone pairs. Their energy is very sensitive to the position of the bridging Cl atoms. It may be that the experimental disordered structure is rather imprecise with respect to the position of these atoms. Unfortunately, a full optimization of their positions is not possible at the EH level. However, it should be noted that it is possible to increase significantly the HOMO/LUMO gap by displacing these atoms toward less symmetrical bridging positions.

Conclusions. In conclusion, the complex $[PhCH_2NMe_3]_2[Bi_2Cl_4(\mu\text{-}Cl_2)\{\mu\text{-}Fe(CO)_4\}]$ (**1**) reported in this paper is observed to have a novel structure and unusual stability in light of the high nucleophilicity of the iron carbonyl anion and the Lewis acidity of the bismuth chloride fragments. The bismuth atoms, despite their attachment to a highly reducing iron carbonyl fragment, retain all chloride ligands and a geometrical arrangement typical of Bi(III). Extended Hückel calculations on an idealized model of **1** have shown that, although the iron carbonyl fragment remains highly charged, there is a significant degree of electron transfer to the Bi_2Cl_6 moiety. This electron density appears to be highly delocalized over the chloride ligands of this unit, and this may give a rationale for the observed stability of the complex.

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Supporting Information Available: Full tables of data collection and refinement parameters, atomic coordinates, bond distances and angles, anisotropic thermal displacement parameters, and hydrogen atom coordinates and thermal ellipsoid plots of the minor anionic component and the unique counterion with atom labels (8 pages). Ordering information is given on any current masthead page.

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