Carbonylchromium Derivatives of Bismuth: New Syntheses and Relevance to C–O Activation

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Abstract: We have discovered a series of novel pentacarbonylchromium derivatives of bismuth from the reactions of $NaBiO_3$ with $[Cr(CO)_6]$ in KOH/MeOH solutions. When the reaction was carried out at room temperature, the highly charged $[Bi\{Cr(CO)_5\}_4]^{3-}$ (**1**) was obtained, whose structure was shown by X-ray analysis to possess a central bismuth atom tetrahedrally coordinated to four $[Cr(CO)_5]$ groups. As the reaction was heated at 80 °C, the methyl-substituted complex $[MeBi\{Cr(CO)_5\}_3]^{2-}$(**2**) was obtained, presumably via the C–O activation of MeOH. Further reactions of **1** with CH_2Cl_2 or $CH{\equiv}CCH_2Br$ form the halo-substituted complexes $[XBi\{Cr(CO)_5\}_3]^{2-}$($X = Cl$, **3**; Br, **4**), respectively. On the other hand, the reactions of **1** with RI ($R = Me$, Et) led to the formation of the alkyl-substituted complexes $[RBi\{Cr(CO)_5\}_3]^{2-}$($R = Me$, **2**; Et). The formation of complexes **1**–**4** is discussed, presumably via the intermediate bismuthinidene $[Bi\{Cr(CO)_5\}_3]^-$ or the trianion $[Bi\{Cr(CO)_5\}_3]^{3-}$.

Keywords: bismuth · carbonyl ligands · C–O activation · chromium

Introduction

Although Hieber et al. published the general syntheses of main-group–iron carbonyl complexes several decades ago, this methodology only worked nicely for the Fe system.[1, 2] Recently, the Mn system was studied by using K_2TeO_3 and $[Mn_2(CO)_{10}]$ in superheated MeOH; this gave rise to a series of tellurium-bridging manganese carbonylates.[3] For the early transition metal Cr, the use of E_2O_3 ($E = As$, Sb) and $[Cr(CO)_6]$ in concentrated KOH/MeOH led to complexes of the type $[HE\{Cr(CO)_5\}_3]^{2-}$[4] but unfortunately not for their congener Bi.

Whereas Bi-Fe-CO and Bi-Co-CO complexes are well-known,[5, 6] previously reported Bi-Cr-CO complexes are more rare: $[Cr(CO)_5BiR_3]$ ($R = Me$, Et, cyclohexyl, Ph, *t*Bu),[7] $[Bi\{Cr(CO)_3Cp\}_3]$,[8] and $[Ph_2Bi\{Cr(CO)_5\}_2]^-$.[5g] Very recently, a *closo*-$[(\mu_3\text{-}Bi)_3Cr_2(CO)_6]^{2-}$ cluster anion has been discussed.[9] Herein we report a route to a series of novel carbonylchromium complexes of bismuth: $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ ($[Et_4N]_3$-**1**), $[Et_4N]_2[MeBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**2**), $[Et_4N]_2[ClBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**3**), and $[Et_4N]_2[BrBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**4**) and the relevance to the C–O activation of MeOH.

Results and Discussion

Syntheses of $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ $[Et_4N]_2[MeBi\{Cr(CO)_5\}_3]$: By varying the sources of bismuth oxides and bases and the concentration of the bases applied, we have successfully discovered a facile route to the rare class of bismuth–chromium carbonyl complexes $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ ($[Et_4N]_3$-**1**]) and $[Et_4N]_2[MeBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**2**) from the reaction of $NaBiO_3$ and $[Cr(CO)_6]$ in a highly concentrated KOH methanolic solution under the different reaction conditions (Scheme 1).

$[Et_4N]_3$-**1** was afforded in high yield from the reaction solution at ambient temperature followed by metathesis with $[Et_4N]Br$. Complex **1** is extremely reactive and its formulation as $[Bi\{Cr(CO)_5\}_4]^{3-}$ is well supported by spectroscopic characterization and elemental analyses. After numerous attempts at crystallization, the structure of **1** was finally confirmed by single-crystal X-ray analysis (see Figure 1) to possess a tetrahedral μ_4-$BiCr_4$ core geometry in which each Cr atom is further coordinated with five terminal carbonyl ligands. Complex **1** can be viewed as a central Bi^V ion tetrahedrally coordinated to four $[Cr(CO)_5]^{2-}$ groups or alternatively be described as a complex consisting of a Bi^{3-} ligand coordinated through a lone pair of electrons to the $16\,e^-$ $[Cr(CO)_5]$

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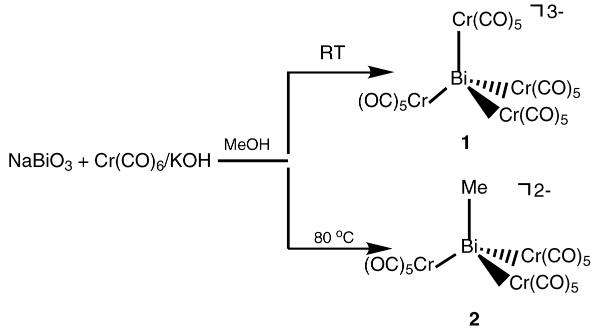


Scheme 1. Synthesis of **1** and **2** from $NaBiO_3$ and $[Cr(CO)_6]$/KOH.

moieties. The assignment of the oxidation state of Bi is not unambiguous because of the small difference in the electronegativities of Bi and Cr.

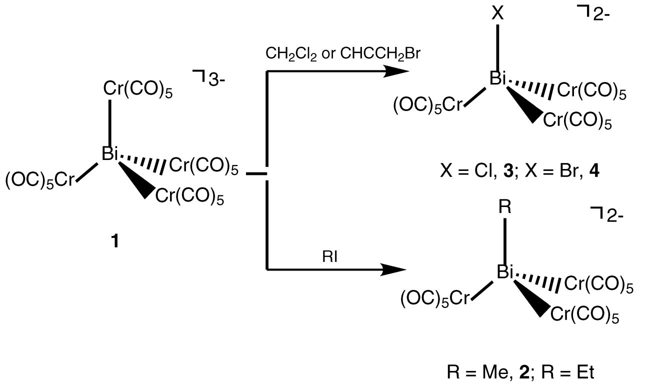
By refluxing the reaction solution at 80 °C, surprisingly, the methyl-substituted bismuth complex $[MeBi\{Cr(CO)_5\}_3]^{2-}$ (**2**) was obtained. The X-ray analysis of $[Et_4N]_2$-**2**, which was carried out at 150 K (see Figure 2), shows that the central bismuth atom is tetrahedrally coordinated to three $[Cr(CO)_5]$ moieties and one Me group. The ^1H and ^{13}C NMR spectra of **2** display signals at $\delta = 2.15$ and -30.40 ppm, respectively, for the methyl group attached to the central bismuth atom.

The formation of **2** is believed to result from the C–O bond cleavage of MeOH, which is rare in the literature. Related examples were observed in the hydrothermal syntheses of telluride complexes $[M_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$($M = Fe$, Ru)[10] and $[Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$[11] by the employment of superheated MeOH solution in sealed tubes. Note that the activation of C–O in this study is achieved under milder conditions. The cleavage of the C–O bond of alcohol is further confirmed by the fact that the corresponding Et-substituted bismuth complex $[EtBi\{Cr(CO)_5\}_3]^{2-}$ is obtained under similar conditions in EtOH solution. The ^1H NMR spectrum of $[Et_4N]_2[EtBi\{Cr(CO)_5\}_3]$ gives a triplet signal at $\delta = 1.680$ ppm and a quartet resonance signal at $\delta = 1.681$ ppm, and the ^{13}C NMR spectrum displays resonances at $\delta = -30.27$ and $\delta = 17.92$ for the ethyl group attached to the bismuth center.

Abstract in Chinese:

我們利用$NaBiO_3$與$Cr(CO)_6$在鹼性的甲醇溶液反應下，成功地合成一系列新穎的含鉍之鉻羰基化合物。當反應控制在室溫下進行時，可以獲得高電子價數的化合物 $[Bi\{Cr(CO)_5\}_4]^{3-}$ (**1**)，並且經由X-光單晶繞射分析，可知其結構是一以鉍原子為中心鍵結四個鉻羰基片斷的四面體。若將反應的溫度提高到80 °C，則產生了甲基取代的化合物 $[MeBi\{Cr(CO)_5\}_3]^{2-}$ (**2**)，推測其形成係由活化甲醇的碳-氧鍵而產生。之後，我們更進一步的研究利用CH_2Cl_2或$CH\equiv CCH_2Br$與化合物 1 反應，分別得到鹵基取代的化合物$[XBi\{Cr(CO)_5\}_3]^{2-}$ ($X = Cl$, **3**; Br, **4**)。另一方面，利用 RI ($R = Me$, Et) 與化合物 1 反應，則可得到烷基取代的化合物$[RBi\{Cr(CO)_5\}_3]^{2-}$ ($X = Me$, **2**; Et)。我們並探討生成化合物**1-4**的反應途徑，推測化合物**1-4**的形成是經由反應中間體 $[Bi\{Cr(CO)_5\}_3]^-$或$[Bi\{Cr(CO)_5\}_3]^{3-}$。

Reactivity of 1: Upon stirring in CH_2Cl_2, $[Et_4N]_3$-**1** converts to the chloro-substituted compound $[Et_4N]_2[ClBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**3**; Scheme 2), which has also been structurally characterized by X-ray analysis (see Figure 3). $[Et_4N]_3$-**1** also reacts with $CH\equiv CCH_2Br$ to give the bromo-substituted compound $[Et_4N]_2[BrBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**4**). Moreover, $[Et_4N]_3$-**1** can react with alkyl halides RI ($R = Me$, Et) to form the alkyl-substituted bismuth complexes $[Et_4N]_2[RBi\{Cr(CO)_5\}_3]$ ($R = Me$, **2**; $R = Et$). This reaction type is parallel to that of the tetrahedral bismuth complex $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with alkyl halides.[5d, e] However, the reaction of **1** toward organic halides is very sensitive to organic reagents with Cl or Br functionality due to the ease of formation of the halo-substituted bismuth complexes.



Scheme 2. Reactions of **1** with organic halides.

Structures of $[Me_4N]_3$-1·CH_3CN, $[Et_4N]_2$-2, $[Et_4N]_2$-3·CH_2Cl_2, and $[Et_4N]_2$-4: The structures of **1**–**4** are depicted in Figure 1–4; selected bond lengths and angles are listed in Table 1. As shown, the structures of **1**–**4** can basically each be considered as a central bismuth atom tetrahedrally bonded to four $[Cr(CO)_5]$ groups (**1**) or three $[Cr(CO)_5]$ groups and one other substituent, namely Me (**2**), Cl (**3**), or Br (**4**).

Very few three-coordinate bismuth complexes are known in which the lone pair on the naked bismuth center remains unavailable for further coordination.[2, 5] Only in a few cases is the naked bismuth center four-coordinate to transition metal carbonyl fragments;[2, 5] examples of the type μ_4-BiM_4 with no M–M bonds are limited to $[Bi\{Fe(CO)_4\}_4]^{3-}$ and $[Bi\{Co(CO)_4\}_4]^-$.[6] Complexes **1**–**4** provide a novel class of four-coordinate bismuth compounds, and more importantly, complex **1** represents the first Bi-Cr-CO tetrahedral complex with the rare μ_4-BiM_4 bonding mode.

For comparison, the average Bi–Cr distances and the average Cr-Bi-Cr bond angles of complexes **1**–**4** and related compounds are listed in Table 2. Note that the average Bi–Cr distances in **1** and **2** are 2.925 and 2.816 Å, respectively, which are significantly larger than the only other Bi–Cr distances reported previously in $[Ph_2Bi\{Cr(CO)_5\}_2]^-$ (2.750(2) Å),[5g] $[Ph_3BiCr(CO)_5]$ (2.705(1) Å),[7c] $[Ph_2Bi\{Cr(CO)_5\}\{Fe(CO)_4\}]^-$ (2.722(2) Å),[5g] and $[Bi\{Fe_2(CO)_8\}\{Fe(CO)_4\}\{Cr(CO)_5\}]^-$ (2.718(2) Å).[5j] This is indicative of the weaker Bi–Cr bonds due to steric hindrance of $[Cr(CO)_5]$ groups. The Bi–Cr distances decrease as the number of $[Cr(CO)_5]$ groups and as the size of substituent ligands become smaller. Additionally,

Table 1. Selected bond lengths [Å] and angles [°] for $[Me_4N]_3$-**1** · CH_3CN, $[Et_4N]_2$-**2**, $[Et_4N]_2$-**3** · CH_2Cl_2, and $[Et_4N]_2$-**4**.

$[Me_4N]_3[Bi\{Cr(CO)_5\}_4] \cdot CH_3CN$ ($[Me_4N]_3$-**1** · CH_3CN)			
Bi–Cr1	2.935(1)	Bi–Cr2	2.932(2)
Bi–Cr3	2.905(1)	Bi–Cr4	2.929(2)
Cr1-Bi-Cr2	109.70(4)	Cr1-Bi-Cr3	113.03(4)
Cr1-Bi-Cr4	105.95(4)	Cr2-Bi-Cr3	108.76(5)
Cr2-Bi-Cr4	112.19(5)	Cr3-Bi-Cr4	107.23(4)
$[Et_4N]_2[MeBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**2**)			
Bi1–C16	2.289(3)	Bi1–Cr1	2.8123(5)
Bi1–Cr2	2.8170(5)	Bi1–Cr3	2.8195(5)
C16-Bi1-Cr1	101.59(8)	C16-Bi1-Cr2	99.61(9)
Cr1-Bi1-Cr2	115.54(2)	C16-Bi1-Cr3	101.45(9)
Cr1-Bi1-Cr3	114.29(2)	Cr2-Bi1-Cr3	119.74(2)
$[Et_4N]_2[ClBi\{Cr(CO)_5\}_3] \cdot CH_2Cl_2$ ($[Et_4N]_2$-**3** · CH_2Cl_2)			
Bi–Cr1	2.740(2)	Bi–Cr2	2.804(2)
Bi–Cr3	2.763(2)	Bi–Cl1	2.678(3)
Cr1-Bi-Cr2	118.32(5)	Cr1-Bi-Cr3	119.61(5)
Cr1-Bi-Cl1	98.82(7)	Cr2-Bi-Cr3	115.69(6)
Cr2-Bi-Cl1	98.34(8)	Cr3-Bi-Cl1	98.34(8)
$[Et_4N]_2[BrBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**4**)			
Bi–Br	2.798(1)	Bi–Cr1	2.792(2)
Bi–Cr2	2.761(2)	Bi–Cr3	2.777(2)
Br-Bi-Cr1	99.90(5)	Br-Bi-Cr2	99.76(5)
Br-Bi-Cr3	99.14(5)	Cr1-Bi-Cr2	117.49(5)
Cr1-Bi-Cr3	116.99(5)	Cr2-Bi-Cr3	116.99(5)

the Cr-Bi-Cr angle of **1** is smallest among **1**–**4** due to the steric effect of the other three $[Cr(CO)_5]$ groups. The Cr-Bi-Cr angle of **3** is slightly larger than that of **4** owing to the smaller size of Cl versus Br. The Bi–C bond in **2** is 2.289(3) Å, which is comparable to that (2.339(1) Å) in $[Bi_2W_2(CO)_8(\mu\text{-}BiMe\{W(CO)_5\})]$[12] and that (2.32(9) Å) in $[i\text{Bu}Bi\{Fe(CO)_4\}_3]^{2-}$.[5d]

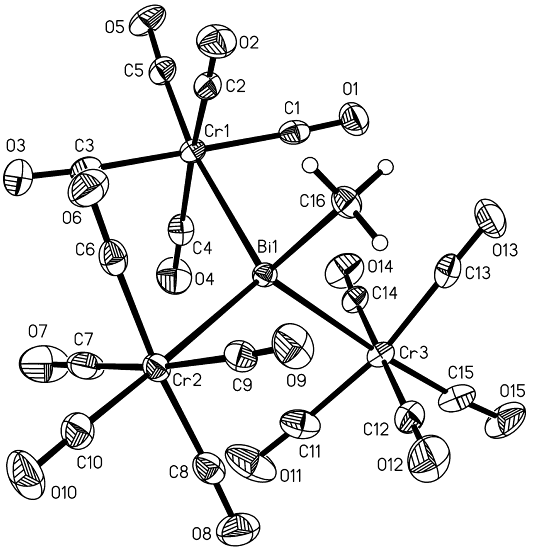


Figure 2. Structure of the dianion **2** (ORTEP diagram; 30% thermal ellipsoids).

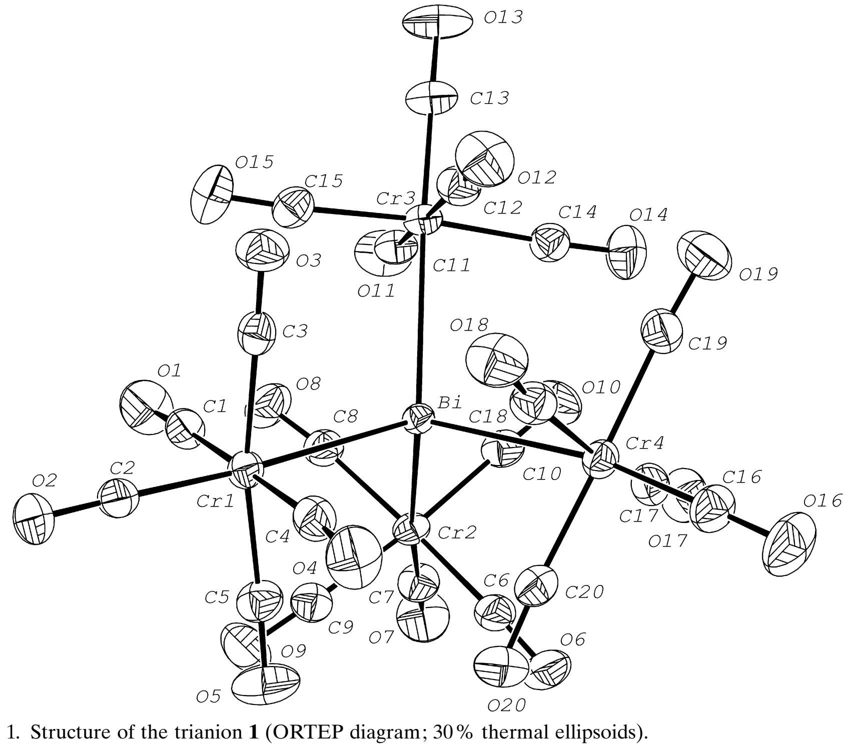


Figure 1. Structure of the trianion **1** (ORTEP diagram; 30% thermal ellipsoids).

Formation of the Bi–Cr complexes: The halogenation of **1** may be proposed to occur via the intermediate bismuthinidene $[Bi\{Cr(CO)_5\}_3\ ]^-$, which is derived from the loss of a $[Cr(CO)_5]^{2-}$ fragment of **1**, followed by the attack of the incoming chloride or bromide group. This assumption is based on the fact that the chloroarsinidene complex $[ClAs\{Cr(CO)_5\}_2]$ can be attacked by Lewis bases to form adducts.[13] The bismuthinidene $[Bi\{Cr(CO)_5\}_3]^-$ is reminiscent of the extremely air-sensitive stibinidene,[14] $[Sb\{Cr(CO)_5\}_3]^-$. An alternative mechanism might involve the loss of the neutral $[Cr(CO)_5]$ group from **1**, leading to the formation of the intermediate anion $[Bi\{Cr(CO)_5\}]^{3-}$ followed by the redox processes and the attack of halides. The formation of $[Bi\{Cr(CO)_5\}]^{3-}$ is also conceivable in the alkylation of **1**.

$[Bi\{Cr(CO)_5\}_3]^-$ may also presumably represent an intermediate in the formation of **1** and **2** in the reaction of $NaBiO_3$ with $Cr(CO)_6$/KOH/MeOH. Complex **1** may result from the attack of $[Cr(CO)_5]^{2-}$ on the bismuth atom of $[Bi\{Cr(CO)_5\}_3]^-$, while complex **2** is derived from the attack of OMe^- on the carbonyl carbon atom followed by elimination of CO_2 and then migration of the Me^- group onto the bismuth center. Alternatively, the formation of $[Bi\{Cr(CO)_5\}]^{3-}$ as the intermediate, accompanied by redox processes is also possible. The site of attack on the bismuth center or the carbonyl carbon atom is controlled by the softness of the nucleophiles. It was proposed that the yield of **2** would be increased if the reaction were conducted under a CO atmosphere; however, the yield of **2** did not increase significantly when we carried out the reaction under a CO

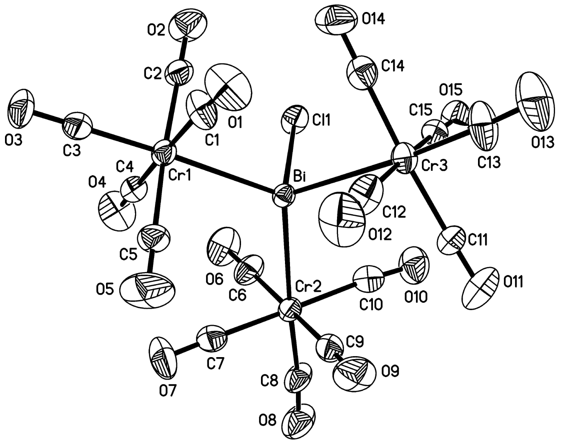


Figure 3. Structure of the dianion **3** (ORTEP diagram; 30% thermal ellipsoids).

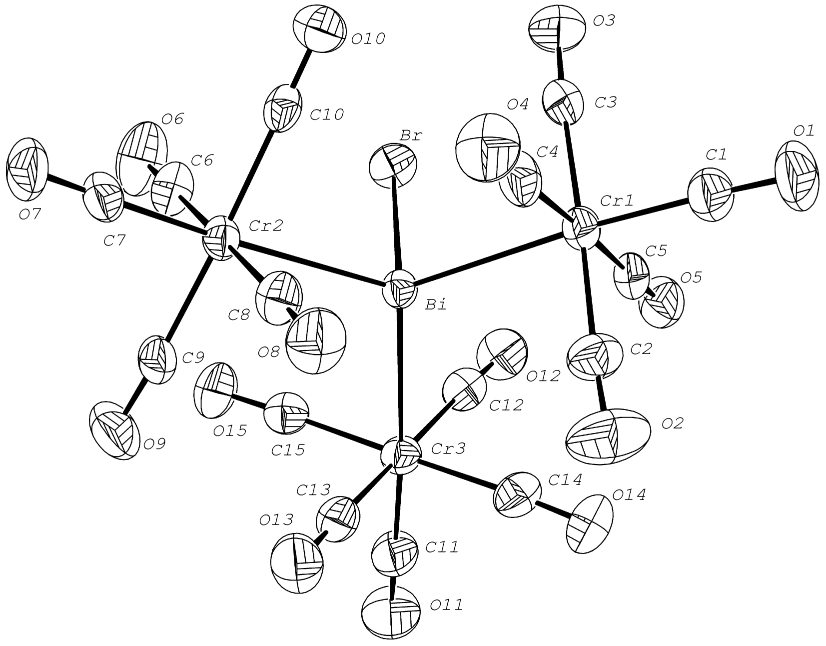


Figure 4. Structure of the dianion **4** (ORTEP diagram; 30% thermal ellipsoids).

Table 2. Average Bi–Cr distances [Å] and Cr-Bi-Cr bond angles [°] in complexes **1**–**4** and other related complexes.

Compounds	Bi–Cr	Cr-Bi-Cr
$[Me_4N]_3$-**1** · CH_3CN[a]	2.925	109.48
$[Et_4N]_2$-**2**[a]	2.816	116.52
$[Et_4N]_2$-**3** · CH_2Cl_2[a]	2.769	117.81
$[Et_4N]_2$-**4**[a]	2.777	117.28
$[Ph_2Bi\{Cr(CO)_5\}_2]^-$[5g]	2.750	125.48
$[Ph_3BiCr(CO)_5]$[7c]	2.705	

[a] This work.

pressure. The decreased efficiency of CO_2 elimination may be the reason for this outcome because of the external CO pressure applied. However, other possible mechanisms involving more complicated atom- and electron-transfer processes cannot be excluded.

Conclusion

This work describes the discovery of a new series of carbonylchromium derivatives of bismuth and the rare example of the highly charged complex $[Bi\{Cr(CO)_5\}_4]^{3-}$ with the μ_4-Bi bonding mode. Furthermore, the reactivity of $[Bi\{Cr(CO)_5\}_4]^{3-}$ with organic halides is investigated and the possible routes to the formation of **1**–**4** are discussed. This study demonstrates that the novel C–O bond activation of alcohol can be promoted by the simple system of $NaBiO_3$ and $Cr(CO)_6$/KOH, presumably via the intermediate bismuthinidene $[Bi\{Cr(CO)_5\}_3]^-$ or the trianion $[Bi\{Cr(CO)_5\}_3]^{3-}$. Further work on useful applications of this system is in progress.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[15] Solvents were purified, dried, and distilled under nitrogen prior to use. $NaBiO_3$ (ACROS), $[Cr(CO)_6]$ (Strem), Et_4NBr (Lancaster), $CH{\equiv}CCH_2Br$ (Lancaster), were used as received. IR spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in CaF_2 cells. The ^1H and ^{13}C NMR spectra were taken on a JEOL 400 instrument at 399.78 and 100.53 MHz, respectively. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei (Taiwan).

Synthesis of $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ ($[Et_4N]_3$-1): MeOH (20 mL) was added to a mixture of $NaBiO_3$ (0.217 g, 0.78 mmol), KOH (5.589 g, 99.6 mmol), and $[Cr(CO)_6]$ (0.685 g, 3.11 mmol). The mixture was allowed to stir for 14 h at ambient temperature, and the resulting greenish-brown solution was filtered and concentrated to the appropriate volume; the product was then precipitated by addition of Et_4NBr (0.825 g, 3.93 mmol) in aqueous solution. The precipitate was washed with deionized water and THF several times and was then extracted with MeCN to give the greenish-brown sample of $[Et_4N]_3$-**1**. Yield: 0.81 g, 0.59 mmol; 76% (based on Bi). Crystals suitable for X-ray analysis were grown from MeCN by using the $[Me_4N]^+$ salts. IR (MeCN): $\tilde{\nu}_{co} = 1982$ (vs), 1930 (w), 1899 (s), 1859 (w), 1826 (s) cm^{-1}; elemental analysis (%) calcd for $[Me_4N]_3$-**1** · CH_3CN: C 32.92, H 3.17, N 4.52; found: C 32.78, H 3.10, N 4.33.

Synthesis of $[Et_4N]_2[MeBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-2): MeOH (20 mL) was added to a mixture of $NaBiO_3$ (0.180 g, 0.64 mmol), KOH (5.880 g, 105 mmol), and $[Cr(CO)_6]$ (0.582 g, 2.58 mmol). The mixture was allowed to stir for 18 h at 80 °C. The solution was filtered and concentrated, and the product was then precipitated by the addition of Et_4NBr in aqueous solution. The precipitate was then washed with deionized water several times and extracted with THF to give the reddish-brown sample of $[Et_4N]_2$-**2**. Yield: 0.42 g, 0.40 mmol; 62% (based on Bi). IR (THF): $\tilde{\nu}_{CO} = 1993$ (vs), 1917 (vs), 1854 (s) cm^{-1}; elemental analysis (%) calcd for $[Et_4N]_2$-**2**: C 36.24, H 4.09, N 2.64; found: C 35.97, H 3.76, N 2.53; ^1H NMR (400 MHz, $[D_6]$DMSO, 298 K): $\delta = 2.15$ ppm (s, CH_3); ^{13}C NMR (100 MHz, $[D_6]$DMSO, 298 K): $\delta = -30.40$ ppm (the chemical shifts for $[Et_4N]^+$ are not given).

Table 3. Crystallographic data for $[Me_4N]_3[Bi\{Cr(CO)_5\}_4]\cdot CH_3CN$ ($[Et_4N]_3$-**1**$\cdot CH_3CN$), $[Et_4N]_2[MeBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**2**), $[Et_4N]_2[ClBi\{Cr(CO)_5\}_3]\cdot CH_2Cl_2$ ($[Et_4N]_2$-**3**$\cdot CH_2Cl_2$), and $[Et_4N]_2[BrBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**4**).

	$[Et_4N]_3$-**1**$\cdot CH_3CN$	$[Et_4N]_2$-**2**	$[Et_4N]_2$-**3**$\cdot CH_2Cl_2$	$[Et_4N]_2$-**4**
empirical formula	$C_{34}H_{39}BiCr_4N_4O_{20}$	$C_{32}H_{43}BiCr_3N_2O_{15}$	$C_{32}H_{42}BiCl_3Cr_3N_2O_{15}$	$C_{31}H_{40}BiBrCr_3N_2O_{15}$
F_w	1240.65	1060.66	1166.01	1125.52
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P1$	$P2_1/n$
crystal dimensions [mm]	0.50 × 0.35 × 0.20	0.25 × 0.15 × 0.10	0.60 × 0.50 × 0.25	0.40 × 0.15 × 0.08
a [Å]	12.174	20.5885(1)	9.835(2)	12.110(2)
b [Å]	12.260(8)	11.3531(2)	11.913(2)	16.029(4)
c [Å]	19.564(4)	17.8053(2)	12.192(2)	22.424(2)
α [°]	89.60(3)		112.96(3)	
β [°]	75.25(2)	96.307(1)	113.27(3)	102.22(1)
γ [°]	60.70(4)		93.93(3)	
V [Å^3]	2438(2)	4136.68(9)	1165.6(4)	4254(1)
Z	2	4	1	4
ρ_{calcd} [g cm^{-3}]	1.69	1.703	1.661	1.76
$\mu(Mo_{K\alpha})$ [cm^{-1}]	45.3	50.73	46.75	58.7
diffractometer	Nonius (CAD4)	Bruker SmartCCD	Nonius (CAD4)	Nonius (CAD4)
λ [Å]	0.70930	0.71073	0.71073	0.70930
T [°C]	25	−123	25	25
T_{min}/T_{max}	0.29/0.38	0.43/0.56	0.25/0.18	0.18/0.30
reflections ($I > 2.0\sigma(I)$)	7445	7037	5342	4877
R[a]; Rw[a]	0.028; 0.031			0.040; 0.042
$R1$[b]/$wR2$[c] [$I > 2\sigma(I)$]		0.0203/0.0419	0.0411/0.1098	
$R1$[b]/$wR2$[c] (all data)		0.0280/0.0470	0.0435/0.1124	
Flack parameter			0.099(7)	

[a] The functions minimized during least-squares cycles were $R = \Sigma|F_o - F_c|/\Sigma F_o$ and $Rw = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$. [b] $R1 = \Sigma||Fo| - ||F_c|/\Sigma|F_o||$. [c] $wR2 = [\Sigma[w(F_o - F_c)^2]/\Sigma[w(F_o)^2]]^{1/2}$.

Synthesis of $[Et_4N]_2[EtBi\{Cr(CO)_5\}_3]$: EtOH (20 mL) was added to a mixture of $NaBiO_3$ (0.18 g, 0.64 mmol), KOH (5.73 g, 102 mmol), and $[Cr(CO)_6]$ (0.83 g, 3.95 mmol). The mixture was allowed to stir for 18 h at 80 °C. The solution was filtered and concentrated, and then the product was precipitated by the addition of Et_4NBr in aqueous solution. The precipitate was then washed with deionized water several times and extracted with THF to give the reddish-brown sample of $[Et_4N]_2[EtBi\{Cr(CO)_5\}_3]$. Yield: 0.33 g, 0.31 mmol; 48 % (based on Bi). IR (THF): $\tilde{\nu}_{CO} = 1994$ (vs), 1914 (vs), 1849 (s) cm^{-1}; elemental analysis (%) calcd for $[Et_4N]_2[EtBi\{Cr(CO)_5\}_3]$: C 36.88, H 4.22, N 2.61; found: C 36.32, H 3.91, N 2.66; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K): $\delta = 1.69$ (t, J = 16 Hz; CH_3), 2.44 ppm (q, J = 16 Hz; CH_2); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 298 K): $\delta = -30.27$ (CH_2), 17.92 ppm (CH_3) (the chemical shifts for $[Et_4N]^+$ are not given).

Reaction of $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ ($[Et_4N]_3$-1) with CH_2Cl_2: CH_2Cl_2 (20 mL) was added to a sample of $[Et_4N]_3$-**1** (0.24 g, 0.18 mmol). The mixed solution was allowed to stir for 14 h at room temperature. The resulting greenish-brown solution was filtered and the solvent was removed under vacuum. The residue was extracted with THF and recrystallized by Et_2O/CH_2Cl_2 to give $[Et_4N]_2[ClBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**3**). Yield: 0.09 g, 0.08 mmol; 44 % (based on $[Et_4N]_3$-**1**). IR (THF): $\tilde{\nu}_{CO} = 2009$ (vs), 1930 (vs), 1867 (s) cm^{-1}; elemental analysis (%) calcd for $[Et_4N]_2[ClBi\{Cr(CO)_5\}_3]$: C 34.44, H 3.73, N 2.59; found: C 33.81, H 3.82, N 2.55.

Reaction of $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ ($[Et_4N]_3$-1) with $CH{\equiv}CCH_2Br$: $CH{\equiv}CCH_2Br$ (0.1 mL, 1.32 mmol) was added to a solution of $[Et_4N]_3$-**1** (0.33 g, 0.24 mmol) in MeCN (20 mL) in an ice/water bath. The mixture was stirred in an ice/water bath for 2 h. The resultant solution was filtered to collect the filtrate, and the solvent was removed under vacuum. The residue was extracted with THF, and the extract was recrystallized with THF/Et_2O to give $[Et_4N]_2[BrBi\{Cr(CO)_5\}_3]$ ($[Et_4N]_2$-**4**). Yield: 0.22 g, 0.20 mmol; 81 % (based on $[Et_4N]_3$-**1**). IR (THF): $\tilde{\nu}_{CO} = 2007$ (vs), 1932 (vs), 1922 (vs), 1867 (s) cm^{-1}; elemental analysis (%) calcd for $[Et_4N]_2[BrBi\{Cr(CO)_5\}_3]$: C 33.08, H 3.58, N 2.49; found: C 33.07, H 3.48, N 2.73.

Reaction of $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ ($[Et_4N]_3$-1) with MeI: MeI (0.04 mL, 0.64 mmol) in CH_3CN (20 mL) was added to a sample of $[Et_4N]_3$-**1** (0.52 g, 0.38 mmol). The mixed solution was allowed to stir for 40 min at room temperature. The resulting purplish-red solution was filtered and the solvent was removed under vacuum. The residue was extracted with THF and recrystallized by THF/Et_2O to give $[Et_4N]_2$-**2**. Yield: 0.25 g, 0.24 mmol; 63 % (based on $[Et_4N]_3$-**1**)

Reaction of $[Et_4N]_3[Bi\{Cr(CO)_5\}_4]$ ($[Et_4N]_3$-1) with EtI: EtI (0.04 mL, 0.50 mmol) in CH_3CN(20 mL) was added to a sample of $[Et_4N]_3$-**1** (0.41 g, 0.30 mmol). The mixed solution was allowed to stir for 2.5 h at room temperature. The resulting purplish-red solution was filtered and the solvent was removed under vacuum. The residue was extracted with THF and recrystallized by THF/Et_2O to give $[Et_4N]_3[EtBi\{Cr(CO)_5\}_3]$. Yield: 0.29 g, 0.27 mmol; 90 % (based on $[Et_4N]_3$-**1**).

X-ray structural characterization of complexes $[Me_4N]_3$-1$\cdot CH_3CN$, $[Et_4N]_2$-2, $[Et_4N]_2$-3$\cdot CH_2Cl_2$, and $[Et_4N]_2$-4: A summary of selected crystallographic data for $[Me_4N]_3$-**1**$\cdot CH_3CN$, $[Et_4N]_2$-**2**, $[Et_4N]_2$-**3**$\cdot CH_2Cl_2$, $[Et_4N]_2$-**4** are given in Table 3. All crystals were mounted on glass fibers with Epoxy cement. Data collection of $[Me_4N]_3$-**1**$\cdot CH_3CN$ and $[Et_4N]_2$-**4** was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation at 25 °C employing the $\theta/2\theta$ scan mode. Cell parameters were obtained from 25 reflections with 2θ angle in the range 18.52–24.14° for $[Me_4N]_3$-**1**$\cdot CH_3CN$, $1.00 < \theta < 25.00$° for $[Et_4N]_2$-**2**, $1.92 < \theta < 27.47$° for $[Et_4N]_2$-**3**$\cdot CH_2Cl_2$, $19.04 < 2\theta < 25.08$° for $[Et_4N]_2$-**4**. A ψ scan absorption correction was made.[16] Data reduction and structural refinement were performed using the NRCC-SDP-VAX packages,[17] and atomic scattering factors were taken from *International Table for X-ray Crystallography*.[18] Data collection for $[Et_4N]_2$-**2** and $[Et_4N]_2$-**3**$\cdot CH_2Cl_2$ was carried out on a SMART CCD diffractometer. A SADABS scan absorption correction was made,[19] and all calculations were performed using SHELXTL packages.[20] All the non-hydrogen atoms were refined with anisotropic temperature factors. CCDC-181785 ($[Me_4N]_3$[**1**]$\cdot CH_3CN$), CCDC-172341 ($[Et_4N]_2$[**2**]), CCDC-172342 ($[Et_4N]_2$[**3**]$\cdot CH_2Cl_2$) and CCDC-181786 ($[Et_4N]_2$[**4**]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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