4926 *Organometallics* 1993, *12*, 4926–4929

Reactions of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with Alkyl Halides or Dihalides: A General Method for the Synthesis of Anionic Complexes of the Type $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ and the Cyclic Complexes $R_2Bi_2Fe_2(CO)_8$

Minghuey Shieh,* Yeantarn Liou, and Bor-Wen Jeng

Department of Chemistry, National Taiwan Normal University,
Taipei 11718, Taiwan, Republic of China

Received July 6, 1993⊗

The reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with alkyl halides or dihalides appears to be a general synthesis of the anionic complexes $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ or the cyclic complexes $R_2Bi_2Fe_2(CO)_8$. In the case of MeI, EtI, and $PhCH_2Br$, $R_2Bi_2Fe_2(CO)_8$ are obtained directly, which are proposed to result from dimerization of $RBiFe(CO)_4$ derived from the corresponding anionic complexes. As the reactivity of alkyl halides or dihalides decreases, the anionic compounds can be isolated and further treated with HOAc to form the cyclic complexes. This methodology offers a convenient route for the synthesis of organo derivatives of the anionic complex and the cyclic compound. These reactions proceed in high yield, are predictable, and can tolerate some functional groups such as Cl and Br.

Introduction

Bismuth-containing transition metal carbonyl clusters have received considerable attention for several years. The interesting structures and bonding modes of these clusters have been extensively investigated.[1,2] Nevertheless, the reactivity of these structurally characterized clusters has received little study. It is known that the introduction of a main group element into transition metal complexes often alters their reactivity. Although the reaction of the mononuclear complexes $Fe(CO)_4^{2-}$ and $HFe(CO)_4^-$ with organic reagents is well documented,[3] the reactions of main group element–transition metal clusters with organic reagents remain rare. Therefore, the exploration of this area is of great interest and challenge. We have recently isolated and structurally characterized an anionic complex, $[i\text{-}BuBi\{Fe(CO)_4\}_3]^{2-}$, from the reaction of the previously characterized cluster $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ (1)[4] with *i*-BuBr.[5] To understand better the characteristics of the reaction, we investigated reactions of cluster 1 with a series of alkyl halides or dihalides. With various alkyl halides, the reaction provides a good methodology for synthesis of anionic complexes of the type $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ and cyclic complexes, $R_2Bi_2Fe_2(CO)_8$.

Results

We have recently reported that the reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ (1) with *i*-BuBr leads to the formation of $[Et_4N]_2[i\text{-}BuBi\{Fe(CO)_4\}_3]$.[5] It is noted that the reactivity of the alkyl halide plays an important role in the reaction. Thus, various alkyl halides and dihalides were employed to react with cluster 1 in CH_3CN. As can be seen from Table I, the alkylation of 1 is a facile process for the synthesis of anionic complexes or cyclic complexes and generally proceeds in good yield. For comparison, the important experimental data are compiled in Tables II and III.

Reactions with MeI, $PhCH_2Br$, and EtI. The reaction of 1 with an excess of MeI in MeCN at room temperature for 5 min produces Me_2CO, $Fe(CO)_5$, and the previously reported complexes $Me_2Bi_2Fe_2(CO)_8$[6] and $[Et_4N][BiFe_3(CO)_{10}]$.[7] Under similar conditions, treatment of 1 with $PhCH_2Br$ gives $(PhCH_2)_2CO$, $Fe(CO)_5$, $(PhCH_2)_2Bi_2Fe_2(CO)_8$, and $[Et_4N][BiFe_3(CO)_{10}]$. The yields of ketones in these two reactions are 27% and 33% (based on Fe), respectively. Analogous reaction with EtI produces mainly $Fe(CO)_5$, $Me_2Bi_2Fe_2(CO)_8$, and $[Et_4N][BiFe_3(CO)_{10}]$ and a small amount of Et_2CO. Accordingly, the reaction with MeI, EtI, and $PhCH_2Br$ basically produces R_2CO, $Fe(CO)_5$, $R_2Bi_2Fe_2(CO)_8$, and $[Et_4N][BiFe_3(CO)_{10}]$ (R = Me, $PhCH_2$, Et) (eq 1).

$$[Bi\{Fe(CO)_4\}_4]^{3-} + RX \rightarrow R_2Bi_2Fe_2(CO)_8 + [BiFe_3(CO)_{10}]^- + Fe(CO)_5 + R_2CO \quad (1)$$

$$R = Me, X = I; R = Et, X = I; R = PhCH_2, X = Br$$

In the reaction with $PhCH_2Br$, the isolation of pure $(PhCH_2)_2Bi_2Fe_2(CO)_8$ is not successful because $PhCH_2Br$ (and $PhCH_2)_2CO$ are not easily separated from the desired compound by column chromatography. This problem is avoided when the reaction is conducted in MeCN with the less reactive $PhCH_2Cl$, which allows the isolation of the anionic product $[PhCH_2Bi\{Fe(CO)_4\}_3]^{2-}$. Further careful acidification of this complex results in a pure cyclic complex. In this case, no dibenzyl ketone is produced.

---

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts*, November 1, 1993.

[1] For recent reviews, see: Norman, N. C. *Chem. Soc. Rev.* **1988**, *17*, 269. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. Whitmire, K. H. *J. Coord. Chem.* **1988**, *17*, 95. Whitmire, K. H. *J. Cluster Sci.* **1991**, *2*, 231.

[2] Shriver, D. F.; Kaesz, H. D.; Adams, R. C. *The Chemistry of Metal Cluster Complexes*; VCH Publishers: New York, 1990.

[3] Brunet, J.-J. *Chem. Rev.* **1990**, *90*, 1041–1059 and references therein.

[4] Churchill, M. R.; Fettinger, J. C.; Whitmire, K. H.; Lagrone, C. B. *J. Organomet. Chem.* **1986**, *303*, 99–109.

[5] Shieh, M.; Liou, Y.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1993**, *32*, 2212.

[6] Whitmire, K. H.; Shieh, M.; Cassidy, J. *Inorg. Chem.* **1989**, *28*, 3164–3170.

[7] Whitmire, K. H.; Lagrone, C. B.; Churchill, M. R.; Fettinger, J. C.; Biondi, L. V. *Inorg. Chem.* **1984**, *23*, 4227–4232.

0276-7333/93/2312-4926$04.00/0

Table I. Reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_3]$ with Alkyl Halides or Dihalides

entry	products[a]	yield, %[b]
MeI	$Me_2Bi_2Fe_2(CO)_8$	40
$PhCH_2Br$	$(PhCH_2)_2Bi_2Fe_2(CO)_8$	c
EtI	$Et_2Bi_2Fe_2(CO)_8$	54
i-PrI	$[Et_4N]_2[i\text{-}PrBi\{Fe(CO)_4\}_3]$	98
n-BuBr	$[Et_4N]_2[n\text{-}BuBi\{Fe(CO)_4\}_3]$	87
i-BuBr[5]	$[Et_4N]_2[i\text{-}BuBi\{Fe(CO)_4\}_3]$	85
$PhCH_2Cl$	$[Et_4N]_2[PhCH_2Bi\{Fe(CO)_4\}_3]$	79
$Br(CH_2)_3Cl$	$[Et_4N]_2[Cl(CH_2)_3Bi\{Fe(CO)_4\}_3]$	92
$Br(CH_2)_4Br$	$[Et_4N]_2[Br(CH_2)_4Bi\{Fe(CO)_4\}_3]$	c

[a] All products are isolated by solvent separation techniques or column chromatography and fully characterized by other spectroscopic methods. [b] The yields are calculated on the basis of Bi. [c] The compound is not isolated.

Reactions with *i*-PrI, *n*-BuBr, and *t*-BuBr. In reactions of 1 with *i*-PrI and *n*-BuBr in MeCN the anionic complexes $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ (R = *i*-Pr, *n*-Bu) are produced with no observation of ketones (eq 2). However, treatment of 1 with *t*-BuBr fails to give the alkylated product.

$$[Bi\{Fe(CO)_4\}_4]^{3-} + RX \rightarrow [RBi\{Fe(CO)_4\}_3]^{2-} \quad (2)$$

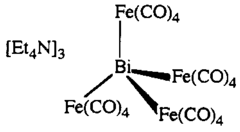
$$R = i\text{-}Pr, X = I; R = n\text{-}Bu, X = Br$$

$R_2Bi_2Fe_2(CO)_8$ (R = *i*-Pr, *n* = Bu) complexes can be obtained by careful treatment of $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ with MeI, but their isolation is difficult because of the formation of $Me_2Bi_2Fe_2(CO)_8$ as a side product. When $[Cu(MeCN)_4]BF_4$ is employed in place of MeI, $[Et_4N][BiFe_3(CO)_{10}]$ is obtained. Further reaction of $[Et_4N][BiFe_3(CO)_{10}]$ with MeI forms $Bi_2Fe_3(CO)_9$[8] but not the desired cyclic complex. However, acidification of $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ (R = *i*-Pr, *n*-Bu) with HOAc readily affords the cyclic complexes, $R_2Bi_2Fe_2(CO)_8$, exclusively.

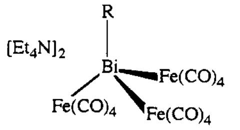
Reactions with $Br(CH_2)_2Br$, $Cl(CH_2)_3Cl$, $ClCH_2ClCH_2CH_3$, $Cl(CH_2)_3Br$, and $Br(CH_2)_4Br$. In the extension of the reaction to dihaloalkanes, it was found that treatment of 1 with 1,2-dibromoethane gives the oxidized product $[Et_4N][BiFe_3(CO)_{10}]$. Treatment with 1,2-dichloropropane or 1,3-dichloropropane fails to give an alkylated compound, while the reaction with 3-chloro-1-bromopropane readily generates the alkylated complex $[Et_4N]_2[Cl(CH_2)_3Bi\{Fe(CO)_4\}_3]$. Similarly, the reaction with 1,4-dibromobutane produces $[Et_4N]_2[Br(CH_2)_4Bi\{Fe(CO)_4\}_3]$. It is noted that the functionalized cyclic compounds $\{Cl(CH_2)_3\}_2Bi_2Fe_2(CO)_8$ and $\{Br(CH_2)_4\}_2Bi_2Fe_2(CO)_8$ also can be obtained by acidification of the corresponding anionic complexes with HOAc.

Discussion

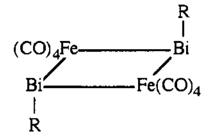
Structures of $[RBi\{Fe(CO)_4\}_3]^{2-}$ and $R_2Bi_2Fe_2(CO)_8$. The core geometry of cluster $[Bi\{Fe(CO)_4\}_4]^{3-}$ (1)[4] can be considered as a central bismuth(V) ion tetrahedrally coordinated to four $Fe(CO)_4{}^{2-}$ fragments. Basically, the anionic complex $[i\text{-}BuBi\{Fe(CO)_4\}_3]^{2-}$ is structurally similar to the anion of cluster 1 except that one $Fe(CO)_4{}^{2-}$ is replaced by one *i*-Bu⁻ group.[5] On the basis of similar IR absorption patterns and NMR spectral data, the cluster anions $[RBi\{Fe(CO)_4\}_3]^{2-}$ are assumed to possess isomorphous structures. Analogous to the reported $Me_2Bi_2Fe_2(CO)_8$,[6] $Ph_2Bi_2Fe_2(CO)_8$,[9] and $(i\text{-}Bu)_2Bi_2Fe_2(CO)_8$,[5] each cyclic complex $R_2Bi_2Fe_2(CO)_8$ is believed to contain a Bi_2Fe_2 parallelogram with one R group bonded to each bismuth atom in the *trans* orientations in the solid state. In solution, as also seen in the case of $Me_2Bi_2Fe_2(CO)_8$,[6] the cyclic complexes exhibit two sets of R resonances each in the ¹H NMR spectrum, which may suggest the existence of *cis–trans* isomers in solution. However, the kinetic study on this issue does not allow us to draw any significant conclusion because of the instability of the complexes in the solution.



$[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ (1)



$[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$



$R_2Bi_2Fe_2(CO)_8$

Reactions with Alkyl Halides. From the above results, it is concluded that $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ (1) is

Table II. Important Data for the Anionic Complexes, $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$

compd	IR, ν(CO) (MeOH), cm⁻¹	¹H NMR, ppm[a]
$[Et_4N]_2[i\text{-}BuBi\{Fe(CO)_4\}_3]$[5,b]	2030 (w), 2012 (w), 1979 (s), 1909 (vs br)	3.52 (d, 2H), 2.29 (m, 1H), 0.95 (d, 6H)
$[Et_4N]_2[PhCH_2Bi\{Fe(CO)_4\}_3]$[c]	2037 (w), 2015 (w), 1988 (s), 1925 (vs br)	7.19–7.17 (m, 2H), 7.06–7.03 (m, 3H), 4.62 (s, 2H)
$[Et_4N]_2[n\text{-}BuBi\{Fe(CO)_4\}_3]$[b]	2032 (w), 2012 (w), 1978 (s), 1901 (vs br)	3.43 (t, 2H), 2.06 (m, 2H), 1.37 (m, 2H), 0.981 (t, 3H)
$[Et_4N]_2[Cl(CH_2)_3Bi\{Fe(CO)_4\}_3]$[d]	2037 (w), 2015 (w), 1981 (s), 1896 (vs br)	3.80 (t, 2H), 3.28 (t, 2H), 2.60 (m, 2H)

[a] Chemical shifts not given for $[Et_4N]^+$. [b] Chemical shifts for these compounds are reported as ppm vs CD_2Cl_2. [c] Chemical shifts for these compounds are reported as ppm vs DMSO-d_6. [d] Chemical shifts for these compounds are reported as ppm vs acetone-d_6.

Table III. Important Data for the Cyclic Complexes, $R_2Bi_2Fe_2(CO)_8$

compd	mp °C	IR, ν(CO) (hexane), cm⁻¹	¹H NMR, ppm vs $CDCl_3$
$(i\text{-}Bu)_2Bi_2Fe_2(CO)_8$[5]	140	2034 (s), 1986(vs)	3.93 (d, 2H), 2.37 (m, 1H), 1.02 (d, 6H); 3.80 (d, 2H), 2.22 (m, 1H), 0.998 (d, 6H)
$Et_2Bi_2Fe_2(CO)_8$	120	2036 (s), 1986 (vs)	3.98 (q, 2H), 1.69 (t, 3H); 3.84 (q, 2H), 1.79 (t, 3H)
$(PhCH_2)_2Bi_2Fe_2(CO)_8$[a]	117	2038 (s), 1981 (vs)	7.29–6.95 (m, 5H), 4.99 (s, 2H); 7.29–6.95 (m, 5H), 4.78 (s, 2H)
$(i\text{-}Pr)_2Bi_2Fe_2(CO)_8$	255	2036 (s), 1987 (vs)	3.70–3.30 (m, 1H), 1.83 (d, 6H); 3.70–3.30 (m, 1H), 1.72 (d, 6H)
$(n\text{-}Bu)_2Bi_2Fe_2(CO)_8$	154	2036 (s), 1987 (vs)	4.01 (t, 2H), 2.04 (m, 2H), 1.54 (m, 2H), 0.96 (t, 3H); 3.87 (t, 2H), 1.94 (m, 2H), 1.44 (m, 2H), 0.94 (t, 3H)
$[Cl(CH_2)_3]_2Bi_2Fe_2(CO)_8$[a]	91	2037 (s), 1981 (vs)	3.68 (t, 2H), 2.76–2.72 (m, 2H), 2.19–2.15 (m, 2H); 3.61 (t, 2H), 2.76–2.72 (m, 2H), 2.19–2.15 (m, 2H)
$[Br(CH_2)_4]_2Bi_2Fe_2(CO)_8$	310	2036 (s), 1987 (vs)	3.91 (t, 2H), 3.46 (t, 2H), 2.02–1.95 (m, 4H); 3.77 (t, 2H), 3.43 (t, 2H), 2.02–1.95 (m, 4H)

[a] Chemical shifts for these compounds are reported as ppm vs DMSO-d_6.

a reactive species that is easily transformed into cyclic complexes, $R_2Bi_2Fe_2(CO)_8$, upon reaction with highly reactive electrophiles. As the reactivity of the reagent decreases, anionic complexes $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ are isolated. This suggests that the anionic complex may represent an intermediate in these alkylation reactions.

The mechanism of these alkylation reactions is not clear. It is not unlikely that the reaction occurs via loss of one $Fe(CO)_4$ fragment followed by the attack of the central bismuth atom on the alkyl group to give the anionic complex. The cyclic complexes $R_2Bi_2Fe_2(CO)_8$ might be considered to result from dimerization of $RBiFe(CO)_4$ derived from the anionic complexes.

As seen in the case of $Fe(CO)_4^{2-}$,[3] the ease of the formation of the ketones follows the reactivity of the alkyl halides. In the presence of PPh_3, a mixture of $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ is isolated along with $Fe(CO)_5$. In agreement with the earlier report,[10] we found that $Fe(CO)_5$ is unreactive toward alkyl halides under our conditions. It is very likely that the ketone arises from reaction of the alkyl halide with the unsaturated "$Fe(CO)_4$" produced in the reaction in a fashion similar to that observed for the methylation of $[HFe(CO)_4]^-$.[11] The observation of $Fe(CO)_5$ in our reactions is probably attributable to the decomposition of the unsaturated "$Fe(CO)_4$", which was also seen in a previous study.[11]

The side products $[Et_4N][BiFe_3(CO)_{10}]$ and $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$ can be considered to be the disproportionation products of 1[12] or decomposition products of the alkylated anionic complexes. The test reactions carried out in our laboratory show that the alkylation of these two complexes does not give the alkylated cyclic complexes, and the oxidation of the alkylated anionic complexes forms $[Et_4N][BiFe_3(CO)_{10}]$ or $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$. This explains the formation of $[Et_4N][BiFe_3(CO)_{10}]$ and $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$ in these reactions.

Although the synthesis of cyclic complexes (Me and Ph derivatives) has been reported by the other two methods,[6,9] our method described here is convenient and general for a series of alkyl halides and dihalides. It is worth mentioning that the intermolecular interaction of the cyclic complexes becomes greater as the organic chain increases, which causes the generation of a polymeric product under appropriate conditions.[13] A detailed examination is now in progress.

Reactivity of Alkyl Halides or Dihalides. In general, primary and secondary alkyl bromides or iodides are reactive toward complex 1. *t*-BuBr does not react with 1 due to the steric effect. Of great interest is that the reaction can tolerate some unmasked functional groups such as Cl and Br. In the case of 1-bromo-3-chloropropane, the chloropropylated bismuth complex $[Et_4N]_2[Cl(CH_2)_3Bi\{Fe(CO)_4\}_3]$ is obtained, which indicates that the reactivity of the carbon attached to the Br atom is greater than that of the carbon attached to the Cl atom, which is similar to what was found in the reaction of $Fe(CO)_4^{2-}$ with 6-chloro-1-bromohexane.[14] The cyclic complex $\{Br(CH_2)_4\}_2Bi_2Fe_2(CO)_8$ is another example of a complex bearing Br functional groups which would provide active sites for further reactions.

Conclusion

Although the reactions of cluster anionic complexes usually are very complicated, the reaction of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with a series of alkyl halides or dihalides can be rationalized and predictable. Since very few bismuth–alkyl iron clusters are known, this reaction provides a convenient and systematic synthesis of bismuth–alkyl complexes of type $[Et_4N]_2[RBi\{Fe(CO)_4\}_3]$ and $R_2Bi_2Fe_2(CO)_8$. The principal advantages of this reaction are high yields and toleration of some unmasked functional groups which should be useful for further reactions. Continuing examination of $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ with other organic reagents is of interest.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques. Solvents were purified, dried, and distilled under nitrogen prior to use. The compound $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$ (1) is prepared according to the published method.[4] Infrared spectra were recorded on a Jasco 700 IR spectrometer as solutions in CaF_2 cells. Mass spectra were obtained on a Finnigan MATTSQ-46C mass spectrometer at 30 or 20 eV. ^1H NMR spectra were taken on a JEOL 400 (400-MHz) instrument. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan.

Reaction of 1 with CH_3I. A 1.0-mL (16-mmol) aliquot of CH_3I was syringed into a green solution of 1.270 g (1 mmol) of 1 in 20 mL of MeCN. The solution was stirred for 10 min, after which time it became reddish-brown. The solution was filtered and solvent removed under vacuum. The volatile products, $Fe(CO)_5$ and acetone, were collected, and the quantitative IR analysis showed the yield of the acetone was 27% based on Fe. The residue was extracted into 100 mL of hexane to give 0.158 g (0.2 mmol) of $Me_2Bi_2Fe_2(CO)_8$[6] (40% based on Bi). The residue was extracted into CH_2Cl_2 giving 0.39 g of $[Et_4N][BiFe_3(CO_{10}]$.[7]

Reaction of 1 with EtI. To a solution of 2.358 g (1.856 mmol) of 1 in 25 mL of MeCN was added 1.5 mL (22 mmol) of EtI. The resulting solution was stirred at room temperature for 24 h to give a reddish-brown solution. The latter was filtered and the solvent was removed under vacuum. The volatile product, $Fe(CO)_5$, was collected and identified by its IR spectrum. The residue was extracted into 180 mL of hexane to give 0.401 g of $Et_2Bi_2Fe_2(CO)_8$ (54% based on Bi). IR (ν_{CO}, hexane): 2036 (s), 1986 (vs) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.98 (q, 2H, $J = 7.8$ Hz), 1.69 (t, 3H, $J = 7.8$ Hz); 3.84 (q, 2H, $J = 7.8$ Hz), 1.79 (t, 3H, $J = 7.8$ Hz). Mass (EI): M^+ at *m/e* 812 with consequent loss of two Et groups $[M^+ - n(29)]$ and the regular loss of CO groups $[M^+ - n(28)]$. Anal. Calcd for $Et_2Bi_2Fe_2(CO)_8$: C, 17.75; H, 1.24. Found: C, 17.69; H, 1.07. Mp: 120 °C dec. The residue was then extracted into ether giving 0.122 g (0.155 mmol) of $[Et_4N][BiFe_3(CO)_{10}]$[7] (15% based on Bi).

Reaction of 1 with $PhCH_2Br$. A 1.0-mL (8.7-mmol) aliquot of $PhCH_2Br$ was quickly syringed into a green solution of 0.786 g (0.618 mmol) of 1 in 12 mL of MeCN. After stirring for 45 min, the solution was filtered and the solvent removed under vacuum. The volatile $Fe(CO)_5$ was collected and identified by IR. The residue was extracted into 180 mL of hexane, and the hexane extracts were chromatographed to give 0.044 g of $(PhCH_2)_2CO$ (33% based on Fe). The hexane extracts contained the neutral compound $(PhCH_2)_2Bi_2Fe_2(CO)_8$ but this could not be isolated by column chromatography. IR (νCO, hexane): 2036 (s), 1984 (vs) cm^{-1}.

Reaction of 1 with $PhCH_2Cl$. A 1.00-mL (9-mmol) aliquot of $PhCH_2Cl$ was syringed into a green solution of 1.270 g (1 mmol) of 1 in 30 mL of MeCN. The solution was stirred for 45 h, after

---

(8) Churchill, M. R.; Fettinger, J. C.; Whitmire, K. H. *J. Organomet. Chem.* **1985**, *284*, 13.

(9) Cassidy, J. M.; Whitmire, K. H. *Inorg. Chem.* **1991**, *30*, 2788–2795.

(10) Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227.

(11) Whitmire, K. H.; Lee, T. R.; Lewis, E. S. *Organometallics* **1986**, *5*, 987.

(12) Whitmire, K. H.; Shieh, M.; Lagrone, C. B.; Robinson, B. H.; Churchill, M. R.; Fettinger, J. C.; See, R. F. *Inorg. Chem.* **1987**, *26*, 2798–2807.

(13) Shieh, M.; Liou, Y. Unpublished results.

(14) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

which time it became reddish–brown. The solution was filtered, and the solvent was removed under vaccum. The volatile $Fe(CO)_5$ was collected and identified by IR. The residue was washed with hexane and then extracted into CH_2Cl_2 to give 0.84 g (0.79 mmol) of $[Et_4N]_2[PhCH_2Bi\{Fe(CO)_4\}_3]$ (79% based on Bi). IR (ν_{CO}, MeOH): 2037 (w), 2015 (w), 1988 (s), 1925 (vs br) cm^{-1}. ^{1}H NMR (400 MHz DMSO-d_6, 298 K): δ 7.19–7.17 (m, 2H), 7.06–7.03 (m, 3H), 4.62 (s, 2H). Anal. Calcd for $BiFe_3C_{35}H_{47}N_2O_{12}$: C, 39.50; H, 4.45; N, 2.63. Found: C, 39.32; H, 4.41; N, 2.55.

Synthesis of $(PhCH_2)_2Bi_2Fe_2(CO)_8$. To 1.04 g (0.97 mmol) of $[Et_4N]_2[PhCH_2Bi\{Fe(CO)_4\}_3]$ was added about 10 mL of HOAc. The solution was stirred for 24 h, giving a reddish-brown solution. The solvent was removed under vacuum, and the residue was extracted with several 40-mL portions of hexane to give 0.102 g (0.108 mmol) of $(PhCH_2)_2Bi_2Fe_2(CO)_8$ (21.6% based on Bi). IR (ν_{CO}, hexane): 2038 (s), 1981 (vs) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 7.29–6.95 (m, 5H), 4.99 (s, 2H); δ 7.29–6.95 (m, 5H), 4.78 (s, 2H). Mass (EI): M$^+$ at m/e 936 with consequent loss of two $PhCH_2$ groups [M$^+$ − n(91)]. Anal. Calcd for $(PhCH_2)_2Bi_2Fe_2(CO)_8$: C, 28.23; H, 1.51. Found: C, 28.59; H, 1.61. Mp: 117 °C dec. The residue was then extracted with CH_2Cl_2, yielding 0.36 g of the previously reported $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$.[12]

Reaction of 1 with *i*-PrI. To a green solution of 1.270 g (1 mmol) of 1 in 35 mL of MeCN was quickly added 1.1 mL (12 mmol) of *i*-PrI. The solution was stirred for 24 h, after which time it became reddish-brown. The solution was filtered, the solvent was removed under vacuum, and the volatile $Fe(CO)_5$ was identified by IR. The residue was washed with 40 mL of hexane and then extracted with CH_2Cl_2 to give about 1.00 g (0.98 mmol) of $[Et_4N]_2[i\text{-}PrBi\{Fe(CO)_4\}_3]$ (98% based on Bi), which was identified by its IR spectrum. IR (ν_{CO}, CH_2Cl_2): 2032 (w), 2010 (w), 1976 (vs), 1893 (vs br) cm^{-1}.

Synthesis of $(i\text{-}Pr)_2Bi_2Fe_2(CO)_8$. To 1.00 g (0.98 mmol) of $[Et_4N]_2[i\text{-}PrBi\{Fe(CO)_4\}_3]$ was added about 5 mL of HOAc. The solution was stirred for 27 h to give a reddish-brown solution. The solvent was removed under vacuum, and the residue was extracted into several 40-mL portions of hexane to give 0.045 g (0.054 mmol) of $(i\text{-}Pr)_2Bi_2Fe_2(CO)_8$ (11% based on Bi). IR (ν_{CO}, hexane): 2036 (s), 1987 (vs) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.70–3.30 (m, 1H), 1.83 (d, 6H, J = 5.8 Hz); δ 3.70–3.30 (m, 1H), 1.72 (d, 6H, J = 5.8 Hz). Mass (EI): M$^+$ at m/e 840 with consequent loss of two Pr groups [M$^+$ − n(43)] and the regular loss of CO groups [M$^+$ − n(28)]. Anal. Calcd for $Bi_2Fe_2C_{14}H_{14}O_8$: C, 20.02; H, 1.68. Found: C, 20.25; H, 1.79. Mp: 225 °C dec. The residue was extracted with CH_2Cl_2, yielding 0.15 g of the previously reported $[Et_4N][BiFe_3(CO)_{10}]$.[7]

Reaction of 1 with *n*-BuBr. A 1.40-mL (12-mmol) amount of *n*-BuBr was syringed into a green solution of 1.270 g (1 mmol) of 1 in 40 mL of MeCN. The solution was heated at 40 °C for 48 h, after which time it became reddish-brown. The solution was filtered and the solvent was removed under vacuum. The volatile $Fe(CO)_5$ was detected by IR. The residue was washed with hexane and ether and then recrystallized from THF/CH_2Cl_2 to give 0.90 g (0.87 mmol) of $[Et_4N]_2[n\text{-}BuBi\{Fe(CO)_4\}_3]$ (87% based on Bi). IR (ν_{CO}, MeOH): 2032 (w), 2012 (w), 1978 (s), 1901 (vs br) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 3.43 (t, 2H, J = 8.6 Hz), 2.06 (m, 2H), 1.37 (m, 2H), 0.981 (t, 3H, J = 7.3 Hz). Anal. Calcd for $BiFe_3C_{32}H_{49}N_2O_{12}$: C, 37.31; H, 4.79; N, 2.72. Found: C, 35.53; H, 4.52; N, 2.55.

Synthesis of $(n\text{-}Bu)_2Bi_2Fe_2(CO)_8$. To 0.90 g (0.87 mmol) of $[Et_4N]_2[n\text{-}BuBi\{Fe(CO)_4\}_3]$ was added about 5 mL of HOAc. After stirring for 24 h, the solution became reddish-brown. The solvent was removed under vacuum, and the residue was extracted into several 40-mL portions of hexane to give 0.099 g (0.14 mmol) of $(n\text{-}Bu)_2Bi_2Fe_2(CO)_8$ (32% based on Bi). IR (ν_{CO}, hexane): 2036 (s), 1987 (vs) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.01 (t, 2H, J = 7.5 Hz), 2.04 (m, 2H), 1.54 (m, 2H), 0.96 (t, 3H, J = 7.1 Hz); δ 3.87 (t, 2H, J = 7.5 Hz), 1.94 (m, 2H), 1.44 (m, 2H), 0.94 (t, 3H, J = 7.1 Hz). Mass (EI): M$^+$ at m/e 868 with consequent loss of two Bu groups [M$^+$ − n(57)] and the regular loss of CO groups [M$^+$ − n(28)]. Anal. Calcd for $Bi_2Fe_2C_{16}H_{18}O_8$: C, 22.14; H, 2.09. Found: C, 21.89; H, 1.98. Mp: 154 °C dec. The residue was extracted with CH_2Cl_2, yielding 0.24 g of the previously reported $[Et_4N][BiFe_3(CO)_{10}]$.[7]

Reaction of 1 with *t*-BuBr. A 1.36-mL (12-mmol) aliquot of *t*-BuBr was syringed into a green solution of 1.270 g (1 mmol) of 1 in 40 mL of MeCN. The solution was heated at 40 °C for 20 h, after which time it became greenish-brown. The solution was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and extracted with CH_2Cl_2, giving 0.543 (0.345 mmol) of $[Et_4N][BiFe_3(CO)_{10}]$ (70% based on Bi).

Reaction of 1 with $Br(CH_2)_2Br$. A 0.50-mL (6-mmol) aliquot of $Br(CH_2)_2Br$ was syringed into a green solution of 1.270 g (1 mmol) of 1 in 40 mL of MeCN. The solution was stirred for 1 day, after which time it became greenish-brown. The solution was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and extracted with CH_2Cl_2 to give 0.156 g (0.198 mmol) of $[Et_4N][BiFe_3(CO)_{10}]$.[7]

Reaction of 1 with $Cl(CH_2)_3Cl$. To a green solution of 1.270 g (1 mmol) of 1 in 40 mL of MeCN was added 1.10 mL (12 mmol) of $Cl(CH_2)_3Cl$. The solution was heated at 40 °C for 5 days to give a greenish-brown solution. The solution was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and extracted into CH_2Cl_2 to give mostly $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$.[12]

Reaction of 1 with $Cl(CH_2)_3Br$. A 2.40-mL (24-mmol) aliquot of $Cl(CH_2)_3Br$ was quickly syringed into a green solution of 2.540 g (2 mmol) of 1 in 40 mL of MeCN. The solution was heated at 40 °C for 40 h, after which time it became reddish-brown. The solution was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and ether and recrystallized from THF/CH_2Cl_2 to give 1.94 g (1.84 mmol) of $[Et_4N]_2[Cl(CH_2)_3Bi\{Fe(CO)_4\}_3]$ (92% based on Bi). IR (ν_{CO}, MeOH); 2037 (w), 2015 (w), 1981 (s), 1896 (vs br) cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6, 298 K): δ 3.80 (t, 2H), 3.28 (t, 2H), 2.60 (m, 2H). Anal. Calcd for $BiFe_3C_{31}H_{46}N_2O_{12}Cl$: C, 35.44; H, 4.41; N, 2.67. Found: C, 35.23; H, 4.24; N, 2.58.

Synthesis of $\{Cl(CH_2)_3\}_2Bi_2Fe_2(CO)_8$. To 1.94 g (1.84 mmol) of $[Et_4N]_2[Cl(CH_2)_3Bi\{Fe(CO)_4\}_3]$ was added about 5 mL of HOAc. The solution was stirred for 40 h to give a reddish-brown solution. The solvent was removed under vacuum and the residue extracted with several 40-mL portions of hexane to give 0.182 g (0.2 mmol) of $\{Cl(CH_2)_3\}_2Bi_2Fe_2(CO)_8$ (22% based on Bi). IR (ν_{CO}, hexane): 2037 (s), 1981 (vs) cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 3.68 (t, 2H), 2.76–2.72 (m, 2H), 2.19–2.15 (m, 2H); δ 3.61 (t, 2H), 2.76–2.72 (m, 2H), 2.19–2.15 (m, 2H). Mass (EI): M$^+$ at m/e 908 with consequent loss of two $Cl(CH_2)_3$ groups [M$^+$ − n(77)] and the regular loss of CO groups [M$^+$ − n(28)]. Anal. Calcd for $Bi_2Fe_2C_{14}H_{12}O_8Cl_2$: C, 18.50; H, 1.33. Found: C, 18.72; H, 1.37. Mp: 91 °C dec. The residue was then extracted with CH_2Cl_2, yielding 0.63 g of the previously reported $[Et_4N]_2[Bi_2Fe_4(CO)_{13}]$.[12]

Synthesis of $\{Br(CH_2)_4\}_2Bi_2Fe_2(CO)_8$. A 1.44-mL (12-mmol) aliquot of $Br(CH_2)_4Br$ was syringed into a green solution of 1.270 g (1 mmol) of 1 in 25 mL of MeCN. The solution was stirred for 40 h, after which time it became reddish-brown. The solution was filtered, and the solvent was removed under vacuum. The residue was washed with hexane and ether to give an oil (IR (ν_{CO}, CH_3CN): 1984 (s), 1903 (vs br) cm^{-1}) which was treated with 5 mL of HOAc for 17 h. The solvent was removed under vacuum and the residue extracted with hexane to give 0.041 g of $\{Br(CH_2)_4\}_2Bi_2Fe_2(CO)_8$ (8% based on Bi). IR (ν_{CO}, hexane): 2036 (s), 1987 (vs) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.91 (t, 2H, J = 7.8 Hz), 3.46 (t, 2H, J = 6.3 Hz), 2.02–1.95 (m, 4H); δ 3.77 (t, 2H, J = 7.8 Hz), 3.43 (t, 2H, J = 6.3 Hz), 2.02–1.95 (m, 4H). Mass (EI): M$^+$ at m/e 1024 with consequent loss of two $Br(CH_2)_4$ groups [M$^+$ − n(135)] and the regular loss of CO groups [M$^+$ − n(28)]. Anal. Calcd for $Bi_2Fe_2C_{16}H_{16}O_8Br_2$: C, 18.73; H, 1.56. Found: C, 18.73; H, 1.79. Mp: 310 °C dec.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 82-0208-M-003-007).

OM9304570