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New Weakly Coordinating Anions 3:[†] Useful Silver and Trityl Salt Reagents of Carborane Anions

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Abstract: New silver and trityl salts of large, exceptionally inert, weakly coordinating carborane anions are reported. The anions include the 10-vertex carborane *closo*-$CB_9H_{10}^-$, **1**, its pentabrominated derivative *closo*-6,7,8,9,10-$Br_5CB_9H_5^-$, **2**, the 12-vertex hexabrominated derivative *closo*-7,8,9,10,11,12-$Br_6CB_{11}H_6^-$, **3**, the cobalt(III) bis(dicarbollide) ion $Co(1,2\text{-}C_2B_9H_{11})_2^-$, **4**, and its hexabrominated derivative $Co(8,9,12\text{-}Br_3\text{-}1,2\text{-}C_2B_9H_8)_2^-$, **5**. X-ray structures have been determined for Ag[**1**] and Ag(η_2-toluene)[**2**]. Halide abstraction reactions with these silver salts have been explored with respect to the labile complex $IrCl(CO)(PPh_3)_2$. Ag[**2**] forms an Ir → Ag metal–metal-bonded adduct rather than undergoing metathesis. The adduct has been characterized by X-ray crystallography and shows η^3 bonding to Ag^+ via bromine atoms from the $Br_5CB_9H_5^-$ anion. The more coordinating anion **4** leads unexpectedly to $[Ir(CO)(PPh_3)_3]$[**4**] from $IrCl(CO)(PPh_3)_2$ and $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}p\text{-xylene})]$[**4**] from $Fe(Cp)(CO)_2I$, both of which have been characterized by X-ray crystallography. This work shows that the gain in stability arising from bromination of carborane anions does *not* occur at the expense of increased coordinating ability, despite the addition of lone pairs. Rather, bromination leads to decreased nucleophilicity. This unexpected result has been confirmed by ranking anions Y^- in order of their increasing carbonyl stretching frequencies in compounds of the type $FeCp(CO)_2Y$. This shows that $Br_6CB_{11}H_6^-$, **3**, is the least coordinating anion in the series, substantially less than SbF_6^-. The size, solubility, inertness, and low nucleophilicity of this and related carborane anions suggest wide and varied applications throughout organic and inorganic metathesis and cation chemistry.

Introduction

New silver(I) salts and new trityl salts, especially having those weakly nucleophilic counterions, are finding immediate applications in metathesis, catalysis, and oxidation chemistry. Some recent examples include trityl salts of tetraphenylborate anion[1] and its fluorinated analogues.[2-4] These are very useful as hydride and methyl abstraction reagents in organosilicon and organotransition metal chemistry. Silver salts of polyteflate anions have proved to be particularly useful for demonstrating coordination of chlorocarbon solvents.[5] More generally, reagents which lead to cations having weakly coordinating anions have led to a number of useful homogeneous polymerization catalysts,[6-10] to novel coordination chemistry of osmium,[11] to a diverse Lewis acid chemistry with organo-transition metal complexes,[12] and to useful new electrolytes.[13]

Our own work has focused on reagents derived from the 12-vertex carborane anion $CB_{11}H_{12}^-$, whose stability, large size, and lack of lone pairs make it one of the least coordinating anions.[14] Its silver salt is a useful halide abstraction reagent and, where thwarted, leads to interesting insight into the mechanisms of halide metathesis reactions.[15] We recently introduced a new weakly coordinating anion, the 10-vertex pentabrominated carborane, *closo*-6,7,8,9,10-$Br_5CB_9H_5^-$, whose trityl salt has allowed one of the closer approaches yet to the synthesis of a silylium ion (R_3Si^+).[16] The 12-vertex hexabrominated carborane, *closo*-7,8,9,10,11,12-$Br_6CB_{11}H_6^-$, does even better. X-ray, ^{29}Si NMR, and reactivity data on *i*-$Pr_3Si(Br_6CB_{11}H_6)$ indicate that this anion is perhaps the least nucleophilic and most inert anion presently known.[17] The search for larger, more inert and more weakly coordinating anions continues to attract much attention[18] as the limits of cationic electrophilic chemistry and coordinative unsaturation are extended. Of the known classes of weakly coordinating anions (oxo and fluoro anions, tetraarylborates, carbanions, polyoxometalates, and carboranes)[19] it is the carboranes which are perhaps the most amenable to further elaboration. We have recently described the derivatization of $CB_{11}H_{12}^-$ via electrophilic substitution at boron and lithiation/alkylation at carbon.[20] In the present paper, we report the synthesis and characterization of silver and trityl salts of various carborane anions, selected for their size, inertness, and solubility characteristics. They include the 10-vertex *closo*-$CB_9H_{10}^-$, **1**,[21,22] and its pentabrominated derivative *closo*-6,7,8,9,10-$Br_5CB_9H_5^-$, **2**,[16] the 12-vertex hexabrominated derivative *closo*-7,8,9,10,11,-

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[†] Part 2: see ref 20.

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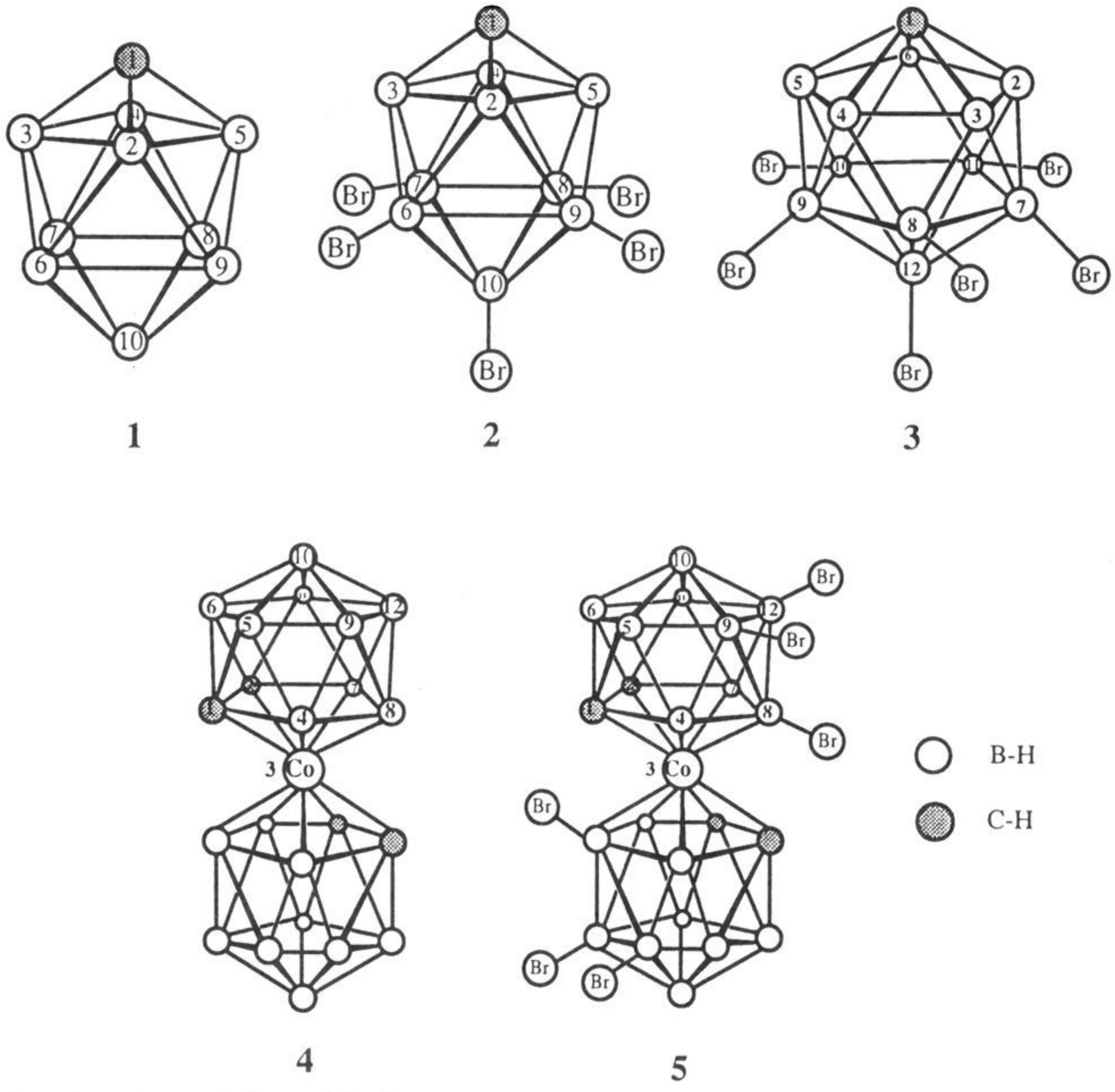

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Figure 1. Drawings of the five anions **1–5** discussed in this paper.

12-Br$_6$CB$_{11}$H$_6^-$, **3**,[15,17,23] and the cobalt(III) bis(dicarbollide) ion Co(1,2-C$_2$B$_9$H$_{11}$)$_2^-$, **4**,[24] and its hexabrominated derivative Co-(8,9,12-Br$_3$-1,2-C$_2$B$_9$H$_8$)$_2^-$, **5**.[24,25] These are illustrated in Figure 1. X-ray crystal structures have been obtained for the silver(I) complexes of the two 10-vertex ions **1** and **2**. In addition, silver salt metathesis chemistry with respect to IrCl(CO)(PPh$_3$)$_2$ and Fe(Cp)(CO)$_2$I has been explored in the search for isolable intermediates and to bring out differences in the nucleophilicity of the anions. The crystal structures of some unexpected products are reported.

Experimental Section

NMR spectra were recorded on a Bruker WP-270 or Bruker AM-360 spectrometer using BF$_3$·OEt$_2$ as external standard for ^{11}B. IR spectra were recorded on a IBM IR/30S FT instrument. Elemental analyses were performed by Oneida Research Services, New York. Ag(Br$_6$-CB$_{11}$H$_6$),[15] Cs(CB$_9$H$_{10}$),[21,22] Cs[Co(C$_2$B$_9$H$_{11}$)$_2$],[24] and Cs[Co-(Br$_3$C$_2$B$_9$H$_8$)$_2$][24,25] were prepared by literature methods. All solvents were distilled from Na/benzophenone inside the glovebox. Other reagents were purchased by Aldrich and used as supplied. Recrystallizations and metathesis reactions were performed in an inert atmosphere glovebox in dried solvents as previously described.[15]

Ag(*closo*-CB$_9$H$_{10}$), Ag[1]. Cs(CB$_9$H$_{10}$) (1.01 g, 4.00 mmol) was dissolved in hot water (50 mL), and Ag(NO$_3$) (0.71 g, 4.18 mmol) was dissolved in cold water (3 mL). The solutions were quickly cooled and mixed at 0 °C. The resulting grey-yellow precipitate was filtered off, washed with cold water, and dried under vacuum for 2 days. Recrystallization from toluene gave 0.80 g of pale green-yellow crystals (88%), some of which were suitable for X-ray diffraction. Since the product is expected to be colorless, the color is ascribed to an unknown trace impurity that cannot be detected by NMR spectroscopy. ^{11}B NMR (C$_6$D$_6$): 13.05 (d, 1B), −18.15 (d, 4B), −25.48 (d, 4B). ^{11}B NMR (acetone-d_6): 17.81 (d, 1B), −18.18 (d, 4B), −25.23 (d, 4B). ^{13}C NMR (C$_6$D$_6$): 68.64 (s, 1C). IR (KBr): 3103 m, 2558 vs, br, 1136 m, 1095 m, 983 s, 676 m cm^{-1}. Anal. Calcd for CB$_9$H$_{10}$Ag: C, 5.28; H, 4.44. Found: C, 5.20; H, 4.35. See X-ray section.

Reaction of Ag[1] with Trityl Bromide. Equimolar portions of Ag[**1**] and trityl bromide were mixed in acetonitrile-d_3 in an attempt to prepare [Ph$_3$C][**1**]. AgBr was removed by filtration and weighed (~1 equiv). ^{1}H NMR of the filtrate indicated triphenylmethane as the sole organic product (7.26–7.10 m, 15H; 5.50 s, 1H). We were unable to isolate the boron-containing product. ^{1}H NMR: 4.84 (s, br). ^{11}B NMR: 29.90 (d, 1B), −13.66 (d, 1B), −16.39 (d, 1B), −18.80 (d, 3B), −21.73 (d, 1B), −24.37 (d, 3B). Reaction in other solvents (e.g. toluene, nitrobenzene) gave products with similar ^{11}B NMR spectra.

Cs(*closo*-6,7,8,9,10-Br$_5$CB$_9$H$_5$), Cs[2]. Cs(CB$_9$H$_{10}$) (1.26 g, 5.0 mmol) was dissolved in glacial acetic acid (50 mL) and refluxed with bromine (40 g, 250 mmol) for 3 days. The solvent was removed, and 100 mL of water was added to give a white precipitate. Recrystallization from hot water gave 2.89 g of off-white crystals (89%). ^{11}B NMR (acetone-d_6): 21.83 (s, 1B), −11.90 (s, 4B), −11.90 (d, 4B). ^{1}H NMR: 5.26 (s, br). IR (KBr): 3105 m, 2603 s, 1104 s, 1081 s, 998 s, 979 s, 798 s cm^{-1}.

Ag(*closo*-6,7,8,9,10-Br$_5$CB$_9$H$_5$)(η^2-C$_7$H$_8$), Ag(tol)[2]. This compound was prepared in a similar manner to Ag[**1**] using Cs(Br$_5$CB$_9$H$_5$) (2.16 g, 3.34 mmol) and Ag(NO$_3$) (0.568 g, 3.34 mmol) except that the reaction mixture was not cooled. Recrystallization from toluene/*n*-hexane gave colorless crystals (1.88 g, 84%), including crystals suitable for X-ray diffraction. ^{11}B NMR (acetone-d_6): 21.81 (s, 1B), −11.73 (s, 4B), −11.73 (d, 4B, accidental degen). IR (KBr): 3112 w, 2601 s, 1105 m, 1084 s, 1000 m, 981 m cm^{-1}. Anal. Calcd for C$_8$H$_{13}$B$_9$Br$_5$Ag: C, 13.46; H, 1.84. Found: C, 13.58; H, 2.24. See X-ray section. The coordinated toluene can be removed under vacuum.

[Ph$_3$C][*closo*-6,7,8,9,10-Br$_5$CB$_9$H$_5$], Trityl[2]. Trityl bromide (0.468 g, 1.45 mmol) in toluene (10 mL) was added to Ag[**2**] (0.90 g, 1.45 mmol) dissolved in toluene (10 mL) and acetonitrile (30 mL). After stirring for 1.5 h, the pale yellow precipitate of AgBr was filtered off. The

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Table 1. Summary of Crystal Data and Intensity Collection Parameters

compound	Ag[**1**]	Ag(tol)[**2**]	$IrCl(CO)(PPh_3)_2 \cdot Ag$[**2**]·tol	$[Ir(CO)(PPh_3)_3]$[**4**]	[CpFe(p-xylene)][**4**]
formula	$AgCH_{10}B_9$	$AgC_8H_{13}B_9Br_5$	$AgIrC_{45}B_9Br_5ClOP_2$	$CoIrC_{59}H_{67}B_{18}OP_3$	$FeCoC_{17}H_{37}B_{18}$
molecular weight (mol)	227.3	713.9	1494.2	1330.8	550.9
space group	$P2_1/m$	$P2_1/n$	$P2_1/a$	$P2_1$	$P2_1/a$
molecules per unit cell	2	4	4	2	4
a (Å)	6.770(6)	11.750(9)	23.54(4)	11.151(7)	12.916(23)
b (Å)	9.120(9)	9.726(5)	12.07(3)	21.689(40)	29.813(34)
c (Å)	6.731(7)	17.746(12)	20.62(4)	13.238(37)	7.365(5)
β (deg)	103.38(8)	99.46(6)	119.4(1)	100.99(16)	102.41(11)
V (Å^3)	404.4(7)	2000(2)	5087(17)	3143(11)	2769(6)
calculated density (g cm^{-3})	1.87	2.38	1.96	1.41	1.33
wavelength (Å) used for data collection (Mo Kα)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
sin θ/λ limit (Å^{-1})	0.538	0.538	0.538	0.538	0.538
scan technique	ω	ω	ω	ω	ω
total number of reflections measured	3354	3180	7792	4788	6348
number of reflections used in structural analysis $I > 3\sigma(I)$	722	976	2336	3482	1400
number of variable parameters	97	210	344	369	381
final agreement factors	$R(F) = 0.047$	$R(F) = 0.067$	$R(F) = 0.078$	$R(F) = 0.044$	$R(F) = 0.063$

filtrate was reduced to a small volume under vacuum and the orange product crystallized out by cooling to −30 °C (0.94 g, 85%). ^{1}H NMR (acetone-d_6): 7.23 (m, 15H), 5.18 (s, br, 1H). ^{13}C NMR: 209.7, 154.0, 130.4, 129.9, 127.8, 47.2. ^{11}B NMR: 22.0 (s, 1B), −12.0 (s, 4B), −12.0 (d, 4B). IR (KBr): 3100 w, 2587 s, br, 1581 s, 1481 s, 1449 s, 1356 s, 1295 s, 1084 s, 995 s, 978 s, 700 s cm^{-1}. Anal. Calcd for $C_{20}H_{20}Br_5B_9$: C, 31.72; H, 2.66. Found: C, 31.61; H, 2.57.

[Ph_3C][*closo*-7,8,9,10,11,12-$Br_6CB_{11}H_6$], Trityl[3]. This was prepared in a similar manner to trityl[**2**], and orange-yellow crystals were isolated in 81% yield. ^{1}H NMR (acetone-d_6: 7.33-7.14 (m, 15H), 3.31 (s, br, 1H). ^{11}B NMR: −1.42 (s, 1B), −9.40 (s, 5B), −19.54 (d, 5B). ^{13}C NMR: 210.0, 148.6, 130.5, 129.7, 128.2, 43.5. IR (KBr): 3070 w, 2594 s, 1581 s, 1481 s, 1449 s, 1358 s, 1294 s, 873 s, 701 s cm^{-1}. Anal. Calcd for $C_{20}H_{21}B_{11}Br_6$: C, 27.94; H, 2.46. Found: C, 28.25; H, 2.38.

Ag[Co(1,2-$C_2B_9H_{11}$)$_2$], Ag[4]. Solutions of $Cs[Co(C_2B_9H_{11})_2]$ (6.90 g, 15.1 mmol) in hot water (500 mL) and $Ag(NO_3)$ (2.56 g, 15.1 mmol) in water (10 mL) were mixed. The resulting yellow precipitate was filtered off, washed with hot water, and dried under vacuum. Recrystallization from toluene with *n*-hexane vapor diffusion gave yellow crystals (5.93 g, 91%). ^{11}B NMR (C_6D_6): 3.56 (d, 2B), 1.57 (d, 2B), −5.81 (m, 8B), −16.40 (d, 4B), −21.16 (d, 2B). IR (KBr): 3043 w, 2552 vs, br, 1098 m, 987 m cm^{-1}. Anal. Calcd for $C_4B_{18}H_{22}AgCo$: C, 11.13; H, 5.14. Found: C, 10.54; H, 5.40.

[Ph_3C][Co(1,2-$C_2B_9H_{11}$)$_2$], Trityl[4]. A toluene solution (25 mL) of trityl bromide (0.808 g, 2.50 mmol) was added to a solution of Ag[**4**] (1.08 g, 2.50 mmol) in acetonitrile (25 mL). After stirring for 2 h the pale yellow precipitate of AgBr was removed by filtration. Concentration of the filtrate and cooling to −30 °C gave orange crystals, which were vacuum dried (1.32 g, 87%). ^{1}1H NMR (acetone-d_6): 7.20 (m, 15 H). ^{13}C NMR: 209.8, 145.3, 130.6, 128.8, 126.7, 50.7. ^{11}B NMR: 12.82 (d, 1B), 11.18 (d, 1B), 5.02 (d, 1B), 2.30 (d, 1B), −4.89 (m, 8B), −16.85 (d, 2B), −18.20 (d, 2B), −21.17 (d, 1B), −22.66 (d, 1B). IR (KBr): 2049 m, 3026 m, 2558 vs, br, 1494 s, 1451 s, 1100 s, 9855, 755 s, 734 s, 700 s cm^{-1}. Anal. Calcd for $C_{23}H_{37}B_{18}Co$: C, 48.71; H, 6.58. Found: C, 50.00; H, 6.67.

Ag[Co(8,9,12-Br_3-1,2-$C_2B_9H_8$)$_2$], Ag[5]. A solution of Cs[Co(8,9,-12-Br_3-1,2-$C_2B_9H_8$)$_2$] (4.41 g, 4.74 mmol) in 95% ethanol (60 mL) was added to $Ag(NO_3)$ (0.81 g, 4.76 mmol) dissolved in water (10 mL). The resulting yellow precipitate was filtered off, washed with hot water, and dried under vacuum (3.75 g, 87%). ^{11}B NMR (acetone-d_6): 5.68 (s, 2B), 3.68 (d, 2B), −1.83 (s, 4B), −4.65 (d, 4B), −17.11 (d, 4B), −23.31 (d, 2B). IR (KBr): 3047 m, 2596 vs, br, 1101 s, 1009 s, 982 s, 953 s, 862 vs cm^{-1}. Anal. Calcd for $C_4H_{16}B_{18}Br_6AgCo$: C, 5.31; H, 1.78. Found: C, 5.58; H, 1.47.

[Ph_3C][Co(8,9,12-Br_3-1,2-$C_2B_9H_8$)$_2$], Trityl[5]. This was prepared in a similar manner to trityl[**4**] and isolated as an orange powder (76%). ^{1}H NMR (acetone-d_6): 7.24 (m, 15H), 4.64 (s, br, 4H). ^{13}C NMR: 210.0, 148.0, 130.5, 128.9, 127.5, 53.1. ^{11}B NMR: 5.77 (s, 2B), 3.90 (d, 2B), −1.54 (s, 4B), −4.45 (d, 4B), −17.04 (d, 4B), −23.36 (d, 2B). IR (KBr): 3047 m, 2594 s, br, 1581 s, 1481 s, 1449 s, 1358 s, 1294 m, 862 s cm^{-1}. Anal. Calcd for 0.5 toluene solvate $C_{26.5}H_{35}B_{18}Br_6Co$: C, 29.29; H, 3.25. Found: C, 29.29; H, 3.01.

$IrCl(CO)(PPh_3)_2 \cdot Ag(Br_5CB_9H_5)$. Ag[**2**] (0.065 g, 0.104 mmol) was added to a solution of $IrCl(CO)(PPh_3)_2$ (0.078 g, 0.10 mmol) in toluene (15 mL). There was no precipitate after 3 days. *n*-Hexanes vapor diffusion resulted in orange-yellow crystals (0.085 g, 61%). Recrystallization from hot toluene gave crystals suitable for X-ray crystallography. ^{1}H NMR (C_6D_6): 8.24–8.15 (m, 15H), 7.58–7.40 (m, 15H), 5.14 (s, br, 1H). ^{11}B NMR: 22.13 (s, 1B), −11.08 (d, 8B). IR (KBr): 3056 w, 2588 s, 2010 m (impurity, probably $[Ir(CO)(PPh_3)_3]^+$), 1979 s, br, 1480 s, 1435 s, 1094 s, 999 m, 980 m, 692 s, 522 s cm^{-1}. Anal. Calcd for $C_{38}H_{35}AgB_9Br_5ClIrOP_2$: C, 32.56; H, 2.52. Found: C, 32.94; H, 2.52. See X-ray section. The rhodium analogue $RhCl(CO)(PPh_3)_2 \cdot Ag(Br_5CB_9H_5)$ was prepared in a similar manner and showed very similar NMR and IR spectra ($\nu CO = 1995$ cm^{-1}). Anal. Calcd for $C_{38}H_{35}AgB_9Br_5ClOP_2Rh$: C, 34.77; H, 2.69. Found: 34.76; H, 2.29.

$[Ir(CO)(PPh_3)_3][Co(1,2\text{-}C_2B_9H_{11})_2]$. Under preparative conditions similar to above, equivalent amounts of $IrCl(CO)(PPh_3)_2$ and Ag[**4**] were stirred overnight. The white precipitate of AgCl was removed by filtration, and an orange solid was isolated by *n*-hexanes diffusion. ^{11}B NMR (C_6D_6): 3.56 (d, 2B), 1.32 (d, 2B), −6.02 (d, 8B), −16.71 (d, 4B), −21.21 (d, 2B). IR (KBr): 3056 w, 2562 vs, br, 2005 s, 1971 s, 1481 s, 1425 s, 1096 s, 744 m, 522 s cm^{-1}. Recrystallization from toluene gave orange crystals suitable for X-ray diffraction.

$[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}p\text{-}(CH_3)_2C_6H_4][Co(1,2\text{-}C_2B_9H_{11})_2]$. A toluene solution (10 mL) of Ag[**4**] (0.086 g, 0.20 mmol) was added to $Fe(Cp)(CO)_2I$ (0.061 g, 0.20 mmol) in toluene (40 mL). After stirring for 4 days, the AgI precipitate was filtered off, the filtrate was reduced to 8 mL, and *n*-hexane vapor diffusion led to orange crystals (0.101 g, 80%). ^{11}B NMR (acetone-d_6): 6.89 (d, 2B), 1.72 (d, 2B), −5.11 (d, 4B), −5.65 (d, 4B), −16.89 (d, 4B), −22.47 (d, 2B). IR (KBr): 3107 w, 3043 w, 2562 vs, br, 1460 m, 1419 m, 1098 m, 982 s, 860 s cm^{-1}. Anal. Calcd for $[Fe(\eta^5\text{-}C_5H_5)\eta^6\text{-}p\text{-}(CH_3)_2(C_6H_4)][Co(1,2\text{-}C_2B_9H_{11})_2] \cdot C_6H_5CH_3$, $C_{23}H_{43}B_{18}CoFe$: C, 43.92; H, 6.73. Found: C, 42.98; H, 6.68.

The *p*-xylene analogue was prepared by dissolving this product in hot *p*-xylene. Slow evaporation gave single crystals suitable for X-ray diffraction (see below).

Reactions with $FeCp(CO)_2I$. Toluene solutions of $FeCp(CO)_2I$ and the five silver salts Ag[**1**]–Ag[**5**] were monitored by IR spectroscopy at 1:1 molar ratios. Upon mixing, νCO values were observed at 2046, 2004 for **1**; 2047, 2005 for **2**; 2047, 2004 for **3**; 2048, 2006 for **4**, and 2045, 2003 cm^{-1} for **5**. The solutions were monitored over periods of several hours to record the in-growth of new, higher frequency νCO bands corresponding to $FeCp(CO)_2Y$ (Y = **1**–**5**). This was accompanied by precipitation of AgI.

X-Ray Structure Determinations. All crystals were mounted in thin-walled glass capillaries using Paratone-N oil. Diffraction data on five compounds were collected on a Syntex P2$_1$ diffractometer under the conditions indicated in Table 1. Crystallographic examinations led to the cell constants and space groups. Absorption correction procedures were applied to the intensity data. Structures were slowed by Patterson or direct methods. Approximate positions for all hydrogen atoms were found in subsequent difference Fourier syntheses. Final refinement cycles utilized anisotropic thermal parameters for all nonhydrogen atoms. Table 1 summarizes the crystal data, intensity collection, and final refinement parameters.

Results and Discussion

Silver Salts. The preparation of silver(I) salts of the anions **1-5** is readily achieved via Ag(NO$_3$) metathesis in aqueous solution. Only in the case of CB$_9$H$_{10}^-$, **1**, was it necessary to use a lowered temperature for the synthesis, although, even then, the appearance of a colored trace impurity in Ag[**1**] was apparent. This is similar to our earlier observations with the 12-vertex anion CB$_{11}$H$_{12}^-$ vis-à-vis its hexabrominated derivative Ag[**3**]; the parent anion decomposes somewhat during synthesis of its silver salt, while the more stable halogenated form is quite thermally stable. We have traced this instability to the B–H bond that is antipodal to carbon in the polyhedron.[20] It is susceptible to hydride abstraction, a problem that is obviated by bromination in the anions **2**, **3**, and **5**. Thus, the three salts with brominated anions, Ag[**2**], Ag[**3**], and Ag[**5**], are amongst the most chemically stable silver salts known. The other property important to their utility as reagents is solubility. In this regard, the silver salts of **1–4** all show workable toluene solubility. On the other hand, the largest anion, **5**, leads to a silver salt with very little arene solvent solubility. This limits its usefulness, and as a consequence, we have not explored its metathesis chemistry as far as with the other anions. Despite this, the solubility characteristics of **5** in other solvents have been cleverly exploited for other applications.[26]

The solution structures of the silver salts, where sufficiently soluble for ^{11}B NMR spectroscopy, are as expected. Coordination of the anions to silver in toluene or benzene is indicated by ^{11}B shifts that differ significantly from the free ion, particularly in the 10-position of Ag[**1**], where there is an upfield shift of ca. 17 ppm relative to Cs[**1**]. On the other hand, in acetone or acetonitrile, ionic formulations of the type [Ag(solvent)$_x$]$^+$Y$^-$ are indicated by ^{11}B shifts that typically do not differ significantly from those in the cesium or trityl salts.

The crystal structures of the silver salts of carborane anions are not particularly predictable, and each anion shows individual features not previously observed. Some time ago we reported the crystal structure of Ag(benzene)(CB$_{11}$H$_{12}$). It showed an unusual η^1 coordination of the arene and 12,7-bridging of the anion to give three-coordinate silver in a zigzag linear polymeric structure.[27] More recently, we showed that the analogous mono-12-brominated species Ag(benzene)BrCB$_{11}$H$_{11}$) was four-coordinate. Arene bonding was again of the unusual η^1 type. The anion forms bridging B–Br and B–H contacts to silver in a 3D network solid.[20] In the present work, we find that Ag[**1**] crystallizes without coordinated (or lattice) arene, while Ag[**2**] reverts to a somewhat more normal η^2 coordination of the arene. Both have carborane anions acting as bridging ligands in polymeric chain structures, but the coordinate details are unique to each anion.

Figure 2 shows the coordination around silver in the polymeric chain structure of Ag[**1**]. The essence of the structure is that the negatively polarized end of the CB$_9$H$_{10}^-$ anion acts as a bridging ligand to silver via the B–H bond antipodal to carbon (B10) and adjacent B–H bonds from the B6–B9 tetragonal belt. The stability of this solid-state structure apparently overrides other lattices having a coordinated arene, which is presumably the structural motif present in the solution from which it was crystallized. The coordinate geometry approximates linear two-coordination except that the anions provide η^2-like coordination from an adjacent pair of B–H bonds. The silver atom is closer to B6 (2.496(3) Å) than B10 (2.578(2) Å), but this does not indicate site nucleophilicity on the carborane cage. Rather, it reflects the fact that the B10–H bond is shared by two silver atoms. As with the B12–H bond in CB$_{11}$H$_{12}^-$, the B10–H bond in CB$_9$H$_{10}^-$, also antipodal to carbon, is expected to be the most electron rich extremity of the anion, and this is reflected in the most downfield ^{11}B NMR resonance. Both Ag···B distances in Ag[**1**] are shorter than those in Ag(benzene)(CB$_{11}$H$_{12}$),[27] consistent with the approximation of two-coordination rather than three. The coordinated hydrogen atoms have been located with reasonable precision. The Ag–H–B bond angles of 104.1(4)° and 86.1(3)° are smaller than those observed in Ag(benzene)(CB$_{11}$H$_{12}$), again consistent with a strong interaction in a situation of lower effective coordination number. We had previously found a correlation between M–H–B angles in *closo*-carboranes and steric congestion at the metal.[15] The Ag–H distances to H6 and H6″ (~1.92 Å) are short, while those to H10 and H10″ are long (~2.27, 2.42 Å) when compared to Ag(benzene)(CB$_{11}$H$_{12}$). These dimensions are again consistent with stronger binding of the 10-vertex anion but with shared bonding of B–H10 to two silver atoms.

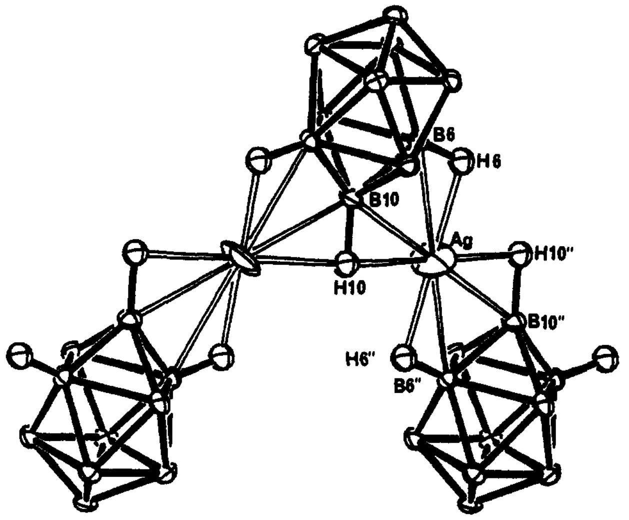

Figure 2. Perspective view (ORTEP) of the coordination sphere around the silver atom in Ag[**1**], showing a portion of the infinite Ag···[**1**]···Ag···[**1**] zigzag chain. Only those hydrogen atoms bonded to silver are shown. The Ag atom is disordered. Bond distances are Ag–B6 = 2.496(3), Ag–B6″ = 2.499(3), Ag–B10 = 2.578(2), Ag–B10″ = 2.593(2), Ag–H6 = 1.921(5), Ag–H6″ = 1.910(5), Ag–H10 = 2.270(7), AG–H10″ = 2.420(7) Å.

The coordinate geometry about silver in Ag(tol)[**2**] is shown in Figure 3. It is made up of η^2-toluene, a bidentate dibromo interaction with one Br$_5$CB$_9$H$_5^-$ ion, and a more nearly monodentate bromo interaction with a neighboring ion. The anions act as bridging ligands to a zigzag linear chain of silver ions, an increasingly familiar motif in silver carborane structures. The η^2 coordination of toluene has rather long Ag–C distances of about 2.62 Å. Typically, η^2-arene coordination is characterized by unsymmetrical bonding with one Ag–C distance at 2.47 ± 0.02 Å and another at 2.6–2.9 Å.[28] The more nearly symmetrical compromise in this case may be the result of both coordinate and crystal-packing requirements. The coordination of the anion is notable on two counts. Firstly, the bridging disposition is quite unsymmetrical, making it "belong" more to one silver atom than another. This is true of both denticity and bond length. The bidentate binding is characterized by Ag–Br bond lengths of ~2.78 Å, whereas the monodentate interaction is weaker at 2.842(6) Å. Secondly, in the bidentate interaction, the Ag–Br10 and Ag–Br6 bond lengths are indistinguishable (2.783(6) and 2.775(6), respectively). If the electron density arguments of the previously discussed all-hydrido anions carried over to the brominated ions, one might expect the B10–Br bond (antipodal to C) to be the most electron rich and therefore the most strongly coordinated. However, either the electron density difference

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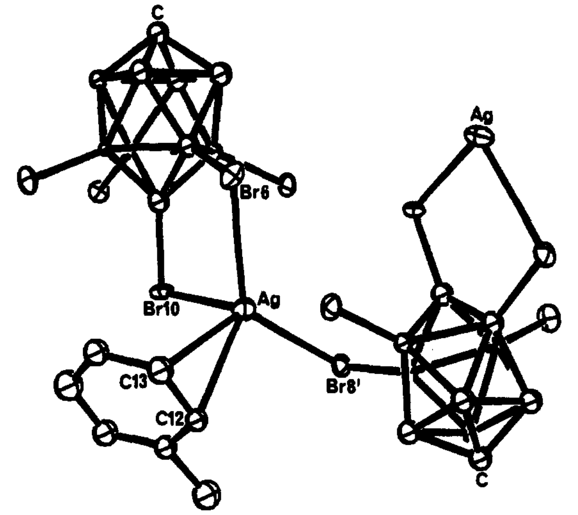

Figure 3. Perspective view (ORTEP) of the coordination sphere around the silver atom in Ag(tol)[**2**], showing a portion of the infinite [2]···Ag(tol)···[**2**]···Ag(tol) zigzag chain. Bond distances are Ag–Br6 = 2.775(6), Ag–Br10 = 2.783(6), Ag–Br8′ = 2.842(6), Ag–C12 = 2.618(36), Ag–C13 = 2.642(38) Å.

between B10 and those in the tetragonal belt (6–9) has been ameliorated by bromination or steric effects are preventing its observation. It is reasonable to view the coordination to silver as a lone pair on bromine, and this contrasts with the bonding pair of a B–H bond on an all-hydrido anion. This probably attenuates some of the disparity of electron density at boron. Also, and perhaps most importantly in view of the 6-bromo- rather than 10-bromo-coordinated anion **2** in (i-Pr)$_3$Si[**2**],[16] the Br(6–9) atoms are more sterically accessible than Br10. The Ag–Br8 distance to the more weakly bound anion (2.842(6) Å) is considerably longer than the Ag–Br separation of 2.642(1) Å in Ag(benzene)(12-BrCB$_{11}$),[20] emphasizing that, relatively, it is a moderate to weak interaction. This means that this structure more nearly approaches that of a discrete molecular complex than any of the other chain structures. It is possible that this feature contributes to the excellent solubility of Ag[**2**] in toluene.

Trityl Salts. The silver(I) salts are useful for forming trityl salts by reaction with trityl bromide. This is successful for the three brominated ions **2**, **3**, and **5** and the cobalt(III) bis(dicarbollide) **4**. The all-hydrido anions **1** and $CB_{11}H_{12}^-$ undergo complicated reactions when their silver salts are treated with Ph_3CBr in various solvents, presumably because of the sensitive B–H bond antipodal to carbon. Invariably, some precipitate of AgBr is observed, but in no case have we been successful in isolating clean boron-containing products. The cleanest reaction seems to be that of Ag($CB_{11}H_{12}$) with Ph_3CBr in acetonitrile. The apparent stoichiometry of an equivalent of AgBr and Ph_3CH as products and the ^{11}B NMR spectrum of a singlet at 3.15, a doublet at −11.9, and a doublet at −15.8 with a ratio 1:5:5 suggest a symmetrical B12–B12 coupling product according to the equation

$$2AgCB_{11}H_{12} + 2Ph_3CBr \rightarrow 2AgBr + 2Ph_3CH + C_2B_{22}H_{22}$$

A related electrochemical oxidation of $CB_9H_{10}^-$ to the symmetrical dimer $C_2B_{18}H_{18}^{2-}$ has been reported, but $CB_{11}H_{12}^-$ is apparently inert to the conditions used.[29]

The utility of the trityl salts in hydride abstraction metathesis chemistry is currently being explored, particularly with respect to organosilane chemistry.[16,17] At this stage we note that one particular trityl salt, [Ph_3C][**2**], has sufficient solubility in toluene that hydride abstractions can be carried out quite readily in very low dielectric media. The only other stable trityl salt that we know to have this property is the perfluorinated tetraphenylborate salt [Ph_3C][$B(C_6F_5)_4$].[4,10,16]

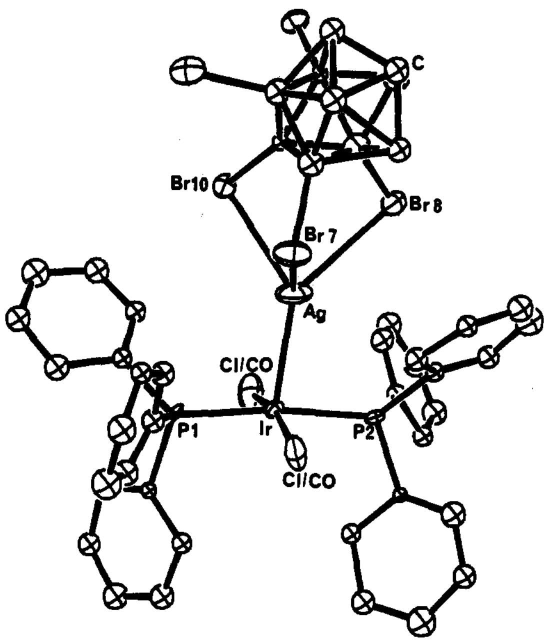

Figure 4. Perspective view (ORTEP) of $(Ph_3P)_2Ir(CO)Cl·Ag$[**2**]. The chlorine atom and CO group are disordered. Bond distances are Ir–Ag = 2.631(5), Ir–P1 = 2.283(12), Ir–P2 = 2.283(11), Ir–Cl = 2.446(19), Ag–Br7 = 2.973(6), Ag–Br8 = 2.949(8), Ag–Br10 = 2.752(8) Å.

Halide Metathesis Chemistry. The dearth of mechanistic work on silver salt metathesis in organo-transition metal chemistry, in sharp contrast to organic chemistry,[30] made our recent discovery of Ir → Ag adducts[31] and Fe–X–Ag halide-bridged intemediates[15] quite unexpected. The essential finding was that very weakly nucleophilic anions can have a profound effect on the mechanism and outcome of halide abstraction reactions with silver salts AgY. In a qualitative manner, the outcome of an attempted metathesis reaction of AgY with $IrCl(CO)(PPh_3)_2$ or $Fe(Cp)(CO)_2I$ gives information on the relative nucleophilicity or coordinating ability of Y^-. It was of interest to compare the reactivity of the silver salts of **1**, **2**, **4**, and **5** with the known reactivity of **3** and its unbrominated precursor $CB_{11}H_{12}^-$ to see if trends in anion stability, nucleophilicity, and ligation ability could be deduced.

While the relatively labile chloride ligand[32] in $IrCl(CO)(PPh_3)_2$ is readily abstracted with silver perchlorate or triflate, less coordinating anions lead instead to Ir → Ag donor–acceptor metal–metal bonded adducts $(PPh_3)_2(CO)ClIr·AgY$.[31] We can now add anions **1**, **2**, and **5** to the latter group along with **3** and its unbrominated parent $CB_{11}H_{12}^-$. None of these silver salts give AgCl precipitates with $IrCl(CO)(PPh_3)_2$ in toluene solution. In the case of **2** we have isolated the adduct with both iridium and rhodium and characterized the iridium complex by X-ray crystallography. Figure 4 shows that $(PPh_3)_2(CO)ClIr·Ag(Br_5\text{-}CB_9H_5)$ adopts the expected silver–iridium Lewis acid–base structure. Bond lengths and bond angles around the iridium atom are within 0.06 Å and 6°, respectively, of those in the previously characterized adduct with Ag($CB_{11}H_{12}$).[31] There is disorder of the chloride and carbonyl ligands. The novel feature of the X-ray structure is the η^3 coordination of the anion. The three Ag–Br distances range from 2.752(8) to 2.973(6) Å. These are comparable to those in Ag(tol)[**2**], where there is also a total of three Ag–Br interactions. In the three complexes of **2** that are now known[16] all three possible coordination modes of the anion,

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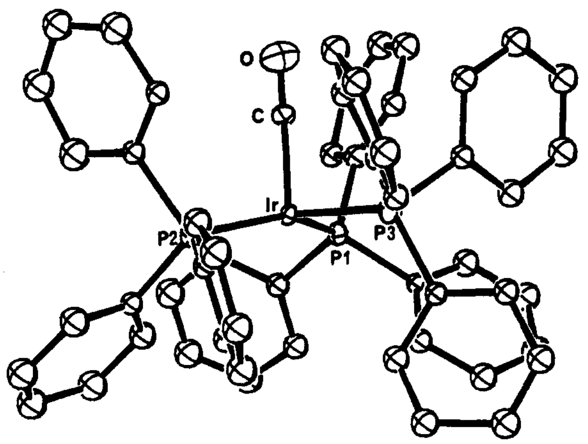

Figure 5. Perspective view (ORTEP) of $[(Ph_3P)_3Ir(CO)]^+$ in $[(Ph_3P)_3Ir(CO)][4]$. Bond distances are Ir–P1 = 2.327(4), Ir–P2 = 2.353(5), Ir–P3 = 2.426(4), Ir–C3 = 1.915(11) Å.

η^1, η^2, and η^3, are now illustrated. In addition, the anion can fill both mononuclear coordination sites as well as bridging sites.

On the other hand, the bis(dicarbollide) ion **4** seems to express a higher coordinating ability than **1**, **2**, **3**, or **5**. Treatment of $IrCl(CO)(PPh_3)_2$ with Ag[**4**] in toluene gives immediate precipitation of AgCl. Isolation of the resulting orange iridium product was suggestive of simple metathesis to give $IrX(CO)(PPh_3)_2$ ($X = Co(C_2B_9H_{11})_2^-$; νCO 1971 cm^{-1}), but the appearance of a growing second νCO at 2005 cm^{-1} indicated further reaction. Upon standing, a disproportionation reaction occurs to give $[Ir(CO)(PPh_3)_3][Co(C_3B_9H_{11})_2]$ as the major product. It was characterized by X-ray crystallography, and the cation is illustrated in Figure 5. The steric congestion in this d^8 ion leads to considerable distortion from square planar toward tetrahedral, as has been previously observed in related complexes such as $[Ir(MePPh_3)_4]^+$.[33]

The precipitation of AgCl from $IrCl(CO)(PPh_3)_2$ and AgY for Y = **4**, but not for Y = **1**, **2**, **3**, and **5**, coupled with the observation of ligand disproportion promoted by **4** suggests a greater nucleophilicity for this anion. It is possible that this arises from a superior ability to take up several coordination sites, thereby promoting the displacement of other ligands (CO, PPh_3), only to be completely displaced itself in the final major product.

Further evidence for this behavior is found in the reaction Ag[**4**] with $Fe(Cp)(CO)_2I$. In previous studies we have observed that, at a certain threshold of weak nucleophilicity, halide-bridged intermediates of the type $Fe(Cp)(CO)_2I\cdot AgY$ were long-lived prior to ultimate metathesis to give $Fe(Cp)(CO)_2Y$.[14] The same is true for all the anions **1–5**, judging from νCO at 2046 ± 2 and 2004 ± 2 cm^{-1} when 1:1 mixture of their silver salts are mixed with $FeCp(CO)_2I$ in toluene. These values are the same as the earlier characterized species $FeCp(CO)_2I\cdot Ag(CB_{11}H_{12})$ (2048, 2006 (toluene); 2044, 1994 cm^{-1} (KBr)).[14] The values are increased from those of the starting material $FeCp(CO)_2I$ (2038, 1994 cm^{-1}), reflecting a loss of electron density at iron. Upon standing, AgI begins to precipitate and new νCO bands appear at higher frequencies, consistent with the formation of metathesis products of the type $FeCp(CO)_2Y$ (Y = **1–5**). The νCO values for these products give a very useful ranking of anion nucleophilicity; the higher νCO, the less donating the anion and the higher the degree of ionicity in the Fe–Y bond. As shown in Table 2, these indicate that the three all-hydrido anions $CB_9H_{10}^-$, **1**, $CB_{11}H_{12}^-$, and the bis(dicarbollide), **4**, have roughly comparable electron-donating ability and are similar to SbF_6^-. The brominated ions are *less* donating and decrease in the order **5** > **2** > **3**. That the hexabromo-12-vertex anion, **3**, is the least coordinating anion in this series is consistent with our findings in R_3SiY chemistry. For Y = **3**, the ^{29}Si NMR shift is the furthest downfield.[17]

Table 2. Carbonyl Stretching Frequencies for $FeCp(CO)_2Y$ Systems

Y	ν_{CO} in toluene (cm^{-1})
I^-	2038, 1994
$Co^{III}(C_2B_9H_{11})_2^-$, **4**	2059, 2030
$CB_{11}H_{12}^-$	2067, 2031
$CB_9H_{10}^-$, **1**	2070, 2030
ClO_4^-	2071, 2027
SbF_6^-	2073, 2030
$Co^{III}(Br_3C_2B_9H_8)_2^-$, **5**	2116, 2058
$Br_5CB_9H_5^-$, **2**	2122, 2073
$Br_6CB_{11}H_6^-$, **3**	2128, 2088

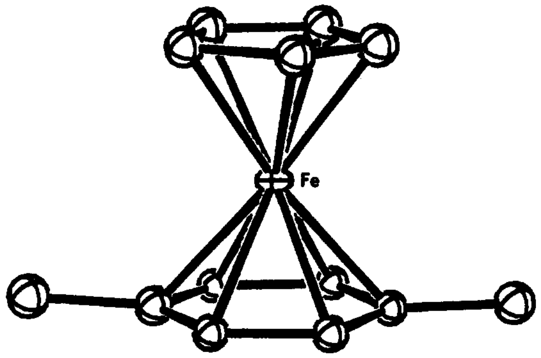

Figure 6. Perspective view (ORTEP) of $[\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xylene})]^+$ in $[CpFe(p\text{-xylene})][4]$. Bond distances (average) are Fe–C (C_5 ring) = 2.083(8), Fe–C (C_6 ring) = 2.119(5), Fe–C (C_5 ring plane) = 1.678, Fe–C (C_6 ring plane) = 1.548 Å.

When a toluene solution of $Fe(Cp)(CO)_2[4]$ is left standing for 5 days, orange crystals which lack νCO are formed. The product is consistent with the formulation [Fe(Cp)(toluene)][**4**]. Replacement of the solvent with *p*-xylene led to crystals of [Fe(Cp)(*p*-xylene)][**4**] suitable for X-ray crystallography. The cation is shown in Figure 6 and confirms that complete replacement of the carbonyl and halide ligands has occurred. The overall result is similar to the chemistry of $Fe(Cp)(CO)_2X/AlX_3$ systems, which led to the original preparation of $[Fe(Cp)(arene)]^+$ salts.[34] The dimensions of the cation show no unexpected differences from closely related species that have been crystallographically characterized.[35] The bis(dicarbollide) anion **4** in both structures is not different from that already reported.[36]

Conclusion

The new silver salts and trityl salts reported in this paper have a combination of features that makes them potentially useful for a wide range of synthetic and mechanistic metathesis chemistry in both organic and inorganic chemistry. The stability of the brominated anions is particularly noteworthy. We have yet to find any evidence for bromide extraction with electrophiles. Yet, the powerfully electrophilic silicon in $i\text{-}Pr_3Si^{\delta+}(Br_6CB_{11}H_6)^{\delta-}$ will abstract chloride from dichloromethane or dichlorobenzene and fluoride from fluorobenzene.[17]

The lowered nucleophilicity of the brominated carboranes is even more noteworthy. One might have expected that bromination of $CB_{11}H_{12}^-$, for example, would *increase* its nucleophilicity by (a) adding lone pairs and (b) increasing the dipole. But the νCO data of Table 2 clearly show a large decrease in electron donation from Y^- to iron in $FeCp(CO)_2Y$. The origin of this decreased nucleophilicity probably lies in a steric effect. Unexpectedly, in

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the X-ray structure of i-$Pr_3Si(Br_6CB_{11}H_6)$,[17] it is a bromine atom from the 7–11 positions in the pentagonal belt rather than the 12-bromo atom that is coordinated to silicon. Apparently, the five bromine atoms in the pentagonal belt prevent the approach of the i-Pr_3Si^+ moiety to the lone pairs on the 12-bromo substituent. Evidence that the bromine atom antipodal to carbon is indeed the most basic comes from the structure of $IrCl(CO)(PPh_3)_2 \cdot Ag$[**2**]. Here, in η^3 bonding of $Br_5CB_9H_5^-$ to the unhindered Ag^+ cation, the Ag–Br10 distance (2.752(8) Å) is shorter than the Ag–Br7 and Ag–Br8 distance (2.973(6) and 2.949(8) Å, respectively).

Applications of trityl[**2**] and trityl[**3**] to the silylium ion problem[15,17] foreshadow a number of other possible applications in catalysis, weak ligand chemistry, electrolyte effects, crystallization, and other areas where the inert properties of spectator anions are critically important. Future work will be directed toward the synthesis of even less nucleophilic anions, other reagents derived from them (e.g. strong oxidants, strong acids, etc.), and coordinatively unsaturated cations.

Acknowledgment. We thank Velia Mitro for assistance. This work was supported by the National Science Foundation (CHE89-17666 and CHE92-23260).

Supplementary Material Available: Tables of bond lengths SI–SV, bond angles SVI–SX, anisotropic thermal parameters SXI–SXV, calculated hydrogen atomic coordinates SXVI–SXVIII, and final atomic coordinates SXIX–SXXIII for the five X-ray structures Ag[**1**], Ag(toluene)[**2**], $IrCl(CO)(PPh_3)_2 \cdot Ag$[**2**], $[Ir(CO)(PPh_3)_3]$[**4**], and [Fe(Cp)(p-xylene)][**4**], respectively, and Figures S1–S6 showing the atom-numbering schemes (45 pages). This material is contained in may libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Structure factor tables are available from the authors.