

ative E-map searching (FIND) routine of SHELXTL. Unless otherwise noted, anisotropic temperature factors were used for all non-hydrogen atoms. Hydrogen atoms were given isotropic temperature factors,  $U = 0.07 \text{ \AA}^2$ . Those defined by the molecular geometry were inserted at calculated positions and not refined; unless otherwise noted, methyl groups were treated as rigid  $\text{CH}_3$  units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Final refinement was on  $F$  by cascaded least-squares methods (full-matrix least-squares). Weighting schemes of the form  $W = 1/\sigma^2(F) + gF^2$  were used and shown to be satisfactory by a weight analysis. Computing was with SHELXTL (Sheldrick, 1983) on a Data General DG30 [SHELX-76 on an IBM 3081-D]. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables (1974). It has been our general experience with these compounds that X-ray scattering is relatively weak, and  $\text{PF}_6^-$  groups are frequently disordered, needing special treatment during refinement. As a result, final  $R$  values are often fairly high with significant residual electron density in the vicinity of these groups.

For complex **3** two Cu atoms are in special position 4c ( $m$  symmetry), and four P atoms are also in 4c. Two had well-defined  $F_6$  groups around them, but for the others (P(3), P(4)), these groups were highly disordered and half-occupancy F atoms were used; the highest residual peaks were in this area. H atoms of methyl groups were not visible on difference Fourier syntheses and were omitted. One molecule of MeCN was located, in position 4c.

For complex **4**, both  $\text{PF}_6^-$  groups were treated as rigid regular octahedra with six ( $\text{PF}_6^-$  (2)) fluorine atoms given 0.5 occupancy, all refined anisotropically. They were supplemented by nine (occupancy 0.25) and four F's (occupancy 0.5) for (1) and (2), respectively, refined individually and isotropically. The hand of the individual chiral crystal chosen was checked by refinement of  $\delta f''$  multiplier.

For complex **5**, after various attempts at refinement with part-occupancy F atoms, one  $\text{PF}_6^-$  group was treated as a rigid octahedron with F-F distance 1.536 Å; group (2) was satisfactory with individual atoms. The six highest residuals on the electron density map are located in the vicinity of  $\text{PF}_6^-$  (1). The hand of the individual chiral crystal chosen was checked by refinement of a  $\delta f''$  multiplier.

For complex **7a**, the crystal was found to contain one molecule of MeCN, which was refined isotropically.

Complex **7b** is isomorphous with **7a**, though the structures were solved independently. It also contains one molecule of MeCN, refined isotropically.

Complex **8a** has cell dimensions similar to **7a** and **7b**, and the Cu is in a very similar position (allowing for a shift of 0.5 in  $y$ ). However, the  $\text{PF}_6^-$  groups occupy different locations in the cell. The crystal contains a highly disordered solvent molecule (MeOH) modeled by one O and

three C atoms, all with occupancy 0.5, refined isotropically.

For complex **12**, the systematic absence gives a choice of  $P2_1/m$  (with molecular  $m$  symmetry) or  $P2_1$ .  $P2_1/m$  was chosen initially, and the structure was successfully solved by Patterson and Fourier methods. Refinement with all non-H atoms anisotropic converged at  $R = 0.074$ ,  $R_w = 0.082$ . One of the saturated six-membered rings was found to be disordered between chair and boat forms (C(1) and C(111) at 0.5 occupancy). However, all the central atoms of the  $\text{C}_{12}$  chain had extremely high temperature factors, and it seemed possible that they represented the superposition of two alternative positions of the molecule each lacking a mirror plane. Space group  $P2_1$  was therefore investigated, starting from the final  $P2_1/m$  coordinates, with the central part of the chain omitted. Refinement in this space group converged at  $R = 0.064$ ,  $R_w = 0.070$ ; but to avoid instability, the refinement had to be damped; it was also necessary to apply a weak constraint to the length of the C-C bonds in the chain between C(12) and C(12A) bond (1.54 Å, esd 0.070). The resulting positions of the chain atoms depart significantly from mirror symmetry and show torsion angles that imply greater stability for the chain. In view of this, of the lower  $R$  value in  $P2_1$ , and of the high thermal parameters for the chain atoms in  $P2_1/m$ , we prefer the non-centrosymmetric refinement. However, the choice is clearly difficult to make, and this refinement does produce differences in equivalent bond lengths in the metal cyclidene portion of the molecule (which probably does not depart appreciably from mirror symmetry). Structural results are presented for the  $P2_1$  structure, but coordinates and bond lengths for the  $P2_1/m$  refinement are included in the supplementary material, and the dimensions in Table II relating to the cyclidene ring are based on this refinement.

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**Supplementary Material Available:** Tables E1-E9 covering crystallographic data for new structures, including atomic coordinates and isotropic thermal parameters as well as a listing of full bond lengths and angles, anisotropic thermal parameters, H-atom coordinates, and structure factors for **3-5**, **7a**, **7b**, **8a**, **8b**, and **12** and coordinates and bond lengths and angles for centrosymmetric refinement of **12** (50 pages); structure factors for **3-5**, **7a**, **7b**, **8a**, **8b**, and **12** (162 pages). Ordering information is given on any current masthead page.

## Observations on Silver Salt Metathesis Reactions with Very Weakly Coordinating Anions

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**Abstract:** Silver salt metathesis reactions using the very weakly nucleophilic anion  $\text{B}_{11}\text{CH}_{12}^-$  reveal several unexpected features of this otherwise familiar reaction. In contrast to  $\text{AgClO}_4$ , which undergoes rapid metathesis with  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , the silver carborane salt  $\text{Ag}(\text{B}_{11}\text{CH}_{12})$  forms a very stable 1:1 adduct having iridium to silver metal-metal bonding. With  $\text{Fe}(\text{Cp})(\text{CO})_2\text{I}$ , a long-lived, isolable intermediate is formed during the first minutes of reaction. The stoichiometry is also 1:1 but the structure is almost certainly that of a halide-bridged adduct:  $\text{Fe}(\text{Cp})(\text{CO})_2\text{I}\cdot\text{Ag}(\text{B}_{11}\text{CH}_{12})$ . Eventual metathesis occurs depositing AgI and giving  $\text{Fe}(\text{Cp})(\text{CO})_2(\text{B}_{11}\text{CH}_{12})$ , which has been the subject of an X-ray crystal structure determination. This work shows that the role of the counterion to silver is much more important to the mechanism and outcome of silver halide abstraction reactions than has previously been recognized and sets the stage for detailed mechanistic studies.

Silver salt metathesis is a time-honored method of halide ion abstraction. Its origins date back to the very earliest days of coordination chemistry. By Werner's time, silver nitrate was already the standard test to differentiate between free and complexed chloride.<sup>3</sup> In modern times, the availability of numerous

silver salts of weakly coordinating anions,  $\text{AgY}$  ( $\text{Y} = \text{ClO}_4^-, \text{SbF}_6^-$  etc.), has kept silver salt metathesis the widely preferred method of halide ion abstraction from labile sources. Perhaps because of its historic familiarity, its stoichiometric simplicity, or its common role as a means to other ends, silver salt metathesis

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reactions have received very little mechanistic attention in the primary literature of inorganic chemistry, and we have been unable to find a textbook of mechanistic inorganic chemistry that makes anything more than a passing reference to the subject. This contrasts with organic chemistry, where silver salt catalysis of alkyl halide reactivity was probed in considerable detail during the 1960s and 1970s.<sup>4</sup> Quite complex rate laws were discovered in a number of cases with rate-determining roles for silver and/or its anion  $Y^-$  such that these studies became a textbook example of how substitution chemistry can be a good deal more complex than simple  $S_N1$  or  $S_N2$  processes.<sup>5</sup> This indication that the silver metathesis reactions of inorganic chemistry might also be mechanistically complex has failed to have much influence over the years, and the prevailing dogma, to which, until recently, we must admit to having accepted, had basically two roles for silver, an active (kinetic) one or a passive (thermodynamic) one, and no significant role for a weakly coordinating anion  $Y^-$ .

Our recent observations with the silver salt of one of the least nucleophilic and least coordinating anions known at this time, the icosahedral carborane  $B_{11}CH_{12}^-$ ,<sup>6</sup> have indicated that silver ion can play quite unexpected roles in metathesis reactions. Moreover, in a growing number of cases, the nature of the counterion  $Y^-$  is critical in determining the outcome of a metathesis attempt. For example, with  $IrCl(CO)(PPh_3)_2$  and  $Ag(B_{11}CH_{12})$  we have found that donor-acceptor metal-metal bonding thwarts the otherwise apparently straightforward metathesis reaction observed with the analogous perchlorate salt.<sup>7</sup> With  $Fe(Cp)(CO)_2I^8$  and  $Ag(B_{11}CH_{12})$  we can readily isolate a halide-bridged adduct that is quite different from the dimeric intermediate  $[Fe(Cp)(CO)_2]_2I^+$  previously isolated,<sup>9</sup> but is consistent with one identified in solution by Graham.<sup>10</sup> In this paper we expand upon our preliminary note<sup>7</sup> to show how  $AgY$  studies with  $IrCl(CO)(PPh_3)_2$  and  $Fe(Cp)(CO)_2X$  reveal new features of silver ion metathesis reactions. By isolating structural models for likely intermediates, this work expands upon the Lewis acid/base adduct concepts developed by Shriver<sup>11</sup> and sets the stage for more detailed mechanistic studies.

### Experimental Section

All reactions and manipulations were carried out in a Vacuum Atmospheres glovebox under  $He$  ( $H_2O$ ,  $O_2 \leq 1$  ppm) except for work with chlorocarbon solvents, which was done with serum stopper/canula techniques. Glassware was flamed or used from a hot oven ( $150^\circ C$ ).  $CDCl_3$  was dried by passage through a short column of activated alumina and stored over molecular sieves. Other solvents were distilled from  $Na$ /benzophenone (except for fluorobenzene from  $CaH_2$ ) inside the glovebox. NMR spectra were recorded on IBM WP-270SY or JEOL FX-90Q instrumentation using  $BF_3 \cdot OEt_2$  and  $P(OCH_3)_3$  as external standards for  $^{11}B$  and  $^{31}P$  spectra, respectively. IR spectra were recorded on IBM IR/32 FTIR or Perkin-Elmer 281 spectrometers using KBr disks or Nujol mulls prepared inside the glovebox. Elemental analyses were performed by Galbraith Labs, Knoxville, TN. The following chemicals were obtained from Aldrich Chemical Co. and used without purification:  $Ag(CF_3SO_3)$ ,  $AgBF_4$ ,  $AgSbF_6$ ,  $AgClO_4$ ,  $Fe(Cp)(CO)_2I$ , and  $[Fe(Cp)(CO)_2]_2$ . The following were prepared by literature methods:  $IrCl(CO)(PPh_3)_2$ ,<sup>12</sup>  $AgB_{11}CH_{12}$ ,<sup>13</sup>  $Fe(Cp)(CO)_2Br$ ,<sup>14</sup>  $Fe(Cp)(CO)_2Cl$ ,<sup>15</sup> and  $Cs(B_{11}CH_6Br_6)$ .<sup>16</sup>

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$AgCPh(CF_3SO_2)_2$ . A solution of  $HCPH(SO_2CF_3)_2$ <sup>17</sup> (0.5 g, 1.4 mmol) in methanol (10 mL) was treated with excess silver carbonate. After the effervescence had subsided, the reaction mixture was filtered, evaporated, and dried under vacuum. The white solid was recrystallized first from dry ether and then from toluene/hexanes (0.4 g, 60%). Anal. Found: C, 33.44; H, 2.33. Calcd for a 1.0 toluene solvate  $C_{15}H_{13}AgF_6O_4S_2$ : C, 33.16; H, 2.41.

$Ag(B_{11}CH_6Br_6)$ . Silver nitrate (0.23 g, 1.3 mmol) in water (5 mL) was added to  $Cs(B_{11}CH_6Br_6)$  (1 g, 1.3 mmol) dissolved in hot water. The resulting white precipitate was filtered off, washed with hot water, and dried under vacuum. Recrystallization was achieved from toluene/hexanes by vapor diffusion (0.9 g, 90%). Anal. Found: C, 1.75; H, 0.84; Br, 66.14. Calcd for  $Ag(B_{11}CH_6Br_6)$ : C, 1.66; H, 0.84; Br, 66.19.  $^{11}B$  NMR ( $C_7D_8$ ): -5.8 (s, 1), -14 (s, 5), -24 (s, 5).

$Fe(Cp)(CO)_2(B_{11}CH_{12})$ . A toluene solution (10 mL) of  $Fe(Cp)(CO)_2I$  (68 mg, 0.23 mmol) was added to  $Ag(B_{11}CH_{12})$  (62 mg, 0.23 mmol) in toluene (5 mL). There was no immediate precipitate. After ca. 5-10 min, an orange solid had precipitated and the supernatant had changed from red to orange. Upon continued stirring for ca. 7 days the orange precipitate was replaced by yellow ( $AgI$ ), the first appreciable amount being visible after ca. 45 min. The precipitate was removed by filtration through a fine frit, and the product crystallized from the brown solution by slow diffusion of hexanes over a period of 2-3 days. The brown crystals were collected by filtration, washed with hexanes, and dried under vacuum (56 mg, 70%). Anal. Found: C, 29.98; H, 5.18; B, 37.22. Calcd for  $C_8H_{17}FeB_{11}O_2$ : C, 30.02; H, 5.36; B, 37.16. An analogous reaction occurs with the corresponding chloride and bromide. The reactions follow a similar time course.

**Halide-Bridged Intermediate.** The initial orange precipitate from the above reaction was collected by filtration after 5-10 min, washed with hexanes, and dried under vacuum. Additional product was collected from the filtrate for a total yield of 66 mg (65%). Anal. Found: C, 17.18; H, 2.79; B, 21.43; I, 22.44. Calcd  $C_8H_{17}FeAgB_{11}O_2$ : C, 17.31; H, 3.09; B, 21.88; I, 22.87. The corresponding chloride was prepared in an analogous manner, with elemental analysis indicating 0.5 toluene solvate. Anal. Found: C, 23.82; H, 3.90; Cl, 6.91. Calcd for  $C_{11.5}H_{21}FeAgClB_{11}O_2$ : C, 24.08; H, 3.94; Cl, 7.29. The corresponding bromide was prepared in an analogous manner for spectroscopic identification. Similar reactions of  $Fe(Cp)(CO)_2I$  with  $AgSbF_6$ ,  $AgBF_4$ ,  $Ag(CF_3SO_3)$ , and  $AgClO_4$  were carried out with fluorobenzene or toluene as solvent but prompt infrared spectroscopy always indicated mixtures of starting material, intermediate, and/or metathesis product. When the reactions were allowed to proceed to completion, the metathesis products could be readily isolated and characterized spectroscopically.

$IrCl(CO)(PPh_3)_2 \cdot Ag(B_{11}CH_{12})$ . A toluene solution (5 mL) of  $Ag(B_{11}CH_{12})$  (42 mg, 0.17 mmol) was added to  $IrCl(CO)(PPh_3)_2$  (135 mg, 0.17 mmol) in toluene, and the mixture was stirred for ca. 30 min. The bright lemon-colored solution changed to orange-yellow, and vapor diffusion of hexanes resulted in yellow crystals, which were washed with hexanes and vacuum-dried (110 mg, 62%). Anal. Found: C, 45.95; H, 4.41; Cl, 3.26; P, 5.93. Calcd for 0.5 toluene solvate  $C_{41.5}H_{44.5}IrAgB_{11}OP_2$ : C, 46.22; H, 4.31; Cl, 3.28; P, 5.75. Crystals suitable for X-ray diffraction were grown from fluorobenzene with vapor diffusion of hexanes over a 2-day period. Anal. Found: C, 47.20; H, 4.89; P, 5.93. Calcd for 0.5 fluorobenzene solvate  $C_{41}H_{44.5}IrAgB_{11}OP_2F$ : C, 47.15; H, 4.29; P, 5.92.

Similar reactions were carried out with  $IrCl(CO)(PPh_3)_2$  and  $AgSbF_6$ ,  $AgBF_4$ ,  $AgCPh(CF_3SO_2)_2$ , and  $Ag(B_{11}CH_6Br_6)$ , the latter two in fluorobenzene instead of toluene to increase solubility of the product. The hexafluoroantimonate was characterized by elemental analysis as a bis-(fluorobenzene) solvate. Anal. Found: C, 44.57; H, 3.34; Cl, 2.42; P, 4.76. Calcd for  $C_{37}H_{30}IrClAgP_2SbF_6$ : C, 44.73; H, 3.07; Cl, 2.69; P, 4.70.  $^{31}P$  NMR ( $C_7D_8$ ) -46.22 (s). The corresponding  $CPh(CF_3SO_2)_2$  compound was also characterized by analysis: Found: C, 46.62; H, 3.25. Calcd for 0.75 toluene solvate: C, 46.89; H, 3.15. The remaining species were characterized spectroscopically.

$[Ir(acetone)(CO)(PPh_3)_2]B_{11}CH_{12}$ . To a toluene suspension (10 mL) of  $IrCl(CO)(PPh_3)_2$  (85 mg, 0.11 mmol) was added  $Ag(B_{11}CH_{12})$  (28 mg, 0.11 mmol) in toluene (10 mL). The resulting solution of the 1:1 adduct was stirred for 5 min to ensure there was no anomalous  $AgCl$  precipitate. Dry acetone (3-4 mL) was added, producing an  $AgCl$  precipitate, which was removed by filtration after 15 min (12 mg, 80%). The acetone was largely removed by reducing the volume of the solution under vacuum, and vapor diffusion of hexanes produced yellow crystals, which were washed with hexanes and dried under vacuum (72 mg, 73%). Anal.

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Table I. Crystallographic Data for FeCp(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>)

FeO <sub>2</sub> C <sub>8</sub> B <sub>11</sub> H <sub>17</sub>	Z = 4
MW = 319.98	space group P2 <sub>1</sub> /c
a = 7.418 (2) Å	T = 293 K
b = 10.774 (2) Å	λ = 0.71073 Å
c = 19.838 (4) Å	μ = 0.940 mm <sup>-1</sup>
β = 89.98 (2)°	R(F <sub>o</sub> ) = 0.033
V = 1585.5 Å <sup>3</sup>	R <sub>w</sub> (F <sub>o</sub> ) = 0.045

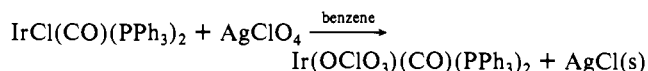
Found: C, 52.11; H, 5.30; P, 6.51. Calcd for acetone solvate C<sub>44</sub>H<sub>54</sub>IrP<sub>2</sub>B<sub>13</sub>: C, 52.06; H, 5.12; P, 6.55. Substitution of CH<sub>2</sub>Cl<sub>2</sub> or tetrahydrofuran for acetone in this experiment produced no AgCl after 1 week.

Ir(CF<sub>3</sub>SO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>. A fluorobenzene solution (10 mL) of Ag-(CF<sub>3</sub>SO<sub>3</sub>) (120 mg, 0.5 mmol) was added to IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> (364 mg, 0.5 mmol) in fluorobenzene (10 mL). After ca. 30–60 s, a white precipitate of AgCl was formed, and after an additional stirring for 15 min, the solution was filtered. Addition of hexanes to the filtrate produced lemon yellow crystals that were filtered off and washed with hexanes (317 mg, 76%). Anal. Found: C, 50.73; H, 3.50; P, 7.68. Calcd for C<sub>38</sub>H<sub>30</sub>IrF<sub>3</sub>P<sub>2</sub>SO<sub>4</sub>: C, 50.40; H, 3.43; P, 6.93.

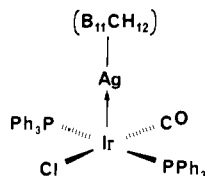
**Crystal Structure Determination.** Crystals of FeCp(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>) were mounted in thin-walled glass capillaries. Crystallographic examination led to the cell constants and the monoclinic space group reported in Table I. Complete intensity collection and refinement parameters are reported in Table SI (supplementary material). The structure was solved by a combination of Patterson and direct methods (DIRDIF).<sup>18</sup> Approximate positions for all hydrogen atoms were found in subsequent difference Fourier syntheses. Final refinement cycles utilized anisotropic thermal parameters for all heavy atoms. Coordinates of all hydrogen atoms were refined and were well behaved during least-squares refinement at least in part as the result of the high-resolution data set (max 2θ = 68° with Mo data). All refined atomic coordinates are reported in Table II. Final values of thermal parameters and complete tabulations of bond distances and bond angles are given in Tables SII–SV. The carbon atom (C8) in the B<sub>11</sub>CH<sub>12</sub><sup>-</sup> anion is readily distinguishable from the boron atoms by the ca. 0.09 Å shorter B–C versus B–B bonds and by the more reasonable thermal parameters.

## Results and Discussion

**Metal–Metal – Bonded Adducts.** The most unexpected outcome of the exploration of the metathesis reactions of Ag(B<sub>11</sub>CH<sub>12</sub>) with halide complexes has been the lack of AgCl precipitation with the labile complex IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>. It has been known for some time that metathesis proceeds rapidly when silver perchlorate is used.<sup>19</sup>



and we find the same is true with silver triflate, Ag(CF<sub>3</sub>SO<sub>3</sub>). However, with the silver salts of less nucleophilic anions such as the carborane B<sub>11</sub>CH<sub>12</sub><sup>-</sup>, its hexabromo-substituted analogue B<sub>11</sub>CH<sub>6</sub>Br<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, or the phenylbis((trifluoromethyl)sulfonyl) carbanion Ph(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>C<sup>-</sup>, there is no precipitation of AgCl even after several days. Instead, there is rapid 1:1 adduct formation which, by X-ray crystallography in the case of Ag-(B<sub>11</sub>CH<sub>12</sub>),<sup>7</sup> has been shown to involve iridium to silver metal–metal bonding: The carbonyl stretching frequency increases some



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Table II. Fractional Coordinates for FeCp(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>)<sup>a</sup>

atom	x	y	z
Fe	0.692191 (24)	0.066426 (18)	0.669713 (9)
O(1)	0.30444 (19)	0.02728 (20)	0.68121 (10)
O(2)	0.77674 (28)	-0.06858 (15)	0.79350 (7)
C(1)	0.90921 (23)	0.15305 (17)	0.62126 (8)
C(2)	0.74429 (27)	0.19543 (17)	0.59391 (9)
C(3)	0.6469 (3)	0.25171 (17)	0.64674 (13)
C(4)	0.74785 (28)	0.24161 (17)	0.70666 (10)
C(5)	0.91195 (23)	0.18220 (17)	0.68961 (9)
C(6)	0.45472 (24)	0.04105 (18)	0.67675 (10)
C(7)	0.74355 (25)	-0.02020 (18)	0.74461 (8)
C(8)	0.77426 (25)	-0.42015 (14)	0.55667 (9)
B(1)	0.6068 (3)	-0.33612 (18)	0.52195 (11)
B(2)	0.8363 (4)	-0.30768 (18)	0.50227 (9)
B(3)	0.96593 (27)	-0.33998 (19)	0.57465 (12)
B(4)	0.59572 (26)	-0.38745 (17)	0.60662 (11)
B(5)	0.81659 (28)	-0.38883 (17)	0.63893 (10)
B(6)	0.67052 (26)	-0.26542 (17)	0.65867 (8)
B(7)	0.53945 (25)	-0.23256 (18)	0.58556 (12)
B(8)	0.72949 (20)	-0.14185 (14)	0.60570 (7)
B(9)	0.6912 (3)	-0.18309 (17)	0.52033 (9)
B(10)	0.91272 (25)	-0.18511 (17)	0.55387 (9)
B(11)	0.90177 (23)	-0.23549 (17)	0.63843 (9)
H(C1)	0.999 (3)	0.1052 (23)	0.5962 (12)
HC(2)	0.706 (3)	0.1814 (26)	0.5458 (12)
H(C3)	0.522 (4)	0.2843 (28)	0.6349 (15)
H(C4)	0.707 (3)	0.2675 (23)	0.7456 (12)
H(C5)	1.0137 (28)	0.1622 (19)	0.7218 (10)
H(C8)	0.7874 (29)	-0.4962 (23)	0.5418 (11)
H(B1)	0.511 (3)	-0.3837 (22)	0.4818 (11)
H(B2)	0.891 (3)	-0.3352 (23)	0.4541 (11)
H(B3)	1.101 (4)	-0.3857 (27)	0.5708 (12)
H(B4)	0.500 (3)	-0.4546 (20)	0.6198 (11)
H(B5)	0.855 (4)	-0.4581 (25)	0.6745 (15)
H(B6)	0.596 (3)	-0.2363 (26)	0.7024 (12)
H(B7)	0.394 (4)	-0.1938 (28)	0.5924 (13)
H(B8)	0.711 (3)	-0.0335 (21)	0.6131 (11)
H(B9)	0.651 (3)	-0.1126 (23)	0.4821 (11)
H(B10)	1.020 (3)	-0.1225 (22)	0.5361 (10)
H(B11)	1.0018 (25)	-0.2062 (20)	0.6744 (9)

<sup>a</sup>The estimated standard deviations of the least significant digits are given in parentheses.

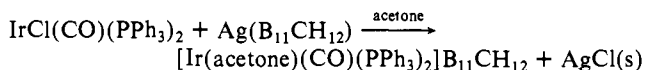
Table III. Spectroscopic Data

compd	ν(CO) (KBr), cm <sup>-1</sup>	NMR
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ·Ag(B <sub>11</sub> CH <sub>12</sub> )	2003	<sup>31</sup> P, <sup>a</sup> -46.09 <sup>11</sup> B, -13.3 (1), -14.9 (10)
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ·AgSbF <sub>6</sub>	2000	<sup>31</sup> P, <sup>a</sup> -46.22
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ·Ag(CPh(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> )	1991	
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ·Ag(B <sub>11</sub> CH <sub>6</sub> Br <sub>6</sub> )	1999	<sup>31</sup> P, <sup>a</sup> -45.03 <sup>11</sup> B, -1.9 (1), -9.2 (5), -10.1 (5)
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ·AgBF <sub>4</sub>	1989	<sup>31</sup> P, <sup>a</sup> -44.23
Ir(CF <sub>3</sub> SO <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	1977	<sup>31</sup> P, <sup>a</sup> -50.37
[Ir(acetone)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ](B <sub>11</sub> CH <sub>12</sub> )	1987 <sup>c</sup>	<sup>31</sup> P, <sup>a</sup> -52.34
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	1945	<sup>31</sup> P, <sup>a</sup> -47.64
Fe(Cp)(CO) <sub>2</sub> Cl	2049, 1989	<sup>1</sup> H, <sup>b</sup> 5.04
Fe(Cp)(CO) <sub>2</sub> Br	2035, 1970	<sup>1</sup> H, <sup>b</sup> 5.03
Fe(Cp)(CO) <sub>2</sub> I	2020, 1960	<sup>1</sup> H, <sup>b</sup> 5.01
Fe(Cp)(CO)(CO)(B <sub>11</sub> CH <sub>12</sub> )	2065, 2026	<sup>1</sup> H, <sup>b</sup> 5.23
Fe(Cp)(CO) <sub>2</sub> ClAg(B <sub>11</sub> CH <sub>12</sub> )	2057, 2008	<sup>1</sup> H, <sup>b</sup> 5.14
Fe(Cp)(CO) <sub>2</sub> BrAg(B <sub>11</sub> CH <sub>12</sub> )	2057, 2008	<sup>1</sup> H, <sup>b</sup> 5.14
Fe(Cp)(CO) <sub>2</sub> IAg(B <sub>11</sub> CH <sub>12</sub> )	2044, 1994	<sup>1</sup> H, <sup>b</sup> 5.15
Fe(Cp)(CO) <sub>2</sub> FBF <sub>3</sub>	2072, 1994	<sup>1</sup> H, <sup>b</sup> 5.26
[Fe(Cp)(CO) <sub>2</sub> ] <sub>2</sub> [BF <sub>4</sub> ]	2064, 2050, 2017 <sup>d</sup>	<sup>1</sup> H, <sup>b</sup> 5.38 <sup>e</sup>
Fe(Cp)(CO) <sub>2</sub> FSbF <sub>5</sub>	2074, 2030	<sup>1</sup> H, <sup>b</sup> 5.30
Fe(Cp)(CO) <sub>2</sub> (OCIO <sub>3</sub> )	2071, 2009	<sup>1</sup> H, <sup>b</sup> 5.20
Fe(Cp)(CO) <sub>2</sub> (CF <sub>3</sub> SO <sub>3</sub> )	2068, 2017	<sup>1</sup> H, <sup>b</sup> 5.22
Fe(Cp)(CO) <sub>2</sub> I·AgBF <sub>4</sub>	2052, 1994	

<sup>a</sup>C<sub>6</sub>H<sub>6</sub>. Add +140 ppm to convert to H<sub>3</sub>PO<sub>4</sub> standard. <sup>b</sup>CDCl<sub>3</sub>. <sup>c</sup>ν(C=O) 1680 cm<sup>-1</sup>; cf. free acetone (ν(C=O) 1750 cm<sup>-1</sup>). <sup>d</sup>CH<sub>2</sub>Cl<sub>2</sub>; ref 9 and 10. <sup>e</sup>References 9 and 10.

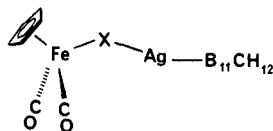
30–50 cm<sup>-1</sup> upon adduct formation (Table III), indicating electron density shift from iridium to silver. As discussed earlier,<sup>7</sup> this particularly clear example of donor–acceptor metal–metal bonding suggests that the filled d<sub>z<sup>2</sup></sub> orbital of iridium is a much more attractive Lewis base to silver than is a lone pair on the chloro ligand. This attractive d<sup>8</sup>–d<sup>10</sup> metal interaction contrasts with the apparently repulsive Ag<sup>+</sup>–Rh interaction observed in somewhat related compounds.<sup>20</sup> Trinuclear M–Ag–M adducts are also known.<sup>21,22</sup>

Although a rigorous separation of kinetic and thermodynamic factors cannot be made at this time, the unconsummated metathesis reaction does provide a measure of threshold nucleophilicity for weakly coordinating anions. We can group the anions B<sub>11</sub>CH<sub>12</sub><sup>-</sup>, B<sub>11</sub>CH<sub>6</sub>Br<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, and Ph(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>C<sup>-</sup> together as less nucleophilic (and presumably less coordinating) than ClO<sub>4</sub><sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, at least with respect to silver salt ionization of the iridium–chlorine bond in IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>. Only in donor solvents such as acetone does metathesis proceed, and then the product is a cationic species with coordinated solvent, similar to the known<sup>23</sup> acetonitrile cation [Ir(CH<sub>3</sub>CN)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>:



Neither dichloromethane nor tetrahydrofuran has the polarity and/or donor capacity to promote ionization or metathesis.

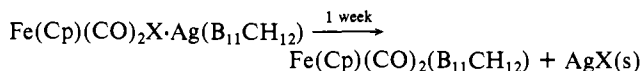
**Halide-Bridged Intermediates.** Silver tetrafluoroborate metathesis with Fe(Cp)(CO)<sub>2</sub>I is one of the few metathesis reactions that has been the subject of a mechanistic investigation.<sup>10</sup> NMR evidence pointed to the initial formation of a silver adduct formulated as [Fe(Cp)(CO)<sub>2</sub>I·Ag]BF<sub>4</sub>. Interestingly, when the reaction is carried out with Ag(B<sub>11</sub>CH<sub>12</sub>) in an arene solvent, an orange 1:1 adduct precipitates from solution during the first 5–15 min. This species has sufficient stability to allow isolation in analytical purity and characterization by <sup>1</sup>H NMR and IR spectroscopies. Despite a sustained effort we have been unable to obtain single crystals of X-ray quality. Nevertheless, it is likely that the structure is a halide-bridged species of the following type:



The <sup>1</sup>H NMR resonance of the Cp ring in CDCl<sub>3</sub> solution moves from near 5.01 ppm to near 5.15 ppm upon adduct formation (Table III). This downfield shift is consistent with a deshielding from electron density loss, and the progression continues to the final metathesis products (5.20–5.30 ppm in Fe(Cp)(CO)<sub>2</sub>Y, where Y<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>, B<sub>11</sub>CH<sub>12</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>). Considerable care had to be taken in these experiments to minimize the presence of water and prevent the formation of the known<sup>24</sup> solvated cation [Fe(Cp)(CO)<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup>. The infrared characterization of the silver adduct showed a similar progression in the ν(CO) frequencies consistent with stepwise loss of electron density from iron. The starting iodide Fe(Cp)(CO)<sub>2</sub>I has frequencies at 2020 and 1960 cm<sup>-1</sup>, which increase to 2044 and 1994 cm<sup>-1</sup> in the silver adduct Fe(Cp)(CO)<sub>2</sub>I·Ag(B<sub>11</sub>CH<sub>12</sub>), increasing further to 2065 and 2026 cm<sup>-1</sup> in the ultimate metathesis product Fe(Cp)(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>). The trends with other halides are similar (Table III). When other silver salts such as the BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> salts are used in place of Ag(B<sub>11</sub>CH<sub>12</sub>), infrared spectroscopy indicates that the intermediate is formed (e.g., for the BF<sub>4</sub><sup>-</sup> salt ν(CO) can be detected at 2052 and 1994 cm<sup>-1</sup> after a few minutes of reaction time) but none of these intermediates has the stability necessary to characterize it to the same level as

the carborane products. The intermediate is written as the neutral adduct Fe(Cp)(CO)<sub>2</sub>X·Ag(B<sub>11</sub>CH<sub>12</sub>) rather than the ionic [Fe(Cp)(CO)<sub>2</sub>X·Ag]B<sub>11</sub>CH<sub>12</sub> because the ν(B–H) infrared frequency shows a clear splitting suggestive of B<sub>11</sub>CH<sub>12</sub><sup>-</sup> coordination (2560 vs 2380 cm<sup>-1</sup>). The splitting is more pronounced than that of Fe(Cp)(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>), which is known to have coordinated B<sub>11</sub>CH<sub>12</sub><sup>-</sup>, so we can be reasonably certain that the splitting does not arise from site asymmetry in an ionic lattice.

The intermediate 1:1 adduct in this reaction is quite long-lived. At room temperature 1 h elapses before any significant amount of silver halide precipitate can be seen in the reaction mixture, and typically a week is required for complete metathesis in an arene solvent:



Infrared spectroscopy on aged samples of the intermediate shows that the metathesis reaction proceeds even in the solid state. The conversion is somewhat faster for the chloride than the iodide in both solution and the solid state. Also, the metathesis proceeds faster in dichloromethane than in toluene. This may be due to increased polarity but may also be due to better solubility of the intermediate in dichloromethane. The ultimate product under dry conditions is the metathesis product Fe(Cp)(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>), which has been characterized by X-ray crystallography (vide infra).

A usually unwanted “dimer” intermediate, [Fe(Cp)(CO)<sub>2</sub>]<sub>2</sub>I<sup>+</sup>, has been observed in previous explorations of the Fe(Cp)(CO)<sub>2</sub>I metathesis reaction.<sup>9,10,25</sup> Its crystal structure has been determined<sup>9</sup> and identifies it as a halide-bridged adduct formed from one molecule of the starting material and one molecule of some metathesis intermediate formed subsequent to silver adduct formation. It has been suggested<sup>10</sup> that when the silver adduct breaks up to give AgI and the presumed unsaturated (or solvated) intermediate [Fe(Cp)(CO)<sub>2</sub>]<sup>+</sup>, the iodine atom of Fe(Cp)(CO)<sub>2</sub>I is a competitive nucleophile with BF<sub>4</sub><sup>-</sup> for the vacant site. Indeed, the back-reaction proceeds: Fe(Cp)(CO)<sub>2</sub>I reacts with Fe(Cp)(CO)<sub>2</sub>(FBF<sub>3</sub>) to give [FeCp(CO)<sub>2</sub>]<sub>2</sub>I<sup>+</sup>BF<sub>4</sub><sup>-</sup>. However, in our studies with B<sub>11</sub>CH<sub>12</sub><sup>-</sup> replacing BF<sub>4</sub><sup>-</sup>, we find no evidence for formation of [Fe(Cp)(CO)<sub>2</sub>]<sub>2</sub>I<sup>+</sup> either during metathesis or in a purposeful back-reaction attempt. A mixture of Fe(Cp)(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>) and Fe(Cp)(CO)<sub>2</sub>I in toluene is inert, whereas the corresponding BF<sub>4</sub><sup>-</sup> reaction in benzene<sup>9</sup> or dichloromethane<sup>10</sup> is the preferred method of synthesis of the iodo-bridged “dimer”. This is another good example of how the nature of the weakly coordinating anion influences the pathway of a reaction and suggests that decomposition of the aforementioned silver adduct Fe(Cp)(CO)<sub>2</sub>I·Ag(B<sub>11</sub>CH<sub>12</sub>) to metathesis products may occur via an intramolecular extrusion of AgI without ionization.

**Metathesis Product Structure.** Fe(Cp)(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>) is readily soluble in arene solvents and recrystallizes nicely from fluorobenzene to give brown single crystals suitable for X-ray crystallography. As expected from this solubility and as suggested by the split ν(B–H) frequency in the infrared spectrum, the carborane anion is coordinated to iron. Figure 1 shows the molecular structure and reveals a stereochemistry about Fe that is not very different from that found in the closely related structures Fe(Cp)(CO)<sub>2</sub>Y, where Y = PhC≡C<sup>-</sup>,<sup>26</sup> σ-Cp<sup>-</sup>,<sup>27</sup> C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub><sup>-</sup>,<sup>28</sup> HO<sub>2</sub>CCH<sub>2</sub><sup>-</sup>,<sup>29</sup> C<sub>4</sub>H<sub>5</sub>SO<sub>2</sub><sup>-</sup>,<sup>30</sup> HCO<sub>2</sub><sup>-</sup>.<sup>31</sup> In these six structures the OC–Fe–CO angles span a narrow range of 89–96°. The present compound falls near the middle of this range at 93.7°. Selected

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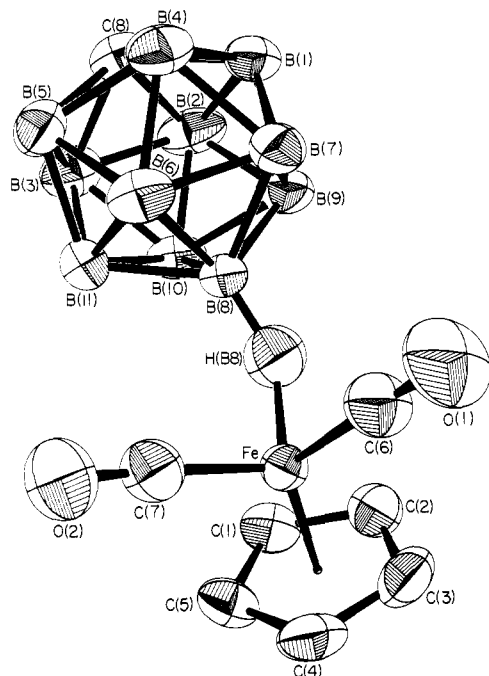


Figure 1. Molecular structure of  $\text{Fe}(\text{Cp})(\text{CO})_2(\text{B}_{11}\text{CH}_{12})$ .

Table IV. Selected Bond Distances and Angles in  $\text{Fe}(\text{Cp})(\text{CO})_2(\text{B}_{11}\text{CH}_{12})^a$

type	dist, Å	type	dist, Å
Fe-Ct	1.703	Fe-C(5)	2.090 (2)
Fe-C(1)	2.094 (2)	Fe-C(6)	1.788 (2)
Fe-C(2)	2.084 (2)	Fe-C(7)	1.796 (2)
Fe-C(3)	2.075 (2)	Fe-B(8)	2.593 (2)
Fe-C(4)	2.066 (2)	Fe-H(B8)	1.563 (22)
angle	deg	angle	deg
CtFeC(6)	125.36	C(7)FeH(B8)	102.6 (8)
CtFe(7)	122.47	FeC(6)O(1)	178.76 (20)
CtFeH(B8)	114.34	FeC(7)O(2)	176.19 (18)
C(6)FeC(7)	93.74 (9)	FeH(B8)B(8)	141.1 (18)
C(1)FeH(B8)	92.3 (8)		

values of bond distances and bond angles are given in Table IV. Complete tabulations are given in Tables SIII and SIV of the supplementary material.

Since the hydrogen atoms were located with reasonable precision, we are able to make some comments on the Fe-H-B coordinate bond. Consideration of the geometry of the complex leads us to conclude that the stated values involving the coordinated hydrogen atom (H(B8)) are unlikely to differ by more than three times the reported estimated standard deviation; changing the bonding parameters by more than that amount leads to unreasonable values.

We first note that although open M-H-B bonds are relatively rare,<sup>32</sup> all examples<sup>6,7,33</sup> of coordinated  $\text{B}_{11}\text{CH}_{12}^-$  are found to have a similar coordination geometry. Furthermore, in all species it is found that the boron atom of the carborane that is antipodal to the carbon atom is the closest boron atom to the metal atom. Thus the most hydridic B-H bond is the one that always interacts with the metal. The Fe-H(B(8))-B(8) bond angle is  $141(2)^\circ$ ; the equivalent bond has been found to be bent in all of the metallo complexes of this carborane, with values ranging between  $114^\circ$  in  $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6$  to  $151(3)^\circ$  in  $[\text{Fe}(\text{TPP})\text{B}_{11}\text{CH}_{12}]$ . Larger values of this bond angle appear to result from steric effects that limit the normal approach of the carborane anion. Such steric

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Table V. Iron-Carbon Distances in  $\text{Fe}(\text{Cp})(\text{CO})_2\text{Y}$  Compounds

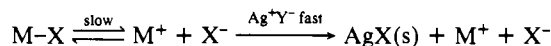
Y	av Fe-C(CO), Å	av Fe-C(Cp), Å	ref
$\sigma\text{-Cp}$	1.70 (3)	2.08 (3)	27
$\text{CH}_2\text{CO}_2\text{H}$	1.72 (3)	2.16 (2)	29
$\text{SO}_2\text{C}_6\text{F}_5$	1.74 (3)	2.08 (3)	28
C=CPh	1.754 (7)	2.099 (8)	26
$\text{SO}_2\text{C}_4\text{H}_5$	1.776 (16)	2.094 (13)	30
$\text{HCO}_2$	1.783 (4)	2.096 (3)	31
$\text{B}_{11}\text{CH}_{12}$	1.792 (3)	2.082 (2)	this work

considerations may be the reason that the B(8)-H(B(8)) bond does not radiate precisely outward from the cage but rather is tipped about  $10^\circ$  off axis so as to increase the distances of B(6) and B(11) from the other (carbonyl) atoms of the complex. The B-H distance of the coordinated hydrogen atom ( $1.18(2)$  Å) is as long as any other B-H distance in the anion (range =  $1.06\text{--}1.18$  Å, average =  $1.10(4)$  Å). This distance is slightly shorter than that found for the two complexes<sup>7,33</sup> in which hydrogen atoms are definitively located; in those two complexes a coordinated B-H distance of  $1.25$  Å was found. The Fe-H distance is  $1.56(2)$  Å. This distance is significantly shorter than  $1.82(4)$  Å distance found for coordination to the "hard" metal atom in the iron(III) porphyrinate  $[\text{Fe}(\text{TPP})(\text{B}_{11}\text{CH}_{12})]$ . The distance is comparable, however, to that found in a series of "soft" ferrocaboranes, where Fe-H =  $1.56$  or  $1.61$  Å.<sup>33</sup>

A further feature of interest in the present structure is to examine whether there are criteria for judging the ionicity or strength of interaction of the anion  $\text{B}_{11}\text{CH}_{12}^-$ . One might expect that the less coordinating the anion, the more  $\text{Fe}(\text{Cp})(\text{CO})_2\text{Y}$  would show character of the formal  $[\text{Fe}(\text{Cp})(\text{CO})_2]^+$  cation. This might involve a greater charge attraction of the  $\text{Cp}^-$  ligand and a concomitant lengthening of the Fe-C(CO) bonds (since  $\pi$ -back-bonding is expected to decrease with increasing positive charge). Although the differences are relatively small and in some cases the precision of the crystallography is not as high as one would like, the numbers in Table V do suggest that such a correlation might be found if more structures with weakly coordinating anions were known. The Fe-C(CO) bond in the present compound is the longest known, and the average Fe-C(Cp) bond is at the short end of the range. This is in accord with the idea that when  $\text{Y} = \text{B}_{11}\text{CH}_{12}^-$ , the weakly coordinating anion imposes the greatest degree of ionicity to the Fe-Y bond in  $\text{Fe}(\text{Cp})(\text{CO})_2\text{Y}$ .

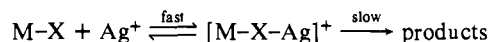
**Metathesis Mechanisms.** One must conclude from this work that the mechanisms of silver salt metathesis reactions are many and varied and that the nucleophilicity of the counterion is much more important than previously recognized. Lowering the nucleophilicity of the anion to new limits has not only slowed metathesis reactions down and allowed the isolation of intermediates but in some cases has stopped them completely.

In principle, the simplest metathesis mechanism would be a dissociative  $\text{S}_{\text{N}}1$  type process with silver and its anion playing purely passive roles with respect to the rate-determining step:



We are unaware of a proven case of this mechanism. Assistance by a coordinating solvent is more likely and may be quite common.<sup>35,36</sup>

More commonly, silver ion may provide an electrophilic rate enhancement consistent with a halide-bridged acid-base intermediate:



There is an extensive literature for M-X being an alkyl halide,<sup>4</sup> and Graham's study<sup>10</sup> together with the present work on Fe-

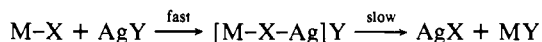
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(35) See, for example: Ballivet-Tkatchenko, D.; Bremard, C. *J. Chem. Soc., Dalton Trans.* **1983**, 1143.

(36) Note also: Colson, M. R.; Noirot, M. D.; Miller, M. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1988**, *110*, 6886.

(Cp)(CO)<sub>2</sub>I firmly establishes silver ion involvement in organo-transition-metal chemistry. Silver ion involvement has also been established in chloride ion abstractions from Ru(CO)<sub>2</sub>(dppm)Cl<sub>2</sub> and apparently involves one-end dissociation of the bidentate phosphine.<sup>37</sup> Of greater novelty, the present findings with IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> show that in the case of coordinatively unsaturated complexes, silver adduct formation may involve metal-to-silver bonding rather than halide-bridge bonding. This had been proposed in the Ru(CO)<sub>2</sub>(dppm)Cl<sub>2</sub> system cited above. Interestingly, the crystal structure of the Ag(PPh<sub>3</sub>)<sup>+</sup> adduct of [PtCl<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>2-</sup> shows a hybrid, nonclassical structure; the silver atom is bonded primarily to chlorine (Ag-Cl = 2.47 Å) but also to platinum (Ag-Pt = 2.79 Å).<sup>38</sup> Whether metal-metal-bonded adducts are actual intermediates in silver metathesis reactions remains to be determined but they must certainly be considered, particularly in d<sup>8</sup> square-planar complexes where the filled d<sub>z<sup>2</sup></sub> orbital can apparently confer a high basicity on the metal.

Of much wider impact is the very active role that weakly coordinating anions play in silver salt metathesis reactions. It seems likely that in a large number of silver-assisted ionizations the nucleophilicity Y<sup>-</sup> will be rate determining.<sup>39</sup>



In organic chemistry, these reactions have been referred to as Y<sup>-</sup>-S<sub>N</sub>1-Ag<sup>+</sup> when they lead to carbocation ion formation<sup>8</sup> but

(37) Smith, G.; Cole-Hamilton, D. J.; Gregory, A. C.; Gooden, N. G. *Polyhedron* 1982, 1, 97.

(38) Uson, R.; Fornies, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Thomas, M. *Inorg. Chem.* 1985, 24, 4651.

(39) Both Ag<sup>+</sup> and anion influences on halide solvolysis rates of RuCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>(Cp) have been mentioned: Treichel, P. M.; Vincenti, P. J. *Inorg. Chem.* 1985, 24, 228.

there can clearly be many variants with respect to the nature of [M-X-Ag]Y and the precise role of Y in influencing the outcome of a reaction and its rate. The lack of metathesis when, for example, IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> or Ph<sub>3</sub>SiCl<sup>40</sup> is treated with Ag(B<sub>11</sub>-CH<sub>12</sub>) compared to the rapid reaction with the corresponding perchlorate is taken as a kinetic result rather than a thermodynamic one. The existence of Fe(Cp)(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>) and its essentially normal stereochemistry argues against the notion that the carborane anion is too bulky to form metathesis products. Rather, its low nucleophilicity relative to perchlorate seems to be the reason for decreased reactivity. This is probably the result of a unique characteristic. The anion is large and has no lone pairs of electrons. Only tetraphenylborate rivals this although its electron-rich arene rings are well-known to act as ligands. Future work will endeavor to put these concepts on a more quantitative basis.

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**Supplementary Material Available:** Table SI, complete crystallographic details of the structure solution of FeCp(CO)<sub>2</sub>(B<sub>11</sub>CH<sub>12</sub>), Table SII, anisotropic thermal parameters, and Tables SIII-SV, complete tabulations of bond distances and bond angles (7 pages); tables of observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

(40) Liston, D. J.; Reed, C. A., to be published.

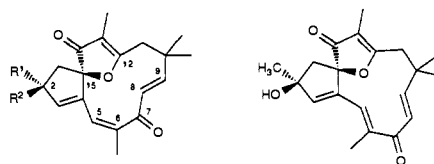
## Total Synthesis of (+)-Hydroxyjatrophone A and (+)-Hydroxyjatrophone B

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**Abstract:** A full account of the first total synthesis of (+)-hydroxyjatrophone A (2) and (+)-hydroxyjatrophone B (3), two antileukemic diterpene macrocycles isolated from *Jatropha gossypifolia*, is presented. Central to the synthetic strategy was an intramolecular Mukaiyama acetal-aldol reaction that generated the 11-membered ring. Of paramount interest with respect to the hydroxyjatrophones was the compatibility of the highly sensitive, tertiary allylic hydroxyl group with the required end-game transformations. Completion of this synthetic venture dramatically demonstrates the versatility of our jatrophone synthetic strategy.

In 1983 we reported, in collaboration with Cordell, the structures of hydroxyjatrophones A, B, and C (2-4),<sup>1</sup> three new antileukemic diterpene macrocycles, isolated from *Jatropha gossypifolia*, a plant used ethnomedicinally for the treatment of cancer.<sup>2</sup> This work reflected one aspect of our longstanding interest in the secondary metabolites of *J. gossypifolia*, which has also resulted in the first (and to this date the only) total synthesis of (±)-jatrophone (1),<sup>3</sup> as well as the total synthesis of the structurally related jatropholones A and B.<sup>4</sup>



Jatrophone (1): R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = H  
Hydroxyjatrophone A (2): R<sup>1</sup> = OH, R<sup>2</sup> = CH<sub>3</sub>  
Hydroxyjatrophone B (3): R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = OH  
Hydroxyjatrophone C (4)

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A central underlying theme of our synthetic program is the development and execution of strategies that are not single target