heterobimetallic complexes. Additional chemical and physical properties will be detailed in our full paper.

Supplementary Material Available: A listing of the data in ref 9, details of the X-ray data collection and structural refinement of **4**, tables of crystallographic data, atomic coordinates, bond lengths, bond and torsion angles, and anisotropic thermal parameters, and a figure showing the numbering of atoms in **4** (16 pages); a listing of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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Donor–Acceptor Metal–Metal Bonding Instead of Metathesis with Vaska's Compound and the Silver(I) Salt of the Weakly Coordinating Anion B₁₁CH₁₂⁻

Sir:

While exploring the candidacy of the unusually stable carborane anion $B_{11}CH_{12}^-$ for a role as the least coordinating anion,[1] we have obtained an unexpected result when a seemingly straightforward halide abstraction reaction was attempted with Vaska's compound, $IrCl(CO)(PPh_3)_2$. Silver salt metathesis is a widely preferred method of halide ion abstraction from labile coordination compounds, and the formation of the perchlorato analogue of Vaska's compound is a typical example:[2]

$$IrCl(CO)(PPh_3)_2 + AgClO_4 \xrightarrow{\text{benzene}}$$
$$Ir(OClO_3)(CO)(PPh_3)_2 + AgCl(s)$$
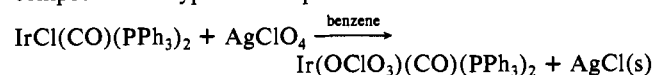
In contrast, when a toluene solution of $IrCl(CO)(PPh_3)_2$ is treated with the silver carborane salt $Ag[B_{11}CH_{12}]$,[3] there is no precipitate of AgCl. This obviously has important implications for the mechanism of the metathesis reaction. However, a slight lemon to orange color change is discernable and product workup and elemental analysis indicated 1:1 adduct formation.[4] The IR spectrum showed an increase in ν(CO) from 1950 to 1990 cm⁻¹ (KBr), indicating a decrease of electron density on iridium. Recrystallization from fluorobenzene gave yellow single crystals of a hemisolvate, whose X-ray structure has been determined.[5]

Figure 1 shows the nature of the adduct. The iridium to silver metal–metal bond is one of the clearest illustrations to date of pure donor–acceptor metal–metal bonding. The Ir–Ag bond length (2.683 (1) Å) can be compared to the Pt–Ag distance of 2.77 Å in $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$, which is considered to indicate a quite respectable bond strength.[6] A precedent for this reaction
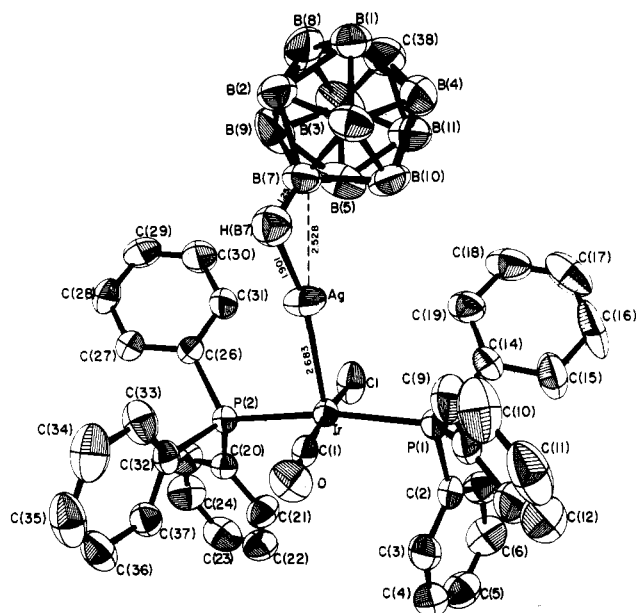

Figure 1. Computer-drawn (ORTEP2) diagram of IrCl(CO)(PPh₃)₂·Ag-(B₁₁CH₁₂). Bond distances around silver are shown. Bond distances at iridium are Ir–P(1) = 2.341 (1) Å, Ir–P(2) = 2.346 (1) Å, Ir–Cl = 2.343 (1) Å, Ir–C(1) = 1.829 (5) Å and C(1)–O = 1.137 (5) Å. The coordinated hydrogen atom H(B7) was located with reasonable certainty in difference Fourier maps.

can be found in the intramolecular Ag⋯Ir interaction observed in a triazenido analogue of Vaska's compound;[7] despite the entropic advantage, however, the bonding is considerably weaker (2.87 Å). While donor–acceptor adduct formation is a widely used synthetic strategy for metal–metal bond formation, the concept is frequently ambiguous when the structure of the adduct is examined.[8] Often the Lewis base donor has no obvious lone pair (e.g. $Co(CO)_4^-$ is tetrahedral), and its structural reorganization upon adduct formation is typical of a formal one- or two-electron oxidation (e.g. Co approaches a trigonal-bipyramidal geometry in $(CO)_4Co-Ag(ttas)^9$).[9] In the present complex the donor, iridium, scarcely changes its geometry from the planarity of the starting material. The P–Ir–P and Cl–Ir–C angles are 169.23 (4) and 173.6 (1)°, respectively, the iridium atom is displaced by only 0.16 Å from the mean plane of the donor atoms, and the metal–ligand bond lengths (see caption to Figure 1) are close to those of IrCl-$(CO)(P(o\text{-tol})_3)_2$.[10] This suggests that the filled d_{z^2} orbital on iridium should be viewed in the traditional manner of a lone pair of electrons. Such a clear illustration of donor–acceptor or Lewis acid–base character in a metal–metal bond is conceptually useful in classifying the different types of metal–metal bonds. Another example can be found in the recently reported octaethylporphyrin species (OEP)Rh–In(OEP), which has a notably small rhodium atom displacement from the porphyrin plane toward the indium atom.[11] We also note the conceptual relationship between the present findings and the BF_3 and SO_2 Lewis acid adducts of Vaska's compound.[12]

In the present reaction, the choice made by the electron-deficient silver atom for iridium over chloride in adduct formation indicates that the iridium atom is the most basic site in Vaska's compound.

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(4) Anal. Calcd for the 0.5 toluene solvate C₄₁.₅H₄₆ClAgIrOP₂B₁₁: C, 46.22; H, 4.31; P, 5.75; Cl, 3.28. Found: C, 45.95; H, 4.41; P, 5.93; Cl, 3.26.
(5) Crystal data: IrAgClP₂C₃₈B₁₁H₄₂O·0.5C₆H₅F, monoclinic, space group *C2/c*, *a* = 37.405 (3) Å, *b* = 12.037 (1) Å, *c* = 20.672 (2) Å, *β* = 107.53 (1)°, *Z* = 8. The structure was solved by direct methods (MULTAN 78) and refined by full-matrix least-squares techniques to a final R_1 = 0.028 and R_2 = 0.033 for 6757 observed reflections with $F_o > 3\sigma(F_o)$, collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation at ambient temperature (293 K). ρ_{calcd} = 1.543 g cm⁻¹; ρ_{measd} = 1.54 g cm⁻¹.
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It is interesting to contrast this with the case for Fe(Cp)(CO)$_2$I, where spectroscopic evidence points to silver adduct formation via an iodide donor.[13] This can be understood in terms of coordinative saturation of the iron atom. A hybrid case occurs with [PtCl$_2$(C$_6$F$_5$)$_2$]$^{2-}$, where an [Ag(PPh$_3$)]$^+$ adduct takes an intermediate structure; the silver atom is bonded primarily to Cl but also to Pt.[6]

The present findings raise some interesting questions about the mechanism(s) of silver salt metathesis reactions and suggest the possibility of metal–metal-bonded intermediates. The unconsummated metathesis seen with Ag[B$_{11}$CH$_{12}$] and IrCl(CO)-(PPh$_3$)$_2$ suggests that the carborane anion has extremely low nucleophilicity.[14] Space-filling models do not support the possibility that the steric bulk of B$_{11}$CH$_{12}^-$ prevents the formation of Ir(B$_{11}$CH$_{12}$)(CO)(PPh$_3$)$_2$. The anion has a smaller coordination bite than PPh$_3$. The low nucleophilicity of B$_{11}$CH$_{12}^-$ is the result of having no lone pairs and a very effective delocalization of charge. Only in donor solvents such as acetone does metathesis proceed, and then the product is the ionic [Ir((CH$_3$)$_2$CO)-(CO)(PPh$_3$)$_2$][B$_{11}$CH$_{12}$].[15] In this case the solvent is probably the entering nucleophile, which displaces Cl$^-$ so that precipitation of AgCl can drive the reaction. These results suggest that previously used weakly coordinating anions (BF$_4^-$, ClO$_4^-$, etc.) play a much more significant role in silver salt metathesis reactions than has been heretofore appreciated. For example, while AgClO$_4$ undergoes instant metathesis with Ph$_3$SiCl in benzene, we find that Ag[B$_{11}$CH$_{12}$] is inert. This suggests that the nucleophilicity of the anion is rate-determining. With FeCp(CO)$_2$I and Ag-[B$_{11}$CH$_{12}$] in toluene we get rapid 1:1 adduct formation,[16] presumably with iodide as the donor to silver as suggested by Graham.[13a] The precipitation of AgI and ultimate formation of the metathesis product Fe(Cp)(B$_{11}$CH$_{12}$)(CO)$_2$ takes several hours. Again, this suggests a rate-determining role for the anion even when heterolysis of the metal–halide bond is apparently assisted by bridging to silver. It is becoming clear that there can be considerably more mechanistic complexity to a metathesis reaction than is implied by its simple stoichiometry. The B$_{11}$CH$_{12}^-$ anion should be able to play a very useful role in detailed studies of metathesis mechanisms.

Supplementary Material Available: Fractional crystal coordinates (Table IS), anisotropic thermal parameters (Table IIS), fixed hydrogen atom positions (Table IIIS), bond distances and angles for the coordination, respectively (Tables IVS and VS), and bond distances and angles for the phosphine and carborane anion, respectively (Tables VIS and VIIS) (13 pages); a listing of observed and calculated structure amplitudes (×10) (22 pages). Ordering information is given on any current masthead page.

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(14) Excess Ag[B$_{11}$CH$_{12}$] gives some AgCl precipitate after several days, accompanied by decomposition.
(15) Anal. Calcd for IrC$_{41}$H$_{48}$B$_{11}$P$_2$O$_2$: C, 52.06; H, 5.12; P, 6.55. Found: C, 52.11; H, 5.30; P, 6.51. IR (KBr): 2550 (BH), 1978 (CO), 1632 (C=O) cm^{-1}.
(16) Anal. Calcd for C$_8$H$_{17}$AgIrFeIO$_2$B$_{11}$: C, 17.31; H, 3.09; I, 22.89. Found: C, 17.18; H, 2.79; I, 22.44. IR (KBr): 2042, 1990 (CO) cm^{-1}.

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Soluble Metal Selenides. Synthesis and Structure of the Tridecaselenidodivanadate Anion, V$_2$Se$_{13}^{2-}$

Sir:

Soluble salts of transition-metal selenium anions (M$_x$Se$_y$)$^{z-}$ are rare, the known examples being MSe$_4^{2-}$ (M = Mo,[1] and W[2]) and Fe$_2$Se$_{12}^{2-}$[3] and the recently reported W$_3$Se$_9^{2-}$, W$_2$Se$_9^{2-}$, and W$_2$Se$_{10}^{2-}$ ions.[4] Even the related sulfur anions (M$_x$S$_y$)$^{z-}$ are limited in number, and among these most have M = Mo or W.[5] Of the sulfur and selenium anions in the vanadium triad only VS$_4^{3-}$[6] and (M$_6$S$_{17}$)$^{4-}$ (M = Nb, Ta)[7] are known. We recently showed that some of the accessible anions in the W/Se system[4] differ markedly from those known in the W/S system. As a continuation of our efforts to discover new transition-metal selenium anions and to assess the relation of such ions to known solid-state materials, we report here the synthesis and structure of the V$_2$Se$_{13}^{2-}$ ion. This ion has both bridging and terminal Se$_2$ ligands as well as a bridging Se$_5$ ligand.

Dropwise addition of a toluene solution (20 mL) of bis(dimethyloctylsilyl) selenide[8] (3.5 g) into a mixture of NH$_4$VO$_3$ (0.5 g), (NEt$_4$)Cl (2.1 g), and triethylamine (10 mL) in acetonitrile (20 mL) caused an immediate color change from white to brown. After stirring the solution at room temperature for 2 days, we obtained a precipitate from the brown solution. This brown material was readily recrystallized as black hexagonal-shaped plates suitable for X-ray characterization by slow diffusion of ether into acetonitrile.[9] Spectroscopic data suggested that this product is a vanadium–selenium compound.[10] The detailed nature of (NEt$_4$)$_2$(V$_2$Se$_{13}$) was established by single-crystal X-ray diffraction methods.[11]

The V$_2$Se$_{13}^{2-}$ ion (Figure 1) has pseudo-C_s symmetry with heptacoordination at the V atoms. The V–V distance of 2.779 (5) Å is consistent with the presence of a V–V bond. The V atoms are bridged by two Se$_2$ ligands to form a V$_2$(μ-η^2-Se$_2$)$_2$ core with average V–Se and Se–Se distances of 2.518 (6) and 2.305 (7) Å, respectively. The two V atoms are also linked by a μ-Se$_5$ unit with an average V–Se distance of 2.505 (2) Å and two types of Se–Se bonds, two around the apical Se atom and two involving the Se atoms bonded to the V atoms, with average values of 2.350 (11) and 2.428 (3) Å, respectively. The coordination sphere of each V atom is completed by an unsymmetrically coordinated η^2-Se$_2$ ligand, with average V–Se distances of 2.403 (6) and 2.597 (9) Å and an average Se–Se distance of 2.334 (3) Å. The V$_2$-

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(8) Bis(dimethyloctylsilyl) selenide was prepared by mixing a 2:1 ratio of dimethyloctylsilyl chloride (Aldrich) and Li$_2$Se in THF. Filtration of this suspension after stirring for 2 days at room temperature gave a yellowish solution. After solvent removal at 0.1 mmHg a clear yellow liquid remains, yield 90%.
(9) Recrystallization was performed by standard layering techniques in 8-mm glass tubes. In addition to the black hexagonal plates, white crystals of (NEt$_4$)Cl were also obtained. Elemental analysis (Galbraith Laboratories, Inc.) of the crude product shows an expected low percentage of V and Se. The ratio found (Se:V = 6.1:1) is consistent with the formulation V$_2$Se$_{13}^{2-}$. From the percentage of vanadium in the crude sample a 20% yield of (NEt$_4$)$_2$(V$_2$Se$_{13}$) is estimated.
(10) IR (Nujol, CsI): ν(V–Se), ν_2(Se–Se) 392 (m), 340 (m), 320 (w), 298 (w) cm^{-1}. Attempts to obtain the ^{77}Se NMR spectrum of V$_2$Se$_{13}^{2-}$ failed owing to the quadrupole nature of adjacent ^{51}V nuclei; $I = {}^7/_2$, natural abundance 99.76%. No characteristic bands in the electronic spectrum were obtained from a DMF solution of the compound.
(11) Crystal data for (NEt$_4$)$_2$(V$_2$Se$_{13}$), C$_{16}$H$_{40}$N$_2$Se$_{13}$V$_2$: orthorhombic, D_2^4-$P2_12_12_1$, Z = 4, a = 11.82 (2) Å, b = 13.20 (2) Å, c = 22.25 (3) Å, V = 3471 Å^3 at −150 °C; 6679 reflections measured out to 2θ(Mo Kα_1) = 50°; R = 0.053 on 2237 reflections having $F_o^2 > 3\sigma(F_o^2)$.