

## Communications

## Increasing the Reactivity of Vaska's Compound. Oxidative Addition of Chlorobenzene at Ambient Temperature

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**Summary:** Silylium ion-like reagents,  $R_3Si^{\delta+}$  (carborane $^{\delta-}$ ), are successful where silver salts fail in abstracting chloride ion from  $IrCl(CO)(PPh_3)_2$  in arene solvents. Replacement of chloride by a very weakly coordinating carborane anion such as  $CHB_{11}H_5Cl_6^-$  promotes unusually facile oxidative addition of chlorobenzene, giving the coordinatively unsaturated  $IrCl(CO)(C_6H_5)(PPh_3)_2]^+$  cation. Other arene solvents promote disproportionation with loss of a phosphine ligand to give labile  $Ir(I)$  cations of the type  $[Ir(arene)(CO)(PPh_3)]^+$ , having three latent vacant coordination sites.

Vaska's compound,  $IrCl(CO)(PPh_3)_2$ ,<sup>1</sup> has taken a central place in providing paradigms of reactivity and catalysis in organotransition-metal chemistry because it combines the reactivity of a vacant site with the driving force for oxidative addition of a great variety of substrates.<sup>2,3</sup> This paper addresses the question of how the reactivity of Vaska's compound might be enhanced by replacing the chloride ligand with a very weakly coordinating anion and by making additional vacant sites more accessible. One of the contemporary challenges for reactive metal complexes is to more easily activate strong bonds such the C-Cl bonds in chloroarenes for cross coupling and functionalization reactions.<sup>4-12</sup>

Ligand loss from  $IrCl(CO)(PPh_3)_2$  is difficult to accomplish. Silver salts do not abstract chloride from  $IrCl(CO)(PPh_3)_2$  unless the halide is replaced by a moderately coordinating anion or solvent (e.g., triflate<sup>13</sup> or  $CH_3CN$ <sup>14</sup>), largely defeating the purpose of latent vacant site creation. With very weakly coordinating anions such as carboranes based on  $CHB_{11}H_{11}^-$ , and less coordinating solvents such as benzene, metathesis is arrested at the adduct stage, e.g., metal-metal-bonded species of the type (anion)Ag· $IrCl(CO)(PPh_3)_2$  are isolated with silver carborane salts.<sup>13</sup> Recently, trialkylsilyl reagents with very weakly coordinating carborane anions,  $R_3Si$ (carborane), have emerged as a potent class of halide abstracting reagents. They have been used to abstract halides from strong bonds in HCl to produce

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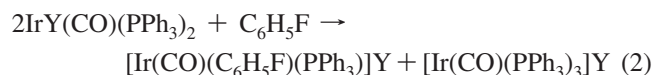
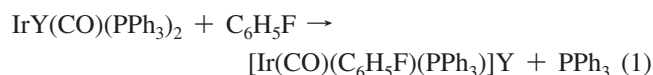
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the strongest known Brønsted acids, H(carborane),<sup>15</sup> and fluoroalkanes to produce fluoro carbocations.<sup>16</sup> We now show they can be used to abstract chloride from Vaska's compound, producing a considerably more reactive species. Comparable chemistry might be expected with silyl reagents based on the very weakly coordinating, more available, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> anion,<sup>17,18</sup> but salts of this anion are typically more difficult to crystallize for X-ray structural characterization than carborane salts, and the R<sub>3</sub>Si{B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>} reagents themselves are reportedly hard to isolate and store.<sup>19</sup> They may also be contaminated with silane in the unrecognized form of the [R<sub>3</sub>Si-H-SiR<sub>3</sub>]<sup>+</sup> cation.<sup>20</sup>

Upon mixing equimolar fluorobenzene solutions of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> and Et<sub>3</sub>Si(CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>) at -20 °C, halide metathesis proceeds over 1 h, as indicated by the appearance of Et<sub>3</sub>SiCl in the <sup>1</sup>H NMR spectrum (0.8, 1.2 ppm). The <sup>31</sup>P NMR signal at 24.5 ppm is gradually replaced by one at 27.7 ppm and there is little change in the yellow color, consistent with preservation of the Ir(I) oxidation state. Crystallization by addition of cold hexanes gives 72% isolated yield of a product whose elemental analysis indicates formulation as the metathesis product, Ir(CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**). The CO stretching frequency in the IR spectrum (KBr) increases from 1951 cm<sup>-1</sup> in Vaska's compound to 1978 cm<sup>-1</sup> in **1**, reflecting an increased positive charge at iridium, although the increase is not significantly different from that of the triflate analogue (1977 cm<sup>-1</sup>).<sup>13</sup> Varying the carborane anion to CHB<sub>11</sub>Cl<sub>11</sub><sup>-</sup> or CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub><sup>-</sup> in attempts to obtain single crystals for X-ray analysis were unsuccessful, although the synthetic results were similar. Collectively, these properties indicate that **1** is the long-sought, weakly coordinating anion analogue of Vaska's compound. The three-coordinate, coordinatively unsaturated cation [Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> remains elusive. The closer similarity of the IR bands (KBr) of the carborane anion in **1** to those in the corresponding Cs<sup>+</sup> or Ag<sup>+</sup> salts than to those in the specifically coordinated Et<sub>3</sub>Si(CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>) suggests that the icosahedral carborane anion in **1** is relatively unperturbed by coordination and therefore quite weakly coordinated. Coordination may be bidentate, as in IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>), where weak bonding between iridium and halide substituents on the carborane anion has been demonstrated by X-ray crystallography.<sup>21</sup>

Although **1** is not ionic, it is expected to have ion-like reactivity. There is an analogy to ion-like trialkylsilylium carboranes in main-group chemistry<sup>22</sup> or ZrCp<sub>2</sub>R{B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>} in early-transition-metal chemistry.<sup>23</sup> Such compounds do not contain free R<sub>3</sub>Si<sup>+</sup> or ZrCp<sub>2</sub>R<sup>+</sup> ions, respectively, but nevertheless react as though they do. The increased reactivity of **1** relative to the parent chloride (or the triflate and acetonitrile analogues) is reflected in reaction with almost any solvent, even dichloromethane, which over several hours at room temperature leads to hydride-containing products (<sup>1</sup>H NMR δ -23 ppm) that have yet to be fully characterized. We now describe characterizable products that are formed with solvents that are normally inert toward Vaska-type systems.

When **1** is dissolved in fluorobenzene at room temperature, the new species **2** is formed (<sup>31</sup>P NMR 7.1 ppm, ν(CO) 2004 cm<sup>-1</sup>) along with disproportionation products: free PPh<sub>3</sub> (<sup>31</sup>P -4.3 ppm) and the well-known [Ir(CO)(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> cation (<sup>31</sup>P 15.6 d, 18.2 t ppm, J<sub>PP</sub> = 29 Hz; ν(CO) 1991 cm<sup>-1</sup>).<sup>24</sup> When the reaction is followed by <sup>31</sup>P NMR spectroscopy at 10 °C, the concentration of free PPh<sub>3</sub> is observed initially to be almost equal to that of **2** but it decays to insignificance over minutes, with concomitant formation of the Ir(CO)(PPh<sub>3</sub>)<sub>3</sub><sup>+</sup> cation. This indicates that **1** is labile with respect to substitution of the carborane by fluorobenzene (i.e., eq 1 is fast) and that the formation of Ir(CO)(PPh<sub>3</sub>)<sub>3</sub><sup>+</sup> is the result of subsequent, slower substitution of solvent by two triphenylphosphine ligands to give the eventual overall stoichiometry of eq 2 (Y = CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub><sup>-</sup>).



Consistent with the coordinated fluorobenzene formulation of **2**, more basic arene solvents such as benzene and toluene give rise to similar chemistry at even lower temperatures. Yellow arene-coordinated salts can be isolated and manually separated from orange crystals of [Ir(CO)(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> salts for X-ray structure determination (Table 1). The structures of the cations in the benzene complex [Ir(CO)(C<sub>6</sub>H<sub>6</sub>)(PPh<sub>3</sub>)] [CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>·C<sub>6</sub>H<sub>6</sub> (**3**) and the toluene complex [Ir(CO)(CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)] [CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>] (**4**) are shown in Figure 1. The η<sup>6</sup>-arene has displaced the anion and one PPh<sub>3</sub> ligand to give a formally saturated complex. The Ir-C<sub>av</sub> distance to benzene in **3** is 2.331(5) Å, longer than 2.28(1) Å in the [Ir(diene)(p-xylene)]<sup>+</sup> cation,<sup>25</sup> which indicates relatively weak binding. More importantly, the arenes in **3** and **4** are essentially planar, whereas strongly coordinated arenes in transition-metal complexes are typically significantly puckered.<sup>26</sup> This also suggests relatively weak binding of the arenes. The lability of the arenes is indicated by gradual decomposition of **2-4** in dichloromethane solution at room temperature to give hydride-containing products (<sup>1</sup>H δ -23 ppm). The solids are air sensitive.

A viable synthetic procedure to obtain bulk **4** in 70% yield was achieved by carrying out the reaction of equimolar amounts of Et<sub>3</sub>Si(CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>) with IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> in toluene at -50 °C and precipitating the product with cold hexanes. Although elemental analyses were 1-3% outside normally acceptable values, essential bulk purity was indicated by <sup>31</sup>P NMR spectroscopy on freshly dissolved samples with appropriate temperature control (see the Supporting Information). The series of [Ir(arene)(CO)(PPh<sub>3</sub>)]<sup>+</sup> cations for arene = fluorobenzene, benzene, toluene have <sup>31</sup>P NMR signals all within a very narrow range (5.8-7.7 ppm in CD<sub>2</sub>Cl<sub>2</sub>) and their ν(CO) IR bands at 2004, 1995, and 1990 cm<sup>-1</sup> (KBr), respectively, are consistent with an isostructural series with gradually increasing basicity of the arene.

An indication of the lability and complexity of the disproportionation equilibria in the present system is reflected in the unexpected crystallization of a dicarbonyl complex as a minor product (3-5%) when a reaction mixture of Et<sub>3</sub>Si(CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>)

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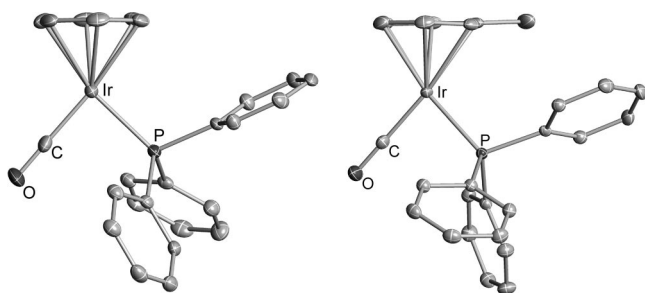
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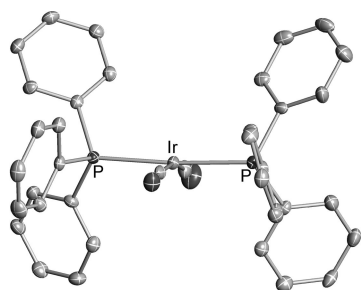
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Table 1. Crystal Data

|  | 3  | 4  | 5   | 6  |
|--|--|--|---|--|
| formula  | C <sub>32</sub> H <sub>33</sub> B <sub>11</sub> Cl <sub>6</sub> OPIr | C <sub>27</sub> H <sub>29</sub> B <sub>11</sub> Cl <sub>6</sub> OPIr | C <sub>39</sub> H <sub>36</sub> B <sub>11</sub> Br <sub>6</sub> IrO <sub>2</sub> P <sub>2</sub> | C <sub>44</sub> H <sub>36</sub> B <sub>11</sub> Cl <sub>12</sub> IrOP <sub>2</sub> |
| formula wt                                       | 988.36   | 924.28   | 1389.19   | 1379.18  |
| space group                                      | monoclinic, P2 <sub>1</sub> /c                                       | monoclinic, P2 <sub>1</sub> /n                                       | monoclinic, P2 <sub>1</sub> /n  | triclinic, P $\bar{1}$   |
| unit cell dimens                                 |  |  |   |  |
| <i>a</i> (Å)                                     | 17.9090(16)  | 8.3919(4)  | 9.1707(10)  | 12.3768(16)  |
| <i>b</i> (Å)                                     | 13.3238(11)  | 29.9794(16)  | 23.557(3)   | 13.7609(17)  |
| <i>c</i> (Å)                                     | 16.8338(15)  | 14.0388(8)   | 21.908(3)   | 17.074(2)  |
| $\alpha$ (deg)                                   | 90   | 90   | 90  | 75.545(5)  |
| $\beta$ (deg)                                    | 102.007(5)   | 96.183(3)  | 93.6401(14)   | 82.187(5)  |
| $\gamma$ (deg)                                   | 90   | 90   | 90  | 77.793(5)  |
| <i>V</i> (Å <sup>3</sup> )                       | 3928.9(6)  | 3511.4(3)  | 4723.4(9)   | 2741.7(6)  |
| temp (K)   | 100(2)   | 100(2)   | 100(2)  | 100(2)   |
| <i>Z</i>   | 4  | 4  | 4   | 2  |
| no. of rflns                                     |  |  |   |  |
| collected  | 69 940   | 30 347   | 36 438  | 38 943   |
| indep  | 11 981   | 9276   | 10 402  | 16 572   |
| <i>R</i> (int)                                   | 0.0603   | 0.0250   | 0.0385  | 0.0193   |
| <i>R</i> 1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | 0.0340   | 0.0199   | 0.0284  | 0.0184   |
| w <i>R</i> 2 (all data)                          | 0.0684   | 0.0443   | 0.0842  | 0.0438   |

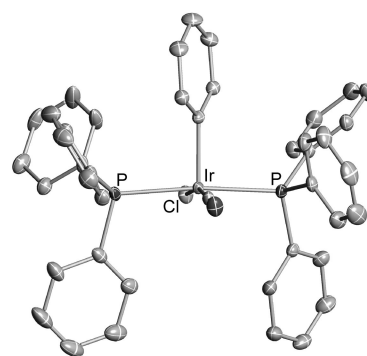


**Figure 1.** Crystal structures of the [Ir(CO)(PPh<sub>3</sub>)(arene)]<sup>+</sup> cations **3** with benzene (left) and **4** with toluene (right). H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.



**Figure 2.** Crystal structure of the Ir(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup> cation in **5**:  $\angle$ C–Ir–C = 165.6°,  $\angle$ P–Ir–P = 175.4°. H atoms on PPh<sub>3</sub> ligands are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

and IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> is left to stand in toluene at room temperature in a closed system. As shown in Figure 3, [Ir(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] (**5**) has a distinctly bent *trans*-dicarbonyl structure with a C–Ir–C bond angle of 165.6°. *Trans* d<sup>8</sup> dicarbonyls are very rare and, when they do occur, can be unusual in having nonplanar geometries.<sup>27</sup> This has been traced to stabilization of the d<sub>z<sup>2</sup></sub> and d<sub>xy</sub> orbitals in bent structures having *trans*  $\pi$ -acceptor ligands. Curiously, the isoelectronic rhodium cation with tris(2,4,6-trimethoxyphenyl)phosphine ligands has planar coordination.<sup>28</sup> Possibly, the greater steric bulk of the phosphines in this case overrides any electronic tendency for



**Figure 3.** Crystal structure of the [IrCl(C<sub>6</sub>H<sub>5</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation in **6**:  $\angle$ Cl–Ir–C(O) = 168.2°,  $\angle$ P–Ir–P = 173.2°. H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

nonplanarity. Thus, cation **5** joins a small but growing class of nonplanar structures of d<sup>8</sup> 16-electron compounds.<sup>29</sup>

The displacement of a strongly bound triphenylphosphine ligand by an arene solvent molecule in **2–4** deserves comment. It must arise from competition in **1** between coordination of the weakly coordinating anion and the arene solvent, possibly via initial  $\eta^2$  coordination, but we have not been able to observe any such preequilibrium by NMR spectroscopy.  $\eta^6$ -Coordination of the arene enables it to ultimately displace the phosphine, taking up three formal coordination sites. Tridentate “pincer-type” ligands have recently been very successful for developing activation and catalytic chemistry using *two* coordination sites at iridium(I).<sup>30</sup> The present work shows conceptually how to hold *three* latent vacant sites ready for use. This is related to solvent-coordinated diene and bidentate phosphine complexes such as [ML<sub>2</sub>(solvent)<sub>2</sub>]<sup>+</sup> (M = Rh, Ir; solvent = O, N donor) which have found considerable utility in late-transition-metal catalysis.<sup>31</sup>

The most interesting observation about the enhanced reactivity of this iridium system is the oxidative addition of chlorobenzene at ambient temperatures. Reports of chloroarene oxidative addition reactions at group 9 metals are not common, and all occur at elevated temperatures.<sup>4–12</sup> The less reactive species

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$\text{Ir}(\text{CF}_3\text{SO}_3)(\text{CO})(\text{PPh}_3)_2$  and  $\text{Ir}(\text{MeCN})(\text{CO})(\text{PPh}_3)_2^+$  are inert to chlorobenzene at room temperature. The chlorobenzene oxidative addition product of **1** is formed within a few minutes when Vaska's compound is treated with a trialkylsilyl carborane in chlorobenzene solvent, even at temperatures as low as  $-20^\circ\text{C}$ . Given the existence of the  $\pi$ -arene complexes **2–4** with fluorobenzene, benzene, and toluene, respectively, it is likely that the formation of **6** proceeds via an analogous  $\pi$ -arene complex of chlorobenzene and that this coordination provides a low-energy pathway for oxidative addition at the Ph-Cl bond. The addition is irreversible. With  $\text{CHB}_{11}\text{Cl}_{11}^-$  as the counterion for best crystallization, single crystals of  $[\text{IrCl}(\text{C}_6\text{H}_5)(\text{CO})(\text{PPh}_3)_2][\text{CHB}_{11}\text{Cl}_{11}]$  (**6**) were isolated and characterized by X-ray crystallography (Figure 3, Table 1). This reveals a rare example of coordinative unsaturation in a  $d^6$  cation. The geometry is square pyramidal with the phenyl group at the apex and is similar to more abundant neutral five-coordinate  $d^6$  complexes of ruthenium and osmium.<sup>32</sup> The possibility of this reaction proceeding via silyl rather than iridium activation of chlorobenzene can be excluded. Chloroarenes have been shown to undergo simple substitution of the carborane anion in  $\text{R}_3\text{Si}(\text{carborane})$  compounds, forming  $\sigma$ -coordinated chloroarene species of the type  $[\text{R}_3\text{Si}(\text{chloroarene})]^+$ , which are stable at room temperature.<sup>20</sup>

In summary, the long-sought replacement of chloride in Vaska's compound by a very weakly coordinating anion has been achieved. This activates iridium toward oxidative addition of chlorobenzene at ambient temperature. Other arene solvents promote disproportionation into a variety of labile cations, creating up to three latent vacant coordination sites. These observations should be generally useful for enhancing oxidative addition reactivity and, more specifically, for improving the catalytic activation of chlorobenzene, a readily available synthon and chemical waste disposal target.

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**Supporting Information Available:** Text, figures, and tables giving synthetic and characterization details, including  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{11}\text{B}$  NMR spectra that establish the bulk purity of **1–6** and CIF files giving full X-ray data for **3–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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