

## Metal Ion Assisted Derivatization of Buckminsterfullerene in the Gas Phase

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The development of new materials and new compounds based on  $C_{60}$  and other fullerenes is currently an area of intense study.<sup>1–6</sup> Paralleling these studies in the condensed phase are gas-phase studies in which ionic fullerene derivatives are generated. It has been demonstrated in the gas phase, for example, that  $C_{60}^{2+}$  reacts with nitriles to form adduct products,<sup>7</sup> and  $C_{60}^-$  reacts with  $NO_2$  to form  $C_{60}NO_2^-$ .<sup>8</sup> We have previously generated some externally bound  $MC_{60}^+$  ( $M = Fe, Co, Ni, Cu, Rh, La,$  and  $VO$ ) ions<sup>9,10</sup> and are particularly interested in the effect of  $C_{60}$  as a ligand on metal ion reactivity and whether the derivatization of  $C_{60}$  can be catalyzed by the metal center. In this paper, we report the reactions of  $CoC_{60}^+$  with some simple  $C_2$ – $C_4$  hydrocarbons and, in particular, the reactions with cyclopropane ( $c-C_3H_6$ ) in which  $C_{60}$  derivatives are formed.

All of the experiments were performed in an Extrel FTMS-2000 Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) equipped with a 3 T superconducting magnet.<sup>11</sup>  $C_{60}$  was introduced into the source side of the dual FT-ICR cell using a solids probe at 350 °C. The temperature of the ion source was kept at 230 °C to maintain a static background  $C_{60}$  pressure of  $\sim 1.0 \times 10^{-8}$  Torr. Background argon pressure at  $\sim 5.0 \times 10^{-6}$  Torr was used as the collision gas for thermalization and for collision-induced dissociation (CID) experiments.<sup>12</sup>  $CoC_{60}^+$  was generated by first forming  $Co^+$  by laser desorption of the pure metal target using a Nd:YAG laser<sup>13</sup> and then allowing it to react with background  $C_{60}$ , yielding both the charge transfer product,  $C_{60}^+$ , and the condensation product,  $CoC_{60}^+$ . The latter was then isolated using FT-ICR ion ejection techniques<sup>14</sup> and allowed to react with a neutral organic molecule which was introduced into the ion trap via either a leak valve or a pulsed valve.<sup>15</sup> For the rate constant measurements, the pressures of propene and cyclopropane were measured using standard procedures for calibrating the ion gauge (Bayard–Alpert) for the sensitivity toward the two neutral molecules.<sup>16</sup> The error in the pressure measurements is conservatively estimated at  $\pm 50\%$  and is the biggest source of error in the rate constant measurements.

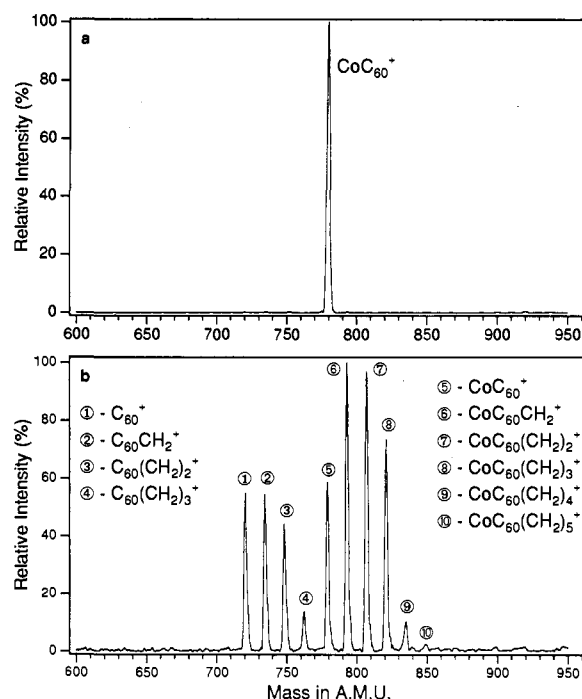
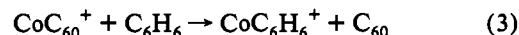


Figure 1. (a) Isolation of  $C_{60}Co^+$  using ion ejection techniques. (b) Pulsing in cyclopropane to a maximum pressure of on the order of  $10^{-5}$  Torr, then allowing an 800 ms time delay.

$CoC_{60}^+$  undergoes a direct attachment reaction with background  $C_{60}$  to form  $Co(C_{60})_2^+$ <sup>17</sup> and with pulsed-in ethylene, propene, 1-butene, and isobutene to form  $C_nH_{2n}CoC_{60}^+$ , exclusively (reaction 1 for  $n = 2$ –4). These  $C_nH_{2n}CoC_{60}^+$  ions undergo ligand displacement (reaction 2) with  $C_{60}$  to form  $Co(C_{60})_2^+$  and, upon CID, yield  $CoC_{60}^+$  at low activation energies ( $\sim 4$  eV center-of-mass), with  $C_{60}^+$  appearing at higher activation energies ( $\sim 6$  eV center-of-mass). Both of these results strongly suggest that the alkene groups in  $C_nH_{2n}CoC_{60}^+$  are bound to the metal center. It is also observed that  $CoC_{60}^+$  undergoes ligand displacement (reaction 3) with benzene to form  $CoC_6H_6^+$ .



As shown in Figure 1, upon pulsing in cyclopropane to isolated  $CoC_{60}^+$ , two sets of major products, metalated  $CoC_{60}(CH_2)_{1-4}^+$  and unmetalated  $C_{60}(CH_2)_{0-3}^+$ , are formed.  $CoC_{60}(CH_2)_5^+$  was also observed, but its intensity was insufficient for further study. The intensity ratio of the metalated ions to the unmetalated ions typically remained the same when various cooling times (0.5–2 s) were applied before pulsing in cyclopropane, indicating that the reactant ions were thermalized to the source temperature prior to reacting with  $c-C_3H_6$ . The major reaction pathways, generalized in reactions 4 and 5, were determined by double-resonance experiments<sup>14</sup> in which cyclopropane was leaked in at a static background pressure of  $\sim 1.6 \times 10^{-6}$  Torr. Upon continuous ejection of  $CoC_{60}(CH_2)_3^+$  during the reaction time, for example, the unmetalated  $C_{60}(CH_2)_3^+$  was not formed.  $CoC_{60}(CH_2)_3^+$  and  $C_{60}(CH_2)_{2,3}^+$  were not observed when  $CoC_{60}(CH_2)_2^+$  was continuously ejected. Similarly,  $C_{60}^+$  was the only product ion observed when  $CoC_{60}CH_2^+$  was continuously ejected. Reactions 4 and 5 were also verified by first isolating each of the metalated ions and then allowing them to react with pulsed-in

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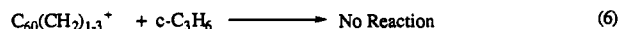
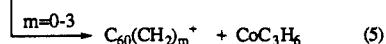
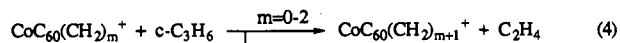
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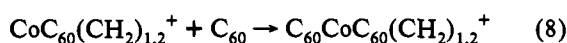
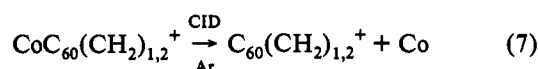
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cyclopropane. Upon pulsing in cyclopropane to isolated  $\text{CoC}_{60}(\text{CH}_2)_2^+$ , for example,  $\text{C}_{60}(\text{CH}_2)_{2,3}^+$  and  $\text{CoC}_{60}(\text{CH}_2)_3^+$  were observed. For each of the  $\text{CoC}_{60}(\text{CH}_2)_{0-2}^+$  ions, the branching ratios for reactions 4 and 5 were about 80–90% and 10–20%, respectively, while the reactive portion of  $\text{CoC}_{60}(\text{CH}_2)_3^+$  undergoes reaction 5, exclusively.



CID of  $\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$  yields unmetalated  $\text{C}_{60}(\text{CH}_2)_{1,2}^+$  at low activation energies (reaction 7,  $\sim 6$  eV center-of-mass), with  $\text{C}_{60}^+$  being formed at higher activation energies ( $\sim 10$  eV center-of-mass). The absence of any  $\text{Co}^+$  in the CID of  $\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$  suggests that  $\text{IP}(\text{Co}) = 7.864 \text{ eV}^{18} > \text{IP}[\text{C}_{60}(\text{CH}_2)_{1,2}]$ , which can be compared to  $\text{IP}(\text{C}_{60}) = 7.61 \text{ eV}^{19}$ . In addition,  $\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$  react with  $\text{C}_{60}$  to form  $\text{C}_{60}\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$ , exclusively (reaction 8), in contrast to ligand displacement (reaction 2). These results



strongly suggest that these  $\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$  ions involve coordination of cobalt to a derivatized  $\text{C}_{60}$ . Furthermore, CID ( $\sim 10$  eV center-of-mass) of the  $\text{C}_{60}(\text{CH}_2)_{1-3}^+$  buckminsterfullerene derivatives yields  $\text{C}_{60}^+$ , exclusively, indicating that the  $\text{CH}_2$  moieties in  $\text{C}_{60}(\text{CH}_2)_2^+$  and  $\text{C}_{60}(\text{CH}_2)_3^+$  are bonded together presumably to form a four-membered and a five-membered ring with  $\text{C}_{60}$ , respectively.

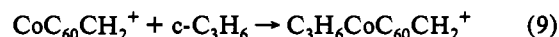
Interestingly, upon CID,  $\text{CoC}_{60}(\text{CH}_2)_3^+$  yields  $\text{CoC}_{60}^+$  at low activation energies ( $\sim 4$  eV center-of-mass), while  $\text{C}_{60}(\text{CH}_2)_3^+$  and  $\text{C}_{60}^+$  become prominent at higher activation energies. At  $E(\text{cm}) = 40$  eV, for example,  $\text{CoC}_{60}^+:\text{C}_{60}(\text{CH}_2)_3^+:\text{C}_{60}^+ = 34\%:53\%:13\%$ . In contrast to  $\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$ , which react with  $\text{C}_{60}$  to form  $\text{C}_{60}\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$ , exclusively,  $\text{CoC}_{60}(\text{CH}_2)_3^+$  reacts with  $\text{C}_{60}$  to form both  $\text{C}_{60}\text{CoC}_{60}(\text{CH}_2)_3^+$  and  $\text{Co}(\text{C}_{60})_2^+$ . In addition, unlike  $\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$ ,  $\text{CoC}_{60}(\text{CH}_2)_3^+$  is only partially converted to  $\text{C}_{60}(\text{CH}_2)_3^+$  in reaction 5. These results indicate that  $\text{CoC}_{60}(\text{CH}_2)_3^+$  consists of two isomers. About 60% of the population corresponds to cobalt bound to a derivatized  $\text{C}_{60}$ , which fragments upon CID and reacts with  $\text{C}_{60}$  and cyclopropane in the same way as  $\text{CoC}_{60}(\text{CH}_2)_{1,2}^+$ . The other isomer at about 40% of the population is likely to be (propene) $\text{CoC}_{60}^+$ , since it exhibits the same chemistry as the propene condensation product in reaction 1. In particular, both species are unreactive with cyclopropane and undergo  $\text{C}_3\text{H}_6$  displacement with  $\text{C}_{60}$ .

$\text{CoC}_{60}(\text{CH}_2)_4^+$  was only observed when the cyclopropane was pulsed in, suggesting a termolecular reaction. This ion was found to arise from the condensation of  $\text{c-C}_3\text{H}_6$  with  $\text{CoC}_{60}\text{CH}_2^+$ , reaction 9. CID and ligand displacement both resulted in the loss

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of the  $\text{C}_3\text{H}_6$  moiety, indicating that the  $\text{C}_3\text{H}_6$  coordinates the metal and does not derivatize the  $\text{C}_{60}\text{CH}_2$  ligand further. It is not clear at this time, however, whether the  $\text{C}_3\text{H}_6$  is cyclopropane or propene.

It is interesting to consider the nature of the neutral product in the demetalation reaction 5. Reactions 1 and 3 and competitive CID of  $\text{C}_n\text{H}_{2n}\text{CoC}_{60}^+$  species provide the bond energy bracket  $D^\circ(\text{Co}^+-\text{benzene}) = 68 \pm 5 \text{ kcal/mol}^{20} > D^\circ(\text{Co}^+-\text{C}_{60}) > D^\circ(\text{Co}^+-\text{propene}) = 44 \pm 2 \text{ kcal/mol}^{21}$ . This in turn yields  $D^\circ(\text{Co}-\text{C}_{60}^+) > 38 \pm 2 \text{ kcal/mol}$  based on the difference  $\text{IP}(\text{C}_{60}, 7.61 \text{ eV})^{19} - \text{IP}(\text{Co}, 7.864 \text{ eV})^{18} = -0.254 \text{ eV}$  ( $\sim 6 \text{ kcal/mol}$ ). Thus, the neutral product in reaction 5 must be an intact  $\text{CoC}_3\text{H}_6$  with  $D^\circ(\text{Co}-\text{C}_3\text{H}_6) \geq D^\circ(\text{Co}-\text{C}_{60}^+) > 38 \pm 2 \text{ kcal/mol}$ . Nevertheless, both Co and  $\text{Co}^+$  are unreactive with cyclopropane.<sup>22,23</sup> While experimental data on neutral metal–ligand bond energies are still relatively scarce, Mitchell and co-workers have reported  $D^\circ(\text{Ni}-\text{C}_2\text{H}_4) = 35.2 \pm 4.2 \text{ kcal/mol}$  obtained using a kinetic method.<sup>24</sup> Similar values have been obtained for Ni(propene)<sup>25</sup> and nickelacyclobutane,<sup>26</sup> which, together with a

theoretical calculation of  $D^\circ(\text{Rh}-\text{CH}_2\text{CH}_2\text{CH}_2) = 40 \text{ kcal/mol}^{27}$  suggests that our lower limit is reasonable. Since only reaction 1 is observed between  $\text{CoC}_{60}^+$  and propene, and not demetalation,  $\text{CoC}_3\text{H}_6$  may be cobaltacyclobutane. Alternatively, rearrangement to a propene complex, as has been observed for the cobaltacyclobutane cation ( $\text{CoC}_3\text{H}_6^+$ ),<sup>28</sup> is possible due to the 11–14 kcal/mol energy available in the rearrangement of cyclopropane to propene.<sup>23</sup> Demetalation reactions analogous to reaction 5 have been observed previously by Bjarnason and Taylor in the metal-assisted oligomerization of halobenzene and halonaphthalene.<sup>29,30</sup> In these cases, intact metal–ligand complexes have also been proposed.

The rate constants measured for the reactions of  $\text{CoC}_{60}^+$  with cyclopropane and propene are  $1.0 \pm 0.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $1.5 \pm 0.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, and are  $< 1\%$  of the calculated Langevin collision rates.<sup>31</sup> The inefficiency of the reaction with cyclopropane suggests either that it is near thermoneutral or that there is a barrier along the reaction route. Additionally, the charge is expected to be delocalized onto the  $\text{C}_{60}$  due to its lower IP, which could slow reaction.

Finally, reactions of  $\text{MC}_{60}^+$  with other derivatization reagents, such as chlorobenzene, which adds one or more  $\text{C}_6\text{H}_4$  units to  $\text{C}_{60}$ , are currently under investigation.

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