

## Dehydrohalogenation for Facile Generation of Unsaturated Ru(0)

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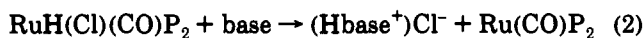
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Dehydrohalogenation (eq 1) is the infrequently encountered reverse of the oxidative addition reaction.<sup>1,2</sup> The reaction of eq 1 is most common with Ir<sup>III</sup> and Rh<sup>III</sup> and often requires Brønsted base to make the reaction exergonic.<sup>3</sup> Dehydrohalogenation of



isoelectronic divalent Fe, Ru, or Os might be challenging, however, since 16-electron compounds of these metals (when zerovalent) have to date only been produced under high-energy conditions (high temperature, UV photon, or matrix isolation). Consider, for example, the high temperatures required for reductive elimination from RuH(Ph)(PMe<sub>3</sub>)<sub>4</sub><sup>4</sup> (135 °C) or RuH<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub><sup>4</sup> (>180 °C) and from OsR<sub>2</sub>(CO)<sub>4</sub><sup>5</sup> when R = H or alkyl (126–163 °C). Once formed, the isoelectronic M(0)L<sub>4</sub> (M = Fe, Ru, Os) are sufficiently high-energy species that they react with C–H bonds.<sup>4,6–8</sup> In the special case of the hydrido halide reagent RuHCl(CO)P<sub>2</sub>,<sup>9</sup> (P = P<sup>t</sup>Bu<sub>2</sub>Me), dehydrohalogenation would yield a most unusual 14-electron transient (eq 2). We report



here evidence for dehydrohalogenation as a route toward low-temperature generation of a highly reactive intermediate.

Addition of <sup>1</sup>BuLi to a toluene solution of RuHCl(CO)P<sub>2</sub> and propylene (1:1:1 mole ratio) at –75 °C gives clean conversion to a single species in which propylene has trapped the primary product of dehydrohalogenation.<sup>10</sup> The single ν<sub>CO</sub> band shows this to be a monocarbonyl, and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, an AB pattern, has a J<sub>AB</sub> value (239 Hz) which requires two mutually trans phosphine ligands. The <sup>1</sup>H NMR spectrum shows a hydride of intensity = 1 (doublet of doublets), two PMe doublets, and four P<sup>t</sup>Bu doublets. The inequivalent P<sup>t</sup>Bu groups show that the molecule has no mirror plane of symmetry containing the P–Ru–P

(1) Grushin, V. V.; Alchrem, I. S.; Vol'pin, M. E. *J. Organomet. Chem.* **1989**, *371*, 403.

(2) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185.

(3) E.g., RhHCl<sub>2</sub>P<sub>3</sub> + NR<sub>3</sub> → RhClP<sub>3</sub> + [HNR<sub>3</sub>]Cl. This reaction is a probable mechanistic step in certain examples of heterolytic splitting of H<sub>2</sub>. See: Brothers, P. J. *Prog. Inorg. Chem.* **1980**, *28*, 1.

(4) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6492. See also: Koola, J. D.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 1450.

(5) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

(6) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433, 7436.

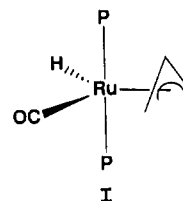
(7) An exception is the transient Fe(dmpe)<sub>2</sub> derived from FeCl<sub>2</sub>(dmpe)<sub>2</sub>, where the high energy input comes from the Na/Hg reagent. See: Chatt, J.; Davidson, J. M. *J. Chem. Soc., Chem. Commun.* **1965**, 843.

(8) Steric "pressure" can facilitate the production of unsaturated Os(0). See: Ermer, S. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1377. Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704.

(9) Gill, D. F.; Shaw, B. L. *Inorg. Chim. Acta* **1979**, *32*, 19. This compound has ν<sub>CO</sub> = 1904 cm<sup>-1</sup>.

(10) <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>): δ 4.56 (m, 1 H), 3.07 (d, J<sub>H1H</sub> = 7.0 Hz, 1 H), 2.10 (m, 1 H), 1.75 (t, J<sub>H1H</sub> = 2.3 Hz, 1 H) (all are allylic, together with one more masked by a <sup>1</sup>Bu resonance), 1.34 (d, P<sup>t</sup>Bu, J<sub>PtH</sub> = 11.5 Hz, 9 H), 1.32 (d, P<sup>t</sup>Bu, J<sub>PtH</sub> = 11.3 Hz, 9 H), 1.30 (d, P<sup>t</sup>Bu, J<sub>PtH</sub> = 11.6 Hz, 9 H), 1.07 (d, P<sup>t</sup>Bu, J<sub>PtH</sub> = 12.2 Hz, 9 H), 0.81 (d, PMe, J<sub>PtH</sub> = 5.5 Hz, 3 H), 0.63 (d, PMe, J<sub>PtH</sub> = 4.6 Hz, 3 H), –8.77 (dd, Ru–H, J<sub>PtH</sub> = 23.5, 31.5 Hz, 1 H). <sup>31</sup>P{<sup>1</sup>H} NMR (146 MHz, C<sub>6</sub>D<sub>6</sub>): δ 63.52, 61.92. IR ν(CO) (in C<sub>6</sub>D<sub>6</sub>): 1887.

unit. Five inequivalent protons of intensity = 1 correspond to an η<sup>3</sup>-allyl group with no molecular mirror plane of symmetry containing the central allyl carbon. All these data are consistent with the product being that of oxidative addition of propylene to Ru(CO)P<sub>2</sub> (structure I).<sup>11–13</sup>



When the reaction is repeated under the above conditions using RuD(Cl)(CO)P<sub>2</sub>, LiC(CH<sub>3</sub>)<sub>3</sub>, and H<sub>3</sub>CCHCH<sub>2</sub>, product I is devoid of deuterium (<sup>1</sup>H and <sup>2</sup>H NMR evidence), which rules out a mechanism where <sup>1</sup>BuLi deprotonates either free or coordinated propylene.<sup>14</sup> It also shows that there is no oxidative addition of the allylic C–H bond when deuteride is still on the metal (these would probably scramble in the Ru(D)(H)(allyl) fragment).

Variable-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy is useful in identifying the product of reaction of RuHCl(CO)P<sub>2</sub> and <sup>1</sup>BuLi. At or below –40 °C, there is complete conversion to a single species exhibiting a sharp singlet at 70.2 ppm.<sup>15</sup> This species is stable for at least 1 h at –40 °C. At –10 °C, within 3 h, there is clean conversion to a mixture whose <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of three signals between 57.2 and 57.4 ppm. These signals are similar to the single resonance for the product (RuH–(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(CO)P<sub>2</sub>) of reaction of PhLi and RuHCl(CO)P<sub>2</sub> in pentane at –10 °C.<sup>16</sup> The 70.2 ppm species thus oxidatively adds toluene solvent. Addition of propylene at –40 °C to the species with the 70.2 ppm <sup>31</sup>P NMR signal provides immediate, complete conversion to I.<sup>17</sup> The same (70.2 ppm) species is also produced from RuHCl(CO)P<sub>2</sub> and <sup>1</sup>BuLi in pentane solvent, ruling out any form of toluene being present in this species. When the reaction is carried out under the same conditions with RuHF(CO)P<sub>2</sub><sup>18</sup> instead of RuHCl(CO)P<sub>2</sub>, the same 70.2 ppm signal is observed and no trace of a doublet structure from coordinated fluorine can be detected. This proves that halide is not present in the species showing the 70.2 ppm <sup>31</sup>P NMR signal. Additionally, when the reaction between RuDCl(CO)P<sub>2</sub> and <sup>1</sup>BuLi is also monitored by <sup>2</sup>H NMR spectroscopy at –40 °C, only (CH<sub>3</sub>)<sub>3</sub>CD is detected.<sup>19</sup>

(11) The identity of this product is supported by independent synthesis of the same material from RuHCl(CO)P<sub>2</sub> and allyl MgCl.

(12) The <sup>31</sup>P NMR inequivalence of the phosphorus nuclei at 25 °C indicates slow interconversion between the structure shown and that with the allyl group pointing toward the other phosphine. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows that the compound decomposes (~60 °C) before site exchange begins to be evident.

(13) For other hydrido allyl compounds, see: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246. Zhuang, J.-M.; Sutton, D. P. *Organometallics* **1991**, *10*, 1516 and references therein.

(14) There is no evidence (<sup>31</sup>P NMR) for propylene binding to RuHCl(CO)P<sub>2</sub> at –80 °C in toluene-*d*<sub>6</sub>.

(15) The <sup>31</sup>P{<sup>1</sup>H} NMR signal of RuHCl(CO)P<sub>2</sub> is broad at –40 °C and below due to slowing of rotation about the Ru–P bonds. Since the 70.2 ppm signal is sharp, it is less crowded than the five-coordinate precursor.

(16) This compound transforms further in pentane at 20 °C within 1 h to a variety of uncharacterized products.

(17) (a) The 70.2 ppm species is also converted to Ru(H)<sub>2</sub>(H<sub>2</sub>)(CO)P<sub>2</sub><sup>17b</sup> by addition of an excess of H<sub>2</sub> at –40 °C. (b) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1.

(18) This compound shows a J(P–F) of 24 Hz (J. Poulton, private communication).

(19) The absence of Me<sub>2</sub>CCHD indicates that reversible β-hydrogen elimination from a Ru<sup>t</sup>Bu intermediate is not involved.

Taken together, these results are consistent with identifying this 70.2 ppm species as  $[\text{Ru}(\text{CO})\text{P}_2]_n$ .<sup>20</sup>

That a hydride and an allyl ligand are *formed* in this reaction emphasizes the high reactivity of the intermediate produced from  $t\text{-BuLi}$  and  $\text{RuHCl}(\text{CO})\text{P}_2$ . A 16-electron reagent ( $\text{ML}_n$ ) cannot oxidatively add propylene and form an  $\eta^3$ -allyl hydride product without dissociation of ligand L. A 14-electron intermediate does have this ability.<sup>21</sup> Dehydrohalogenation is a perhaps underuti-

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(20) Two referees feel that the  $-70^\circ\text{C}$  species could be the five-coordinate product of oxidative addition of a  $t\text{-BuP}$  C-H bond (with the requirement that such oxidative addition is rapidly reversible at  $-70^\circ\text{C}$ ). We feel this to be unlikely since metalation will move the phosphorus chemical shift at least 50 ppm upfield, requiring a rate of  $\sim 10^4\text{ s}^{-1}$  to achieve coalescence.

lized method of producing, under very mild conditions, molecules with a useful combination of characteristics: unsaturated, low-valent, and neutral. We are currently probing the limits of base strength which will permit this dehydrohalogenation and the range of C-H bond types which can be attacked.

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(21) For an example of intramolecular C-H bond cleavage from the unsaturated (photogenerated at 260 nm) species  $\text{Fe}(\text{CO})_3(\text{propene})$ , see: Barnhart, T. M.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5434.