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DIRECTED CLEAVAGE OF *sp*^{2}—*sp* CARBON—CARBON BONDS

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Summary

$RhCl(PPh_3)_3$ can insert into the α-bond of acetylenic ketones, giving stable acylrhodium(III) acetylides. This provides a rare example of homogeneous C—C bond cleavage by a transition metal.

Heterogeneous transition metal catalysts can break carbon—hydrogen bonds, and much recent work has shown soluble metal complexes can also accomplish this feat, particularly when the organic molecule possesses the appropriate directing group [1]. Metal surfaces can also break carbon—carbon bonds, but much less is known about the homogeneous analog of this process. Most examples of C—C bond breaking in solution have involved strained bonds, such as in cyclopropanes or cubane [2—6]. We have found we can direct the cleavage of *sp*^{2}—*sp* bonds of certain acetylenic ketones under very mild conditions.

When $RhCl(PPh_3)_3$ and 8-quinolinyl t-butylacetylenyl ketone (I) [7,8] were heated at 40°C for 10 min in CH_2Cl_2, the initially red solution became yellow and a stable yellow solid (II) could be precipitated with diethyl ether in quantitative yield (m.p. 199—200°C, ^{1}H NMR δ 1.16 ppm, ^{t}Bu). The acetylene and ketone IR bands in I at 2205 and 1645 cm^{-1} were shifted to 2120 and 1670 cm^{-1} in II. The $^{31}P\{^1H\}$ spectrum showed a doublet at —19.35 ppm (downfield from 85% H_3PO_4), $J(Rh—P) = 110$ Hz. The above data, together with the elemental analysis, indicated that II was an acylrhodium(III) acetylide. Chemical confirmation of this structure was obtained by treating II with one equiv. of anhydrous HCl in CH_2Cl_2 at 35°C for 20 minutes. Both NMR and GC showed the formation of t-butylacetylene in high yield. An analogous insertion occurs with $RhCl(PPh_3)_3$ and 8-quinolinyl phenylacetylenyl ketone (IR 2110, 1667 cm^{-1}, m.p. 171—172°C).

The related ligand with an *sp*^{2}—*sp*^{2} carbon—carbon bond, the styryl ketone IV, does not give an insertion product with $RhCl(PPh_3)_3$, even after extended reaction in benzene at reflux. Instead, bidentate coordination through the nitrogen and olefin takes place (olefin multiplet at δ 4.4 ppm, shift of the

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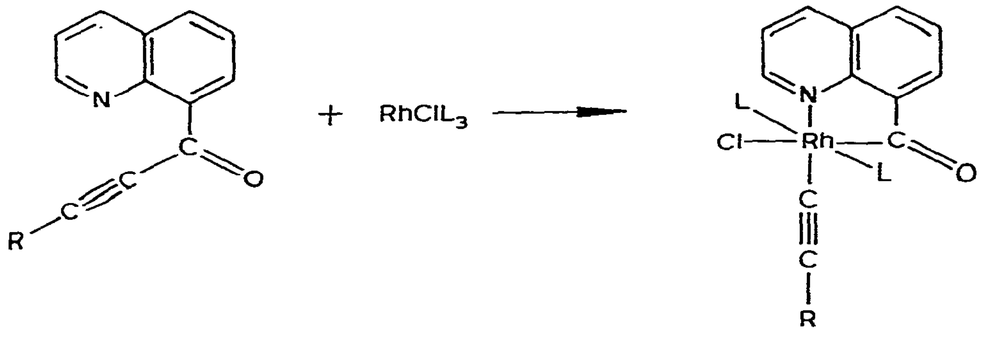
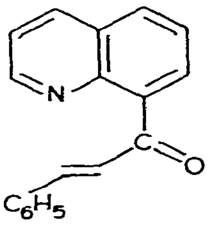


(I)

(II, R = t-Bu ;
III, R = C_6H_5)



(IV)

2-quinolinyl proton to δ 8.45 ppm). Such a π-complex is probably an intermediate in the reaction of I with $RhCl(PPh_3)_3$, but we cannot observe it in the IR at room temperature.

Bisacetylenic ketones are decarbonylated at elevated temperature (140° C) by rhodium(I) compounds [9]. By using a directing group, the quinoline nitrogen, we can trap what is undoubtedly an intermediate in that reaction, as well as increasing the rate of insertion. Although acetylenic ketones can suffer sp^2—sp bond cleavage with strong reducing agents [10], the sp^2—sp carbon—carbon bond is ca. 160 kJ/mol stronger than the sp^3—sp^3 bond in ethane [11].

We believe ketones such as I are good substrates for investigating homogeneous C—C bond breaking. First, chelation, in addition to speeding up insertion, directs the metal to a specific C—C bond. This directing effect may be a strategy which can be used to favor C—C over C—H bond insertion, given the strong preference for five-membered chelate rings in metalated complexes [1]. Second, the α bonds in ketones are somewhat weaker than most other carbon—carbon single bonds [10]. Finally, one may expect the possibility of resonance and the resulting partial double bond character of a metal—acyl bond may strengthen such a bond compared to a simple metal—alkyl bond [12].

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