

C(sp³)-H and C(sp²)-H Bond Activation in the (Pentamethylcyclopentadienyl)rhodium(III) System: Formation of (2,2-Dimethylpropane-1,3-diyl)(pentamethylcyclopentadienyl)(triphenylphosphine)rhodium and Neopentyl(pentamethylcyclopentadienyl)(triphenylphosphine-C²,P)-rhodium

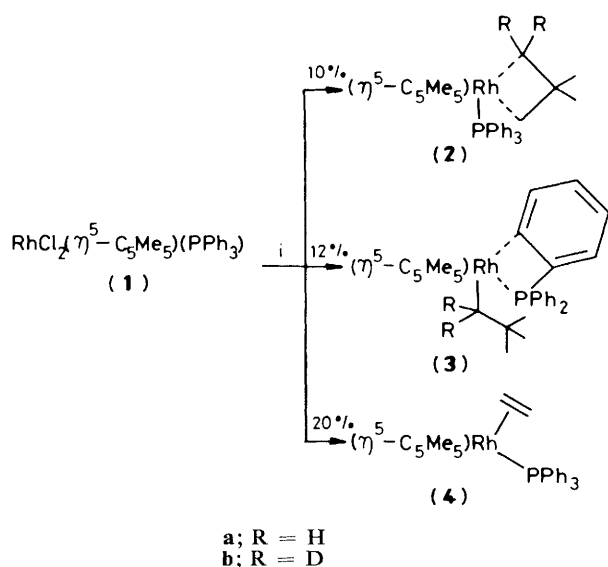
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The rhodacyclobutane $[\text{RhCH}_2\text{CMe}_2\text{CH}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$ and the *ortho*-metallated compound $[\text{RhC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2(\text{CH}_2\text{CMe}_3)(\eta^5\text{-C}_5\text{Me}_5)]$ are formed in the reaction of $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$ with $\text{LiCH}_2\text{CMe}_3$ or $\text{XMgCH}_2\text{CMe}_3$.

Carbon-hydrogen bond activation in neopentyl systems of transition metals has recently emerged as a route to metallacyclobutane derivatives, although it is limited to a few examples.¹⁻³ In our study of the preparation and properties of metallacycles,⁴ we set out to study the reactivity of some Group 8 neopentyl derivatives. We now report the isolation of the first rhodacyclobutane derivative obtained *via* γ -hydrogen abstraction from a neopentyl system: to our knowledge only one rhodacyclobutane complex has been previously reported.⁵

Reaction of $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)]$ (1) with an excess of $\text{LiCH}_2\text{CMe}_3$ or $\text{XMgCH}_2\text{CMe}_3$ in diethyl ether gives a red solution. After elimination of ether and extraction with pentane of the crude reaction product, separation by column chromatography on alumina furnishes three bands. On crystallization from pentane three solid products were isolated: the rhodacyclobutane (2a), the *ortho*-metallated complex (3a), and the ethylene complex (4) (Scheme 1). These products have been characterized by microanalyses, mass spectra, and ¹H n.m.r. spectra. The n.m.r. spectrum of (2a) (60 MHz, C₆D₆) shows resonances at δ 0.11 (3H, s, CH₃), 1.04 (3H, s, CH₃), 0.41 (4H, m, CH₂), 1.58 [15H, d, C₅Me₅, *J*(CH₃-P) 2 Hz], and 7-8 (15H, m, C₆H₅). Compound (2a) decomposes in solution at 40 °C to give 1,1-dimethylcyclopropane quantitatively; on treatment with bromine 1,1-dimethylcyclopropane and 1,3-dibromo-2,2-dimethylpropane are formed (Scheme 2).



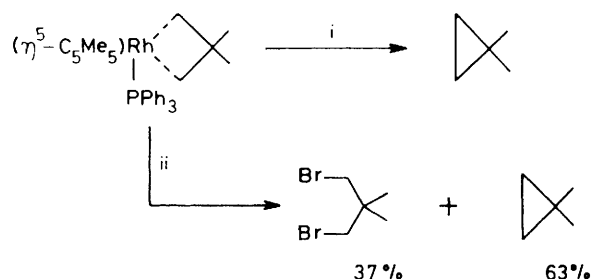
Scheme 1. i, $\text{LiCR}_2\text{CMe}_3$, Et_2O .

The ¹H n.m.r. spectrum of (3a) (60 MHz, C₆D₆) shows resonances at δ 0.76 (9H, s, CH₃), 1.59 [15H, d, C₅Me₅, *J*(CH₃-P) 3 Hz], 2.16 (2H, m, CH₂), and 7-8 (14H, m, C₆H₅). The mass spectrum shows the expected molecular ion peak at *m/z* 570, a peak at 513 (*M*⁺-C₄H₉), a base-peak at 499 (*M*⁺-C₅H₁₁), and a metastable ion at 461.7. Compound (3a) gives neopentyl bromide on reaction with bromine.

Compound (4) has been identified by comparison of its properties with those of an authentic sample prepared according to the literature.⁶

Reaction of (1) with $\text{LiCD}_2\text{CMe}_3$ produces the deuterium disubstituted derivatives (2b) and (3b) and the non-deuteriated complex (4). The latter finding rules out the possibility that ethylene could be formed by coupling of rhodium-carbene fragments derived from carbon-carbon cleavage of the rhodacyclobutane moiety.⁷ Moreover the ethylene-rhodium compound (4) was not formed when the alkylation reaction was carried out in pentane. We suggest that ethylene could be formed by C-O rupture of diethyl ether by the alkylating reagent and then trapped by a rhodium(i) species formed *in situ*. A similar observation was made when a rhodacyclopentane derivative was prepared by allowing (1) to react with $\text{XMg}[\text{CH}_2]_4\text{MgX}$ in diethyl ether.⁶

The mechanism by which (2) and (3) are formed is not yet clear. We know for certain that (2) and (3) are primary products of the reaction (they have been detected in the crude reaction product); (2) and (3) do not seem to interconvert, *i.e.* they are formed independently under the reaction conditions. While different mechanisms are possible for the formation of the *ortho*-metallated compound, the rhodacyclobutane derivative (2) can be assumed to be formed from a dineopentyl-, or, less likely, a halogenoneopentyl-rhodium(III) intermediate. Two mechanisms⁸ are then possible, *i.e.* (i) an oxidative addition to a distal C-H bond of a neopentyl group followed by reductive elimination of neopentane (or HX), or (ii) a four-centred transition state, the metal centre undergoing



Scheme 2. i, $\text{CCl}_2\text{FCF}_2\text{Cl}$, 40 °C; ii, Br_2 , $\text{CCl}_2\text{FCF}_2\text{Cl}$.

no formal change of oxidation state during the reaction. Mechanism (i), in spite of the intervention of a rather exotic rhodium(v) species, is not too unlikely in the light of Maitlis' recent isolation of rhodium(v) organometallic compounds stabilized by $\eta^5\text{-C}_5\text{Me}_5$.⁸

Received, 7th June 1982; Com. 652

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