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REVERSAL OF THE BENZOPHENONE REACTIVITY UPON η^2-COMPLEXATION TO BIS(η^5-CYCLOPENTADIENYL)ZIRCONIUM

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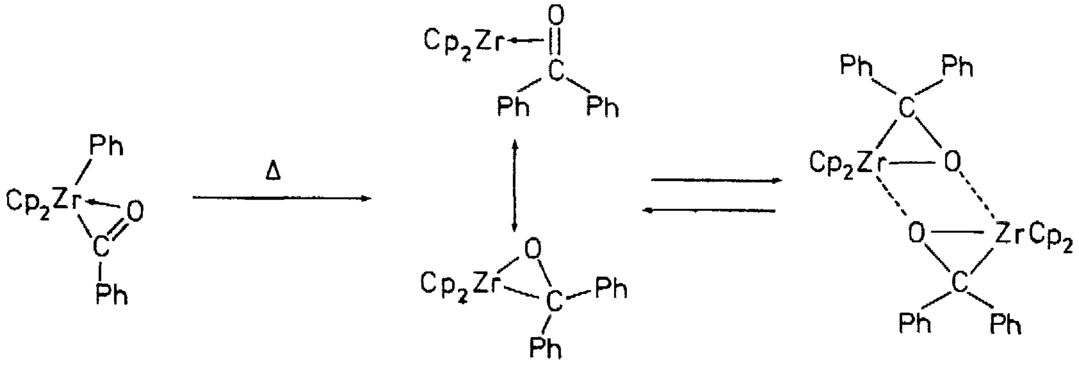
Summary: Reversal of the carbonyl activity of benzophenone, serving as electron donor in single-electron transfer processes and acting as a proton acceptor through the 'carbonyl' carbon atom, is observed upon η^2-complexation to zirconocene.

From the multitude of metal complexes of organic carbonyl compounds only a few examples of 'side on' co-ordination are known[1]. Since little information is available about the influence of π-complexation on the carbonyl activity we prepared the zirconocene η^2-benzophenone complex 2 by thermolyzing phenyl benzoyl zirconocene 1[2] (70°C) and analyzed its chemical reactivity.

2 stands in equilibrium with the thermodynamically favoured dimer 3. From the spectral data [showing the presence of four identical aryl- as well as η^5-cyclopentadienyl groups (n.m.r.), the unusually high 'carbonyl' carbon atom absorption at δ 92.5 p.p.m. in the ^{13}C n.m.r., and the absence of IR-bands in the carbonyl-stretching region above 1600 cm^{-1}] bridging of two monomeric 16 electron units is implied leading to a dimeric structure similar to the one recently described for a titanocene diphenylketene π-complex[3].



1 2 3

Treatment of 2 with water or protic acid yields benzhydrol. With molecular oxygen benzophenone is liberated spontaneously. 2 reacts only at elevated temperatures ($> 100^{\circ}C$) with aromatic hydrocarbons in the sense of an electrophilic aromatic substitution. Surprisingly zirconium-carbon rather than carbon-carbon bond formation is observed, producing an equimolar mixture of m- and p-substitution product 4 using toluene as substrate.

With alkyl halides 2 reacts rapidly under zirconium-halogen bond formation and addition of the alkyl group to the benzophenone moiety with formation of a mixture of the organometallic products 6, 7, and 8 formally derived from 1.2- respectively conjugate (i.e. 1.4- and 1.6-) addition of the alkyl halide across the zirconium-carbon bond in 2. After oxidative workup a mixture of the organic products alkyldiphenylcarbinol (9), ortho- (10), and para-alkylbenzophenone (11) is obtained. The product ratio as well as the observed reaction rates are dependent on the structure of the alkyl halide. As can be seen from the Table, primary alkyl halides react predominantly by 1.2-addition while higher yields of 1.4- and 1.6-addition products are formed from secondary and tertiary alkyl halides. An increasing reactivity towards 2 was found in the sequence ethyl $<$ isopropyl $<$ t-butyl bromide ($k_{rel.}$ = 1 : 4 : 18).

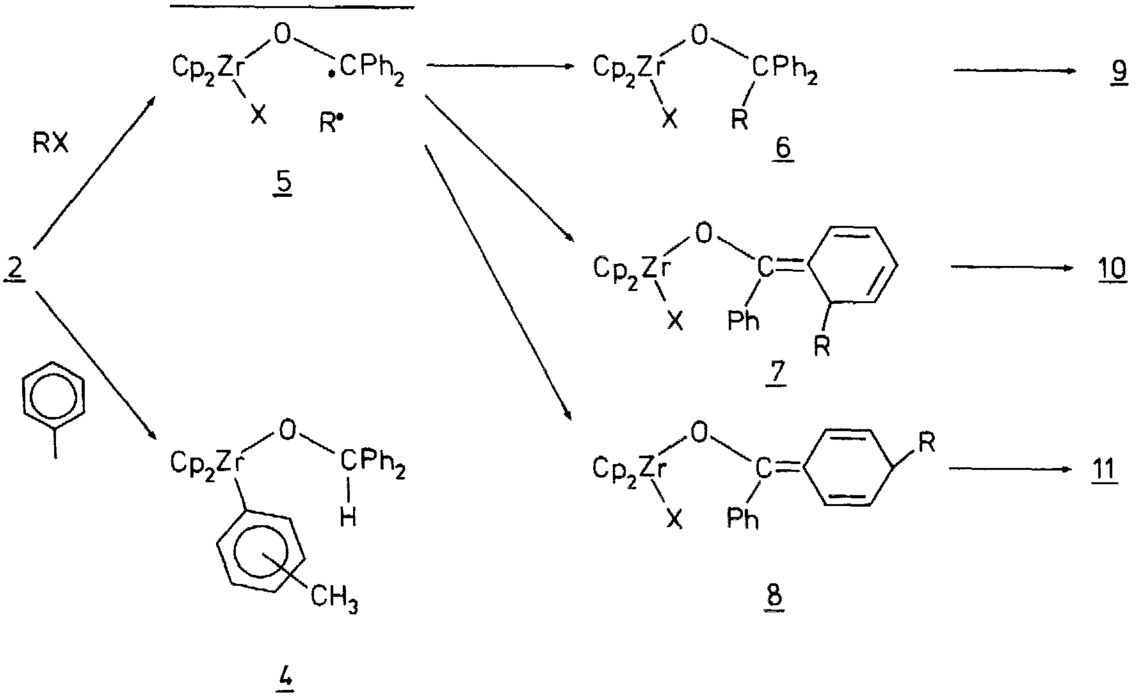


Table 1: Product ratios obtained from addition of alkyl halides[a] to 2

alkyl halide	methyl	ethyl	allyl	propargyl	isopropyl	2-octyl	t-butyl
9	86	88	89	95[b]	67	68	49
10	9	8	4	3	11	13	4
11	5	4	7	2	22	19	47

[a] alkyl bromides, except methyl iodide, [b] 45% allenylic product.

The reactivity pattern exhibited by 2 towards acids and aromatic hydrocarbons can best be understood by assuming a polar reaction mechanism. In both cases the 'carbonyl' carbon atom of the complexed benzophenone serves as a proton acceptor.

The reaction of 2 with alkyl halides, however, takes a different course. The contribution of polar mechanisms appears to the negligible. The absence of alkyl isomerisations found in the products rules out the intermediacy of alkyl zirconium species[4]. Direct nucleophilic displacement of halide ion is contradicted by the observed relative rates. However, a reactivity sequence is observed as expected for a single-electron transfer process, leading to a radical anion / radical cation pair in the rate determining step[5] which subsequently collapses to the caged radical pair 5. The kind of products formed as well as their ratios can easily be understood from this intermediate. Depending on the reactivity of the radical R• product distributions can be found characteristic for either geminate (methyl, prim. alkyl, allyl) or random free radical recombination (t-butyl) or a competition of both (sec. alkyl)[6]. The similarity of the resulting product composition compared to that obtained from the Grignard addition to benzophenone is noteworthy. The postulated radical pathway of the Grignard reaction has been suggested to pass through an analogous intermediate radical pair (exchange cp_2ZrX for MgX in 5)[7]. The strikingly similar reaction patterns followed by such different compounds derived from a main group and a transition metal indicate the general importance of single-electron transfer processes for organometallic reagents.

Upon η^2-complexation to zirconocene benzophenone no longer exhibits a typical carbonyl activity. The observed reversal of the reactivity of this ketone, in the complexed state functioning as a proton acceptor through the 'carbonyl' carbon atom respectively reacting as an electron donor in single-electron transfer processes, in our opinion, is best understood by a description of 2 as a metallaoxiran possessing a strongly polarized zirconium-carbon bond.

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