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Preliminary communication

endo-HYDRIDE ABSTRACTION FROM *exo*-SUBSTITUTED CYCLOPENTADIENECYCLOPENTADIENYLCOBALT; SYNTHESIS OF MONOSUBSTITUTED COBALTICINIUM SALTS

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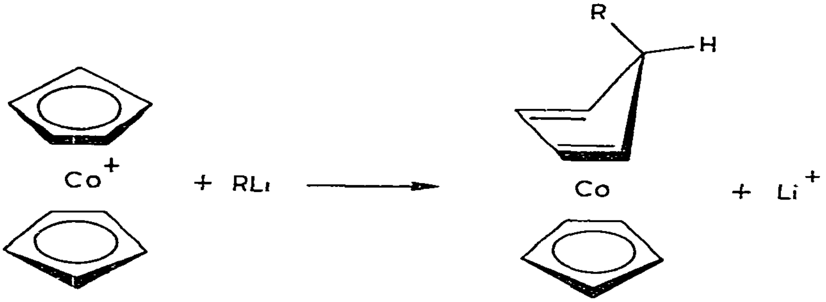
Summary

exo-Methyl- or phenyl-cyclopentadienecyclopentadienylcobalt is very easily obtained when a cobalticinium cation reacts with methyl- or phenyl-lithium. Triphenylmethyl tetrafluoroborate abstracts the *endo*-hydrogen atom from these two complexes, and this enabled us to prepare the corresponding monosubstituted cobalticinium salts.

Ferrocene undergoes electrophilic substitution extremely readily, so that many substituted derivatives can be prepared. Attempts to carry out electrophilic substitution on cobaltocene have invariably led to oxidation yielding the cobalticinium cation. With milder electrophiles the reaction results in nucleophilic addition and gives the *exo*-substituted cyclopentadienecyclopentadienylcobalt [1,2]. These complexes can also be obtained starting from the cobalticinium cation by addition of nucleophiles [3] or starting from the cobalticinium anion by addition of electrophiles [4]. One possible way to substitute cobaltocene seemed to us to be the abstraction of the *endo*-hydrogen atom from these *exo*-substituted cyclopentadienecyclopentadienylcobalt; many fruitless attempts have been made [5,6] and only one successful example has been reported [7], although the method is often used for the isoelectronic cyclopentadienylcyclohexadienyliron [6,8,9]. We report here two examples of such hydride abstraction which allowed us to prepare the monosubstituted cobalticinium cations in good yield.

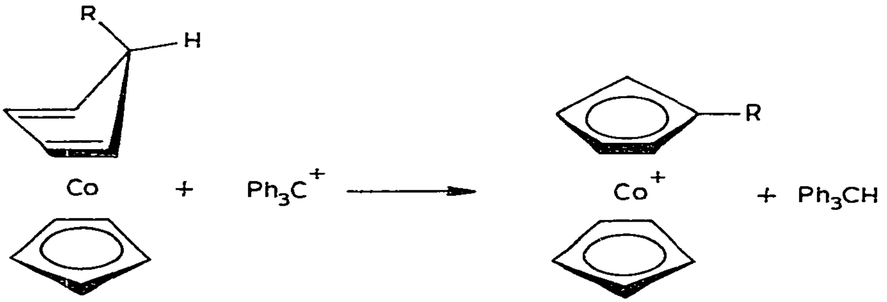
The *exo*-substituted cyclopentadienecyclopentadienylcobalt derivatives (I) (R = Me and Ph) were prepared by adding THF solutions of methyl- or phenyllithium to solution of unsubstituted cobalticinium (reaction i). The *exo* position of the methyl and phenyl groups is easily assigned on the basis of the absence of an absorption at 2760 cm^{-1} in their infrared spectra [10].



(i)

Previous work on the use of triphenylmethyl tetrafluoroborate to convert the cyclopentadienecyclopentadienylcobalt derivatives into cobalticinium cations, had led to the belief that this reagent is stereospecific for removal of the *exo*-hydrogen atoms; transformation of an *exo*-substituted cyclopentadienecyclopentadienylcobalt into substituted cobalticinium salts was claimed to be impossible [5,6]. In contrast, it was shown for the isoelectronic cyclopentadienylcyclohexadienyliron, that $Ph_3C^+ BF_4^-$ could also remove an *endo*-hydrogen atom and gives the corresponding cyclopentadienylareneiron cation [8].

We obtained similar results when $Ph_3C^+ BF_4^-$ was added to a dichloromethane solution of I (R = Me or Ph). The methyl- and phenyl-cobalticinium were isolated in about 80% yield as hexafluorophosphate salts (scheme ii).



(ii)

$[(MeC_5H_4(C_5H_5)Co]^+ PF_6^-$: m.p. (decomp.): 340—341°C; NMR: (CD_3COCD_3 δ(ppm)): 5.80 (5H,s), 5.77 (4H,m), 2.31 (3H,s). Anal.: Found: C, 38.12; H, 3.49; Co, 17.15. $C_{11}H_{12}CoPF_6$ calcd.: C, 37.95; H, 3.47; Co, 16.93%.

$[(PhC_5H_4)(C_5H_5)Co]^+ PF_6^-$: m.p.: 124—125°C; NMR: (CD_3COCD_3, δ(ppm)): 8—7.35 (5H,m), 6.43 (2H,t), 5.97 (2H,t), 5.68 (5H,s). Anal.: Found: C, 47.02; H, 3.53; Co, 14.38. $C_{16}H_{14}CoPF_6$ calcd.: C, 46.85; H, 3.44; Co, 14.36%.

Reactions (i) and (ii) together represent, to our knowledge, the first examples of substitution of the cobalticinium cation by chemical methods. We are now investigating the possibility of using this method more generally.

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