

Cyclobutadiene cobalt complexes as catalysts for insertion of diazo compounds into X–H bonds

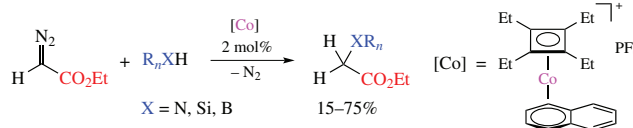
Nikita V. Shvydkiy^{a*} and Dmitry S. Perekalin^{a,b}

^a A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: nikich-shv@mail.ru

^b G. V. Plekhanov Russian University of Economics, 117997 Moscow, Russian Federation

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Novel cyclobutadiene cobalt complex with labile naphthalene ligand [(C₄Et₄)Co(C₁₀H₈)]PF₆ catalyzes the insertion of ethyl diazoacetate into X–H bonds giving the corresponding products in 15–75% yields. The reaction proceeds with primary and secondary aliphatic amines, hydrosilanes and triethylamine borane but not with anilines and alcohols.



Keywords: cyclobutadiene, cobalt complexes, catalysis, diazo compounds, insertion, organosilicon compounds.

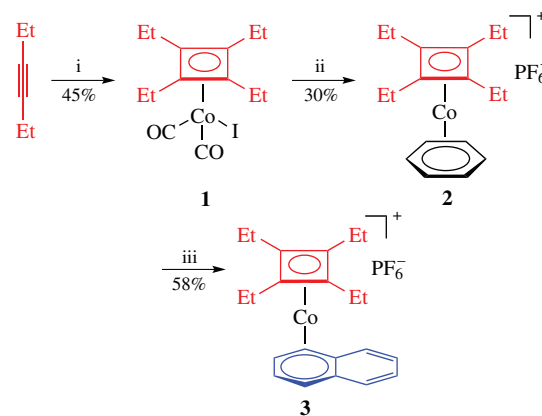
Cyclobutadiene complexes are well known for many transition metals.¹ However, most of the reported compounds have inert sandwich structures^{2,3} and hence they have not been used as catalysts until 2015.⁴ We have previously discovered a simple method for the synthesis of the cyclobutadiene complexes of rhodium with labile ligands, such as [(C₄Et₄)Rh(xylene)]PF₆, [(C₄Et₄)Rh(MeCN)₃]PF₆, and [(C₄Et₄)RhCl]₂.^{4,5} These compounds were proved to be active catalysts for insertion of diazo compounds,⁶ reductive amination,⁷ and cycloisomerization of unsaturated substrates.⁴

One of the trends in modern catalysis is the replacement of catalysts based on expensive platinum metals with more affordable derivatives of 3d metals.^{8,9} Therefore, we decided to investigate the activity of cyclobutadiene cobalt complexes in one of the reactions catalyzed by cyclobutadiene rhodium complexes, namely, the insertion of diazo compounds into X–H bonds. Noteworthy, to the best of our knowledge, cyclobutadiene cobalt complexes are almost unexplored type of the catalysts; the only example is the catalytic oxidation of alkanes.¹⁰

The insertion of diazo compounds into X–H bonds is an efficient approach to the formation of C–X bonds (X = N, O, S, Si, *etc.*),^{11,12} which is often used for the synthesis of bioactive molecules and modifications of natural compounds.^{13,14} This transformation is typically catalyzed by copper and rhodium complexes.¹⁵ Interestingly, despite the widespread use of rhodium catalysts, the related cobalt derivatives have rarely been tested for this reaction.¹⁶ At the same time, cobalt compounds have been reported to catalyze cyclopropanation of olefins with diazo compounds.^{17,18}

Based on the data on the catalytic activity of cyclobutadiene rhodium complexes⁶ we initially tested the analogous benzene complex of cobalt [(C₄Et₄)Co(C₆H₆)]⁺ as a catalyst for model reaction between ethyl diazoacetate (EDA) and *tert*-butylamine. It was found, however, that the desired insertion product was formed only in trace amounts. The possible explanation for this fact is that the displacement of benzene in [(C₄Et₄)Co(C₆H₆)]⁺ complex, which is required for the initiation of the catalytic cycle, is very slow.¹⁹ Therefore, we switched to the related

naphthalene complex [(C₄Et₄)Co(C₁₀H₈)]⁺, which would undergo the displacement of the arene ligand much faster due to the transition from η⁶- to η⁴-coordination.^{20,21} This complex was obtained from 3-hexyne and Co₂(CO)₈ following the protocol developed earlier for the tetramethyl-substituted analogue [(C₄Me₄)Co(C₁₀H₈)]⁺ (Scheme 1).^{22,23} It should be noted that 3-hexyne is readily available and more easy to handle than 2-butyne that was used for assembling C₄Me₄-ligand. Initially, 3-hexyne formed a cyclobutadienyl complex with aluminum chloride, which reacted with cobalt carbonyl giving [(C₄Et₄)Co(CO)₃]⁺.²⁴ This complex was converted *in situ* into the iodide (C₄Et₄)Co(CO)₂I **1** by treatment with NaI in the presence of mild CO-abstracting agent²⁵ Me₃NO · 2 H₂O. The refluxing of **1** with AlCl₃ in benzene produced the benzene complex [(C₄Et₄)Co(C₆H₆)]⁺ **2** in 30% yield. The preparation of complex **2** was not optimized and it was used in further reactions without additional purification. At the final stage of the synthesis, the benzene ligand in **2** was displaced by acetonitrile to form the labile intermediate [(C₄Et₄)Co(MeCN)₃]⁺, which then reacted with naphthalene to give the target complex



Scheme 1 Reagents and conditions: i, AlCl₃, Co₂(CO)₈, C₆H₆, reflux, then Me₃NO/NaI · 2 H₂O (*cf.* ref. 22); ii, KPF₆/H₂O; iii, MeCN, reflux, then C₁₀H₈.

$[(C_4Et_4)Co(C_{10}H_8)]^+ \mathbf{3}$ in 58% yield (for details, see Online Supplementary Materials).

In contrast to benzene derivative **2**, the new naphthalene complex **3** readily promoted decomposition of ethyl diazoacetate (EDA) in THF solution in the presence of acetonitrile (Scheme 2). The addition of acetonitrile was required to displace the naphthalene ligand and to generate active solvate species $[(C_4Et_4)Co(MeCN)_3]^+$.²² The use of this acetonitrile complex as a catalyst itself led to non-reproducible results, apparently due to its sensitivity to oxidation. Thus, the naphthalene complex acts as an air-stable source of the catalytically active species representing a common way of application of arene complexes in catalysis.¹⁹

The reaction of EDA with *tert*-butylamine in the presence of 5 mol% of catalyst **3** provided product **4a** in 70% yield. The main by-products were ethene-1,2-dicarboxylate **5** as the result of the decomposition of EDA, as well as a small amount of $Bu^tN(CH_2COOEt)_2$ as a product of the second insertion of EDA into **4a**. Neither lowering the temperature to $-10^\circ C$ nor slow addition of EDA to the reaction mixture did not significantly suppress these side processes. Similar behaviour has been observed previously for other catalytic systems.²⁶ The yield of the target product **4a** slightly depended on the catalyst loading, in particular, 2 mol% of the catalyst **3** produced 60% yield.

The reaction with secondary amines afforded the corresponding products **4b–d** in 50–75% yields (see Scheme 2). At the same time, aromatic amines such as aniline did not give insertion products. Oxygen-containing nucleophiles such as methanol or *tert*-butyl alcohol gave only traces of the target products. Reaction with silanes provided the products with new C–Si bonds **6a–c**. The product yield dropped for disubstituted silanes (**6c**) in comparison with trisubstituted ones. Finally, the reaction of EDA with triethylamine borane furnished compound **7** thus demonstrating the application of cyclobutadiene cobalt catalyst for the formation of C–B bonds.

Generally, the cyclobutadiene complexes of cobalt catalyze the transformation of EDA similarly to cyclobutadiene complexes of rhodium. In the case of rhodium, 2 mol% of the catalyst provides 67% yield of product **4a** at room temperature, and the process is also complicated by secondary insertion and self-condensation of the diazo component. However, unlike rhodium, cyclobutadiene complexes of cobalt did not catalyze the insertion of less reactive diazo compounds, such as methyl 2-diazo-2-phenylacetate $PhC(=N_2)CO_2Me$ even at $80^\circ C$ (the starting diazo compound can be completely recovered in this case).

In summary, we have shown that cyclobutadiene cobalt complexes can catalyze insertion of diazo esters into N–H, Si–H

and B–H bonds. Naphthalene complex $[(C_4Et_4)Co(C_{10}H_8)]PF_6^- \mathbf{3}$ is more active than the benzene analogue **2** due to the more labile arene ligand. At the same time, the activity of the naphthalene cyclobutadiene complex **3** is notably lower than that of cyclobutadiene rhodium analogues.

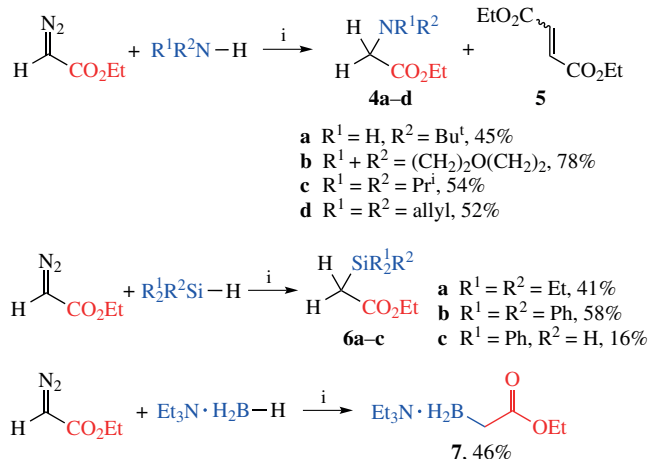
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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.022.

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Scheme 2 Reagents and conditions: i, $[(C_4Et_4)Co(C_{10}H_8)]^+PF_6^- \mathbf{3}$ (2 mol%), MeCN/THF, $0^\circ C$, 1 h, then $-20^\circ C$, 18 h.

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