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Preliminary communication

REDUCTIVE SUBSTITUTION OF COBALTOCENE: DISPLACEMENTS OF A CYCLOPENTADIENYL GROUP ON COBALTOCENE AND REPLACEMENT OF SAME BY A DIENE MOIETY

D.W. SLOCUM*, THEODORE R. ENGELMANN, ROBERT L. FELLOWS, MAREK MORONSKI and STAN DURAJ

Department of Chemistry and Biochemistry, Laboratory of Catalysis, Southern Illinois University, Carbondale, IL 62901 (U.S.A.)

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Summary

Substitution of a cyclopentadienyl ring of cobaltocene by diene, quinone and cyclopentadienone moieties serves as a synthetic procedure for a series of (η^4-ligand)(cyclopentadienyl)cobalt complexes; some speculation as to the involvement of an η^1-cyclopentadienyl intermediate in these transformations is advanced.

Displacement and replacement of cyclopentadienyl rings from metallocenes is well-documented in the case of ferrocene derivatives [1], but is relatively rare in the case of the other metallocenes. Recently, a review article has described the use of alkali metal reductions to induce displacement of cyclopentadienyl rings from not only ferrocene but also cobaltocene and nickelocene [2]. In several cases replacement of the displaced cyclopentadienyl ring with an alkene or diene function was described which resulted in complexes where the transition metal was formally reduced. In contrast our own recent communication outlines the reductive substitution* of nickelocene in which two 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) moieties effect displacement of both cyclopentadienyl rings in nickelocene to produce bis(tetracyclone)nickel(0), but without the agency of alkali metal promotion [3].

In this communication we report a series of reductive substitutions in which a single cyclopentadienyl ring of cobaltocene is replaced by a diene-type moiety to

(Continued on p. C24)

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*We prefer the term "reductive substitution" rather than "reductive C_5H_5-abstraction" [2] since the former describes the actual process which takes place on the metallocene, namely, substitution of the cyclopentadienyl ring by an appropriate moiety with concomitant reduction of the transition metal atom.

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TABLE 1

(η^5-CYCLOPENTADIENYL)(η^4-DIENE)COBALT PRODUCTS PREPARED BY THE REDUCTIVE SUBSTITUTION OF COBALTOCENE

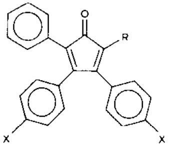
Diene or quinone	CpCo(η^4-diene) product	Reaction temperature (°C)	Reaction period (h)	M.pt (°C) (m.p. lit)	Description	Yield (%)	^{1}H NMR spectra (δ (ppm) in $CDCl_3$)
Duroquinone	1	Reflux [a]	34	274—275 (275 dec. [13])	Orange-red crystals	12.2	2.11s (12) (CH_3); 4.79s (5) (C_5H_5)
1,5-Di-t-butyl-*p*-benzoquinone	2	Reflux [b]	17	212—214	Brown-red crystals	8.0	1.37s (18) (CH_3); 5.27s (5) (C_5H_5); 5.34s (2) (olefin)
Bicyclo[2.2.1]-heptadiene	3	120 [c]	24	59—60 (60—61 [14])	Orange crystals	2.4	0.74t (2) (-CH_2-); 2.83t (4) (olefin); 3.13m (2) (bridgehead); 4.70s (5) (C_5H_5)
1,5-Cyclo-octadiene	4	135 [a]	24	103—104 (103—105 [14])	Yellow crystals	11.1	1.70m (4) (*endo*-H); 2.40m (4) (*exo*-H); 3.45m (4) (olefin) 4.43s (5) (C_5H_5)
1-Methoxy-1,4-cyclohexadiene	5	135 [c]	24		Orange oil, sensitive to light	6.3	2.12s (2) (*endo*-H); [3.10s (*exo* H), 3.01—3.40m (olefin) 3.33s (CH_3)] (8); 4.61s (5) (C_5H_5) [d]
1-Ethyl-1,4-cyclohexadiene	6	Reflux [c]	23	—	—	<1	[0.5—1.8m (*endo*-H), 1.16t (CH_3)] (5); 2.22q (2) (CH_2); 3.02s (2) (*exo*-H); 4.5—4.9m (C_5H_5 + olefin)

[a] In diethylbenzene. [b] In diglyme. [c] No solvent. [d] In C_6D_6.

TABLE 2

(η^5-CYCLOPENTADIENYL)(η^4-CYCLOPENTADIENONE)COBALT PRODUCTS PREPARED BY THE REDUCTIVE SUBSTITUTION OF COBALTOCENE

η^4 =



Cyclopentadienone	CpCo(η^4-cyclopentadienone) product	Reaction temperature (°C)	Reaction period (h)	M.pt. (°C) [c]	Yield (%)	^{1}H NMR spectra (δ (ppm))
X = X′ = H; R = Me	7	135 [b]	35	294—295	7.2	2.01s (3) (CH_3); 4.97s (5) (C_5H_5); 7.33—7.51m (15) (C_6H_5)
X = X′ = OMe; R = Ph	8	135 [b]	39	238—239	22.9	3.89s (6) (CH_3); 4.85s (5) (C_5H_5); 6.60—7.70m (18) (C_6H_5)
X = X′ = Me; R = Ph	9	135 [b]	42	241—242	11.5	2.28s (6) (CH_3); 4.82s (5) (C_5H_5): 6.95—7.82m (18) (C_6H_5)
X = Ph; X′ = H; R = Ph	10	220 [a]	2	196—197	22.0	4.93s (5) (C_6H_5); 7.22—7.82m (24) (C_6H_5)
X = X′ = H; R = Ph	11	220 [a]	2	325—327 [d]	37.0	4.88s (5) (C_5H_5); 7.17m (20) (C_6H_5)
X = X′ = Cl; R = Ph	12	220 [b]	60	299—300	30.5	4.89s (5) (C_5H_5); 7.16—7.77m (18) (C_6H_5)

[a] No solvent. Reaction run as melt. [b] Reaction run in diethylbenzene. [c] All compounds are red crystals from CH_2Cl_2/petroleum ether. [d] Lit. [15] m.p. 327—329°C.

afford a variety of diene(cyclopentadienyl)cobalt complexes. These transformations were accomplished without the use of alkali metals by simply heating the reactants together either neat or in a high boiling solvent. Prior formation of the radical anions of tetracyclone and duroquinone led in fact to apparent destruction of the metallocene. These results compliment and extend the observations of Pruett and Myers [4] two decades ago who described the reaction of a series of acyclic conjugated dienes with cobaltocene to form alkadiene(cyclopentadienyl)cobalt complexes. On balance, this method can now be used, not only to prepare conjugated alkadienecobalt complexes, but also a variety of nonconjugated diene complexes as well as complexes of quinones and tetracyclones.

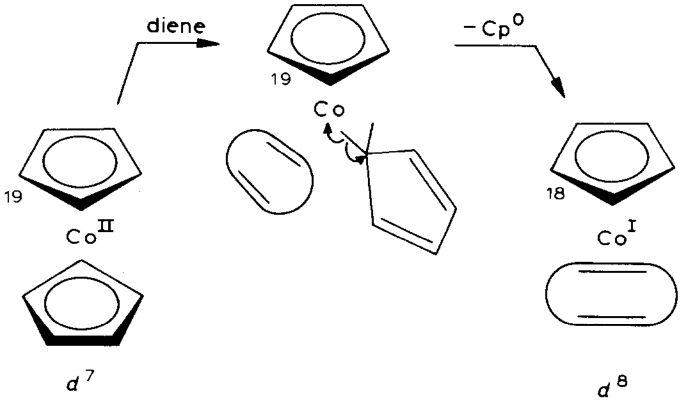
Heretofore preparation of diene(cyclopentadienyl)cobalt complexes has been accomplished by displacements from a number of cyclopentadienylcobalt complexes including cyclopentadienylcobalt dicarbonyl [5] and related materials [6a,b]. A synthesis from cobalt(II) bromide and sodium cyclopentadienide followed by a diene or acetylene has recently appeared [7]. Cobaltocene has only been used one other time as a starting material for such transformations; namely, in a reaction involving intermolecular exchange of ligands between cobaltocene and another organometallic complex [8].

In a typical experiment, equimolar quantities of cobaltocene and the diene were heated together either neat or in diethylbenzene solvent for a specified period (cf. Tables 1 and 2) under an inert atmosphere. The solvent was evaporated and the crude product was chromatographed on an alumina column with the sequence petroleum ether, benzene/chloroform being used for development. In the cases of dienes **5** and **6**, an excess of diene was used as the solvent. The composition of products **1**, **3**, **4** and **11** was substantiated by comparison with samples prepared via procedures recorded in the literature. Compounds **2**, **7**, **8**, **9**, **10** and **12** (all previously unknown) were characterized by IR, NMR and mass spectral analysis as well as elemental analysis. Compounds **5** and **6** were characterized only by spectral analyses due to the paucity of their respective samples.

The cobalt complexes with 1-methoxy- (**5**) and 1-ethyl-1,4-cyclohexadiene (**6**) are noteworthy in that, although relatively unstable, these are the first described organometallic complexes of a 1,4-cyclohexadiene in which the nonconjugated 1,4-diene structure has not been isomerized to the corresponding 1,3-diene during the course of complexation. Several examples of such isomerizations are known [9]. Structure assignments for these complexes are based on observation of the MW ions (234 and 232 for **5** and **6**, respectively) and vinyl proton absorptions (relative area 3) of 4.5—4.9 ppm for the ethyl complex and 3.01—3.40 for the methoxy complex. Conjugated 1,3-diene complexes infallibly afford significantly different chemical shifts for the 1,4- vs. the 2,3-protons [10].

The cobaltocene-duroquinone reactions was studied quite extensively. The reaction was examined in several different highly purified solvents with reactant stoichiometry and reaction times varied. Yields of 10% of complex **1** were obtained by refluxing the equimolar mixture reactants in diethylbenzene for 17 h. Refluxing decalin also gave similar yields of complex **1** as did diglyme. One of the interesting side products of this duroquinone reaction was found to be azulene. Although produced here in trace quantities (<1%), it is known that reaction of the cobalticinium ion with strong bases also produces small quantities of azulene [11].

The examples of reductive substitution described here constitute attachment of a neutral four-electron ligand (diene) to cobalt with displacement of a neutral cyclopentadienyl ligand of formal coordination number one unit greater. Such transformations we believe take place via prior $\eta^5 \rightarrow \eta^1$ rearrangement of a cyclopentadienyl ring followed by coordination of the diene moiety and ultimate dissociation of the η^1-cyclopentadienyl group (Scheme 1). Although ample precedent exists for $\eta^5 \rightarrow \eta^1$ rearrangements or equilibria in a variety of cyclopentadienyl systems [3,12], this may be the first suggestion that such C_5H_5-ring displacements take place via this mechanism. Attempts to detect an η^1-intermediate in this system have thus far proved fruitless, however.



SCHEME 1

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