The Reactivity of Complexed Carbocycles.
XI. Structure and Reactivity of New Cobalt(I) Cycloolefin Complexes with Seven-membered Rings**

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Thermal reaction of $C_5H_5Co(CO)_2$ with cyclohepta-1,3-diene and cyclohepta-1,3,5-triene yields the complexes $C_5H_5CoC_7H_{10}$ (I) and $C_5H_5CoC_7H_8$ (II). Protonation of II or hydride abstraction from I gives the very stable cation $[C_5H_5CoC_7H_9]^+$ (III). Proton abstraction from II with butyllithium leads to $[C_5H_5CoC_7H_7]^-$, which on quenching with D_2O, gives the exodeuterated, $C_5H_5CoC_7H_7D$. While $NaBH_4$ adds to III at C(3), forming $C_5H_5Co(cyclohepta-1,4-diene)$ (IV), tri-isopropylphosphine attacks at C(1), yielding the unsymmetrical addition product. The addition of alkylphosphines to other cationic cobalt complexes was also investigated. ^{13}C chemical shift data for the new complexes are reported which support the structural and stereochemical assignments.

Introduction

In continuation of our research on the reactivity of complexed polyolefins we recently became interested in the stereochemistry of cobalt(I) olefin complexes. It is well established that in compounds like CpCo(cyclooctatetraene) and CpCo(cycloocta-1,3,5-triene) [Cp = cyclopentadienyl] complexation to two nonconjugated double bonds is preferred, the cyclopentadienyl cobalt unit thereby showing a different preference for complexation compared to the isoelectronic $Fe(CO)_3$ moiety. This is further emphasized by our recent report [1, 2] on the synthesis of CpCo(1,2:5,6η-cyclononatetraene), in which the ligand assumes a different coordination mode than in the previously described iron complexes [3].

A paper by Geiger [4] points out, however, that $CpCoC_8H_8$ exists in two forms in a dynamic equilibrium, namely CpCo(1,2:5,6η-cyclooctatetraene) in 75% and CpCo(1-4η-cyclooctatetraene) in 25%, as is evident from the electrochemical behaviour as well as spectroscopic data. The latter complex is fluxional in solution, giving an averaged signal at 94.2 ppm in the ^{13}C NMR for the eightmembered ring (Table I). These results suggested a rather small enthalpy difference for both isomers. We, therefore, started our investigation on the synthesis and stereochemistry of complexes with sevenmembered ring systems to see whether similar equilibria exist.

While this work was in progress, the preparation of CpCo(cyclohepta-1,3-diene) was reported by another group [5]. The authors, however, were unable to prepare the corresponding complexes of cycloheptatriene or cyclohepta-1,4-diene, the successful preparation of which will be described later.

Results and Discussion

On reacting $CpCo(CO)_2$ with cyclohepta-1,3-diene in refluxing n-octane we obtained the complex $CpCoC_7H_{10}$ (I) in good yields as a dark red oil, identical with the product prepared by Reger and Dukes [5]. In contrast to the report by these authors reaction with cycloheptatriene under identical conditions was equally successful, giving moderate yields of a dark red crystalline product with composition $CpCoC_7H_8$ (II). High purity of the starting cobalt complex as well as long reaction times appear to be imperative for the preparation.

^{13}C- as well as ^1H-NMR show this compound unambiguously to be CpCo(1-4η-cycloheptatriene), thereby demonstrating that under these reaction conditions coordination to two conjugated double

II   III   I
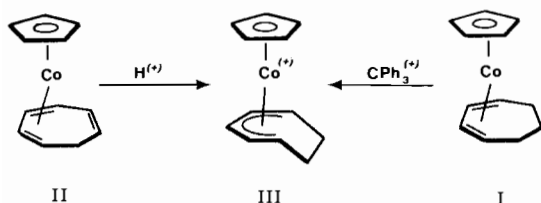
bonds is preferred over the alternate 1,2:5,6η-bonding mode.

Protonation of the uncomplexed double bond in II is easily effected (as in the corresponding iron carbonyl complex) giving almost quantitative yields of the very stable cation $[CpCoC_7H_9]^+$, isoelectronic to the well known cobalticenium salts. This is a further member in the series of stable cycloheptadienyl complexes that we have prepared [6–8]. Another route to this complex is hydride abstraction from I, proceeding equally in good yields. NMR spectra show this complex to have the expected 1,5η-dienyl structure, different from the unstable isomeric complex $[CpCoC_7H_9]^+$ prepared by Lewis and Parkins [9], for which a 1-3:5,6η-bonding mode was proposed.

The ease of preparation of cation III contrasts sharply with the difficulty in obtaining the corresponding cyclohexadienyl species $[CpCoC_6H_7]^+$ by a similar preparative route, as hydride abstraction from $CpCoC_6H_8$ leads directly to $[CpCoC_6H_6]^{2+}$, while the analogue of II, $CpCo(1-4η-C_6H_6)$ is not known.

We also tried to prepare the yet unknown tropylium complex $[CpCo-η^5-C_7H_7]^+$ by hydride abstraction from II. This, however, gave a product mixture that we were unable to separate, as presumably electrophilic attack of $[CPh_3]^+$ at the seven- as well as the fivemembered ring occurs as a side reaction. As an alternative method we attempted the preparation of CpCo(7-methoxycycloheptatriene), which on protonation should yield $[CpCoC_7H_7]^+$, a route successfully used for the preparation of the corresponding iron carbonyl species [10]. Unfortunately, neither thermal nor photochemical treatment of $CpCo(CO)_2$ with 7-methoxycyloheptatriene lead to the desired product. We had more success with the anionic analogue $[CpCo-η^3-C_7H_7]^-$. On treatment of II in THF with butyllithium at low temperatures an instant colour change was observed and the solution turned olive green. On quenching with water the original compound was recovered. As a check experiment, D_2O was used as the quenching agent. This produced the monodeuterated $CpCoC_7H_7D$, for which the ^1H-NMR showed that attack of D^+ had exclusively occurred in exo position. No deuterium scrambling was observed on moderate heating.

Experiments are in progress towards isolation of this interesting mixed sandwich anion $[CpCoC_7H_7]^-$ and its further characterization.
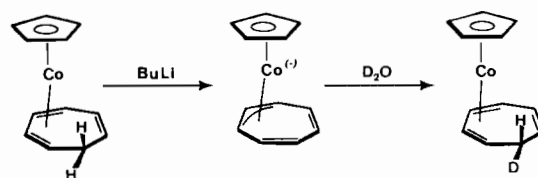
The stereochemistry of nucleophilic attack to cationic metal olefin complexes has received wide attention in recent years and results have been reviewed lately [11]. In connection with our longstanding interest in this field, we also studied nucleophilic addition of H^- as well as trialkylphosphines to cation III.

On treating an aqueous solution of $[CoCoC_7H_9]$-BF_4 with $NaBH_4$ a ready reaction was observed. After chromatographic separation two products were isolated, both of which were not identical with I. The first compound is a low melting orange solid of analytical composition $CpCoC_7H_{10}$. ^1H as well as ^{13}C NMR proved that this complex was CpCo(cyclohepta-1,4-diene) (IV), formed by hydride attack at C(3) of the dienyl system. This complex is stable to at least 100 °C without rearranging to I via a hydrogen shift. The only other transition metal complex of cyclohepta-1,4-diene was reported by Lewis et al. [12], obtained by $NaBH_4$ reduction of $[C_7H_9Fe(C_6H_8)CO]^+$, this product being less stable, however, and rearranging to the 1,3-isomer. In contrast, $[CpCoC_6H_7]^+$ gives only CpCo(cyclohexa-1,3-diene) on hydride reduction, as previously reported by Herberich [13].

The structure of the second product isolated from the reaction mixture was not fully elucidated. A highly complicated structure is, however, inferred from the ^{13}C spectrum showing at least 12 different carbon resonances.

V   III   IV
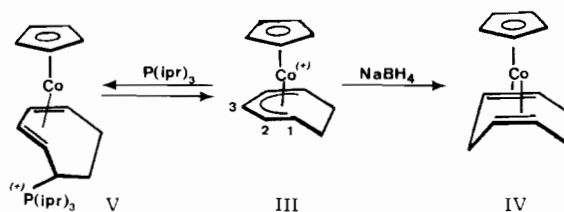
Unusual chemical shifts were observed in the ^{13}C NMR spectra of IV as well as for $[CpCoC_6H_7]^+$ (Tables I, II), both compounds having the similar structural feature of a bent-away methylene group. The two coordinated sp²-carbons adjacent to it appear at much higher field than all other coordinated olefinic carbons. A similar phenomenon is also observed for the cyclopentadiene complexes $CpCoC_5H_6$ and $CpRhC_5H_6$, having the same bent-away methylene group, where the olefinic carbons next to the methylene group again are shifted to

Cobalt(I) Cycloolefin Complexes

TABLE I. ^{13}C NMR Data for Neutral Cobalt Olefin Complexes, in C_6D_6 Proton-Noise Decoupled, Chemical Shifts in ppm Relative to TMS.

Complex	Cp	Olefinic uncoord.		Olefinic coord.		Aliphatic	
CpCo(cyclohepta-1,3-diene) (I)	80.9			80.4	47.7	30.0	
CpCo(cyclohepta-1,4-diene) (IV)	81.7			59.8	22.1	24.2	
CpCo(cycloheptatriene) (II)	80.3	129.7	123.9	86.7	80.7	28.7	
				49.6	45.6		
CpCo(cyclopentadiene)	78.7			76.2	38.3	40.6	
CpCo(cyclohexa-1,3-diene)	82.6			80.5	56.1	28.7	
CpCo(bicyclo[4.2.0]-octa-2,4-diene)	79.1			78.2	59.9	39.0	23.6
CpCo(cycloocta-1,5-diene)	83.8			63.2		32.3	
CpCo(cycloocta-1,3,5-triene)	84.1	136.0		67.8	64.7	32.9	
CpCo(1,2:5,6η-cyclooctatetraene)	84.5	135.5		68.7			
CpCo(1-4η-cyclooctatetranee)	78.9			94.2			

TABLE II. ^{13}C NMR Data for Cationic Cobalt Olefin Complexes, Phosphine Carbons Omitted, in CD_3NO_2, Proton-Noise Decoupled, Chemical Shifts in ppm Relative to TMS, J_{C-P} (Hz) in Brackets.

| Complex	Cp	Olefinic uncoord.		Olefinic coord.			Aliphatic
[CpCoC$_6$H$_7$]$^+$	86.8			93.7	92.5	50.3	23.9
[CpCoC$_7$H$_9$]$^+$ (III)	87.9			101.8	95.6	90.3	34.9
[CpCoC$_6$H$_7$P(ipr)$_3$]$^+$ (VI)	81.8			79.3	78.5 (2)		30.2 (20)
				52.3 (9)	45.6 (11)		28.4 (2)
[CpCoC$_7$H$_9$P(ipr)$_3$]$^+$ (V)	82.7			83.0	80.0		34.8 (24)
				49.1	38.3 (9)		31.3 (11)
							24.3 (3)
[CpCoC$_8$H$_9$P(ipr)$_3$]$^+$ (VII)	86.5	139.5	135.9	68.9	66.2 (17)		40.6 (15)
				61.3 (11)	60.8 (4)		29.6

higher field than the methylene group itself. This has never been observed for complexes where the olefinic carbons are separated by two methylene groups, as in CpCo(1,5-C$_8$H$_{12}$), CpCoC$_6$H$_8$ and [CpCoC$_7$H$_9$]$^+$.

As we had previously observed [6] that addition of triphenylphosphine to [C$_7$H$_9$Mo(CO)$_3$]$^+$ proceeds *via* attack at C(3) to give the symmetrical phosphonium salt [C$_7$H$_9$PPh$_3$]$^+$, we were interested to see whether [CpCoC$_7$H$_9$]$^+$ would react similarly. On addition of triphenylphosphine to III no addition product was isolated, however, although spectroscopic measurements suggested that at least partial addition had occurred [14]. The more basic triisopropylphosphine [P(ipr)$_3$] afforded a stable addition product [C$_7$H$_9$P(ipr)$_3$CoCp]$^+$ (V) in almost quantitative yields. To our surprise the ^{13}C spectrum

of V revealed that attack of the phosphine had occurred exclusively at C(1) of the dienyl system leading to an unsymmetrical addition product (Scheme 3).

An explanation for this unusual regioselectivity of attack by different Lewis bases could be that addition of phosphines is generally a reversible reaction [15] leading ultimately to the thermodynamically most stable addition product, while addition of H$^-$ is irreversible and often kinetically controlled.

The study of nucleophilic addition was extended to other cationic cobalt complexes. Thus [CpCoC$_6$H$_7$]$^+$, [CpCoC$_8$H$_9$]$^+$, and [CpCoC$_8$H$_{11}$]$^+$ react equally smoothly with alkylphosphines. A kinetic study of the addition to the latter molecule has already been
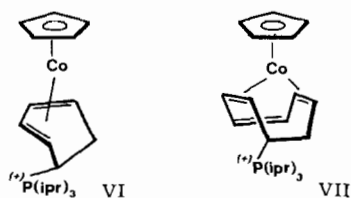
briefly reported by us [14]. The six-membered ring in VI is clearly 1-4η-bonded while VII exhibits 1,2:5,6η-coordination.

[13]C chemical shift data for all new compounds reported here are given in Tables I and II. Data for a series of previously known cobalt olefinic species are also included. A comparison of compounds with similar structural features clearly indicates typical shift patterns for the various geometries involved, facilitating structural assignments of new complexes.

A remarkable versatility for cobalt in its coordination behaviour emerges from the results reported here. While for cyclohexadiene 1-4η-coordination is clearly preferred and cyclononatetraene is so far only known to complex in a 1,2:5,6η-fashion to cobalt [1], seven- as well as eightmembered rings show an interesting ambiguity. For cyclooctatetraene only a small preference is seen for 1,2:5,6η-coordination. While cycloheptadiene forms stable complexes for both isomers, cycloheptatriene is only coordinating in a 1-4η-fashion. A 1,2:5,6η-bonding mode has been suggested for the corresponding rhodium complex [3], which seems also to be realized in (acac)RhC$_7$H$_8$ [16]. In the cationic complex [C$_8$H$_{12}$RhC$_7$H$_8$]$^+$, where several bonding modes have been suggested [17], cycloheptatriene is clearly 1-6η-bonded as derived from our own ^{13}C measurements. It thus emerges that cobalt and rhodium complexes are more versatile in their stereochemical preferences and, possibly, also more sensitive to small conformational changes than the corresponding iron carbonyl species with their pronounced affinity for conjugated diene systems.

Experimental

All experiments were carried out under nitrogen using solvents purified under nitrogen by standard procedures. NMR measurements were made on VARIAN XL-100 (^{13}C), XL-200 and EM-390 instruments (^{1}H). Cycloheptadiene was prepared according to the procedure by Hafner [18]; all previously known cobalt complexes according to the literature [19].

CpCo(cyclohepta-1,3-diene) (I) and Cp(Co(cycloheptatriene) (II)

A mixture of 3 ml (0.022 mol) freshly distilled CpCo(CO)$_2$, 8 ml olefin (0.8 mol), and 50 ml

n-octane is heated at the boiling point under reflux for 60 hours. After cooling the reaction mixture, solvent and excess ligand are distilled off under reduced pressure. The residue is dissolved in little hexane and poured on a alumina column (activity grade III) and chromatographed. The dark red zone is collected and reduced in volume. Repeated recyrstallization at −78 °C from hexane affords dark red crystals for II and a dark red oil for I (M.p. −50 °C). Yield 1.8 g II (37.5%) and 2.7 g I (56.4%). (I) Anal. Found: C, 65.12; H, 6.70%. C$_{12}$H$_{15}$Co calcd.: C, 66.06; H, 6.93%. (II) *Anal.* Found: C, 66.82; H, 6.28%. C$_{12}$H$_{13}$Co calcd.: C, 66.67; H, 6.06%.

[CpCoC$_7$H$_9$]PF$_6$ (III)

1 g of II is dissolved in 5 ml propionic anhydride and treated dropwise with 40% aqueous HBF$_4$ until the dark red colour of the solution disappears. Addition of 100 ml ether precipitates an orange red solid, which is filtered, washed with ether and dried. This is dissolved in 50 ml water and precipitated with a saturated solution of NH$_4$PF$_6$. Recrystallization from hot acetone/water gives orange-red platelets, yield 1.3 gr 77.8%. *Anal.* Found: C, 39.72; H, 3.92; F, 31.45%. C$_{12}$H$_{14}$CoPF$_6$ calcd.: C, 39.80; H, 3.89; F, 31.48%.

CpCo(cyclohepta-1,4-diene) (IV)

1 g of III is suspended in a water/ether two-phase mixture cooled with ice and treated with small portions of NaBH$_4$, until all of III is reacted and the aqueous layer is almost colourless. The ether phase is separated, dried and evaporated. Chromatography on alumina (activity grade III, hexane eluent) produces two bands, the first of which is collected, concentrated and on cooling to −78 °C produces orange needles of IV. Yield 320 mg, 53%. *Anal.* Found: C, 65.92; H, 6.75%. C$_{12}$H$_{15}$Co calcd.: C, 66.06; H, 6.93%.

Isolation of tri-isopropylphosphine adducts (V, VI, VII)

[CpCoC$_6$H$_7$]PF$_6$, [CpCoC$_7$H$_9$]PF$_6$ (in acetone) and [CpCoC$_8$H$_9$]BF$_4$ (generated *in situ* in propionic anhydride solution by treatment of CpCoC$_8$H$_8$ with HBF$_4$) are treated with an excess of tri-isopropylphosphine, stirred for a few minutes and precipitated by addition of ether. Recrystallization from acetone/water. Yields almost quantitative. (V) *Anal.* Found: C, 48.02; H, 6.63; F, 22.01%. C$_{21}$H$_{35}$CoP$_2$F$_6$ calcd.: C, 48.28; H, 6.75; F, 21.82%. (VI) *Anal.* Found: C, 46.98; H, 6.47; F, 22.45%. C$_{20}$H$_{33}$CoP$_2$F$_6$ calcd.: C, 47.25; H, 6.54; F, 22.42%. (VII) *Anal.* Found: C, 55.35; H, 7.21%. C$_{22}$H$_{35}$CoPF$_4$B calcd.: C, 55.48; H, 7.41%.

Acknowledgements

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