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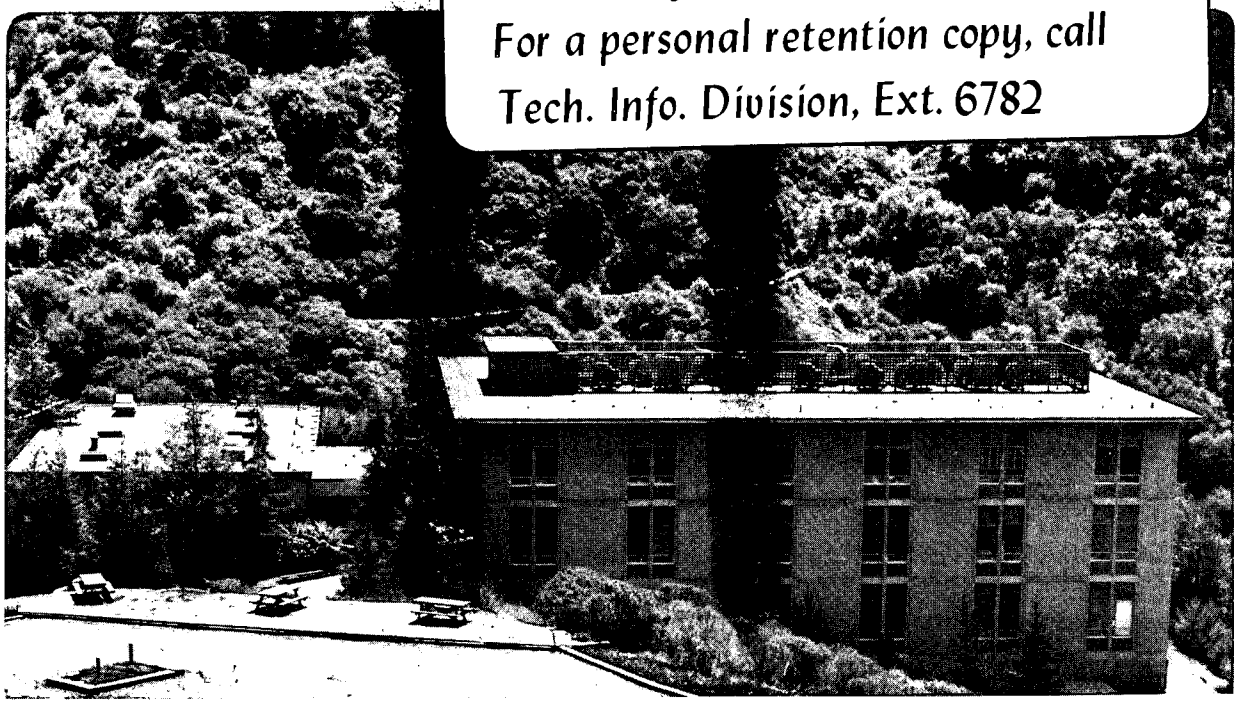

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TRANSITION METAL ACTIVATION OF π-COMPLEXED BENZENE: DOUBLE NUCLEOPHILIC ADDITIONS

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Summary

Treatment of the η^5-cyclopentadienyl-η^6-benzene cobalt dication with sodium methoxide in methanol or sodium cyclopentadienide in tetrahydrofuran gives double, vicinal, and stereospecific (exo) addition to the benzene ring in accord with the Davies-Green-Mingos rules.

There is considerable current interest in the activation of aromatic nuclei towards nucleophilic attack in an effort to develop procedures leading to benzene substitution and functionalization. Such activation may be achieved by complexation of the aromatic substrate to an electron poor or accommodating transition metal center [1,2] followed by addition of a nucleophile. We have been interested in using such a scheme in double nucleophilic

additions to benzenoid aromatics, a virtually unexplored area [3].* An ideal system on which to study such a reaction is the $(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)M^{2+}$ unit (M = Co, Rh, Ir) for three reasons: 1. the dicationic metal should facilitate twofold attack by negatively charged species, 2. the Davies-Green-Mingos rules predict that the successive nucleophilic addition should occur vicinally, stereospecifically exo, and at the six membered ring [5], and 3. mild oxidative demetallation methods are available to liberate the anticipated 1,3-cyclohexadiene ligands [6]. Interestingly, double nucleophilic additions of this type have been unsuccessfully attempted to pentamethyl and ethyltetramethylcyclopentadienyl rhodium and iridium(III) complexes [7]. We now report the reactions of $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Co][BF_4]_2$ 1 and some model studies.

$(\eta^5\text{-}C_5H_5)(\eta^4\text{-}1,3\text{-}C_6H_8)Co$ was prepared by heating 1,4- or 1,3-cyclohexadiene with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in nonane to reflux for 2-4 days in 95% yield, an improvement over the literature procedure [8]. Hydride abstraction gave 1 [9]. We reasoned that those nucleophiles which successfully added to $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_7)Co]$-

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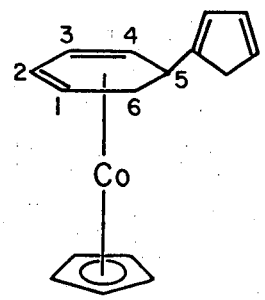
* The reaction of bisbenzene ruthenium perchlorate with hydrides ($NaBH_4$, $LiAlH_4$) gives $(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)Ru$, but this product is likely derived by secondary reaction of the initially formed $(\eta^5\text{-}C_6H_7)$ Ru [3]. Double hydride addition to $[(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)Ir][PF_6]_2$ has been claimed [4].

$[PF_6]$ 2 would be the most likely to succeed in double additions to 1. Single nucleophilic attack on 2 by five nucleophiles (H^-, malonate, $N(CH_3)_2$, $N(C_2H_4)_2O$, OCH_3) had been reported previously and shown to occur with exo-stereoselectivity [10]. We have expanded this list by C_5H_5 (28%), CH_2CN (40%), and $CH_2COC_6H_5$ (78%). (η^5-C_5H_5)cyclopentadienyl(η^5-C_6H_7)Co is formed as a red oil and what appears to be only one isomer assigned structure 3 based on NMR decoupling studies and by comparison with 5: ^{1}H NMR (δ, C_6D_6): 5.9-6.3(m, 3H), 4.8(m, 2H, $H_{2,3}$), 4.45(s, 5H, C_5H_5), 2.6-3.1(m, 3H, $H_{1,4,5}$), 2.54(m, 2H), 1.84(ddd, J = 14, 10, 5Hz, 1H, H_6 endo), 0.70(ddd, J = 14, 5, 3Hz, 1H, H_6 exo).

With these model systems in hand the reactivity of complex 1 was explored. Whereas treatment of this



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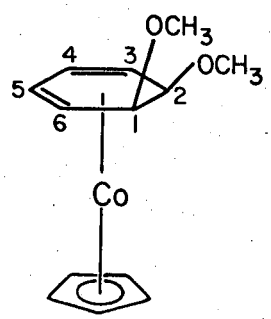

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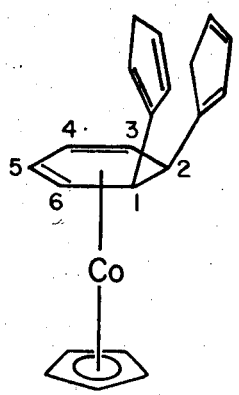

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compound with $NaOCH_3$ (3 equivalents) in THF at 0°C gave only benzene (69%), exposure to $NaOCH_3$ (11 equivalents) in methanol gave an orange solution containing the very unstable adduct 4 which polymerized on standing. Another route to 4 involved treatment of (η^4-1-methoxycyclohexa-1,3-diene)(η^5-C_5H_5)Co [10] with trityl hexafluorophosphate followed by $NaOCH_3$ in methanol.

Due to its sensitivity no reliable yield data could be obtained on 4 but the initial addition appears to be clean based on spectral analysis. The proton NMR spectrum [10] is most informative and proves the structure and stereochemistry of 4: δ (C_6D_6) 4.89(dd, J=4, 3, Hz, 2H), 4.40(s, 5H), 3.70(overlapping dd, J=3,2Hz, 2H), 3.20(s, 6H), 2.87(m, 2H). Decoupling experiments served to corroborate spectral assignments. When the resonance at δ2.87 was irradiated, the peaks at δ4.89 and 3.70 collapsed into singlets. Therefore the resonance at δ2.87 is attributed to protons at positions 3 and 6. Irradiation at δ3.70 did not affect the signal at δ4.89 and collapsed the multiplet at δ2.87 to a doublet of doublets (J=4.5, 3 Hz). Therefore, the resonance at δ3.70 is attributed to $H_{1,2}$ and that at δ4.89 is due to $H_{4,5}$.

Attempts to liberate the unknown ligand cis-5,6-dimethoxycyclohexadiene by oxidative means [6] gave no characterizable products. Significantly, no anisole or catecholdimethylether was detectable.

Assuming that the leaving group ability of the methoxy group was responsible for the instability of 4, we turned our

attention to carbon nucleophiles. Indeed, 1 reacts with NaC_5H_5 in THF to give up to 42% of an inseparable mixture of the unstable bis-adduct 5 and its two double bond isomers (with a respective pair of equal substituents) as a red oil in varying ratios depending on the reaction temperature. However, in this transformation the major product is $[(\eta^5\text{-}C_5H_5)_2Co][BF_4]$ derived by apparent nucleophilic attack on the metal [7] and ligand displacement. The appropriate amount of benzene could also be detected. The ^1H NMR spectrum of the mixture of 5 and its isomers clearly shows that addition has occurred vicinally and exo to the metal: $\delta(C_6H_6)$ 5.9-6.5(m, 6H), 4.75(dd, J=4, 2Hz, 2H, $H_{4,5}$), 4.50(s, 5H), 3.20(t, J=1.5 Hz, 2H, $H_{1,2}$), 2.88(m, 2H, $H_{3,6}$) and narrow multiplets of varying intensity at 2.67, 2.40, 2.27, and 2.05 integrating for a total of four hydrogens. Cyclopentadienyladducts of the type 5 have generated some recent interest since they potentially are novel metal bearing ligands [11, 12] and their structure has been the subject of some controversy.

Since substantial quantities of cobalticinium ion were found in the preparation of 5 the reaction of this species with NaC_5H_5 (THF, 0°C, 1h; 25°C, 2H) was investigated. This produced a 16% yield of a 1:1 mixture of two isomers of cyclopentadienyl-(η^4-cyclopentadiene)(η^5-C_5H_5)Co, a result at variance with the literature [12]: ^1H NMR δ (C_6D_6): 5.6-6.4 (m, 3H), 5.05(m, 2H), 4.67(s, 5H), 3.94(m, 1H), 2.80(m, 2H),

2.65(bs, 1H), 2.52(bs, 1H). These compounds were not observed in the preparation of 5.

Although the above experiments demonstrate for the first time the basic feasibility of effecting double nucleophilic additions to coordinated benzene the generality of this transformation still remains to be demonstrated. Thus, the reaction of 1 with CH_3Li, t-BuLi, CH_3MgI, $NaBH_4$, $P(C_6H_5)_3$, $Li[N(CH(CH_3)_2)_2]$, $Na[OCH(CH_3)_2]$, $HN[CH(CH_3)_2]_2$, KSCN, $H_2NCH_2CH_2NH_2$, NaCN, NaOH, $LiBEt_3H$, $LiCH_2CN$, $LiC{\equiv}CSiMe_3$, $LiCH_2COC_6H_5$, $Li_2[CH_2CO_2]$, $Li[C(CH_3)(CO_2Et)_2]$, and $Li[C(CH_3)_2CN]$ did not yield any detectable amount of desired product but green uncharacterizable precipitates and free benzene.

An improvement of the effectiveness of the method will have to await changes in ligand design or the discovery of a system less prone to ligand displacement.

Experimental

General

Proton NMR spectra were recorded at 90 MHz on a Varian Associates EM-390 NMR instrument in 5mm tubes using an internal proton lock system, or a home-built 250 MHz system. Most measurements for cobalt species required the use of C_6D_6 as solvent rather than CCl_4 or $CDCl_3$ owing to decomposition in chlorinated solvents. Data are reported as chemical shifts (δ) in ppm (multiplicity,

integration) where s=singlet, d=doublet, t=triplet, q=quartet, qn=quintet, m=multiplet, b=broad). Infrared spectra were ob-obtained on a Perkin-Elmer 337 and 597 spectrometer as neat liquid films of arbitrary thickness between sodium chloride plates, as solutions using 0.1mm path length cells (NaCl), or as potassium bromide pellets. Data are reported as $\tilde{\nu}$ values (cm^{-1}); only selected lines are given. Low and high resolution mass spectra (obtained at 70eV) were recorded on AEI-MS and DuPont CEC 21-110B instruments, respectively, on a service basis at the University of California, Berkeley. Only the strongest and/or structurally most important fragmentation peaks are reported in the mass spectra of new compounds. Cp conveniently stands for η^5-C_5H_5. Vacuum line operations were carried out on a high vacuum (mercury diffusion) multiple line apparatus. All chromatographic separations were carried out on alumina [Alfa Products, activated neutral, CAMAG 95+% Al_2O_3, -60 mesh] deactivated with water (4.5% w/w). Thin layer chromatography was accomplished on a pre-coated TLC plastic or aluminum sheet (E. Merck Reagents); a) Aluminum oxide 60 F_{254}, neutral (Type E), layer thickness 0.2mm; b) precoated plastic TLC sheets, Polygram^R Sil G/UV_{254}, layer thickness 0.25mm (Machery-Nagel & Co.); c) precoated TLC glass sheets (Uniplate^R), SilicaGel GHLF, layer thickness 0.25mm (Analtech, Inc.). Visualization was by UV absorption and I_2 vapor.

All reactions were carried out under oxygen-free atmospheres with magnetic stirring in deoxygenated solvents. Solvents (Mallinckrodt, Analytical Reagent Grade) were generally used as supplied excepting THF which was distilled from sodium-benzophenone. Pentane was distilled away from higher boiling residues.

$[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ was prepared according to a literature procedure [13]. $(\eta^5\text{-}C_5H_5)Co(CO)_2$ was purchased from Strem Chemical and used without further purification.

Preparation of η^4-(1,3-cyclohexadiene)-$(\eta^5\text{-}C_5H_5)Co$ [8]

$(\eta^5\text{-}C_5H_5)Co(CO)_2$ and 1,4-cyclohexadiene:

1,4-Cyclohexadiene (2ml, 21.1mmol) and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (1ml, 8.0mmol) were dissolved in nonane (5ml) and the solution heated to reflux for 3.5 d. The cooled mixture was chromatographed on alumina (activity II) with pentane and a red band was eluted. Volatiles were removed by rotary evaporation which yielded 1.282g (0.628mmol, 78.5%) of (1,3-cyclohexadiene) $(\eta^5\text{-}C_5H_5)Co$ as a red crystalline solid; m.p. 38-42°C (lit. [8] 40-42°C). Yields ranged from 60-79%.

$(\eta^5\text{-}C_5H_5)Co(CO)_2$ and 1,3-cyclohexadiene:

1,3-Cyclohexadiene (2ml, 20.98mmol) and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (1ml, 8mmol) in nonane (5 ml) were heated to reflux for 4 d. The cooled mixture was chromatographed on alumina; thus obtained was 1.545g (7.57mmol, 94.7%) of (1,3-cyclohexadiene)$(\eta^5\text{-}C_5H_5)Co$. Yields ranged from 70-95%.

Reaction of $[(\eta^5\text{-Cyclohexadienyl})(\eta^5\text{-}C_5H_5)Co]PF_6$ 2 with Nucleophiles

1. Cyclopentadienyl sodium:

To NaC_5H_5 (0.07g, 0.79mmol) in THF (15 ml) at -78°C was added 2 (0.250g, 0.718mmol). After stirring at -78°C for 1 h, the mixture was warmed to room temperature and stirred under nitrogen overnight. The mixture was then filtered and the volatiles removed by rotary evaporation. The red residue was chromatographed on alumina with pentane. A red band was collected to give 0.05g (0.20mmol, 28%) of $(\eta^5\text{-}C_5H_5)$cyclopentadienyl$(\eta^5\text{-}C_6H_7)Co$ 3 as a red oil: m/e: 268(M^+, 64%), 265(M^+-3H, 100%), 200(M^+-Cp, 51%), 189(Cp_2Co, 32%), 124(CpCo, 31%); ^1H NMR see text; IR(pentane): 3110m, 3045m, 1110m, 1008m, 905m, 895m, 858w, 800s, 722s.
Anal. Found: C, 71.94; H, 6.57. Calcd. for $C_{16}H_{17}Co$: C, 71.64; H, 6.39

2. Lithioacetonitrile:

To diisopropylamine (0.10ml, 0.71mmol) in THF (15ml) at -78°C was added 0.50ml (1.55M in hexane, 0.78mmol) of n-butyllithium. The mixture was warmed and kept at 0°C for 15 min before cooling back to -78°C. To this solution was added acetonitrile (0.040ml, 0.76mmol), the mixture warmed and kept at 0°C for 15 min. After cooling to -78°C, 2 (0.150g, 0.431mmol) was added. An orange solution was obtained which was warmed to room temperature and stirred for 1h. The volatiles were removed by rotary evaporation and the red oil chromatographed on alumina, eluting with pentane. A red band was collected which on evaporation yielded η^4-5-cyanomethyl-1,3-cyclohexadiene$(\eta^5\text{-}C_5H_5)Co$ as a thick red oil (0.042g, 0.172mmol, 40%). m/e: 243(M^+, 26%), 241(M^+-2H, 47%), 203(M^+-CH_2CN, 1.5%), 176(6%), 124 (CpCo, 100%); ^1H NMR (C_6D_6): 4.75(m, 2H), 4.54(s, 5H), 2.80(m, 2H),

2.00(m, 1H), 1.71(dd, J=10, 5Hz, 1H), 1.50(d, J=6Hz, 2H), 0.50(ddd, J=13, 3, 2 Hz); IR(film): 3030w, 2990w, 2922w, 2826w, 2183s (ν_{CN}), 1638s, 1598s, 1417m, 1108m, 1010m, 806s.

Anal. Found: C, 64.68; H, 5.41. Calcd. for $C_{14}H_{13}CoN$: C, 64.21; H, 5.80.

3. Acetophenone Anion:

To diisopropylamine (0.070ml, 0.50mmol) in THF (20ml) at -78°C was added 0.30ml (1.55M in hexane, 0.47mmol) n-butyllithium. The solution was warmed and kept at 0°C for 15 min. After cooling back to -78°C acetophenone (0.056ml, 0.48mmol) was added. The mixture was then kept at 0°C for 15 min and cooled back to -78°C. To this solution was added 2 (0.150g, 0.431mmol). The mixture was kept at -78°C for 0.5 h and then warmed to room temperature. After stirring for another 0.5 h, solvent was removed by rotary evaporation and the red residue chromatographed on alumina eluting with ether. A red band was collected which when concentrated and cooled (0°C) gave red crystals of η^4-5-(2-oxo-2-phenylethyl)cyclohexadiene(η^5-C_5H_5)-Co (0.10g, 0.335mmol, 78%), m.p. 151-153°C. m/e: 322(M^+, 46%), 320(M^+-2H, 46%), 255(M^+-Cp-2H, 100%); ^{1}H NMR (C_6D_6): 7.70(m, 2H), 7.0(m, 3H), 4.75(m, 2H), 4.48(s, 5H), 2.95-2.30(m, 5H), 1.99(ddd, J=15, 9, 4.5Hz, 1H), 0.50(m, 1H); IR(KBr): 3036w, 2998w, 2940w, 2920w, 2900w, 2870w, 2838w, 1674s (ν_{CO}), 1592w, 1579w, 1448m, 1400m, 1349m, 1325w, 1290m, 1250w, 1198m, 1168w, 1159w, 1109m, 1053w, 1020w, 1000w, 990w, 983w, 953m, 814s, 808s, 758s, 690s.

Anal. Found: C, 70.93; H, 5.88. Calcd. for $C_{19}H_{19}CoO$: C, 70.61; H, 5.94.

Synthesis of η^4-1,2-Dimethoxy-3,5-cyclohexadiene Cyclopentadienyl Cobalt

1. From $[\eta^6(C_6H_6)(\eta^5-C_5H_5)](BF_4)_2$ and $NaOCH_3$:

To sodium methoxide (0.222g, 4.11mmol) in degassed methanol (20ml) at 0°C was added 1 (0.150g, 0.399mmol). A yellow solution was immediately obtained. The ice bath was removed and the mixture stirred for 5-10 min. The solvent was removed by rotary evaporation and the black-orange residue extracted with diethyl ether (50ml). The red solution was filtered and solvent was removed by rotary evaporation. The red oil was vaccum dried to give 0.066g (crude yield: 0.25mmol, 63%) of (5,6-dimethoxycyclohexa-1,3-diene)$(\eta^5-C_5H_5)$Co 3. m/e: 264(M^+, 33%), 262(M^+-2H, 15%), 232(M^+-CH_3OH, 48%), 202(M^+-2CH_3O, 46%), 76(100%); High resolution m/e: Found 264.0547. Calcd. for $C_{13}H_{17}CoO_2$: 264.0560; ^1H NMR see text; IR(film): 3100w, 3044w, 3009w, 2970w, 2929m, 2902m, 2810m, 2012m, 1960m, 1590w, 1490w, 1465w, 1442w, 1402m, 1340m, 1262m, 1185w, 1065s, 950w, 900w, 800s, 760w, 700m.

2. From η^4-5-Methoxycyclohexa-1,3-diene$(\eta^5-C_5H_5)$Cobalt:

To 5-Methoxycyclohexa-1,3-diene$(\eta^5-C_5H_5)$Co [10] (0.352g, 1.504mmol) in dichloromethane (20ml) at -78°C was added trityl hexafluorophosphate (0.588g, 1.51mmol). The mixture was warmed to room temperature and pentane added to precipitate out 0.515g of an orange solid.

When 0.092g of the crude orange solid was reacted with sodium methoxide (0.037g, 0.68mmol) in methanol at room temperature for 0.5 h followed by solvent removal by rotary evaporation, the ^1H NMR spectrum of the residue in C_6D_6 indicated a 3:1 ratio of η^4-cyclohexa-1,3-diene-$(\eta^5-C_5H_5)$Co and η^4-5,6-dimethoxycyclohexa-1,3-diene)$(\eta^5-C_5H_5)$Co.

Preparation of 5,6-Dicyclopentadienyl-η^4-cyclohexa-1,3-diene-(η^5-C_5H_5) Cobalt 5.

To NaC_5H_5 (0.090g, 1.02mmol) in THF (20ml) at -78°C was added $[(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)Co](BF_4)_2$ 1 (0.150g, 0.399mmol) and the mixture stirred for 1 h before the red solution was warmed to room temperature. The solvent was removed by rotary evaporation and the residue chromatographed on alumina eluting rapidly with pentane under a nitrogen pressure. Thus isolated was (5,6-dicyclopentadienyl-η^4-cyclohexa-1,3-diene)(η^5-C_5H_5)Co 5 (0.056g, 0.169mmol, 42%) as an orange oil which darkened when kept at room temperature. m/e: 332(M^+, 13%), 267(M^+-Cp, 9%), 265(M^+-Cp-2H, 36%), 244(100%), 208(M^+-CpCo, 17%), 189(Cp_2Co, 29%). High resolution m/e: Found 332.0969. Calcd. for $C_{21}H_{21}Co$: 332.0975. IR(film): 3060s, 2990s, 2895s, 2895s, 1595m, 1495m, 1362s, 1253m, 1111m, 1000m, 952m, 890s, 850m, 804s, 752m, 745m, 730m, 704m, 679s.

A second band eluted with acetone which was collected to give 0.051g (0.185 mmol, 46%) of $[(\eta^5\text{-}C_5H_5)_2Co]BF_4$.

Reaction of $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ With NaC_5H_5 [12]

To NaC_5H_5 (0.096g, 1.1mmol) in THF (20ml) at 0°C was added $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ (0.225g, 0.674mmol). A red solution was obtained. The mixture was kept at 0°C for 1 h and then warmed to room temperature for 2 h. The solvent was removed by rotary evaporation and the residue chromatographed on alumina eluting

with pentane. An orange band was obtained containing double bond isomers of cyclopentadienyl-(η^4-cyclopentadiene)(η^5-C_5H_5)cobalt. m/e: 254(M^+, 61%), 253(M^+-H, 100%), 252(M^+-2H, 10%), 189(M^+-Cp, 81%), 129(M^+-CpCo-H, 32%), 124(CpCo, 37%); ^{1}H NMR see text.

Acknowledgments

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