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Preliminary communication

PENTAMETHYLCYCLOPENTADIENYLCOBALTBIS(ETHYLENE): A VERSATILE REAGENT IN ORGANOCOBALT SYNTHESIS

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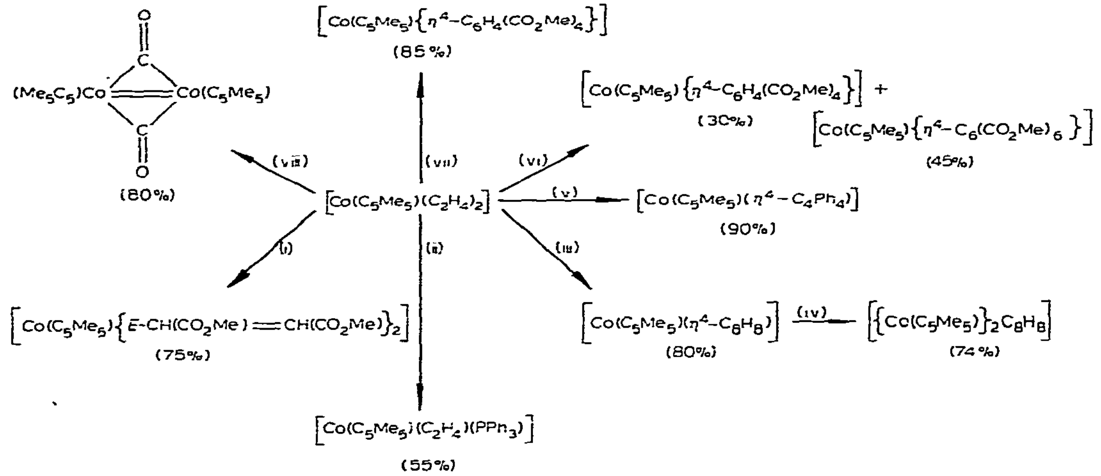
Summary

Cyclopentadienyl- and pentamethylcyclopentadienyl-bis(ethylene)cobalt are synthesized from the respective diiodides $[\{Co(C_5R_5)I_2\}_2]$ by Na/Hg reduction under ethylene. Reaction of $[Co(C_5Me_5)(C_2H_4)_2]$ with dimethylfumarate (DMF), triphenylphosphine, cycloocta-1,5-diene and cycloocta-1,3,5,7-tetraene gives the replacement products $[Co(C_5Me_5)(DMF)_2]$, $[Co(C_5Me_5)(C_2H_4)(PPh_3)]$, $[Co(C_5Me_5)(\eta^4\text{-}C_8H_{12})]$ and $[Co(C_5Me_5)(\eta^4\text{-}C_8H_8)]$ respectively, whereas reaction with acetylenes (RC_2R') affords $[Co(C_5Me_5)(\eta^4\text{-}C_4R_2R'_2)]$, $[Co(C_5Me_5)(\eta^4\text{-}C_6R_3R'_3)]$ and/or $[Co(C_5Me_5)(\eta^4\text{-}C_6H_4R_2R'_2)]$. Reaction of $[Co(C_5Me_5)(C_2H_4)_2]$ with $[Co(C_5Me_5)(CO)_2]$ provides a clean high-yield synthesis of $[\{Co(C_5Me_5)(\mu\text{-}CO)\}_2]$.

Cyclopentadienylcobaltdicarbonyl has been the starting point for much of the organometallic chemistry of cobalt [1]. However, it is not an ideal starting material being moderately inert to carbonyl substitution such that vigorous thermal or photochemical conditions are frequently required for reaction. Our search for a more labile starting material led us to $[Co(C_5Me_5)(C_2H_4)_2]$, a compound of considerable synthetic utility.

Pentamethylcyclopentadienylcobaltbis(ethylene) may be conveniently prepared by rapidly beating a suspension of $[\{Co(C_5Me_5)I_2\}_2]$ [2] in tetrahydrofuran with an excess of 1% sodium amalgam (5 min) under an atmosphere of ethylene. The decanted solution is evaporated at reduced pressure and the residue extracted with petroleum ether. Filtration and crystallization at —78°C affords orange crystals of $[Co(C_5Me_5)(C_2H_4)_2]$ in good yield (70—85%), (^1H NMR (C_6D_6): δ 1.43 (15 H, C_5Me_5), 1.60 and 0.86 ppm (AA'BB', 8 H, inner and outer H of C_2H_4, $|J(AB) + J(AB')|$ 13 Hz); ^{13}C NMR (C_6D_6 : 92.3 (C_5Me_5), 45.1 (C_2H_4) and 9.1 ppm (C_5Me_5)). This material offers considerable advantages over the previously reported $[Co(C_5Me_4Et)(C_2H_4)_2]$ [3] in that as a solid it is sufficiently stable to allow brief handling in the air. Also the ^{1}H and ^{13}C NMR spectra are simpler. The compound may be stored under an inert atmosphere (or preferably under ethylene) for several months at 5°C without significant deterioration.



SCHEME 1. (i) *E*- or *Z*-$CH(CO_2Me)=CH(CO_2Me)$, hexane, reflux; (ii) PPh_3, hexane reflux; (iii) cyclooctatetraene, hexane, reflux; (iv) $[Co(C_5Me_5)(C_2H_4)_2]$, hexane, reflux; (v) PhC_2Ph, hexane, reflux; (vi) $C_2(CO_2Me)_2$, hexane, 20°C; (vii) $C_2(CO_2Me)_2$, toluene, 20°C; (viii) petroleum ether (30—40°), reflux.

Ethylene is easily displaced by a range of ligands in low boiling hydrocarbon solvents (Scheme 1). In many cases the straightforward substitution product is obtained in good yield, though in the case of dimethyl maleate the olefin is isomerized and the corresponding fumarate complex is isolated [4].

When $[Co(C_5Me_5)(C_2H_4)_2]$ reacts with acetylenes (RC_2R') a number of products may be formed (e.g. $[Co(C_5Me_5)(\eta^4\text{-}C_4R_2R_2')]$, $[Co(C_5Me_5)(\eta^4\text{-}C_6R_3R_3')]$ and $[Co(C_5Me_5)(\eta^4\text{-}C_6H_4R_2R_2')]$) depending on the choice of acetylene, solvent, reaction time and conditions. Of particular interest is the cyclo-cotrimerization which yields 1,3-cyclohexadiene products. This reaction is quite general for a wide range of acetylenes (R, R' = alkyl, aryl, CF_3, CO_2Me, $SiMe_3$, etc.) and is enhanced in aromatic solvents. The yields are often excellent, for instance $[Co(C_5Me_5)(\eta^4\text{-}C_6H_4Et_4)]$ is produced in $>$ 90% yield. Other olefins may also be incorporated. For instance, $[Co(C_5Me_5)(CH_2CHMe)_2]$, generated in toluene solution but not isolated, reacts with $C_2(CO_2Me)_2$ to give the corresponding cyclohexadiene complex $[Co(C_5Me_5)\{\eta^4\text{-}C_6H_3Me(CO_2Me)_4\}]$. Although cyclo-cotrimerization of olefins and acetylenes is reported to occur in a number of systems [5] the reaction is by no means common and in many cases is restricted to the more reactive olefins and acetylenes.

When equal quantities of $[Co(C_5Me_5)(CO)_2]$ and $[Co(C_5Me_5)(C_2H_4)_2]$ are allowed to react together in refluxing petroleum ether (b.p. 30—40°C) the green dimer $[\{Co(C_5Me_5)(\mu\text{-}CO)\}_2]$ [6] is formed in excellent yield and separates as the crystalline solid. This represents an interesting alternative to the current syntheses.

Brintzinger and Lee [7] have discussed the utility of $[\{Co(C_5H_5)I_2\}_2]$ in the synthesis of various organocobalt derivatives. We find that reduction of this material by Na/Hg (½%) in THF (—25°C, C_2H_4 1 atm) affords $[Co(C_5H_5)(C_2H_4)_2]$ in good yield (^1H NMR (C_6D_6): δ 4.32 (s, 5 H, C_5H_5), 2.56 and 0.70 ppm (AA'BB'. total 8 H, inner and outer H of C_2H_4, $|J(AB) + J(AB')|$ 13 Hz); ^{13}C NMR (C_6D_6) 85.2 (C_5H_5) and 37.9 ppm (C_2H_4)). Jonas [8] has recently reported briefly the synthesis of this compound from cobaltacene.

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