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Preliminary communication

CYCLOBUTADIENETRICARBONYLCOBALT SALTS

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Summary

Cyclobutadiene- and tetramethylcyclobutadiene-tricarbonylcobalt hexafluorophosphates have been obtained by different methods, each capable of extension to related salts.

In contrast to the extensive work on cyclobutadienetricarbonyliron, little is known about the chemistry of unsubstituted cyclobutadiene complexes of other metals [1]. Moreover the only known cationic complexes of this ligand are also iron compounds, the nitrosyl complexes $[C_4H_4Fe(CO)(NO)L]PF_6$.

We now describe the preparation of cyclobutadienetricarbonylcobalt(I) hexafluorophosphate (Ia) and its triphenylphosphine substitution product Ib from the known cyclobutadienecobalt complexes $C_4H_4Co_2(CO)_6$ and $C_4H_4Co(CO)_2I$, respectively, as well as an entirely different and very facile route to (tetramethylcyclobutadiene)tricarbonylcobalt(I) hexafluorophosphate (Ic).

We have previously shown [2] that simple dienetricarbonylcobalt(I) salts, e.g. those containing butadiene or cyclohexa-1,3-diene as hydrocarbon ligands, can be obtained by oxidation of binuclear dienecobalt carbonyls. We have now found that the long-known [1] cyclobutadiene complex, $C_4H_4Co_2(CO)_6$ is similarly oxidised by triphenylmethyl tetrafluoroborate in dichloromethane solution. The product, initially precipitated with ether, was converted to the more stable hexafluorophosphate salt* Ia using aqueous ammonium hexafluorophosphate. The cation is isoelectronic with butadienetricarbonyliron and with the cation $[C_4H_4Fe(CO)_2NO]^+$ (II) and closely resembles the latter in both the proton chemical shift values (δ $[(CD_3)_2CO]$ 6.08 for compound Ia; 6.14 [3] for the PF_6 salt of cation II) and the carbonyl stretching frequencies (2150(m), 2105(s) and 2133, 2103 cm^{-1}, respectively).

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*Purity of each of the new salts was established by C, H analyses.

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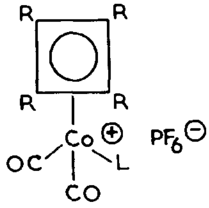
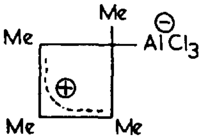


I

a) R=H, L=CO

b) R=H, L=PPh$_3$

c) R=Me, L=CO



III

The triphenylphosphine-substituted analogue Ib was formed by treating the iodo complex, $C_4H_4Co(CO)_2I$, with the phosphine and silver hexafluorophosphate in tetrahydrofuran.

Our route to the tetramethylcyclobutadiene complex Ic is based on the recent work of Hoberg and Riegel [4] who treated the readily available [5] aluminium complex III with tetracarbonylnickel. However, whereas the latter is oxidised with complete loss of carbonyl groups to give the nickel(II) complex $C_4Me_4NiCl_2$ under these conditions, we find that a dichloromethane solution of octacarbonyldicobalt yields the cation $[C_4Me_4Co^I(CO)_3]^+$. This was precipitated, presumably as tetrachloroaluminate, by addition of ether to the reaction mixture and converted to the hexafluorophosphate Ic with aqueous ammonium hexafluorophosphate in 41% yield (δ $[(CD_3)_2CO]$ 2.04; ν(CO) 2110(m), 2075(s); cf. $[C_4Me_4Fe(CO)_2NO]PF_6$: ν(CO) 2102, 2063 cm^{-1}). It is noteworthy that both in the cobalt and in the iron salts the replacement of ring hydrogens by methyls causes significant lowering of the carbonyl stretching frequencies.

The three salts described above are very pale yellow (almost colourless) crystalline solids, soluble in acetone and other polar organic solvents. The only known substituted cyclobutadienetricarbonylcobalt salts are the alkyl- and aryl-alkoxy-substituted complexes recently described by Hughes and his coworkers [6]. Our salts appear to be both more stable (dec. >150°C) and less reactive; thus they do not suffer replacement of the carbonyl groups by benzene under the conditions used by these authors [6]. Further reactivity studies are in progress.

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