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PREPARATION AND CHARACTERISATION OF 1-(2,4-DIMETHYLBICYCLO[2.2.2]OCTYL)PENTACYANOCOBALTATE(III)

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Summary

The preparation and properties of sodium 1-(2,4-dimethylbicyclo[2.2.2]-octyl)pentacyanocobaltate(III) tetrahydrate are described.

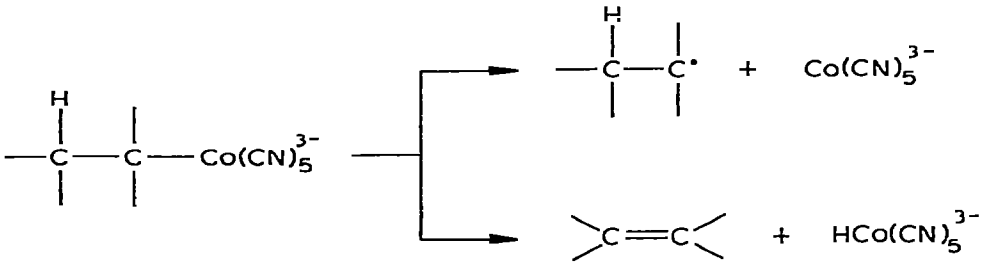
Introduction

In recent years, σ-bonded organotransition-metal complexes have been the subject of much research activity [1]. In particular, σ-bonded organocobalt complexes have attracted special interest [2,3], since it is known that a coenzyme of vitamin B_{12} contains a very stable C—Co σ-bond [4]. The series of alkylpentacyanocobaltate(III) complexes constitutes one group of such compounds [5-8]. The more stable of these contain Co bonded to aromatic sp^2 or primary sp^3 carbon centres, especially those carrying a stabilising cyano, carbonyl or aryl group. Secondary carbon—cobalt complexes are relatively rare [6], and tertiary analogues are non-existent [9] except for two bridgehead C—Co complexes i.e. 1-adamantyl pentacyanocobaltate(III) [10] and the neutral complex tetrakis-(1-norbornyl)cobalt [11]. We report here the preparation and characterisation of another stable complex, 1-(2,4-dimethylbicyclo[2.2.2]octyl)pentacyanocobaltate(III), containing the bridgehead C—Co bond.

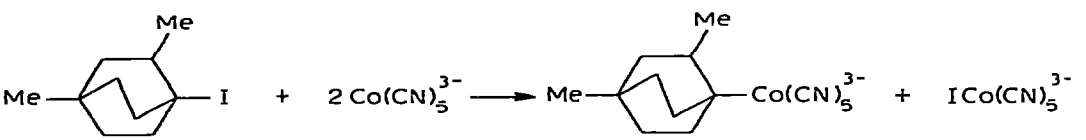
Results and discussion

Evidence has accumulated to indicate that the instability of transition metal—carbon σ bonds is due mainly to bond homolysis, reductive (1,1), (1,2) and (1,n) eliminations or α- and β-elimination of metal hydride, and the coupling of ligands at the transition metal atom [1,12]. Previous work [6-8] has demonstrated that the non-acid catalysed decomposition of alkylpentacyanocobaltates occurs via homolysis and β-elimination of hydridopentacyanocobaltate(III) as shown in Scheme 1:

SCHEME 1

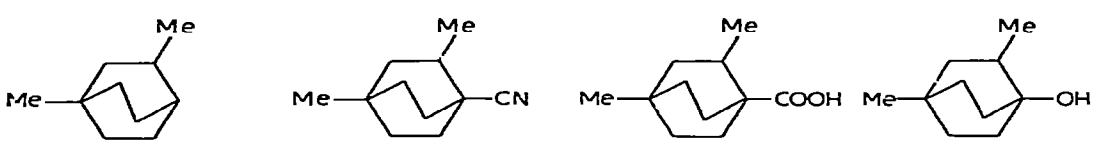


Stability of such complexes can therefore be attained if the system is such that (a) the radical produced by homolysis is of high energy, so that its formation is thermodynamically unfavourable, (b) the β-carbon does not carry groups that are readily transferrable to the cobalt atom, e.g., hydrogen and (c) a double bond is difficult to form between the α- and β-carbons. These conditions can be fulfilled if the alkyl group is a bridgehead carbon centre. We have earlier reported one such compound [10] and we now report the preparation of sodium 1-(2,4-dimethylbicyclo[2.2.2]octyl)pentacyanocobaltate(III). This was prepared by the reaction of 2,4-dimethyl-1-iodobicyclo[2.2.2]octane with sodium pentacyanocobaltate(II). The air stable complex was isolated as yellow crystals in 58% yield. Elemental analyses together with NMR, IR and UV spectral data were consistent with structure (II).



(I) (II)

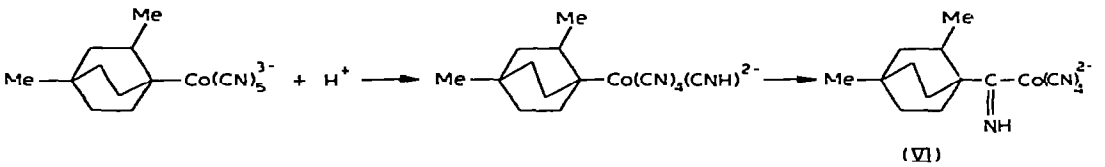
The compound is stable in neutral and alkaline solutions, and is comparable in stability to the analogous methyl [5,13], pyridylmethyl [6] and 1-adamantyl [10] complexes. As in the case of 1-adamantylpentacyanocobaltate [10], bond cleavage is rendered difficult by the presence of a bridgehead carbon centre, because homolysis will give a highly unstable bridgehead radical [14,15] while a 1,2-elimination will give an olefin at a bridgehead position or Bredt compound which is highly strained [16,17]. Thermal decomposition in neutral or basic media gave mainly 1,3-dimethylbicyclo[2.2.2]octane (III), probably formed



(III) (IV) (V) (X)

from a carbanion produced by a heterolytic fission of the carbon—cobalt bond. 2,4-Dimethyl-1-cyanobicyclo[2.2.2]octane (IV) was isolated as a minor product, suggesting that a non-acid catalysed insertion (discussed below) may also be operative.

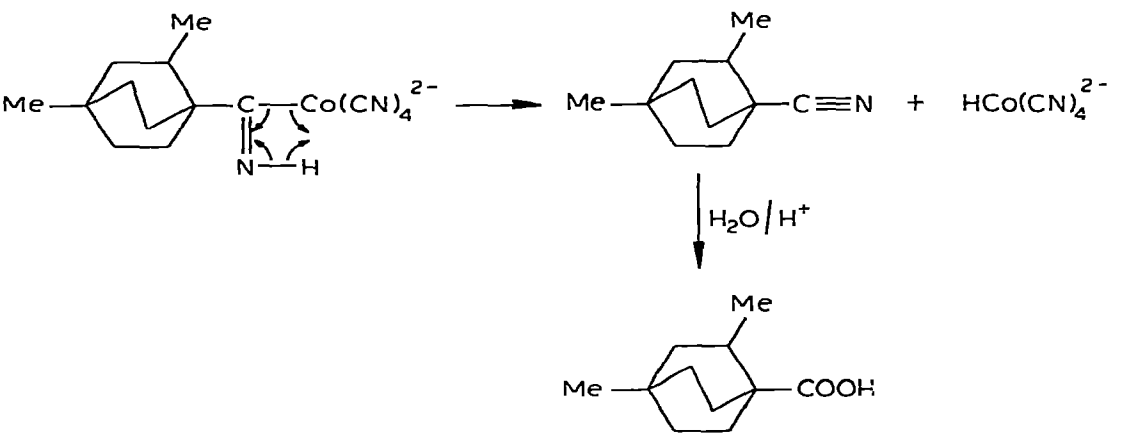
Compared to the methyl and pyridylmethyl analogues, the 1-bicyclo[2.2.2]-octyl complex (II) is less stable in acid medium. An aqueous solution (λ_{max} 280 nm) on acidification immediately develops a pinkish-red coloration (λ_{max} 292 nm) which changes again within minutes to a pale yellow solution (λ_{max} 271 nm), and ultimately decays more slowly to organic products, which consist of ca. 90% of 2,4-dimethyl-1-cyanobicyclo[2.2.2]octane (IV), ca. 10% of 2,4-dimethyl-1-carboxybicyclo[2.2.2]octane (V) and trace amounts of 1,3-dimethylbicyclo-[2.2.2]octane (III). This agrees with previous findings [6,7,9,18] that an acid-catalysed insertion of isonitrile is the main reaction pathway in acidic medium.



(VI)

Like the 1-adamantyl complex [10], but unlike the other non-bridgehead alkyl-pentacyanocobaltates [6,7,18], the isonitrile complex (VI) does not require base-catalysis for decomposition to organic products. The organic nitrile and carboxylic acid may be formed as shown in Scheme 2:

SCHEME 2



The formation of $HCo(CN)_4^{3-}$ is consistent with the air-sensitive nature of the inorganic product that was formed. Addition of base catalyses the decomposition to give organic nitrile.

Experimental

The NMR, IR and UV spectra were recorded on Hitachi—Perkin—Elmer R20B, Hilger and Watts Infrascan and Unicam SP700 instruments respectively. GLC was performed on a Varian Aerograph 1520 instrument using 10ft QF-1 and 20ft SE-30 columns.

Elemental analyses

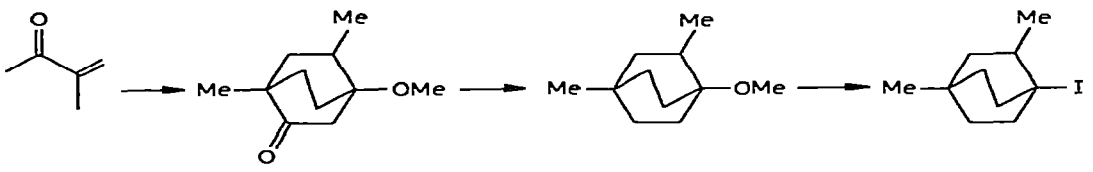
Sodium was analysed as potassium tetraphenylborate after conversion of

the complex to the potassium salt. Cobalt was analysed as $Co(SCN)_4^{2-}$ after decomposition of the complex in 0.1 *M* $HClO_4$ by UV irradiation. Other elemental analyses were performed by Mrs. H.K. Tong of the University of Singapore and the Australian Microanalytical Service of the University of Melbourne.

2,4-Dimethyl-1-iodobicyclo[2.2.2]octane

2,4-Dimethyl-1-iodobicyclo[2.2.2]octane was prepared by a multistep reaction sequence starting from methyl isopropenyl ketone (VII) (Scheme 3).

SCHEME 3



(VII) (VIII) (IX) (I)

Methyl isopropenyl ketone [19] was converted to (VIII) and then (IX), following earlier procedures [20].

2,4-Dimethyl-1-iodobicyclo[2.2.2]octane (I) was prepared from (IX) by the following procedure: To a stirred mixture of (IX) (4 g, 23.81 mmol) and acetyl iodide (13.8 g, 81.17 mmol) under nitrogen, was added 10 drops of stannic chloride. Initially there was a vigorous exothermic reaction. When this reaction subsided the mixture was refluxed for 4 h and then left at room temperature for a further 12 h. The mixture was stirred with 40 ml water and then extracted with 60-80 petroleum ether (6 × 10 ml). The combined ethereal extract was washed with saturated sodium bicarbonate, water and sodium thiosulphate and then dried over sodium sulphate. The solvent was removed and the residue distilled to give a colourless liquid, b.p. 63°/0.7 mm. (3.6 g, 11.36 mmol, 48% yield), $n_D^{23.5°}$ 1.5412. (Found: C, 45.28; H, 6.70; I, 48.02. $C_{10}H_{17}I$ calcd.: C, 45.47; H, 6,48; I, 48.04%.)

1,3-Dimethylbicyclo[2.2.2]octane(III)

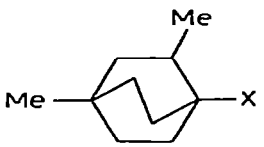
This was obtained by reduction of the iodide (I) by lithium in t-butanol. (Found: C, 87.02; H, 13.08. $C_{10}H_{18}$ calcd.: C, 86.87; H, 13.12%.) Mass spectrum M^+ *m/e* = 138.

1-(2,4-Dimethylbicyclo[2.2.2]octylpentacyanocobaltate(III)

To an aqueous methanolic solution of sodium pentacyanocobaltate(II) (prepared from 24.6 mmol $CoCl_2$ and 145.5 mmol NaCN in 110 ml H_2O and 200 ml MeOH) under nitrogen, was added 2,4-dimethyl-1-iodobicyclo[2.2.2]octane (3.13 g, 12.3 mmol) and the solution stirred 33 h at room temperature until ca. 5% of pentacyanocobaltate(II) was left. The solution was concentrated to ca. 10 ml at reduced pressure, and $K_3Co(CN)_6$ and $K_3Co(CN)_5I$ were precipitated out with methanol—acetone. Fractional crystallisation of the residue in methanol—acetone finally gave the bicyclo[2.2.2]octyl complex as a yellow crystalline solid (ca. 3.4 g, 7.2 mmol, 58% yield). (Found: Co, 12.67; Na, 14.53. $Na_3[C_{10}H_{17}Co(CN)_5] \cdot 4H_2O$ calcd.: Co, 12.61; Na, 14.76%.) $\tau(D_2O)$: 9.39 (s,

TABLE 1

CHARACTERISTIC NMR CHEMICAL SHIFTS[a] OF SOME 2,4-DIMETHYLBICYCLO[2.2.2]OCTANE COMPOUNDS



X	τ(4-Me)	τ(2-Me)[b]
H	9.28	9.07
I	9.28	8.76
CN	9.20	8.84
COOH	9.23	9.08
$Co(CN)_5$	9.39	8.75

[a] Solutions in CCl_4 with TMS as internal standard except for X = $Co(CN)_5$ in D_2O with DDS as internal standard. [b] Doublet, J = 7 Hz.

bridgehead CH_3), 8.75 (d, J = 7 Hz, CH_3), 7.5-9.2 (m, CH_2's) (Table 1). λ_{max} (H_2O) 280-281 nm (ϵ 1.29 × 10^4), λ_{min} (H_2O) 240-242 nm (ϵ 3.62 × 10^3). ν(CN) (cm^{-1}), 2072 vs, 2102 w(sh).

Product studies

Decomposition in dilute sulphuric acid. To the complex (0.11 mmol) dissolved in 0.3 ml water was added 0.3 ml 2 *M* H_2SO_4. A pinkish precipitate was formed. The mixture was left at room temperature for 2 h, after which the organic products were extracted into CCl_4 (5 × 2 ml). The spectrum of the concentrated extract indicated 0.05 mmol (ca. 50%) of total organic material, which was shown by GLC on a 10ft QF1 column to consist of 84% 2,4-dimethyl-1-cyanobicyclo[2.2.2]octane (IV) 9% 2,4-dimethyl-1-carboxybicyclo[2.2.2]-octane (V) and 7% 2,4-dimethyl-1-hydroxybicyclo[2.2.2]octane (X) and a trace of the hydrocarbon (III). (For characteristic NMR chemical shifts of these compounds see Table 1.) Extraction of the aqueous residue after basification with Na_2CO_3 provided another 0.05 mmoles of organic product shown by GLC to consist of more than 90% of the nitrile (IV), the rest being the acid (V).

A larger scale decomposition of the complex (0.15 mmol) in 0.5 *M* H_2SO_4 gave again 90% nitrile (IV) and 10% acid (V), both of which were separated by GLC for analysis and identification. The nitrile (IV) showed ν(CN) 2220 cm^{-1}. Mass spectrum: found M^+ = 163.1360 (calcd. 163.13609). The acid (V) had m.p. 97-98.5°, ν(CN) 2500-3600 (vbr) and 1708 vs cm^{-1}. Mass spectrum: found M^+ = 182.13059 (calcd. 182.13067).

Decomposition in water. The complex (0.1 mmol) was dissolved in 0.3 ml water and left at 70-90° for 2 h. The organic products after extraction into ether were shown by GLC and NMR to contain mainly 1,3-dimethylbicyclo-[2.2.2]octane (III) (50% yield) and the nitrile (IV) (< 5% yield).

Decomposition in dilute sodium carbonate. The complex (0.2 mmol) dissolved in 4 ml 0.5 *M* Na_2CO_3 was left at 60-70° for 5 days, and then extracted with ether. GLC of the concentrated ethereal extracts indicated the presence of

(III) (0.06 mmol, 30%) and (IV) (0.05 mmol, 25%). A repeated decomposition experiment gave (III)/(IV) ratio of 3/2.

Acknowledgements

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