

## 1-ADAMANTYLPENTACYANOCOBALTATE(III)

S. R. GOR and LAI-YOUNG GOR

Department of Chemistry, University of Malaya, Kuala Lumpur (Malaysia)

(Received April 11th, 1972)

### SUMMARY

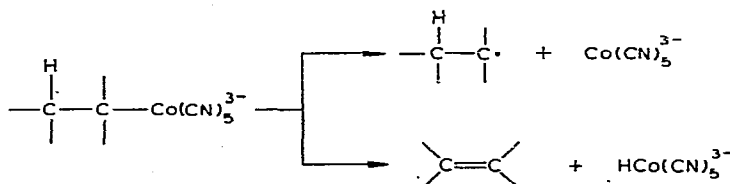
The preparation and properties of potassium 1-adamantylpentacyanocobaltate(III) trihydrate are described.

### INTRODUCTION

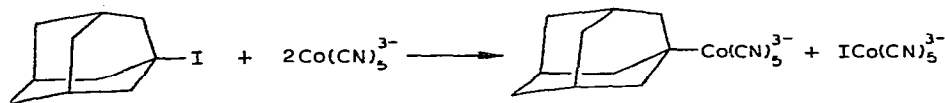
The chemistry of  $\sigma$ -bonded organocobalt complexes has recently attracted considerable attention<sup>1</sup>. This is due partly to interest in the chemistry of vitamin B<sub>12</sub>; a number of simple chemical analogs of this compound in fact have been synthesized<sup>2,3</sup>. Since the first preparation of methylpentacyanocobaltate(III) a number of analogous alkyl complexes have been described<sup>4</sup>. Of these the more stable ones are bonded directly to  $sp^2$  carbon centres or to primary alkyl centres, especially those carrying a stabilizing cyano, carbonyl or aryl group<sup>4-7</sup>. The present paper describes the preparation and properties of a stable pentacyanocobaltate complex which is bonded to a tertiary carbon centre.

### RESULTS AND DISCUSSION

Previous work<sup>5,6</sup> has demonstrated that the non-acid-catalysed decomposition of alkylpentacyanocobaltates occurs by the following pathways. If the alkyl group is a bridgehead carbon centre, these modes of decomposition will be



rendered difficult. One such compound, 1-adamantylpentacyanocobaltate, was prepared by the reaction of excess 1-adamantyl iodide with potassium pentacyanocobaltate. The air-stable complex was isolated in 44% yield as yellow crystals; analysis, NMR, IR and UV spectra obtained were consistent with the structure.



The compound is stable in neutral or alkaline solutions and its stability is comparable with that of methyl and (pyridylmethyl)pentacyanocobaltates<sup>4,5</sup>. It may be noted that the analogous tert-butyl complex is too unstable to be isolated. The stability of the 1-adamantyl derivative is due to the fact that bond cleavage will lead to a bridgehead radical which is known to be unstable<sup>9,10</sup> or an olefin at a bridgehead position which is considerably strained<sup>11,12</sup>. Recently, Bower and Tennent<sup>13</sup> also reported the preparation of some exceptionally stable transition metal bicyclo[2.2.1]hept-1-yls.

The complex is however easily decomposed by acid catalysis; an aqueous solution ( $\lambda_{\max}$  285 nm) on acidification immediately assumes a red coloration ( $\lambda_{\max}$  300 nm), which then rapidly changes to a green solution ( $\lambda_{\max}$  270 nm) and finally decays to give organic products, 1-adamantyl cyanide and 1-adamantanol. These changes are consistent with earlier findings<sup>5,6,8</sup> that protonation and cyanide insertion have taken place. Decomposition in neutral or slightly alkaline solutions is very much slower and gives adamantane and 1-adamantanol probably by heterolytic cleavage.

#### EXPERIMENTAL

The NMR, IR and UV spectra were recorded on Hitachi Perkin Elmer R20B, Hilger and Watts Infracan and Beckman DBG instruments respectively. GLC was performed on a Varian Aerograph 1520 instrument using 2ft. QF-1 and 3ft. SE-30 columns.

#### Preparation of 1-adamantylpentacyanocobaltate

To a solution of 1-adamantyl iodide<sup>14</sup> (2.3 g, 8.8 mmol) in 100 ml of methanol was added under nitrogen an aqueous solution of potassium pentacyanocobaltate (70 ml, 9.5 mmol) and the mixture was stirred for 20 h. On cooling, the excess organic iodide and unreacted  $\text{K}_6\text{Co}_2(\text{CN})_{10}$  were removed by filtration. On concentration to ca. 10 ml,  $\text{K}_3\text{Co}(\text{CN})_6$  and  $\text{K}_3\text{Co}(\text{CN})_5\text{I}$  were precipitated out. After the addition of methanol the adamantyl complex fractionally crystallized out as yellow crystals,  $\text{K}_3[\text{C}_{10}\text{H}_{15}\text{Co}(\text{CN})_5] \cdot 3\text{H}_2\text{O}$  (ca. 1 g, 2.1 mmol, 44% yield). (Found: Co, 11.8, K, 23.3.  $\text{C}_{15}\text{H}_{21}\text{CoK}_3\text{N}_5\text{O}_3$  calcd.: Co, 11.89, K, 23.67%).  $\tau$  ( $\text{D}_2\text{O}$ ) 7.58 (6 H, broad s) and 8.27 (9 H, broad s).  $\lambda_{\max}$  ( $\text{H}_2\text{O}$ ) 288 nm ( $\epsilon$   $1.65 \times 10^4$ ).  $\nu(\text{CN})$  2075 vs, 2090 w and 2105 w  $\text{cm}^{-1}$ .

#### Decomposition products

The complex (0.2 mmol) dissolved in water, 0.5 M sulphuric acid and 0.5 M sodium carbonate, respectively, was kept at 40° for 40 h. The organic products were extracted into ether and analyzed by GLC to give the following results:

- from water, 52% adamantane and 48% 1-adamantanol;
- from dilute sulphuric acid, 6% adamantane, 70% 1-adamantyl cyanide and 10% 1-adamantanol;
- from dilute sodium carbonate 57% adamantane and 43% 1-adamantanol.

## REFERENCES

- 1 J. Halpern, *Accounts Chem. Res.*, 3 (1970) 386.
- 2 G. N. Schrauzer, *Accounts Chem. Res.*, 1 (1968) 97.
- 3 A. Van Den Bergen, K. S. Murray and B. O. West, *J. Organometal. Chem.*, 33 (1971) 89.
- 4 J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, 87 (1965) 5361; 86 (1964) 2311.
- 5 M. D. Johnson, M. L. Tobe and Lai-Yoong Wong, *J. Chem. Soc. A*, (1967) 491; (1968) 923, 929.
- 6 J. Kwiatek, *Catal. Rev.*, 1 (1967) 37.
- 7 J. Halpern and Lai-Yoong Wong, *J. Amer. Chem. Soc.*, 90 (1968) 6665.
- 8 J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, 3 (1965) 421; 3 (1965) 433.
- 9 R. C. Fort and R. E. Franklin, *J. Amer. Chem. Soc.*, 90 (1968) 5266.
- 10 W. H. Chick and S. H. Ong, *J. Chem. Soc. D*, (1969) 216.
- 11 R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, 10 (1971) 262.
- 12 J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, 92 (1970), 948; J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, 92 (1970) 956.
- 13 B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 94 (1972) 2512.
- 14 R. C. Fort and P. v. R. Schleyer, *J. Org. Chem.*, 30 (1965) 789; P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 83 (1961) 2700.

*J. Organometal. Chem.*, 43 (1972)