

## Preliminary communication

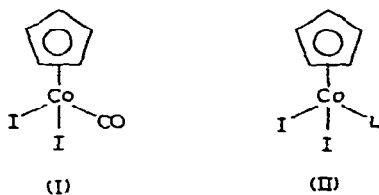
### Cyclopentadienyliodobis(imidazole)cobalt(III) iodide

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In connection with a search for synthetic routes to aza-heterocyclic analogues of the metallocenes, we have had occasion to investigate the reaction of cyclopentadienyliodobis(imidazole)cobalt(III) carbonyl with a series of heterocyclic nitrogen bases.



(a, L = imidazole; b, L = pyrazole; c, L = benzimidazole; d, L = indazole; e, L = benzotriazole)

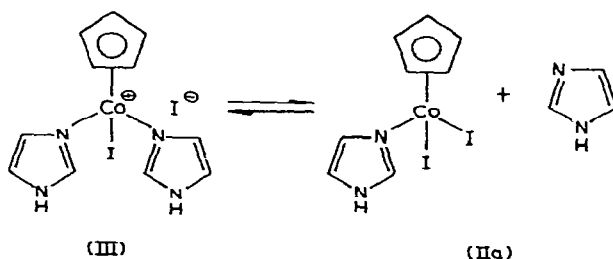
The green crystalline air-stable complexes (Ia-e) were prepared in high yield (see Table 1) by the reaction of equimolar proportions of carbonyl (I) and the appropriate heterocycle in methylene chloride at room temperature. Satisfactory analyses for C, H, Co, I, and N were obtained. The progress of the reaction was followed by monitoring the disappearance of the characteristic IR carbonyl absorption of (I)<sup>1</sup>. Formation of compounds (IIb-e) was essentially complete within 30-90 min. Although indazole and

TABLE I  
 MELTING POINTS AND YIELDS OF THE NEW COMPLEXES

| Compound | m.p.<br>(°C)   | Yield<br>(%) |
|----------|----------------|--------------|
| (IIa)    | 146-147        | 80           |
| (IIb)    | 137-138        | 72           |
| (IIc)    | 127-129        | 89           |
| (IId)    | 178-180        | 78           |
| (IIe)    | 170-180 (dec.) | 62           |

benzotriazole have two non-equivalent potential basic centres, no evidence for isomerism was detected in complexes (II<sub>d</sub>) and (II<sub>e</sub>).

The reaction of carbonyl (I) with imidazole followed an anomalous pattern. Although evolution of carbon monoxide was initially rapid, it thereafter became extremely slow and formation of (II<sub>a</sub>) was not complete until five hours had elapsed. If the reaction mixture was filtered immediately after mixing the reactants a violet-black crystalline complex (III), m.p. 128–129° was isolated. Microanalytical data for (III) were in agreement with an empirical formula of  $C_5H_5Co(C_2H_3N_2)_2I_2$ : (Found: C, 26.06; H, 2.58; Co, 11.19; I, 49.72; N, 10.77. Calc.: C, 25.71; H, 2.55; Co, 11.47; I, 49.39; N, 10.91%). Yield 46% based on (I). Work-up of the filtrate yielded unreacted (I) (50%). Compound (III) was insoluble in non-polar solvents, sparingly soluble in methylene chloride and extremely soluble in water to give a violet solution. The yield of (III) was increased to 90% if a 2/1 ratio of imidazole to (I) was employed. The above data is consistent with the formulation of compound (III) as the iodide salt of the cyclopentadienyliodobis(imidazole)-cobalt(III) cation.



Several cationic six-coordinate cyclopentadienyliodobis(imidazole)cobalt(III) complexes of formula  $[C_5H_5Co(LL)_2I]^+$  are known<sup>1,2</sup> where (LL) is a bidentate chelating ligand. To our knowledge compound (III) is the first example of such a complex involving monodentate ligands alone. The unusual reactivity of imidazole may be related to the fact that it is a stronger base<sup>3</sup> and more powerful nucleophile than the other heterocycles employed in this work.

The monoimidazole complex (II<sub>a</sub>) reacted with one equivalent of imidazole in methylene chloride to give (III) in quantitative yield. Complex (II<sub>a</sub>) may, therefore, be an intermediate in the formation of (III) under our original conditions. If the bis-imidazole complex (III) was stirred in suspension with a methylene chloride solution of one equivalent of carbonyl iodide (I) slow redistribution of the imidazole ligand took place and after ca. five hours, the mono-imidazole complex (II<sub>a</sub>) was isolated in 95% yield. In the absence of carbonyl (I) some 75% of (III) was recovered by filtration. The filtrate contained neutral (II<sub>a</sub>) and other products as yet unidentified. Shaking an aqueous solution of (III) (acidified with dilute sulphuric acid) with methylene chloride also produced (II<sub>a</sub>) although in poor yield. We feel that these reactions are best understood if cationic (III) is assumed to exist in solution in equilibrium with neutral (II<sub>a</sub>) and free imidazole. In the presence of a reagent which can irreversibly bind imidazole (*i.e.* carbonyl (I) or acid) or in solutions such as methylene chloride in which the ionic (III) is virtually insoluble — the equilibrium can be forced in either direction.

The molar conductance of the monoimidazole complex (Ia) (measured at  $10^{-3}$  molar solution in acetone) is  $3.9 \text{ mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$  which agrees well with the value of  $4 \text{ mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$  found by King<sup>1</sup> for the related non-ionic  $\text{C}_5\text{H}_5\text{Co(Py)}_2$ , (Py = Pyridine) in the same solvent. Complex (III) ( $10^{-3}$ – $10^{-4}$  molar in acetone) has a molar conductance of  $\sim 100 \text{ mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$ . This value is low compared to the molar conductance of  $[\text{C}_5\text{H}_5\text{Co}(o\text{-Phenanthroline})\text{I}]^+\text{I}^-$  in acetone which is  $185 \pm 20 \text{ mho} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$  for the same concentration range<sup>1</sup>. A low value for the molar conductance of (III) would be expected, if, as indicated by the chemical evidence, it exists in equilibrium with neutral (Ia) under the conditions of measurement.

The sequence of reactions outlined above suggests a potential route to novel cyclopentadienylcobalt(III) complexes of the type  $[\text{C}_5\text{H}_5\text{CoI(L)L}']^{0 \text{ or } +1}$  containing a pseudo-tetrahedral asymmetric cobalt centre. This possibility, together with a kinetic investigation of the reactions of (III) is currently being explored.

#### REFERENCES

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