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π-CYCLOPENTADIENYL—COBALT COMPLEXES CONTAINING ISOCYANIDE LIGANDS

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Summary

The preparation of neutral, cationic and dicationic π-cyclopentadienyl—cobalt complexes which also contain isocyanide ligands is reported. These include $CpCo(CNR)I_2$, $[CpCo(CNR)_2I]PF_6$ and $[CpCo(CNR_3](PF_6)_2$ (Cp = π-cyclopentadienyl, R = C_6H_4OMe-*p* or Me), and the other new complexes reported have been derived from these by replacement of one or more of the isocyanide groups with other carbon-, nitrogen- or phosphorus-donor ligands. The infrared and NMR spectra of these new compounds are reported and some of their reactions have been explored.

Introduction

π-cyclopentadienyl complexes of manganese, iron and nickel which also contain isocyanide ligands have been known for some time. Examples of such complexes include $CpMn(CNPh)_3$ [1], $CpFe(CNPh)_2I$ [2] and $[CpNi(CNPh)]_2$ [1]. However no cobalt complexes of this type have ever been reported*.

More recently, the reactivity of such complexes has been studied and it has been shown, for example, that $CpFe(CNR)_3^+$ reacts with methylamine, giving the amidinium complex [3] $CpFe(CNR)_2[C(NHMe)NHR]^+$, while $[CpFe(CO)(CNMe)_2]^+$ reacts with the strong nucleophile C_6F_5Li giving the imino—metal complex [4] $CpFe(CO)(CNMe)[C(C_6F_5){=}NMe]$.

It seemed of interest therefore to attempt the preparation of related cobalt complexes for comparative purposes, and in this paper we report the synthesis of a variety of such complexes, including neutral, monopositively and dipositively charged species.

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* Since the completion of the experimental work described in this paper, the preparation of $CpCo(CNC_6H_5)_3^{2+}$ by alkylation of $CpCo(CN)_3$ has been reported [18].

Results and discussion

(a). Preparation of complexes

The complex $CpCo(CO)I_2$ reacts readily with ligands (L) such as Ph_3P or pyridine at room temperature to give derivatives of the type $CpCo(L)I_2$, in which the CO group has been replaced by the ligand L [5,6]. We find that isocyanide ligands react similarly in dichloromethane solution giving the complexes $CpCo(CNR)I_2$ [R = C_6H_4OMe-*p* or Me] in high yield. These are brown, air-stable, crystalline compounds which we have used as starting materials for the preparation of a range of cationic isocyanide-containing derivatives. Relative to the carbonyl ligand in $CpCo(CO)I_2$, the isocyanide ligand in $CpCo(CNR)I_2$ is far less easily displaced by other neutral 2-electron donor ligands and, where reaction with such ligands takes place, it invariably leads to the displacement of one or both of the iodide ions rather than of the isocyanide group. Thus addition of an excess of RNC (R = *p*-$MeOC_6H_4$ or Me) to $CpCo(CNR)I_2$ in dichloromethane solution leads to the formation of $[CpCo(CNR)_2I]I$ which crystallises out on partial evaporation of the solvent. The ionic nature of these complexes is confirmed by conductivity measurements in nitromethane solution. In general the reaction:

$$CpCo(CNR)I_2 + L \rightleftharpoons [CpCo(CNR)(L)I]\,I \qquad (1)$$

reaches an equilibrium position in solution which, for L = organophosphine or isocyanide, lies well to the right (as shown by solution infrared spectra). On the other hand for L = THF or MeCN the equilibrium lies well to the left and indeed no infrared bands which could be attributed to the species $[CpCo(CNR)(L)I]^+$ were observed. It should be noted in this context, however, that both THF and MeCN catalyse the reaction of $CpCo(CNR)I_2$ with $AgPF_6$ in dichloromethane solution (vide infra), and the formation of $[CpCo(CNR)(L)I]I$ (L = THF or MeCN) may well be the first step in this reaction.

Addition of a dichloromethane solution of $AgPF_6$ to solutions of the complexes $CpCo(CNR)I_2$ helps to displace the equilibrium (1) completely over to the right and, by this means, we have been able to prepare a wide range of complexes of the type $[CpCo(CNR)(L)I]PF_6$ (see Table 1). They are dark brown or green crystalline materials which are quite stable in air in the solid state. All are moderately soluble in acetone, nitromethane and dichloromethane (except $[CpCo(CNMe)_2I]I$ which is only slightly soluble) and these solutions are stable in air for long periods. The complexes are slightly soluble or insoluble in water.

Although the complex cations $[CpCo(CNR)(L)I]^+$ are, in general, the predominant species present in solution, the ligands in these cations are quite labile and can rearrange readily. Thus evaporation of a solution of $[CpCo(CNR)(PPh_3)I]I$ (a complex which can be isolated as its PF_6^- salt) leads to the crystallisation of $[CpCo(CNR)_2I]I$, even though this latter complex cannot be detected in solution by infrared spectroscopy.

In a few cases this rearrangement takes place to a significant extent even in solution and, e.g., the attempted preparation of $[CpCo(CNMe)(CNC_6H_4$-

TABLE 1

MICRO-ANALYTICAL DATA[a]

	C	H	N	P
CpCo(CNC$_6$H$_4$OMe-*p*)I$_2$	30.77 (30.56)	2.35 (2.37)	2.67 (2.74)	
[CpCo(CNC$_6$H$_4$OMe-*p*)$_2$I]I	39.40 (39.16)	3.25 (2.97)	4.20 (4.35)	
[CpCo(CNC$_6$H$_4$OMe-*p*)$_2$I]PF$_6$	37.91 (38.09)	3.08 (2.89)	4.39 (4.23)	4.50 (4.68)
[CpCo(CNC$_6$H$_4$OMe-*p*)(PPh$_3$)I]PF$_6$	46.97 (47.05)	3.71 (3.44)	1.92 (1.77)	7.85 (7.83)
[CpCo(CNC$_6$H$_4$OMe-*p*)(PPh$_2$Me)I]PF$_6$	43.04 (42.82)	3.36 (3.46)	1.72 (1.92)	8.25 (8.49)
[CpCo(CNC$_6$H$_4$OMe-*p*)(PPhMe$_2$)I]PF$_6$	37.45 (37.80)	3.29 (3.47)	2.32 (2.10)	8.93 (9.28)
[CpCo(CNC$_6$H$_4$OMe-*p*)(C$_5$H$_5$N)I]PF$_6$	35.46 (35.55)	2.82 (2.82)	4.88 (4.61)	5.25 (5.09)
[CpCo(CNC$_6$H$_4$OMe-*p*)(CO)I]PF$_6$	30.56 (30.19)	2.49 (2.17)	2.89 (2.51)	5.43 (5.56)
[CpCo(CNC$_6$H$_4$OMe-*p*)$_3$](PF$_6$)$_2$	43.09 (42.82)	3.32 (3.22)	5.09 (5.17)	7.94 (7.62)
[CpCo(CNC$_6$H$_4$OMe-*p*)$_2$(PPh$_3$)](PF$_6$)$_2$	49.75 (49.70)	3.81 (3.64)	2.86 (2.97)	9.75 (9.86)
[CpCo(CNC$_6$H$_4$OMe-*p*)(Diphos)](PF$_6$)$_2$	49.61 (49.54)	3.89 (3.84)	1.44 (1.48)	12.84 (13.10)
[CpCo(CNC$_6$H$_4$OMe-*p*)(Bipy)](PF$_6$)$_2$	38.92 (39.28)	2.94 (2.87)	6.06 (5.97)	8.62 (8.81)
[CpCo(CNC$_6$H$_4$OMe-*p*)$_2$(CNMe)](PF$_6$)$_2$	38.86 (38.30)	3.29 (3.07)	5.77 (5.83)	8.00 (8.59)
CpCo(CNMe)I$_2$	20.33 (20.07)	1.86 (1.93)	3.79 (3.34)	
[CpCo(CNMe)$_2$I]I	23.65 (23.50)	2.42 (2.41)	5.77 (6.09)	
[CpCo(CNMe)$_2$I]PF$_6$	22.59 (22.60)	2.52 (2.32)	6.14 (5.86)	6.69 (6.48)
[CpCo(CNMe)(PPh$_3$)I]PF$_6$	42.93 (42.94)	3.38 (3.32)	2.06 (2.00)	8.91 (8.86)
[CpCo(CNMe)(PPh$_2$Me)I]PF$_6$	37.18 (37.70)	3.29 (3.32)	2.23 (2.20)	9.48 (9.72)
[CpCo(CNMe)(C$_5$H$_5$N)I]PF$_6$	28.19 (27.93)	2.64 (2.54)	5.53 (5.43)	6.22 (6.00)
[CpCo(CNMe)(CO)I]PF$_6$	20.89 (20.67)	1.82 (1.73)	3.19 (3.01)	6.79 (6.66)
[CpCo(CNMe)$_3$](PF$_6$)$_2$	24.80 (24.60)	2.91 (2.63)	7.40 (7.82)	11.36 (11.53)
[CpCo(CNMe)$_2$(PPh$_3$)](PF$_6$)$_2$	42.84 (42.76)	3.59 (3.46)	3.82 (3.69)	12.32 (12.25)
[CpCo(CNMe)(Diphos)](PF$_6$)$_2$	46.18 (46.44)	3.72 (3.78)	1.61 (1.64)	14.29 (14.52)
[CpCo(CNMe)(Bipy)](PF$_6$)$_2$	33.30 (33.41)	2.58 (2.64)	7.05 (6.88)	10.00 (10.14)
Co(CNC$_6$H$_4$OMe-*p*)$_4$I$_2$	45.24 (45.47)	3.38 (3.34)	6.53 (6.63)	
Co(CNMe)$_4$I$_2$	19.18 (20.15)	2.89 (2.54)	10.52 (11.75)	
CpCo(CNC$_6$H$_4$OMe-*p*)(SnCl$_3$)$_2$	21.18 (22.08)	1.79 (1.71)	1.70 (1.98)	

[a] Found(calcd.)(%).

OMe-*p*)I]$^+$ in dichloromethane solution, by addition of *p*-MeOC$_6$H$_4$NC to CpCo(CNMe)I$_2$, leads only to a mixture of [CpCo(CNMe)$_2$I]$^+$ and CpCo(CNC$_6$H$_4$OMe-*p*)$_2$I]$^+$ being obtained. Of these two complexes [CpCo(CNMe)$_2$I]$^+$ is the least soluble and crystallises out as its PF$_6^-$ salt on concentration of the solution. The complex cations [CpCo(CNR)$_2$I]$^+$ (R = C$_6$H$_4$-OMe-*p* or Me) can also be crystallised from dichloromethane solutions of CpCo(CNR)I$_2$ by addition of AgPF$_6$ alone.

Another case in which the complex $[CpCo(CNR)(L)I]^+$ is unstable in solution is when L = CO. CO loss from this complex takes place most readily in polar solvents, suggesting perhaps that the solvent actually participates in the reaction. In acetone, for example, the initially green solution of $[CpCo(CNR)(CO)I]PF_6$ can be observed to effervesce and, at the same time, the formation of $[CpCo(CNR)_2I]PF_6$ can be monitored by NMR spectroscopy. However if a solution of $[CpCo(CNR)_2I]PF_6$ is saturated with CO then, as seen from solution infrared spectra, $[CpCo(CNR)(CO)I]PF_6$ is generated. The ease with which these mixed carbonyl—isocyanide complexes of cobalt undergo rearrangement may be contrasted with the relative stability of similar complexes of iron and manganese such as CpFe(CNR)(CO)CN [7], $[CpFe(CNR)_2CO]^+$ [7] and $Mn(CNPh)_3(CO)_2Br$ [2] which appear not to rearrange in solution.

We have not investigated the mechanism of these disproportionation reactions in any detail, but it is noteworthy that the equilibrium (2) is established rapidly from either direction.

$$[CpCo(CNR)(PPh_3)I]^+ + RNC \rightleftharpoons CpCo(CNR)_2I^+ + PPh_3 \qquad (2)$$

This suggests that the presence of low concentrations of free RNC could be responsible for the formation of the cations $[CpCo(CNR)_2I]^+$ from complex cations of the type $[CpCo(CNR)(L)I]^+$. This free RNC could arise either by solvent attack on these latter complexes or via the formation of dimeric species with Co—I—Co bridges. No free isocyanide could, however, be detected in solution by either infrared or NMR spectroscopy.

Naturally in rearrangements of complexes of the type $[CpCo(CNR)(L)I]^+$ another species must be formed in solution apart from $[CpCo(CNR)_2I]^+$, although in no case have we been able to isolate a second product. However, e.g. for L = CO, a π-cyclopentadienyl ^1H NMR resonance at τ 4.1 ppm (deuterioacetone solution) due to this unidentified product appears simultaneously with that due to $[CpCo(CNR)_2I]^+$ as rearrangement takes place.

Treatment of acetone solutions of the complexes $[CpCo(CNR)_2I]PF_6$ with an excess of RNC does not cause any colour change, suggesting that the equilibrium (3) lies well to the left in the absence of $AgPF_6$.

$$[CpCo(CNR)_2I]^+ + CNR \rightleftharpoons [CpCo(CNR)_3]^{2+} + I^- \qquad (3)$$

On addition of a further mole of $AgPF_6$, however, the colour of the solutions change from dark brown to orange or yellow and, on addition of diethyl ether, the complexes $[CpCo(CNR)_3][PF_6]_2$ crystallise out. They may alternatively be prepared directly from $CpCo(CO)I_2$ in dichloromethane solution by addition of RNC in a 3/1 molar ratio followed by 2 moles of $AgPF_6$. Although King [6] has previously reported that addition of 2,2′,2″-terpyridyl to a solution of $CpCo(CO)I_2$ gives an orange-brown precipitate which he claimed to be an impure sample of $[CpCo(C_{15}H_{11}N_3)]I_2$, these isocyanide complexes are, to our knowledge, the first well-characterised dicationic mononuclear complexes containing a cyclopentadienyl ligand to have been reported*. Their for-

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*See footnote on page 137.

TABLE 2

MOLAR CONDUCTIVITIES[a] (ohm^{-1} · cm^{2} · mole^{-1})

	R = C_6H_4OMe-*p*	R = Me
$CpCo(CNR)I_2$	4	4
$[CpCo(CNR)_2I]I$	76	91
$[CpCo(CNR)_2I]PF_6$	88	96
$[CpCo(CNR)(PPh_3)I]PF_6$	84	87
$[CpCo(CNR)(PPh_2Me)I]PF_6$	89	94
$[CpCo(CNR)(PPhMe_2)I]PF_6$	86	
$[CpCo(CNR)(CO)I]PF_6$	85	89
$[CpCo(CNR)(C_5H_5N)I]PF_6$		93
$[CpCo(CNR)_3](PF_6)_2$	187	205
$[CpCo(CNR)_2(PPh_3)](PF_6)_2$	174	197
$[CpCo(CNR)(Diphos)](PF_6)_2$	161	169
$[CpCo(CNR)(Bipy)](PF_6)_2$	160	214
$[CpCo(CNC_6H_4OMe$-*p*$)_2(CNMe)](PF_6)_2$	170	

[a] The conductivities were measured in nitromethane at about 10^{-3} molar concentrations and the values obtained correspond to those expected for 1/1 and 2/1 electrolytes [24]. Allowance was made for the conductivity of the solvent.

mulation as dications is supported by the conductivity data given in Table 2. Their existence as relatively stable complexes is in accord with the known ability of isocyanide ligands, as compared to carbon monoxide, to stabilise relatively high as well as low oxidation states of transition metals [8]. By similar routes we have prepared from $[CpCo(CNR)_2I]PF_6$ the mixed complexes $[CpCo(CNR)_2L](PF_6)_2$ (RNC = *p*-$MeOC_6H_4NC$; L = MeNC, Ph_3P or CO; RNC = MeNC; L = Ph_3P), and from $CpCo(CNR)I_2$ the complexes $[CpCo(CNR)(Diphos)](PF_6)_2$ [Diphos = 1,2-bis(diphenylphosphino)ethane] (Table 1). The analogous 2,2′-bipyridine (Bipy) complexes could not be synthesized in this manner but were obtained from the reaction of [CpCo(Bipy)I]I [6] with one mole of RNC in the presence of two moles of $AgPF_6$.

Some of these dicationic complexes rearrange in solution and e.g. deuterioacetone solutions of $[CpCo(CNC_6H_4OMe$-*p*$)_2(CNMe)]^{2+}$ show additional cyclopentadienyl resonances in their NMR spectra after only a few minutes, which may be assigned to the rearranged products $[CpCo(CNC_6H_4OMe$-*p*$)_3]^{2+}$ and $[CpCo(CNMe)_3]^{2+}$. Equilibrium is established rapidly and there is then no further change in the NMR spectra over a period of several hours. Surprisingly there is no evidence for the formation of $[CpCo(CNC_6H_4OMe$-*p*$)(CNMe)_2]^{2+}$ as a component of the equilibrium mixture. The complex $[CpCo(CNC_6H_4 \cdot OMe$-*p*$)_2(CO)]^{2+}$ rearranges particularly rapidly, and we were unable to prepare an analytically pure sample. The crude yellow product obtained by rapid evaporation of the reaction mixture showed an infrared band at 2161 cm^{-1} attributable to the presence of a CO group. However, recrystallisation of this crude product from dichloromethane solution gave only $[CpCo(CNC_6H_4$-OMe-*p*$)_3](PF_6)_2$. In the case of the analogous MeNC complex not even an impure product could be obtained. This low stability of the carbonyl-containing dicationic species is presumably a result of the rather low electron density at the cobalt atom, which would not favour back-donation from the metal to the CO group.

TABLE 3

INFRARED DATA[a]

	Nujol mull	Dichloromethane solution
$CpCo(CNC_6H_4OMe\text{-}p)I_2$	2144	2177
$[CpCo(CNC_6H_4OMe\text{-}p)_2I]I$	2194, 2180	2209, 2197
$[CpCo(CNC_6H_4OMe\text{-}p)_2I]PF_6$	2203, 2191	2207, 2198
$[CpCo(CNC_6H_4OMe\text{-}p)(PPh_3)I]PF_6$	2198	2188
$[CpCo(CNC_6H_4OMe\text{-}p)(PPh_2Me)I]PF_6$	2187	2183
$[CpCo(CNC_6H_4OMe\text{-}p)(PPhMe_2)I]PF_6$	2181	2180
$[CpCo(CNC_6H_4OMe\text{-}p)(C_5H_5N)I]PF_6$	2184	2197
$[CpCo(CNC_6H_4OMe\text{-}p)(CO)I]PF_6$	2215, 2126, 2114	2217, 2117
$[CpCo(CNC_6H_4OMe\text{-}p)_3](PF_6)_2$	2226(br)	2222(br)
$[CpCo(CNC_6H_4OMe\text{-}p)_2(PPh_3)](PF_6)_2$	2213, 2202	2206
$[CpCo(CNC_6H_4OMe\text{-}p)(Diphos)](PF_6)_2$	2190	2191
$[CpCo(CNC_6H_4OMe\text{-}p)(Bipy)](PF_6)_2$	2212	2222
$[CpCo(CNC_6H_4OMe\text{-}p)_2(CNMe)](PF_6)_2$	2276, 2225(br)	2274, 2224
$[CpCo(CNC_6H_4OMe\text{-}p)_2(CO)](PF_6)_2$	2237, 2161	
$CpCo(CNMe)I_2$	2231, 2218(sh)	2224
$[CpCo(CNMe)_2I]I$	2248	2253, 2246
$[CpCo(CNMe)_2I]PF_6$	2255(br)	2253(br)
$[CpCo(CNMe)(PPh_3)I]PF_6$	2226	2243, 2236
$[CpCo(CNMe)(PPh_2Me)I]PF_6$	2247	2234
$[CpCo(CNMe)(C_5H_5N)I]PF_6$	2238	2248
$[CpCo(CNMe)(CO)I]PF_6$	2275, 2113, 2102	2268, 2114
$[CpCo(CNMe)_3](PF_6)_2$	2289, 2279, 2273	2270[b]
$[CpCo(CNMe)_2(PPh_3)](PF_6)_2$	2267, 2261	2262, 2255
$[CpCo(CNMe)(Diphos)](PF_6)_2$	2249	2245
$[CpCo(CNMe)(Bipy)](PF_6)_2$	2276	2268[b]
$Co(CNC_6H_4OMe\text{-}p)_4I_2$	2175	2179
$Co(CNMe)_4I_2$	2228	2226
$CpCo(CNC_6H_4OMe\text{-}p)(SnCl_3)_2$	2181	2173
$p\text{-}MeOC_6H_4NC$		2128
MeNC		2165

[a] All values are in cm^{-1}: sh shoulder, b broad. [b] In nitromethane.

(b). Infrared and NMR spectra

Infrared data for the new complexes in the 2000 cm^{-1} region are presented in Table 3. The bands observed may be assigned to ν(NC) and are raised in frequency by about 50 - 100 cm^{-1} from the free ligand value.

Similar results have been obtained previously for e.g. the series of cationic platinum complexes $[PtXL_2(CNR)]^+$ (X = halogen, L = organophosphine) and were taken as indicating that the isocyanide ligand is effective in reducing the positive charge on the platinum atom, this then leading to an increase in the CN bond order [9]. It might also be taken as supporting the suggestion that back-donation from the *d*-orbitals of the metal to the CNR group is relatively unimportant compared to e.g. the series of cationic complexes $[M(H)(CNR)(Depe)_2]^+$ (M = Fe, Ru or Os; R = C_6H_4OMe-*p* or CMe_3) in which ν(NC) is lowered by as much as 100 cm^{-1} from the free ligand value (in the case of the iron complexes) [10]. A comparison of the values for individual complexes is probably not very informative in view of the varying symmetry and number of isocyanide ligands present. It is noteworthy, however, that in any two closely related complexes such as $[CpCo(CNR)(CO)I]^+$ and $[CpCo(CNR)(PPh_3)I]^+$ the value of ν(NC) reflects the relative π-acceptor abilities of the other ligands present (as deduced from other infrared studies [11]), and is higher for the CO than the Ph_3P complex in this particular case. The dicationic species in general

TABLE 4

NMR DATA[a]

	R = C_6H_4OMe-*p*		R = Me	
	τC_5H_5	τMeO	τC_5H_5	τMeNC
$CpCo(CNR)I_2$	4.40	6.13	4.55	6.15
$[CpCo(CNR)_2I]I$	3.78[b]	6.18[b]	4.03	6.22
$[CpCo(CNR)_2I]PF_6$	3.70	6.15	3.94	6.19
$[CpCo(CNR)(PPh_3)I]PF_6$	4.06	6.17	4.23	6.52
$[CpCo(CNR)(PPh_2Me)I]PF_6$	4.03	6.14	4.21	6.26
$[CpCo(CNR)(PPhMe_2)I]PF_6$	4.22	6.15		
$[CpCo(CNR)(C_5H_5N)I]PF_6$	3.90	6.13	3.99	6.04
$[CpCo(CNR)(CO)I]PF_6$	3.40	6.13	3.53	6.21
$[CpCo(CNR)_3](PF_6)_2$	3.10	6.14	3.40	6.21, 6.23, 6.26
$[CpCo(CNR)_2(PPh_3)](PF_6)_2$	3.46	6.18	3.76	6.51
$[CpCo(CNR)(Diphos)](PF_6)_2$	3.71	6.25	3.86	6.94
$[CpCo(CNR)(Bipy)](PF_6)_2$	3.31	6.22	3.36	6.36, 6.38, 6.40
$[CpCo(CNC_6H_4OMe\text{-}p)_2(CNMe)](PF_6)_2$	3.26	6.14		6.22
$CpCo(CNC_6H_4OMe\text{-}p)(SnCl_3)_2$	4.05	6.15		

[a] (ppm): All spectra were taken in $(CD_3)_2CO$ unless otherwise stated. [b] $CDCl_3$ solution.

have higher values of ν(NC) than the monocationic species, although there is some overlap between the two series.

NMR data are presented in Table 4. The π-cyclopentadienyl proton resonances for the cationic and dicationic complexes occur at τ values some of which are among the lowest which have been recorded for π-cyclopentadienyl complexes [12,18]. Such values seem only to occur in π-cyclopentadienyl complexes in which the metal atom is in a rather high oxidation state [13], and probably reflect the high positive charge on the metal atom, although other factors may also be involved. Certainly for the complexes reported here there is a general correlation with the infrared data, and those complexes which have the highest values of ν(NC) give the lowest τ values for the π-cyclopentadienyl protons. No coupling was observed at 30° between these protons and the phosphorus atoms in those complexes containing organophosphine ligands. The related nickel complex $\{CpNi(PPh_3)[CNC(CH_3)_3]\}I$ also fails to show such a coupling [14].

The complex $[CpCo(CNC_6H_4OMe\text{-}p)(PPhMe_2)I]^+$ shows a proton resonance due to the phosphorus methyl groups consisting of 4 lines. This is caused by the asymmetric centre at the cobalt atom which leads to non-equivalence of the two methyl groups [15]. By running spectra at 60 MHz as well as at 100 MHz *J*(P—Me) was derived as 12.3 Hz with the chemical shift difference between the two methyl groups being 0.16 ppm at 30°. These values are comparable to those previously found for related rhodium complexes [15].

(c). Reactions

(i). Reduction. The new complexes described in this paper are all formally Co^{III} species and they can be reduced either to Co^{II} or Co^{I} complexes depending on the reaction conditions. Thus if $[CpCo(CNR)_2I]X$ (R = C_6H_4OMe-*p*; X = I or PF_6) is refluxed overnight in either ethanol or methanol, $Co(CNR)_4I_2$ can be crystallised on concentration of the solution, and the same product is formed if an excess of RNC is added to a dichloromethane solution of $[CpCo(CNR)_2I]X$ at room temperature.

Hydrazine is a most versatile reducing agent for these complexes and gives either Co^{II} or Co^{I} products depending upon the solvent used. Thus addition of an excess of hydrazine to an ethanolic solution of $[CpCo(CNR)_2I]X$ (R = C_6H_4OMe-*p* or CH_3; X = I or PF_6) produces an instant colour change from dark brown to orange, and the Co^{I} complex $[Co(CNR)_5]X$ may then be isolated by concentration of the solution [8]. On the other hand if the reaction is carried out in acetone a colour change to dark purple occurs and the Co^{II} complex $Co(CNR)_4I_2$ can be obtained. Even if a pure crystalline sample of this latter complex is dissolved in acetone and a further quantity of hydrazine is added no further reduction from Co^{II} to Co^{I} takes place. This is presumably because the acetone reacts preferentially with the hydrazine to give acetone hydrazone, a reaction which does take place rapidly in the absence of the metal complex.

In none of the above experiments was any evidence obtained for the addition of N—H bonds across the isocyanide ligands as has been observed for complexes of Pd, Pt and Fe [19,20].

(ii). With $SnCl_2$. There has been a report in the literature that the complex $CpFe(CO)_2SnCl_2I \cdot MeOH$ may be prepared [21] by reaction of an excess of $SnCl_2$ with $CpFe(CO)_2I$. Subsequent experiments failed to confirm this observation, however [22], and indicated that because of rapid exchange of halogen bound to tin, $CpFe(CO)_2SnCl_3$ is formed by this means. To obtain further evidence on this point the reaction of $CpCo(CNC_6H_4OMe\text{-}p)I_2$ with an excess of $SnCl_2$ was studied. No reaction takes place in either dichloromethane or acetone solution, even after refluxing for several days, and in refluxing ethanol all the isocyanide ligands were displaced. In chloroform however, the colour of the solution changed from dark brown to orange after several hours at room temperature, and the complex $CpCo(CNC_6H_4OMe\text{-}p)(SnCl_3)_2$ was obtained as a red-brown crystalline material on concentration of the solution. Microanalysis showed that no iodine was present in this compound.

(iii). Reaction with methylamine. The complex $[CpFe(CNC_6H_4OMe\text{-}p)_3]^+$ reacts with methylamine [3] to yield $[CpFe(CNC_6H_4OMe\text{-}p)_2(C\{NHMe\}\text{-}NHC_6H_4OMe\text{-}p)]^+$. The corresponding reaction of $[CpCo(CNC_6H_4OMe\text{-}p)_2I]^+$ with a concentrated solution of methylamine in ethanol does not give an isolable carbene complex of this type. Instead, all the isocyanide ligands are displaced from the metal and analytical data suggest that the complex obtained contains only methylamine and iodide as ligands. Similarly sodium methoxide, which sometimes reacts with coordinated isocyanide ligands to give carbene complexes [23], does not give an isolable complex with any of the new cationic cobalt complexes described in this paper.

Experimental

Infrared spectra were recorded on a Perkin - Elmer 457 grating instrument using caesium bromide plates for Nujol mull spectra and sodium chloride plates for solution spectra. NMR spectra were recorded on a Varian HA 100 spectrometer. Microanalyses were performed by the microanalytical department at Cambridge and conductivity measurements were made using a Wayne - Kerr Universal Conductivity Bridge.

Starting materials were prepared by standard literature methods. CpCo(CO)I_2 was synthesised by the method of King [6]. Methyl isocyanide was prepared by the method of Casanova [16] and (*p*-methoxyphenyl)isocyanide by the method of Ugi and Meyr [17]. The dichloromethane solvent was distilled from calcium chloride before use and all reactions were carried out under nitrogen.

Preparations

(a). CpCo(CNMe)I_2. A solution of methyl isocyanide (104 mg, 2.52 mmole) in dichloromethane (5 ml) was added dropwise to a stirred solution of CpCo(CO)I_2 (1.025 g, 2.52 mmole) in dichloromethane (100 ml) at room temperature. After 24 h the solution was concentrated and then left overnight in the fridge. Yield 87%. It was recrystallised for analysis from dichloromethane/diethyl ether. CpCo(CNC_6H_4OMe-*p*)I_2 was similarly prepared.

(b). [CpCo(CNC_6H_4OMe-*p*)$_2$I]I. A solution of *p*-methoxyphenylisocyanide (117 mg, 0.88 mmole) in dichloromethane (5 ml) was added dropwise to a stirred solution of CpCo(CNC_6H_4OMe-*p*)I_2 (450 mg, 0.88 mmole) in dichloromethane (100 ml) at room temperature. After 24 h the solution was concentrated and left in the fridge overnight. Yield 85%. It was recrystallised for analysis from dichloromethane/diethyl ether. [CpCo(CNMe)$_2$I]I was similarly prepared.

(c). [CpCo(CNC_6H_4OMe-*p*)$_2$I]PF_6. A solution of *p*-methoxyphenylisocyanide (95 mg, 0.71 mmole) in dichloromethane (5 ml) was added dropwise to a stirred solution of CpCo(CNC_6H_4OMe-*p*)I_2 (365 mg, 0.71 mmole) in dichloromethane (100 ml) at room temperature. A solution of silver hexafluorophosphate (180 mg, 0.71 mmole) in dichloromethane (5 ml) was then added to the stirred solution. After 24 h the silver iodide was filtered off, the solution concentrated, and then left overnight in the fridge. Yield 85%. A sample was recrystallised for analysis from dichloromethane/diethyl ether. [CpCo(CNMe)$_2$I]PF_6 was prepared similarly.

(d). [CpCo(CNMe)(PPh_3)I]PF_6. A solution of triphenylphosphine (138 mg, 0.53 mmole) in dichloromethane (5 ml) was added dropwise to a stirred solution of CpCo(CNMe)I_2 (220 mg, 0.53 mmole) in dichloromethane (50 mg, 0.53 mmole) at room temperature. A solution of silver hexafluorophosphate (133 mg, 0.53 mmole) in dichloromethane (5 ml) was then added dropwise and the solution was stirred for 24 h. After filtering off the silver iodide the solution was concentrated and left overnight in the fridge to crystallise. Yield 87%. A sample was recrystallised for analysis from dichloromethane/diethyl ether. The compounds [CpCo(CNR)(L)I]PF_6 (R = C_6H_4OMe-*p*, L = $MePh_2P$, Me_2PhP, Py; R = Me, L = Ph_3P, $MePh_2P$, Py;) were all prepared similarly. The yields varied from 50 to 90%. All recrystallisations were carried out from dichloromethane/diethyl ether.

(e). [CpCo(CNC_6H_4OMe-*p*)(CO)I]PF_6. Carbon monoxide was rapidly bubbled through a stirred solution of CpCo(CNC_6H_4OMe-*p*)I_2 (218 mg, 0.43 mmole) in dichloromethane (20 ml) held at room temperature in a water bath, and a solution of silver hexafluorophosphate (108 mg, 0.43 mmole) was quickly added. The solution was concentrated to about 5 ml by continuing to bubble

carbon monoxide through the solution for a few minutes after the addition of the silver hexafluorophosphate. The silver iodide was quickly removed by centrifuging and diethyl ether was added dropwise until crystallisation began. The solution was then left for 1 h in the fridge, the mother liquor quickly decanted, and the product washed and dried in vacuo. Yield 30 - 40%. [CpCo(CNMe)(CO)I]PF_6 was similarly prepared in 40 - 50% yield. The compounds could not be recrystallised without decomposition.

(f). [CpCo(CNMe)$_3$](PF$_6$)$_2$. A solution of methyl isocyanide (133 mg, 3.24 mmole) in acetone (5 ml) was added to a solution of CpCo(CO)I_2 (439 mg, 1.08 mmole) in acetone (100 ml) at room temperature and then a solution of silver hexafluorophosphate (547 mg, 2.16 mmole) in acetone (5 ml) was added. The solution was stirred for 24 h, centrifuged to remove the silver iodide, concentrated and left in the fridge. Yield 23%. It was recrystallised for analysis from acetone/diethyl ether. [CpCo(CNC_6H_4OMe-*p*)$_3$](PF_6)$_2$ was prepared similarly.

(g). [CpCo(CNC_6H_4OMe-p)$_2$(PPh_3)](PF_6)$_2$. A solution of triphenylphosphine (85 mg, 0.32 mmole) in dichloromethane (5 ml) was added to a solution of [CpCo(CNC_6H_4OMe-*p*)$_2$I]PF_6 (214 mg, 0.32 mmole) in dichloromethane (100 ml) at room temperature. A solution of silver hexafluorophosphate (82 mg, 0.32 mmole) in dichloromethane (5 ml) was then added and the solution was stirred for 24 h. After filtering off the silver iodide the solution was concentrated and put in the fridge. Yield 95%. It was recrystallised from dichloromethane/diethyl ether. [CpCo(CNMe)$_2$(PPh_3)](PF_6)$_2$ was prepared similarly. [CpCo(CNC_6H_4OMe-*p*)$_2$(CNMe)](PF_6)$_2$ was also prepared similarly but in poorer yield. This last complex could not be easily recrystallised.

(h). [CpCo(CNMe)(Diphos)](PF_6)$_2$. A solution of Diphos (182 mg, 0.46 mmole) in dichloromethane (5 ml) was added to a solution of CpCo(CNMe)I_2 (192 mg, 0.46 mmole) in dichloromethane (150 ml) at room temperature. A solution of silver hexafluorophosphate (232 mg, 0.92 mmole) in dichloromethane (5 ml) was then added. After stirring for 24 h the silver iodide was filtered off and the solution concentrated and put in the fridge. Yield 97%. It was recrystallised for analysis from dichloromethane/diethyl ether. [CpCo(CNC_6H_4OMe-*p*)(Diphos)](PF_6)$_2$ was prepared similarly.

(i). [CpCo(CNMe)(Bipy)](PF_6)$_2$. A solution of methyl isocyanide (23.4 mg, 0.57 mmole) in acetone (3 ml) was added to a solution of [CpCo(Bipy)I]I (305 mg, 0.57 mmole) in acetone (50 ml) at room temperature. A solution of silver hexafluorophosphate (289 mg, 1.14 mmole) in acetone was added and the solution was stirred for 24 h. After filtering off the silver iodide the solution was concentrated and put in the fridge. Yield 60%. It was recrystallised for analysis from acetone/diethyl ether. [CpCo(CNC_6H_4-OMe-*p*)(Bipy)](PF_6)$_2$ was prepared similarly but using dichloromethane instead of acetone as the solvent.

(j). CpCo(CNC_6H_4OMe-p)($SnCl_3$)$_2$. A solution of CpCo(CNC_6H_4-OMe-*p*)I_2 (200 mg, 0.39 mmole) in chloroform (30 ml) was stirred at room temperature with $SnCl_2$ (430 mg, 2.25 mmole). After 15 h the solution was filtered, concentrated and put in the fridge. Yield 15%. The compound decomposed on attempted recrystallisation.

References

1 P.L. Pauson and W.H. Stubbs, Angew. Chem. Int. Ed. Engl., 1 (1962) 333.
2 K.K. Joshi, P.L. Pauson and W.H. Stubbs, J. Organometal. Chem., 1 (1963) 51.
3 R.J. Angelici and L.M. Charley, J. Organometal. Chem., 24 (1970) 205.
4 P.M. Treichel and J.P. Stenson, Inorg. Chem., 8 (1969) 2563.
5 R.F. Heck, Inorg. Chem., 4 (1965) 855.
6 R.B. King, Inorg. Chem., 5 (1966) 82.
7 C.E. Coffey, J. Inorg. Nucl. Chem., 25 (1963) 179.
8 F. Bonati and L. Malatesta, Isocyanide Complexes of Metals, Wiley, London, 1969.
9 H.C. Clark and L.E. Manzer, Inorg. Chem., 11 (1972) 503.
10 G.M. Bancroft, M.J. Mays, B.E. Prater and F.P. Stefanini, J. Chem. Soc. A, (1970) 2146.
11 W.A.G. Graham, Inorg. Chem., 7 (1968) 315.
12 M.L. Maddox, S.L. Stafford and H.D. Kaesz, Advan. Organometal. Chem., 3 (1965) 1.
13 M. Cousins and M.L.H. Green, J. Chem. Soc. A, (1969) 16.
14 Y. Yamamato, H. Yamazaki and N, Hagihara, J. Organometal. Chem., 18 (1969) 189.
15 A.J. Oliver and W.A.G. Graham, Inorg. Chem., 9 (1970) 243.
16 J. Casanova, Jun., R.E. Schuster and N.D. Werner, J. Chem. Soc. A, (1963) 4280.
17 I. Ugi and R. Meyr, Chem. Ber., 93 (1960) 239.
18 J.A. Dineen and P.L. Pauson, J. Organometal. Chem., 43 (1972) 209.
19 A. Burke, A.L. Balch, and J.H. Enemark, J. Amer. Chem. Soc., 92 (1970) 2555.
20 A.L. Balch and J. Miller, J. Amer. Chem. Soc., 94 (1972) 417.
21 A.R. Manning, Chem. Commun., (1966) 906.
22 M.J. Mays and S.M. Pearson, J. Chem. Soc. A, (1969) 136.
23 P.M. Treichel, W.J. Knebel and R.W. Hess, J. Amer. Chem. Soc., 93 (1971) 5424.
24 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.