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BASIC METALS

XVI *. INTERCONVERSION OF ALKYL- AND ACYL-COBALT(III) COMPLEXES DERIVED FROM CYCLOPENTADIENYLCARBONYL(TRIMETHYLPHOSPHINE)COBALT(I)

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Summary

The complex $C_5H_5Co(PMe_3)CO$ reacts with alkyl halides to give the acyl complexes $C_5H_5Co(PMe_3)(COR)I$ (R = Me, Et). $[C_5H_5Co(PMe_3)(CO)Me]I$ was shown to be an intermediate in the formation of the acetyl complex, and in solution in more polar solvents the two are in equilibrium, the position of which is dependent upon the solvent polarity. The methyl complex is stable as the PF_6 salt in solution, but reacts readily with PPh_3 to give $[C_5H_5Co(PMe_3)(PPh_3)(COMe)]PF_6$. This also exists in solution in equilibrium with the methyl complex and free PPh_3, and the equilibrium is almost independent of solvent polarity. With acyl halides, the complexes $[C_5H_5Co(PMe_3)(COR)CO]PF_6$ (R = Me, Et, Ph) are formed. They do not appear to form alkyl complexes under mild conditions.

Introduction

During studies on low-valent complexes of transition metals [1] in which the metal possesses pronounced basic character, it was found that the complexes $C_5H_5CoL_2$ (L = PMe_3, PMe_2Ph, $PMePh_2$) undergo oxidative addition with alkyl and acyl halides to give cobalt(III) complexes of the type $[C_5H_5CoL_2Y]X$ (Y = Me, Et, MeCO, PhCO; X = anion) [2]. The reaction of carbonyl complexes

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* For part XV see ref. 1.

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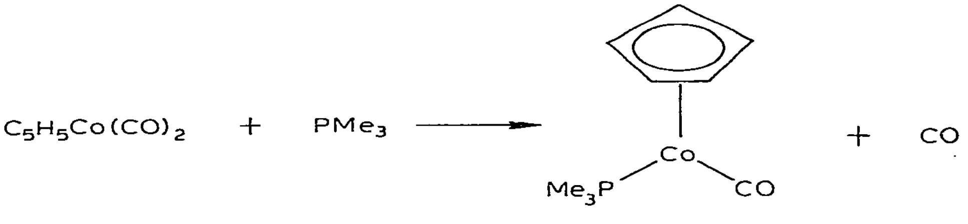
of the type $C_5H_5CoL(CO)$ ($L = PPh_3, PMe_2Ph, PMePh_2, P(C_6H_{11})_3$) with methyl and ethyl iodides giving the complexes $C_5H_5Co(L)(COR)I$ ($R = Me, Et$) have also been described [3].

We have synthesised the complex $C_5H_5Co(PMe_3)(CO)$ (I) which forms a link between the two series above. We report here the preparation of complex I, its reactions with alkyl and acyl halides, and the interconversion of the resulting alkyl- and acyl-cobalt(III) compounds.

Results and discussion

The complex $C_5H_5Co(CO)_2$ [4,5] which at room temperature is a dark red liquid, reacts with an excess of trimethylphosphine with evolution of carbon monoxide to give the new complex I, which is formed in almost quantitative



(I)

yield. It is an orange-red solid which can be recrystallised from n-pentane to give soft needle crystals. The complex is soluble in a very wide range of organic solvents (e.g. pentane, methanol) and the solutions are highly air-sensitive. It is insoluble in water. The solid complex burns instantly on exposure to air, but under pure nitrogen at room temperature it remains analytically pure after several months. The complex shows a carbonyl band in the infrared spectrum at 1923 cm^{-1} (pentane solution). The ^1H NMR spectrum consists of two doublets, from coupling of the methyl groups and the cyclopentadienyl ligand to the ^{31}P nucleus (Table 1).

Whereas $C_5H_5Co(CO)_2$ rapidly undergoes oxidative addition of iodine to give $C_5H_5Co(CO)I_2$ in high yield [6,7] complex I gives phosphine disproportionation in this reaction, the products being $C_5H_5Co(CO)I_2$, $[C_5H_5Co(PMe_3)_2I]I$ [8], and $[C_5H_5Co(PMe_3)_3]I_2$, which has already been reported as the fluoroborate salt [2].

Complex I reacts rapidly with methyl iodide in acetone at room temperature to give the dark brown complex II.

$$C_5H_5Co(PMe_3)(CO) + MeI \rightarrow C_5H_5Co(PMe_3)(COMe)I$$

(I) (II)

During this reaction a yellow precipitate forms and redissolves (see below). Complex II is extremely soluble in acetone, but can be obtained as dark brown, almost black crystals from pentane or even better from ether. It is air-stable in solution. The infrared spectrum shows a band at 1618 cm^{-1} due to the acetyl group.

The ^{1}H NMR spectrum of II is dependent upon the solvent. In solvents such as benzene-d_6 or acetone-d_6 the observed spectra are in agreement with the above structure of complex II (Table 1). The trimethylphosphine and acetyl signals appear in both cases as doublets through coupling to phosphorus, but the cyclopentadienyl group appears as a singlet. A coupling of less than 0.6 Hz would not be observed with the instrument used.

In nitromethane-d_3, extra resonances occur in the spectrum (Fig. 1). There is a second singlet to low field of the cyclopentadienyl resonance of II, a second doublet in the phosphine region, and a further doublet to high field of the phosphine. The chemical shifts of these "extra" resonances together with their integration are entirely consistent with the presence of the cationic complex, $[C_5H_5Co(PMe_3)(CO)Me]I$ (III) formed by displacement of the iodo-ligand by methyl migration to cobalt. From the overall integration complex II is present to the extent of 85% and complex III to 15%. When the spectrum of complex II was recorded in methanol-d_4, a similar situation was found this time with 68% of II and 32% of III. Clearly the formation of III from II is favored by increasing solvent polarity, which is consistent with the ionic nature of complex III.

In view of the behaviour described above the corresponding ethyl complex $C_5H_5Co(PMe_3)(COEt)I$ (IV) was prepared. It shows a band at 1625 cm^{-1} in the infrared spectrum due to the propionyl group. The NMR spectrum in acetone-d_6 nitromethane-d_3, and methanol-d_4 is in all cases that expected for the structure IV indicating that the ethyl analogue of complex III is not formed in more than 3% yield, if at all.

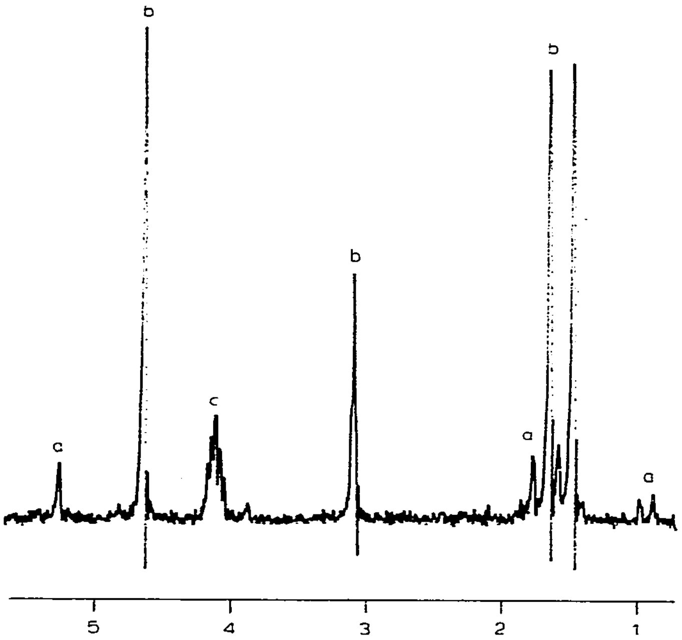


Fig. 1. ^{1}H NMR spectrum of $C_5H_5Co(PMe_3)(COMe)I$ in nitromethane-d_3 at 60 MHz (see text). (a) $[C_5H_5Co(PMe_3)(CO)Me]I$; (b) $C_5H_5Co(PMe_3)(COMe)I$; (c) Solvent.

TABLE 1

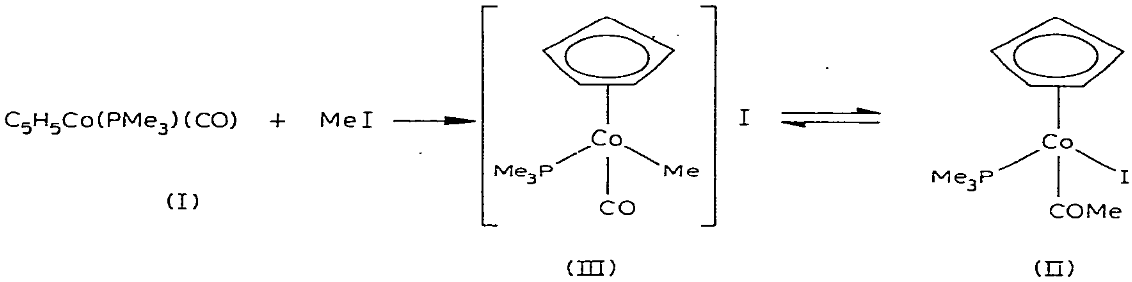
^{1}H NMR SPECTRA OF COMPLEXES I, II, IV—IX (δ in ppm, J in Hz; d, doublet; t, triplet; q, quartet; m, multiplet)

Complex	Solvent	$\delta(C_5H_5)$	J(PH)	$\delta(PMe_3)$	J(PH)	δ(COR)	J(HH)	δ(Me)	J(PH)	$\delta(PPh_3)$
I	C_6D_6	4.35 d	1.4	0.93 d	8.7					
II	CD_3COCD_3	4.65	[a]	1.55 d	9.9	3.07 [b]				
IV	CD_3COCD_3	4.66 d	0.6	1.6 d	9.9	3.5 q [c]	7.0			
V	CD_3NO_2	5.29	[a]	1.66 d	11.2			0.91 d	5.4	
VI [d]	CD_3NO_2	5.01	[a]	1.3 d	9.9	2.66				7.15 [e]
VII	CD_3NO_2	5.33	[a]	1.65 d	11.6	2.73 [f]				
VIII	CD_3COCD_3	5.5 d	0.6	1.71 d	11.4	3.14 q 0.96 t	6.9			
IX	CD_3NO_2	5.48	[a]	1.73 d	11.0	7.19 m				

[a] J(PH) <0.6 Hz. [b] J(PH) 0.8 Hz. [c] J(PH) 1.3 Hz. [d] Also spectrum of V (ca. 15%) and acetone (δ 2.01), see text and Fig. 2. [e] Broad doublet. [f] J(PH) 1.5 Hz.

Complexes analogous to III have already been postulated as intermediates in the reactions of methyl and ethyl iodides with cyclopentadienylcarbonylphosphinecobalt complexes, but direct evidence for such species was obtained only with rhodium and iridium where the stable complexes $[C_5H_5Rh(PPhMe_2)(CO)Me]BPh_4$ and $[C_5H_5Ir(PPh_3)(CO)Me]I$ were isolated [3].

In view of the yellow precipitate observed during the preparation of II from I and methyl iodide, this reaction was repeated in toluene as solvent in which complex III would be expected to be insoluble. In this way a dark yellow complex was isolated in good yield there being little or no formation of complex II. The dark yellow complex shows a carbonyl band at 2035 cm^{-1} in the infrared spectrum and no band in the acyl region. The complex dissolves in acetone-d_6 to give a dark brown solution having the NMR spectrum of complex II in this solvent. In nitromethane-d_3, it shows a mixture of 85% of II and 15% of III exactly as with complex II. From these results it is clear that the dark yellow powder is complex III, and that this is the intermediate in the formation of II from I.



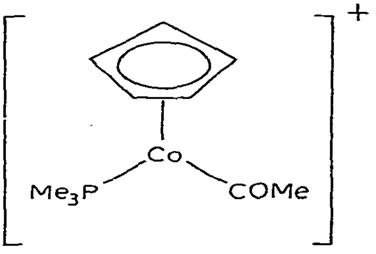
Further, since the solutions obtained from both II and III have the same composition this is clearly the equilibrium mixture. Even in the solid state III reacts to form II almost completely in 48 h at room temperature. This process is slowed only marginally by storage at —25°C. The complex is air-stable over its lifetime and the conversion to II is not affected by storage under nitrogen.

In order to investigate further the stability of the cation in complex III we decided to prepare an analogous complex having a non-coordinating anion. Accordingly, the reaction of I with methyl iodide was carried out in methanol with addition of $AgPF_6$ immediately after the alkyl halide. The complex $[C_5H_5Co(PMe_3)(CO)Me]PF_6$ (V) was obtained in good yield as a yellow powder. It is soluble in polar organic solvents and the solutions are air-stable for at least a few hours. The infrared spectrum shows a carbonyl band at 2040 cm^{-1} and no acetyl band and the NMR spectrum in nitromethane-d_3 is that of the methylcarbonyl species, with no trace of the acetyl compound present (Table 1). The complex in the solid state shows no sign of forming the acetyl even after some weeks.

Complex V can be obtained in quantitative yield by treatment of complex II with $AgPF_6$ and the reverse reaction can be effected with NaI.

$$\underset{(II)}{C_5H_5Co(PMe_3)(COMe)I} \underset{NaI}{\overset{AgPF_6}{\rightleftharpoons}} \underset{(V)}{[C_5H_5Co(PMe_3)(CO)Me]PF_6}$$

Clearly the driving force for acetyl formation is the nucleophilic attack of the iodo ligand on cobalt. Since complex III is already coordinatively saturated, we believe that the 18-electron methyl-carbonyl cation exists in equilibrium with a very small amount of the 16-electron acetyl cation:



In presence of a suitable ligand such as iodide the equilibrium is driven over to the 18-electron complex II. In absence of such a ligand the 18-electron methyl-carbonyl cation is preferred.

If this is so other nucleophiles should convert complex V into the corresponding acetyl. From the reaction of V with triphenylphosphine we have isolated the acetyl complex $[C_5H_5Co(PMe_3)(PPh_3)(COMe)]PF_6$ (VI) as an acetone monosolvate. The complex forms red crystals, readily soluble in polar organic solvents. The infrared spectrum shows a fairly broad band at 1650 cm^{-1} and a sharp band at 1710 cm^{-1}. The former we attribute to the acetyl group and the latter to the acetone. The NMR spectrum of complex VI was recorded in

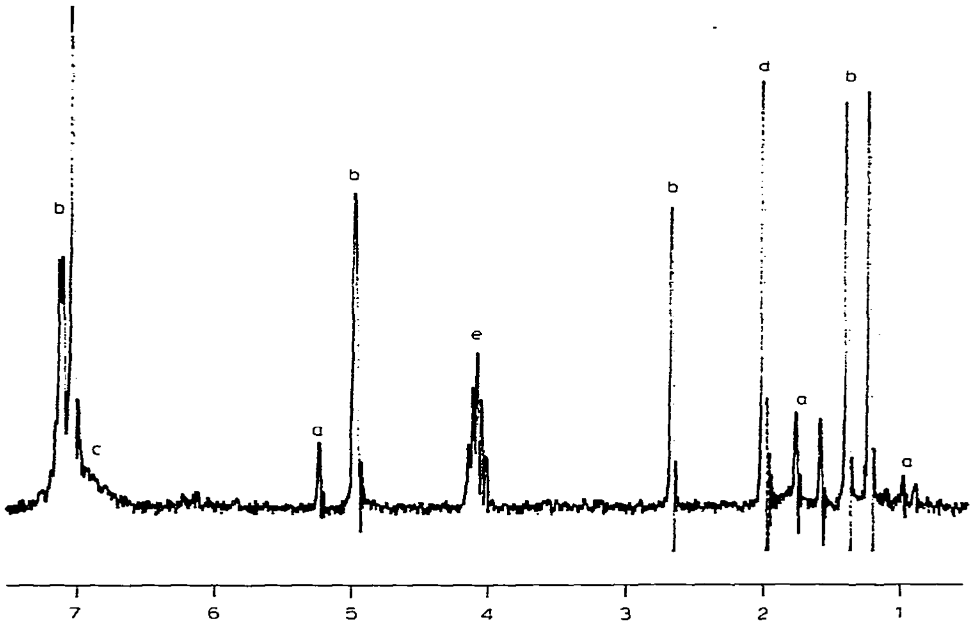


Fig. 2. ^1H NMR spectrum of $[C_5H_5Co(PMe_3)(PPh_3)(COMe)]PF_6 \cdot CH_3COCH_3$ in nitromethane-d_3 at 60 MHz (see text). (a) $[C_5H_5Co(PMe_3)(CO)Me]PF_6$; (b) $[C_5H_5Co(PMe_3)(PPh_3)(COMe)]PF_6$; (c) Free PPh_3; (d) CH_3COCH_3; (e) Solvent.

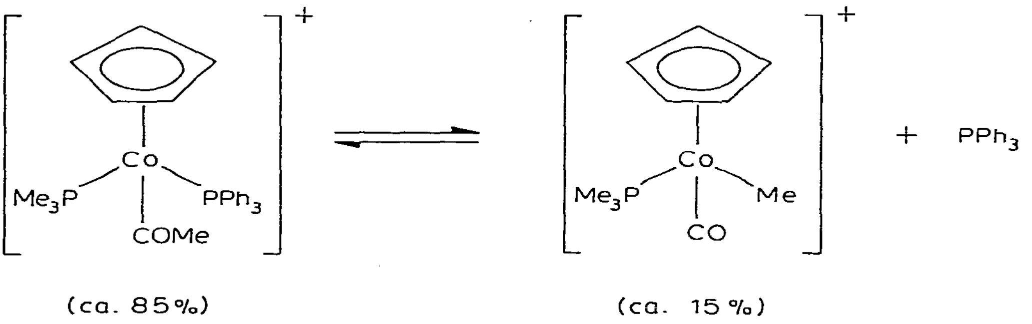
TABLE 2

ELEMENTAL ANALYSES (Found (calcd.) (%)) OF COMPLEXES I, II, IV—IX

Complex	C	H	Co	F	I	P
I[a]	47.22	6.26	26.00			13.50
	(47.35)	(6.18)	(25.87)			(13.59)
II	32.35	4.48	15.38		34.14	8.63
	(32.42)	(4.62)	(15.94)		(34.32)	(8.38)
IV	34.04	4.77	15.41		33.30	8.15
	(34.36)	(5.00)	(15.36)		(33.06)	(8.07)
V	30.67	4.44	15.20	29.53		15.82
	(30.91)	(4.41)	(15.20)	(29.37)		(15.98)
VI	52.24	5.22	8.96			13.03
	(52.52)	(5.41)	(8.33)			(13.13)
VII	36.73	4.81	16.45	20.95		8.84
	(36.86)	(4.78)	(16.48)	(21.22)		(8.66)
VIII	38.54	4.70	15.02	20.19		8.28
	(38.69)	(5.16)	(15.85)	(20.42)		(8.33)
IX	45.87	4.85	14.00	17.95		7.24
	(45.69)	(4.57)	(14.04)	(18.09)		(7.38)

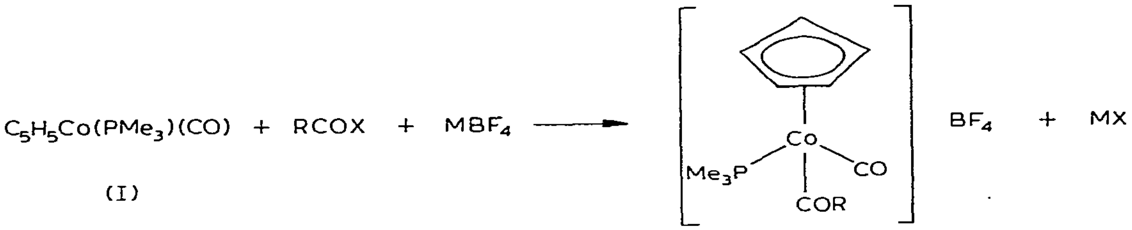
[a] Mol. wt.: Found 219; calcd. 228.1.

acetone-d_6, nitromethane-d_3, and methanol-d_4. The spectra in all three solvents are very similar, an equilibrium of the type observed with complexes II and III occurring (Fig. 2). Comparison of these spectra with that of complex V indicates that the PPh_3 is displaced to form the methyl-carbonyl species. The spectra indicate 83—87% of the acetyl and 17—13% of the methyl-carbonyl complex to be present, the differences being within the error of the integration.



The absence of any solvent dependence of the equilibrium in this case we attribute to the liberation of a neutral ligand as a result of which there is neither a change in charge of the complex nor the effect of solvation of a liberated anion. VI is air-stable in the solid state, but slow oxidation occurs in solution due to phosphine dissociation.

Complex I also undergoes oxidative addition of acyl halides. The complexes $[C_5H_5Co(PMe_3)(COR)CO]BF_4$ (VII, R = Me; VIII, R = Et; IX, R = Ph) were isolated by treatment of I with acetyl chloride, propionyl bromide and benzoyl bromide, respectively, followed by addition of $NaBF_4$ (VII) or $AgBF_4$ (VIII and IX).



(I)

(VII) - (IX) .

The complexes form red crystals which are soluble in polar organic solvents. They are air-stable in the solid state and in solution, and no evidence for loss of carbon monoxide and formation of the methyl-carbonyl cation was found, the NMR spectra indicating that the above structure is maintained in solution (Table 1). In the infrared spectra the complexes show carbonyl and acyl bands at 2040 and 1708 cm^{-1} (VII); 2040 and 1683 cm^{-1} (VIII); and 2038 and 1642 cm^{-1} (IX).

Since these complexes are quite stable in solution it might be expected that complex V would react with carbon monoxide in a manner analogous to its reaction with iodide and PPh_3, leading to complex VII as the PF_6 salt. However, no reaction between V and CO occurred even on prolonged treatment of a solution of V in nitromethane-d_3 at room temperature. At 80°C the NMR spectrum showed that decomposition of V occurred but no well-defined product was formed. We can at present give no adequate explanation for the failure to form VII.

Since the complexes $C_5H_5CoL_2$ [2] readily react with acids to give the hydrides $[C_5H_5CoL_2H]X$ (X = acid anion) we attempted such reactions with complex I, which would be expected to be a weaker base than $C_5H_5Co(PMe_3)_2$. I does not react with NH_4PF_6 or acetic acid as does the bisphosphine complex. With stronger acids (CF_3CO_2H, HPF_6, H_2SO_4, HBF_4) yellow solutions were obtained. Attempts to isolate the yellow species generally produced intractable green oils. With fluoroboric acid in propionic anhydride a very pale yellow, almost colourless solution was obtained from which a bright yellow powder could be isolated by addition of ether. The powder was extremely air-sensitive and reacted immediately with those common solvents in which it was soluble (acetone, nitromethane, methanol) preventing the NMR spectrum from being recorded. In the original propionic anhydride solution, no sign of a hydride resonance could be found. The infrared spectrum of the powder in Nujol showed only very broad bands, suggesting that it was far less pure than its physical appearance indicated, and we are unable to say whether the complex $[C_5H_5Co(PMe_3)(CO)H]BF_4$ was present or not. It should be mentioned that the corresponding rhodium complex $[C_5H_5Rh(PMe_3)(CO)H]BF_4$ has been isolated quite recently by protonation of $C_5H_5Rh(PMe_3)(CO)$ or by ligand displacement of $[C_5H_5Rh(PMe_3)(C_2H_4)H]BF_4$ with CO [1].

Experimental

Infrared spectra were recorded as Nujol mulls on a Perkin—Elmer 457 and ^1H NMR spectra on a Varian T60 using TMS as internal reference.

$C_5H_5Co(CO)_2$ [9] and PMe_3 [10] were prepared according to the literature. Elemental analyses (Table 2) were performed by Miss R. Schedl and Mrs. E. Ullrich of this department and by the Alfred Bernhardt Microanalytical Laboratory. All reactions were carried out under purified nitrogen.

Preparation of $C_5H_5Co(PMe_3)(CO)$ (I)

$C_5H_5Co(CO)_2$ (0.72 ml, 5.6 mmol) and PMe_3 (2.84 ml, 28 mmol) were stirred for 1 h. The nitrogen stream must be as slow as possible because of the volatility of PMe_3. The flask was then connected to a vacuum line and pumped for 30 min to remove excess PMe_3. The product thus obtained was a dark red solid (1.22 g, 96%) which was pure enough for further reactions. It can be recrystallised from n-pentane to give soft orange-red needle crystals below ca. −35°C. Because of its air-sensitivity it was preferred always to prepare and use the complex directly for further reactions, rather than to store and transfer it.

Preparation of $C_5H_5Co(PMe_3)(COMe)I$ (II)

$C_5H_5Co(PMe_3)(CO)$ (1.22 g, 5.4 mmol) was dissolved in acetone (10 ml) and MeI (0.67 ml, 10.8 mmol) was added. The solution was stirred for 1 h, and the acetone was removed. The residue was extracted with ether (40 ml) and the solution was filtered. The filtrate was cooled at −25°C, giving the product as dark brown crystals. These were collected, washed with a little cold pentane, and dried in vacuo (0.87 g, 42%).

Preparation of $C_5H_5Co(PMe_3)(COEt)I$ (IV)

The complex was prepared from $C_5H_5Co(PMe_3)(CO)$ and EtI as for the acetyl analogue, using n-pentane instead of ether for the extraction (0.64 g, 16%).

Preparation of $[C_5H_5Co(PMe_3)(CO)Me]I$ (III)

$C_5H_5Co(PMe_3)(CO)$ (0.61 g, 2.68 mmol) in toluene (5 ml) was stirred for 1 h with MeI (0.34 ml, 5.5 mmol). The resulting yellow precipitate was collected, washed with toluene and ether and dried in vacuo. Yield almost quantitative. Because of the instability of the iodide salt, it was analysed as the PF_6 salt (below).

Preparation of $[C_5H_5Co(PMe_3)(CO)Me]PF_6$ (V)

$C_5H_5Co(PMe_3)(CO)$ (0.61 g, 2.68 mmol) was dissolved in methanol (10 ml). MeI (0.34 ml, 5.5 mmol) was added followed immediately by $AgPF_6$ (1.39 g, 5.5 mmol). After 15 min, the mixture was filtered and the precipitate (AgI and product) was washed with methanol (5 ml). The product was then dissolved out with nitromethane (20 ml). To this was added ether (200 ml) and the solution was cooled at −25°C. The yellow precipitate was collected, washed with ether and dried in vacuo (0.58 g, 59%).

Preparation of $[C_5H_5Co(PMe_3)(PPh_3)(COMe)]PF_6 \cdot CH_3COCH_3$ (VI)

$[C_5H_5Co(PMe_3)(CO)Me]PF_6$ (0.5 g, 1.35 mmol) and PPh_3 (0.53 g, 2.02 mmol) were stirred in acetone (10 ml) for 1 h. The dark red solution was filtered and ether was added to the filtrate until a precipitate began to form. The solution was cooled at —25°C to give the product as red crystals which were an acetone monosolvate. The product was collected, washed with ether and dried in vacuo (0.31 g, 32%).

Preparation of $[C_5H_5Co(PMe_3)(COMe)CO]BF_4$ *(VII)*

$C_5H_5Co(PMe_3)(CO)$ (1.22 g, 5.4 mmol) was dissolved in toluene (10 ml) and MeCOCl (0.8 ml, 10.7 mmol) was added. After 15 min, the toluene was removed and the residue was dissolved in methanol (30 ml). $NaBF_4$ (0.62 g, 5.6 mmol) was added and the mixture was stirred for a further 15 min. It was then filtered and the product was precipitated as an orange powder by the addition of ether. This was collected, washed with ether and dried in vacuo (1.22 g, 60%). It can be obtained as orange crystals from cold methanol.

Preparation of $[C_5H_5Co(PMe_3)(COEt)CO]BF_4$ *(VIII)*

$C_5H_5Co(PMe_3)(CO)$ (0.61 g, 2.68 mmol) was dissolved in toluene (10 ml) and EtCOBr (0.5 ml, 5.55 mmol) was added. After 15 min, the toluene was removed and the residue was dissolved in methanol (10 ml). $AgBF_4$ (0.6 g, 3.8 mmol) was added and the mixture was stirred for 15 min. After filtration, the solution was cooled at —25°C, giving the product as red crystals which were collected, washed with ether and dried in vauo (0.35 g, 35%).

Preparation of $[C_5H_5Co(PMe_3)(COPh)CO]BF_4$ *(IX)*

$C_5H_5Co(PMe_3)(CO)$ (0.61 g, 2.68 mmol) was treated as above with PhCOBr (0.66 ml, 5.6 mmol) in toluene (5 ml). The residue was dissolved in methanol (15 ml) and $AgBF_4$ (0.54 g, 2.72 mmol) was added. After 5 min, the solution was filtered and cooled at —25°C to give the product as red crystals which were collected as above (0.45 g, 39%).

Acknowledgements

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References

1 H. Werner and R. Feser, Angew. Chem., 91 (1979) 171.
2 H. Werner und W. Hofmann, Chem. Ber., 110 (1977) 3481.
3 A.J. Hart-Davis and W.A.G. Graham, Inorg. Chem., 9 (1970) 2658.
4 E.O. Fischer and R. Jira, Z. Naturforsch, B, 9 (1954) 618.
5 T.S. Piper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1955) 165.
6 R.F. Heck, Inorg. Chem., 4 (1965) 855.
7 R.B. King, Inorg. Chem., 5 (1966) 82.
8 A. Spencer and H. Werner, J. Organometal. Chem., 171 (1979) 209.
9 M.D. Rausch and R.A. Genetti, J. Org. Chem., 35 (1970) 3888.
10 W. Wolfsberger and H. Schmidbaur, Synth. Inorg. Met-Org. Chem., 4 (1974) 149.