Journal of Organometallic Chemistry, 221 (1981) 333—337
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTIONS OF MONOCYCLOPENTADIENYLCOBALT CATIONS WITH NUCLEOPHILES

T. AVILÉS and P. ROYO *

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Alcalá de Henares, Madrid (Spain)

(Received June 26th, 1981)

Summary

The reactions of $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ with the nucleophiles $Y^- = CN^-$, N_3^-, MeO^-, H^-, NO_2^- have been investigated. Only for $Y^- = CN^-$ or N_3^- were crystalline products $[Co(\eta\text{-}C_5H_5)(PMe_3)_2Y][PF_6]$ ($Y^- = CN^-, N_3^-$) and $Co(\eta\text{-}C_5H_5)(PMe_3)(CN)_2$ isolated. MeO^- and H^- gave untractable products and with NO_2^- no reaction was observed. Reaction of $Co(\eta\text{-}C_5H_5)(CO)I_2$ with PEt_3 in the stoichiometry 1 : 1, 1 : 2 or 1 : 3 gave the complexes $Co(\eta\text{-}C_5H_5)(PEt_3)I_2$, $[Co(\eta\text{-}C_5H_5)(PEt_3)_2I]I$ and a mixture of $Co(PEt_3)_2(CO)_2I$ and $Co(PEt_3)_2I_2$, respectively.

Introduction

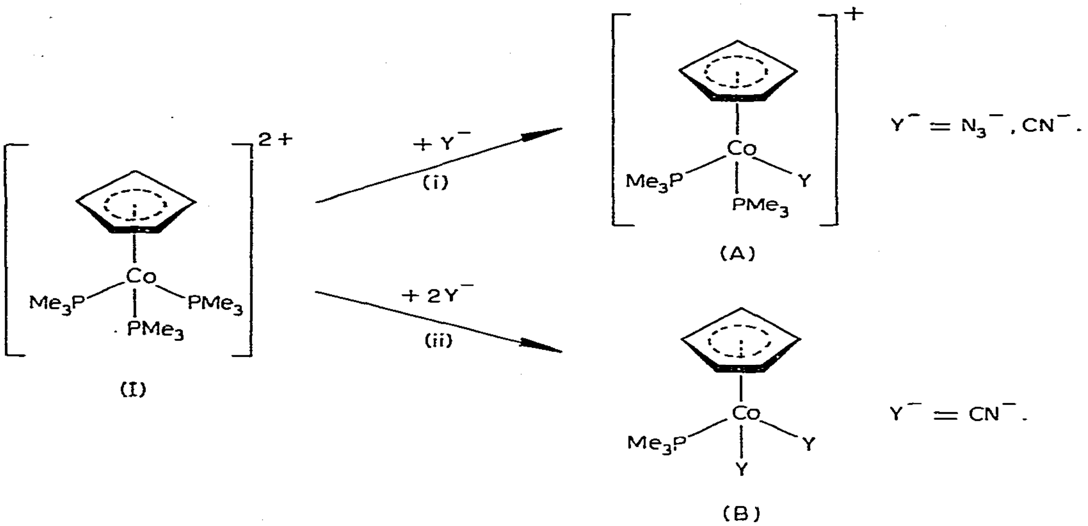
Organotransition metal cations containing unsaturated hydrocarbon ligands undergo nucleophilic addition [1]. We were interested in nucleophilic addition to the cation $[Co(\eta\text{-}C_5H_5)(PMe_3)_3]^{2+}$.

Results and discussion

The reaction of the salt $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ (I) [2], with an excess of KCN gave a crystalline yellow compound, which was characterised as the neutral compound $Co(\eta\text{-}C_5H_5)(PMe_3)(CN)_2$ (II). Similar cyanide complexes have been described previously [3]. When a stoichiometric amount of KCN is used the yellow crystalline salt $[Co(\eta\text{-}C_5H_5)(PMe_3)_2CN][PF_6]$ (III) is obtained. In contrast, treatment of $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ (I) with an excess of KN_3 gave the monosubstituted species $[Co(\eta\text{-}C_5H_5)(PMe_3)_2N_3][PF_6]$ (IV) as dark red crystals. It thus seems that treatment of $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ (I) with nucleophiles such as N_3^- and CN^- gives rise to ligand substitution, yielding mono- and di-substituted species of the types A and B. When an excess of Me^- is used, the disubstituted B species is obtained [4].

0022-328X/81/0000—0000/$02.50

SCHEME 1



(i) $Y^- = CN^-$, in THF for 30 min at room temperature, then reflux for 1 h (75%). $Y^- = N_3^-$, in THF reflux for 48 h (30%). (ii) in THF for 12 h at 60°C (75%)

In an attempt to obtain the analogue of compound I by treatment of $Co(\eta\text{-}C_5H_5)(CO)I_2$ (V) [5], with PEt_3, we found that the reaction proceeded differently. Treatment of V with PEt_3 in the stoichiometries 1 : 1, 1 : 2 and 1 : 3 in fact gave the results shown below:

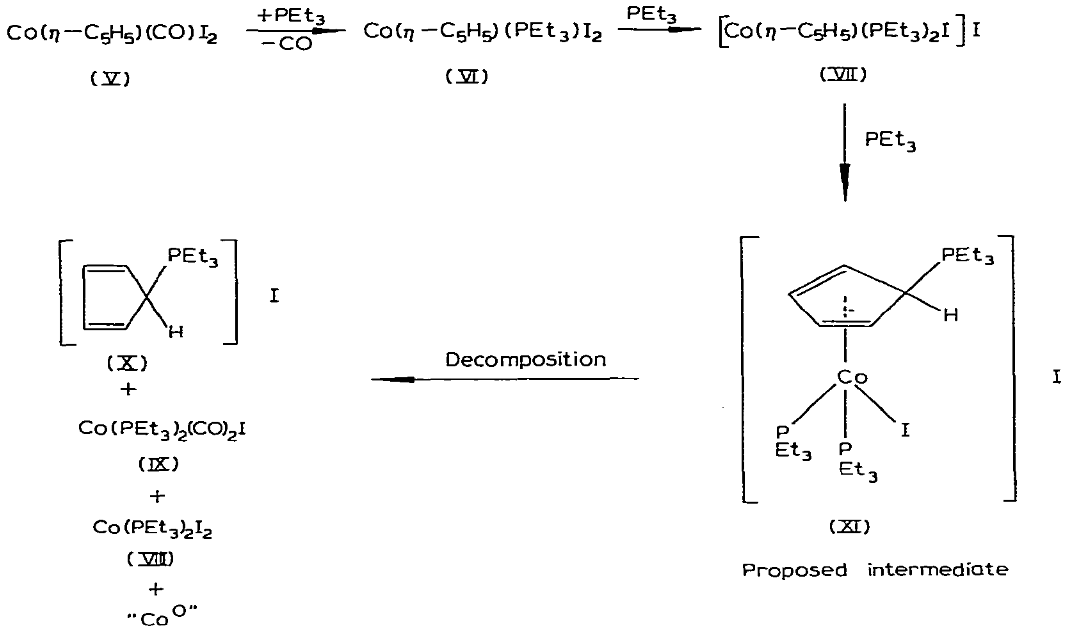
$$Co(\eta\text{-}C_5H_5)(CO)I_2\ (V) \xrightarrow{1\,:\,1\ PEt_3} Co(\eta\text{-}C_5H_5)(PEt_3)I_2\ (VI)$$

$$\xrightarrow{1\,:\,2\ PEt_3} [Co(\eta\text{-}C_5H_5)(PEt_3)_2I]I\ (VII)$$

$$\xrightarrow{1\,:\,3\ PEt_3} \underset{(VIII)}{Co(PEt_3)_2I_2} + \underset{(IX)}{Co(PEt_3)_2(CO)_2I} + \underset{(X)}{[PEt_3(C_5H_5)]I}$$

It is probable that the reactions proceeds through the sequence shown in Scheme 2.

The first mole of PEt_3 displaces the CO ligand, the second mole of PEt_3 displaces an iodo ligand to give the cationic species VII, while the third mole of PEt_3 adds nucleophilically the $\eta\text{-}C_5H_5$ ring to give the intermediate XI (which we were unable to isolate under the conditions employed), which decomposes to give the phosphosnium salt which was isolated as the PF_6^- salt and a cobalt(I) moiety which in the presence of CO gives stable $Co(PEt_3)_2(CO)_2I$ and partially disproportionates to $Co(PEt_3)_2I_2$ and a cobalt(0) residue not identified.



SCHEME 2

Experimental

All reactions and manipulations were carried out under nitrogen or in vacuum. All solvents were dried and distilled. The ^{1}H NMR spectra (Table 1) were recorded using a Bruker (90 MHz) or a Varian (80 MHz) instrument. Microanalyses (Table 2) were determined with a Perkin-Elmer 240 B elemental analyser. Infrared spectra (Table 1) were recorded as KBr pellets on a Perkin-Elmer 599 infrared spectrophotometer.

TABLE 1

SPECTROSCOPIC DATA

Complex	^{1}H NMR [a]
II, $Co(\eta\text{-}C_5H_5)(PMe_3)(CN)_2$ [d]	8.18(9), d ($J(^{31}P$—Me) 12.64), PMe_3; 4.59(5), d ($J(^{31}P—C_5H_5)$ 0.44), C_5H_5 [b]
III, $[Co(\eta\text{-}C_5H_5)(PMe_3)_2CN][PF_6]$ [e]	8;18—8.05(18), c, PMe_3; 4.27(5), s, C_6H_5 [b]
IV, $[Co(\eta\text{-}C_5H_5)(PMe_3)_2N_3][PF_6]$ [f]	8.33—8.10(18), c, PMe_3; 4.29(5), s, C_5H_5 [b]
VI, $Co(\eta\text{-}C_5H_5)(P(CH_2\text{-}CH_2\text{-}CH_3)_3)I_2$	8.76(9), d-t, CH_3; 7.85—7.48(6), c, CH_2 [c]; 4.8(5), s, C_5H_5
XII, $[Co(\eta\text{-}C_5H_5)(P(CH_2\text{-}CH_3)_3)_2I][PF_6]$	8.9—8.5(18), c, CH_3; 7.8—7.55(12), c, CH_2 [b]; 4.27(5), t($J(^{31}P—C_5H_5)$ 0.6) C_5H_5

[a] Data presented as chemical shift (τ), relative intensity (in parentheses), multiplicity (*J* in Hz), assignment.
[b] In $(CD_3)_2CO$. [c] In $CDCl_3$. [d] ν(C—N) = 2120—2110 cm^{-1}. [e] ν(C—N) = 2120 cm^{-1}. [f] ν(N—N—N) = 2035 cm^{-1}.

TABLE 2

ANALYTICAL DATA

Complex	Colour	Analysis found (calcd.) (%)		
		C	H	N
II. $Co(\eta\text{-}C_5H_5)(PMe_3)(CN)_2$	Yellow	47.6 (47.9)	5.6 (6.1)	11.1 (10.8)
III. $[Co(\eta\text{-}C_5H_5)(PMe_3)_2CN][PF_6]$	Yellow	32.2 (32.9)	5.1 (5.1)	3.1 (3.6)
IV. $[Co(\eta\text{-}C_5H_5)(PMe_3)_2N_3][PF_6]$	Dark red	28.5 (28.6)	5.0 (5.0)	9.1 (8.6)
VI. $Co(\eta\text{-}C_5H_5)(PEt_3)I_2$	Black	26.6 (26.8)	4.0 (4.7)	— —
VII. $[Co(\eta\text{-}C_5H_5)(PEt_3)_2I]$ I	Brown	33.2 (33.35)	5.7 (6.2)	—
XII. $[Co(\eta\text{-}C_5H_5)(PEt_3)_2I][PF_6]$	Brown	32.3 (32.6)	5.5 (5.9)	—

Cyano(η-cyclopentadienyl)bis(trimethylphosphine)cobalt hexafluorophosphate

A suspension of $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ (0.34 g, 0.53 mmol) in tetrahydrofuran (20 cm^3) was treated with KCN (0.036 g, 0.55 mmol) and then stirred for 30 min at room temperature. The mixture was stirred for 1 hour under reflux. The solvent was removed under reduced pressure and the yellow residue extracted with dichloromethane (5 × 20 cm^3). The yellow extract was concentrated to give yellow crystals of $[Co(\eta\text{-}C_5H_5)(PMe_3)_2(CN)][PF_6]$ (ca. 75%).

Di(cyano)(η-cyclopentadienyl)(trimethylphosphine)cobalt

A suspension of $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ (0.66 g, 1.03 mmol) in tetrahydrofuran was treated with KCN (0.15 g, 2.30 mmol) and then stirred for 12 hours at 60°C. The solution became light yellow. The solvent was removed under reduced pressure and the yellow residue was crystallised several times from ethanol/pentane and acetone/diethyl ether in order to remove $K[PF_6]$. Pure $Co(\eta\text{-}C_5H_5)(PMe_3)(CN)_2$ was finally obtained as yellow crystals (ca. 75%).

(Azido)(η-cyclopentadienyl)bis(trimethylphosphine)cobalt hexafluorophosphate

A suspension of $[Co(\eta\text{-}C_5H_5)(PMe_3)_3][PF_6]_2$ (0.55 g, 0.84 mmol) in tetrahydrofuran (30 cm^3) was treated with NaN_3 (0.15 g, 2.70 mmol) and then stirred for 48 hours under reflux. The solution became brown. The solvent was removed under reduced pressure and the residue was washed with water and extracted with dichloromethane. Slow removal of dichloromethane under reduced pressure gave red-brown crystals of $[Co(\eta\text{-}C_5H_5)(PMe_3)_2N_3][PF_6]$ (ca. 30%).

Reaction of $Co(\eta\text{-}C_5H_5)(CO)I_2$ with PEt_3, 1 : 1

A solution of $Co(\eta\text{-}C_5H_5)(CO)I_2$ (2.20 g, 5.40 mmol) in toluene (300 cm^3) was treated with PEt_3 (0.80 cm^3, 0.54 mmol). Gas evolution was observed. The solvent was partly removed under reduced pressure. Evaporation gave black crystals of $Co(\eta\text{-}C_5H_5)(PEt_3)I_2$ (ca. 60%).

Reaction of $Co(\eta\text{-}C_5H_5)(CO)I_2$ with PEt_3 1 : 2

A solution of $Co(\eta\text{-}C_5H_5)(CO)I_2$ (1.62 g, 4.00 mmol) in toluene (200 cm^3) was cooled to ca. —20°C and then treated with PEt_3 (1.20, cm^3, 0.96 g, 8.13 mmol) with stirring. Gas evolution was observed. A brown precipitate formed and the solution became yellow. The brown precipitate was filtered off, washed with toluene (4 × 20 cm^3), and extracted with water (ca. 100 cm^3) to give a yellow solution. Addition of $[NH_4][PF_6]$ (1.50 g in 10 cm^3) gave a yellow-brown precipitate. This was crystallised from acetone/diethyl ether to give black crystals of $[Co(\eta\text{-}C_5H_5)(PEt_3)_2I][PF_6]$ (ca. 60%).

Reaction of $Co(\eta\text{-}C_5H_5)(CO)I_2$ with PEt_3, 1 : 3

A solution of $Co(\eta\text{-}C_5H_5)(CO)I_2$ (1.30 g, 3.20 mmol) in toluene (200 cm^3) was treated with PEt_3 (2.50 cm^3, 2.00 g, 16.9 mmol). The colour of the solution changed from the dark purple to yellow, and a pale yellow precipitate immediately separated. This was filtered off, and washed with toluene (3 × 20 cm^3) becoming paler. The pale yellow precipitate was extracted with water, and addition of $[NH_4][PF_6]$ (0.50 g in cm^3) to the solution gave a white precipitate. This was crystallised from acetone/water to give white crystals and comparison of their analytical data, ^1H NMR and IR spectra with those of an authentic sample showed them to be $[(PEt_3)(C_5H_5)][PF_6]$ (ca. 35%). The yellow toluene solution was concentrated in vacuum to ca. 2 cm^3 and water was added. A yellow crystalline compound was formed and was filtered off and recrystallised from light petroleum to give yellow needles. Comparison of the analytical data and IR spectrum of the product with that of an authentic sample showed it to be $Co(PEt_3)_2(CO)_2I$ (ca. 70%).

The colourless water solution was evaporated under reduced pressure to give a blue residue. This was crystallized from toluene/petroleum ether (b.p. 50—70°C) to give tourquoise blue crystals. These were identified as $Co(PEt_3)_2I_2$ by comparison of their analytical data, m.p. and IR spectra with that of an authentic sample (ca. 18%).

Acknowledgment

We greatly appreciate financial support from Comisión Asesora de Investigación Científica y Técnica (Spain).

References

1 S.G. Davies, M.L.H. Green and P.M.P. Mingos, Tetrahedron, 34 (1978) 3047.
2 H. Werner and W. Hofmann, Chem. Ber., 110 (1977) 3481.
3 J.A. Dineen and P.L. Pauson, J. Organometal. Chem., 43 (1972) 209.
4 T. Avilés and M.L.H. Green, J. Chem. Soc. Dalton, (1979) 1119.
5 T.B. King, Inorg. Chem., 5 (1966) 82.