

## NEW NEUTRAL AND CATIONIC CYCLOPENTADIENYLCOBALT COMPLEXES \*

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### Summary

The treatment of the aquocation  $[\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)(\text{H}_2\text{O})]^+$  with neutral and anionic ligands gives new cobalt complexes containing cations  $[\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{L}]^{n+}$ ,  $n = 0$ ; L = CN, CH<sub>3</sub>COO, CF<sub>3</sub>COO and  $n = 1$ ; L = P(*p*-MePh)<sub>3</sub>, NCEt, NCPH, CNCy, dppm and  $\{[\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)]_2(\mu\text{-L-L})\}^{2+}$ , L-L = bipy, dppm. The neutral cyano complex reacts with various electrophiles to give cationic isocyanide complexes containing the cation  $[\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)(\text{CNR})]^+$ , which have been isolated in low yields. Chemical behaviour and structural implications of IR and <sup>1</sup>H and <sup>13</sup>C NMR spectra are discussed.

### Introduction

The intermediate formation of the aquocation  $[\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)(\text{H}_2\text{O})]^+$  was observed during an attempt to obtain the coordinatively unsaturated species by reaction of the neutral iodo complex with AgBF<sub>4</sub> and its X-ray structure was determined [1]. The case of replacement of water in this compound means that it can be used to obtain new monomeric and dimeric cationic complexes. Low yields are obtained when isocyanides are used as ligands, but this type of compound can be synthesized through the electrophilic attack at the cyanide group, as reported for other cyano derivatives [2].

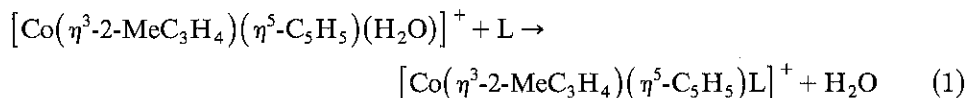
### Results and discussion

The addition of various ligands to freshly prepared solutions of I produces dark red solutions from which crystalline cationic complexes can be isolated by evapora-

\* This paper is dedicated to Professor R. Usón on the occasion of his 60th birthday.

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tion; the reaction is represented in eq. 1.

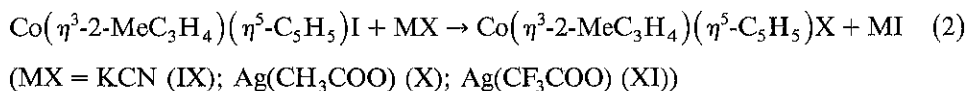


(L = P(*p*-MePh)<sub>3</sub> (II); NCEt (III); NCPH (IV); CNCy (V))

An excess of the ligand in the case of P(*p*-MePh)<sub>3</sub> must be avoided since this leads to lower yields, probably because of further nucleophilic attack by the ligand. In a similar reaction with bipy the dimeric cationic complex  $[\{\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-bipy})]^{2+}[\text{PF}_6]^{2-}$  (VI) was isolated and characterized by IR and NMR spectroscopy.

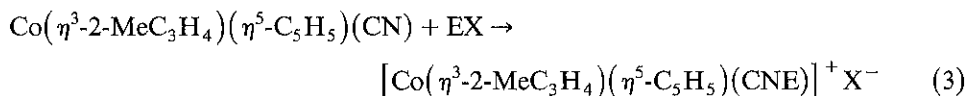
When dppm is used a similar dimeric cation  $[\{\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-dppm})][\text{BF}_4]_2$  (VII) can also be isolated if the exact stoichiometric amount of the ligand is used for the reaction; but in the present case use of an equimolar amount of the ligand leads to the monomeric cation  $[\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{dppm}]^+$  (VIII), which contains the monocoordinate ligand. All the salts are air sensitive but stable as solids under an inert atmosphere. They are soluble in CH<sub>2</sub>Cl<sub>2</sub> and acetone, but insoluble in diethyl ether and aliphatic solvents. Their reactivity decreases on going from phosphorus to nitrogen donor complexes, and complex V, containing isocyanide, is much less stable, and is isolated only in very low yield.

An alternative route to these isocyanide complexes is based on the familiar electrophilic attack on cyanide derivatives [2]. Compound IX can be obtained by reaction of the corresponding iodo complex with KCN, according to eq. 2, and a similar procedure can be used to obtain acetate derivatives.



Complex IX is an air stable solid, whereas X and XI are very easily hydrolyzed and must be manipulated under rigorously anhydrous conditions.

The reaction of the cyanide complex IX with various electrophiles leads to isocyanide complexes, as in eq. 3.



(EX = MeI (XII); SiMe<sub>3</sub>Cl (XIV); PPh<sub>2</sub>Cl (XV))

The reaction with MeI is incomplete in dichloromethane even after a long time, but goes to completion in polar solvents such as acetonitrile. Reaction with PhCH<sub>2</sub>Br does not take place in acetonitrile, and does not go to completion in dichloromethane. Reactions with SiMe<sub>3</sub>Cl and PPh<sub>2</sub>Cl are complete in dichloromethane after stirring for two days, but yields are always low because of the long reaction time required since all these complexes are unstable in solution and decompose to give green solutions with liberation of free isocyanide. Better yields were obtained from the more reactive oxonium salts  $[\text{OR}_3][\text{BF}_4]$  (R = Me (XII); Et (XIII)), with shorter reaction times.

All the complexes were crystallized as salts of bulky cations by addition of NaBPh<sub>4</sub> or NaBF<sub>4</sub>.

## Structural studies

The formulation of all the reported new complexes is in agreement with the experimental analytical data (see Table 1), although deviations are observed for air sensitive compounds.

Complexes II–IV and VIII behave as conductors in acetone with molar conductivities between 115.5 and 120.0  $\Lambda^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , which correspond to 1/1 electrolytes, in accord with the proposed formulation. Complexes V and XII–XV are not stable enough to permit conductivity measurements in acetone.

Complexes VI and VII have molar conductivities between 153.2 and 160.0  $\Lambda^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , in agreement with their formulation as 2/1 electrolytes.

The IR spectra of all the complexes show the characteristic absorptions due to the  $\eta\text{-C}_5\text{H}_5$  group [3]. The presence of the added ligand can be inferred from the presence of its characteristic absorption bands.

TABLE 1  
ANALYSES FOR CYCLOPENTADIENYLCOBALT COMPLEXES

Complex	Analysis (Found. (calc.) (%))		
	C	H	N
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{P}(p\text{-MePh})_3)](\text{BF}_4)$ (II)	61.2 (61.1)	6.1 (5.6)	—
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{NCeEt})](\text{BF}_4)$ (III)	45.2 (44.9)	5.8 (5.3)	4.5 (4.4)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{NCPh})](\text{BF}_4)$ (IV)	52.5 (52.1)	4.8 (4.6)	3.9 (3.8)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNCy})](\text{BF}_4)$ (V) <sup>a</sup>	52.0 (51.3)	6.7 (6.2)	4.1 (3.7)
$\{[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)]_2\text{bipy}\}(\text{PF}_6)_2$ (VI)	42.1 (41.8)	3.1 (3.9)	3.7 (3.5)
$\{[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)]_2\text{dppm}\}(\text{BF}_4)_2$ (VII)	56.5 (56.1)	5.7 (5.4)	—
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)\text{dppm}](\text{BF}_4)$ (VIII)	62.6 (62.8)	6.4 (5.3)	—
$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CN})$ (IX)	59.0 (58.6)	6.4 (5.8)	7.0 (6.8)
$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{OOCCH}_3)$ (X) <sup>a</sup>	53.8 (55.5)	7.2 (6.3)	—
$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{OOCFC}_3)$ (XI)	45.3 (45.2)	4.5 (4.1)	—
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNMe})](\text{BPh}_4)$ (XIIa) <sup>a</sup>	77.0 (77.9)	6.9 (6.5)	2.6 (2.6)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNMe})](\text{BF}_4)$ (XIIb) <sup>a</sup>	44.4 (42.9)	5.1 (4.9)	4.6 (4.6)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNEt})](\text{BF}_4)$ (XIII)	45.0 (44.9)	5.3 (5.8)	4.4 (4.4)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNSiMe}_3)](\text{BF}_4)$ (XIV)	73.9 (74.4)	6.7 (6.9)	2.7 (2.4)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNPh}_2)](\text{BPh}_4)$ (XV)	72.9 (73.0)	6.0 (5.7)	2.1 (2.0)

<sup>a</sup> Discrepancies are due to the great air-sensitivity of the complexes.

TABLE 2

MOST SIGNIFICANT IR ABSORPTIONS FOR CYCLOPENTADIENYLCOBALT COMPLEXES (cm<sup>-1</sup>)

Complex	$\nu(\text{CN})$	$\nu(\text{CNR})$	$\nu_a(\text{CO})$	$\nu_s(\text{CO})$	$\nu(\text{NCR})$
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{NCBt})](\text{BF}_4)$ (III)					2300
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{NCPH})](\text{BF}_4)$ (IV)					2300
$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CN})$ (IX)	2120	-	-	-	
$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{OOCCH}_3)$ (X)	-	-	1640	1380	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{OOCF}_3)]$ (XI)	-	-	1640	1380	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNMe})](\text{BPh}_4)$ (XIIa)	-	2240	-	-	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNMe})](\text{BF}_4)$ (XIIb)	-	2250	-	-	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNEt})](\text{BF}_4)$ (XIII)	-	2220	-	-	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNSiMe}_3)](\text{BPh}_4)$ (XIV)	-	2190	-	-	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNPPH}_2)](\text{BPh}_4)$ (XV)	-	2200	-	-	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{CNCy})](\text{BF}_4)$ (V)	-	2200	-	-	

<sup>a</sup> As KBr disc.

A weak absorption observed at 2300 cm<sup>-1</sup> for complexes III and IV is due to the  $\nu(\text{NC})$  stretching vibration, which is displaced to higher frequencies relative to that for the free ligand as previously reported [4]. The isocyanide complexes V and XII–XV show strong absorptions due to  $\nu(\text{CN})$  at 2190–2250 cm<sup>-1</sup> which are at higher wave numbers than those for the free ligand [5].

Complex IX shows the  $\nu(\text{CN})$  absorption at 2120 cm<sup>-1</sup>, only 40 cm<sup>-1</sup> lower than in the free anion indicating a low  $\pi$ -backbonding interaction. Both carboxylate complexes X and XI show absorptions at 1640 and 1380 cm<sup>-1</sup>, due respectively to  $\nu_a(\text{CO})$  and  $\nu_s(\text{CO})$ , indicating the presence of monocoordinate carboxylate groups. The most significant IR absorption bands are shown in Table 2.

### NMR spectroscopy

Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra are shown in Table 3. All the complexes give <sup>1</sup>H NMR spectra showing resonances due to H<sub>a</sub>, H<sub>s</sub> and the methyl protons of the 2-methyl- $\eta^3$ -allyl group. The Me-allyl resonance appears as a singlet at  $\delta$  0.94–2.35 ppm, with comparatively low values for neutral complexes IX, X ( $\delta$  1.19 ppm) and XI ( $\delta$  0.94 ppm) in benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub>.

The H<sub>s</sub> resonance is also normally observed as a singlet at  $\delta$  4.13–4.98 ppm, but for complex VI at  $\delta$  3.58 ppm and for IX at  $\delta$  3.48 ppm. The H<sub>a</sub> resonance appears as a doublet for complex II, at  $\delta$  1.31 ppm with  $J(\text{P-H}) = 12.89$  Hz, and also for complex VIII, at  $\delta$  1.73 ppm with  $J(\text{P-H}) = 12.82$  Hz, whereas a complex signal is observed for VII at  $\delta$  1.46 ppm. A singlet is observed for the remaining compounds, but with a wide range of values ( $\delta$  1.69–4.36 ppm) depending on the ligands. The <sup>1</sup>H resonance due to the Cp protons appears as a singlet at  $\delta$  5.19–5.82 ppm for all the cationic complexes except complex II; this shows a doublet at  $\delta$  5.23 ppm with  $J(\text{P-H}) = 1.14$  Hz whereas lower values in the range  $\delta$  4.33–4.63 ppm are observed for the neutral complexes IX–XI in benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub>.

Other expected resonances due to the various ligands are observed. Complex II shows a singlet at  $\delta$  2.39 ppm for Me-phenyl and a multiplet for Ph protons. A quadruplet and a triplet are observed for CH<sub>2</sub> and Me protons in complex III, respectively, at  $\delta$  2.56 ( $J(\text{H-H}) = 7.65$  Hz) and 1.13 ppm ( $J(\text{H-H}) = 7.56$  Hz). A

TABLE 3

<sup>1</sup>H AND <sup>13</sup>C NMR DATA FOR CYCLOPENTADIENYLCOBALT COMPLEXES

Complex	<sup>1</sup> H NMR <sup>a</sup>	<sup>13</sup> C NMR <sup>b</sup>
II <sup>c</sup>	1.31(2), d, ( <i>J</i> (H <sub>a</sub> -P) 12.89, H <sub>a</sub> ; 2.25(3), s, Me(allyl); 2.39(3), s, Me(phenyl); 4.35(2), s, H <sub>s</sub> ; 5.23(5), d, ( <i>J</i> (P-H) 1.14) Cp; 7.46(12), c, Ph	10.03, s, CH <sub>2</sub> (Et); 13.78, s, Me(Et); 25.17, s, Me(allyl); 58.26, s, C(1)+C(3)(allyl); 87.68, s, Cp; 112.35, s, C(2)(allyl)
III <sup>d</sup>	1.13(3), t, ( <i>J</i> (H-H) 7.56), Me(Et); 1.87(3), s, Me(allyl); 2.05(2), s, H <sub>a</sub> 2.56(2), q, ( <i>J</i> (H-H) 7.65), CH <sub>2</sub> (Et); 5.02(2), s, H <sub>s</sub> ; 5.27(5), s, Cp	25.09, s, Me(allyl); 58.57, s, C(1)+C(3)(allyl); 88.05, s, Cp; 130.45, (s), C(4)(Ph); 133.61, s, C(3.5)(Ph); 135.59, s, C(2.6)(Ph)
IV <sup>d</sup>	1.97(3), s, Me(allyl); 2.21(2), s, H <sub>a</sub> ; 5.17(2), s, H <sub>s</sub> ; 5.36(5), s, Cp; 7.60(5), c, Ph	
V <sup>d</sup>	1.44(11), c, Cy; 1.96(2), s, Ha; 2.09(3), s, Me(allyl); 4.23, (2) s, H <sub>s</sub> ; 5.30(5), s, Cp	
VI <sup>c</sup>	3.58(4), s, H <sub>s</sub> ; 5.82(10), s, Cp; 7.75-8.98(8), c, bipy	
VII <sup>d</sup>	1.46(4), c, H <sub>a</sub> ; 2.18(6), s, Me(allyl); 3.00(2), t, ( <i>J</i> (P-H) 6.27); PCH <sub>2</sub> P; 4.33(4), s, H <sub>s</sub> ; 4.84(10), s, Cp; 7.24 (20), c, Ph	
VIII <sup>d</sup>	1.73(2), d, ( <i>J</i> (H-P) 12.82) H <sub>a</sub> ; 2.35(3), s, Me(allyl); 3.18(2), d, ( <i>J</i> (P-H) 8.7), PCH <sub>2</sub> P; 4.32(2), s, H <sub>s</sub> ; 5.19(5), s, Cp; 7.57(20), c, Ph	
IX <sup>e</sup>	1.19(3), s, Me(allyl); 2.29(2), s, H <sub>a</sub> ; 3.48(2), s, H <sub>s</sub> ; 4.33(5), s, Cp	
X <sup>f</sup>	1.19(3), s, Me(allyl); 1.70(2), s, H <sub>a</sub> ; 2.00(3), s, OOC-Me; 4.63(5), s, Cp; 4.98(2), s, H <sub>s</sub>	
XI <sup>e</sup>	0.94(3), s, Me(allyl); 1.69(2), s, H <sub>a</sub> ; 4.39(5), s, Cp; 4.82(2), s, H <sub>s</sub>	
XIIa <sup>c</sup>	2.20(3), s, Me(allyl); 2.84(3), s, Me(CNMe); 3.49(2), s, H <sub>a</sub> ; 4.33(2), s, H <sub>s</sub> ; 5.52(5), s, Cp; 6.86(20), c, Ph(BPh <sub>4</sub> )	
XIIb <sup>g</sup>	1.60(3), s, Me(CNMe); 2.11(3), s, Me(allyl); 3.53(2), s, H <sub>a</sub> ; 4.19(2), s, H <sub>s</sub> ; 5.37(5), s, Cp	
XIII <sup>c</sup>	1.39(3), t, ( <i>J</i> (H-H) 7.3), Me(Et); 2.20(3), s, Me(allyl); 3.90(2); q( <i>J</i> (H-H) 7.3), CH <sub>2</sub> (Et); 4.36(2), s, Ha; 5.57(5), s, Cp; 5.60(2), s, H <sub>s</sub>	28.35, s, Me(allyl); 57.14, s, C(1)+C(3)(allyl); 85.05, s, Cp; 124.67, s, C(4), Ph(BPh <sub>4</sub> ); 127.05, s, C(3.5), Ph(BPh <sub>4</sub> ); 133.22, s, C(2.6), Ph(BPh <sub>4</sub> )
XIV <sup>d</sup>	0.06(9), s, Me(SiMe <sub>3</sub> ); 2.03(3), s, Me(allyl); 2.16(2), s, H <sub>a</sub> ; 4.13(2), s, H <sub>s</sub> ; 5.16(5), s, Cp; 7.09(20), c, Ph(BPh <sub>4</sub> )	28.21, s, Me(allyl); 27.03, s, Cp; 57.64, s, C(1)+C(3)(allyl); 124.64; s; 126.89, s; 133.19, s (BPh <sub>4</sub> +CNPPPh <sub>2</sub> )
XV <sup>d</sup>	2.04(3), s, Me(allyl); 2.17(2), s, H <sub>a</sub> ; 4.14(2), s, H <sub>s</sub> ; 5.17(5), s, Cp; 7.10(30), c, Ph(CNPPPh <sub>2</sub> ), (BPh <sub>4</sub> )	

<sup>a,b</sup> Given as chemical shifts in ppm rel. to TMS, (relative intensity), multiplicity (*J* Hz), assignment. <sup>c</sup> In acetone-*d*<sub>6</sub>. <sup>d</sup> In methylene chloride-*d*<sub>2</sub>. <sup>e</sup> In benzene-*d*<sub>6</sub>. <sup>f</sup> In toluene-*d*<sub>8</sub>. <sup>g</sup> In chloroform-*d*<sub>1</sub>.

similar pattern is observed for the ethyl radical in complex XIII, at  $\delta$  3.90 ( $J(\text{H}-\text{H}) = 7.3$  Hz) and  $\delta$  1.39 ppm ( $J(\text{H}-\text{H}) = 7.3$  Hz), respectively.  $^1\text{H}$  resonances for the methyl and trimethylsilyl complexes appear at  $\delta$  1.60 and 0.06 ppm, respectively, and complex signals are observed for the corresponding Ph and Cy groups in the rest of the complexes.

The fact that the bonding of the ppm ligand is different in complexes VII and VIII is evident from the  $^1\text{H}$  and  $^{31}\text{P}$  spectra. Complex VII shows one singlet at  $\delta$  44.30 ppm, as expected for two equivalent P atoms of the ligands forming a bridge, whereas two doublets at  $\delta$  42.65 and  $-26.22$  ppm with  $J(\text{P}-\text{P}) = 51.38$  Hz are observed for complex VIII, indicating that it contains two non equivalent P atoms mutually coupled, the first signal being due to the coordinate and the second to the free P atom.

$^{13}\text{C}$  NMR spectra for complexes III, IV, XIV and XV, with assignments, are shown in Table 3.

## Experimental

All experiments were performed under nitrogen on a vacuum line using Schlenk type glassware. Solvents were dried by standard methods and distilled. Conductivity measurements were made with a LF-42 conductimeter. IR spectra were recorded with Nujol mulls between CsI plates on a Perkin-Elmer 599 spectrophotometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Varian FT-80A instrument. Microanalytical determinations were carried out with a Perkin-Elmer 240B microanalyzer. Deviations in H are due to water incorporated in the  $\text{WO}_3$  added to improve combustion of the samples. A second determination was carried out without addition of  $\text{WO}_3$  for some complexes.  $\text{Co}(\eta^3\text{-}2\text{-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{I}$  was prepared by a published method [6]. The remaining reagents were commercial high purity products and were used without further purification.

*Preparation of  $[\text{Co}(\eta^3\text{-}2\text{-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{L}]^+$  complexes;  $\text{L} = \text{P}(p\text{-MePh})_3$  (II),  $\text{NCEt}$  (III),  $\text{NCPH}$  (IV),  $\text{dppm}$  (VIII)*

$\text{AgBF}_4$  (0.15 g) was added to a  $\text{CH}_2\text{Cl}_2$  (30 ml) solution of I (0.30 g, 0.97 mmol) and the mixture was stirred for 0.5 h, in the absence of light. The  $\text{AgI}$  was filtered off and the filtrate allowed to flow into a  $\text{CH}_2\text{Cl}_2$  (10 ml) solution containing 0.97 mmol of the ligand. The resulting dark red solution was evaporated to dryness and the residue extracted with  $\text{CH}_2\text{Cl}_2$ . Evaporation of the solvent and addition of petroleum ether (II) or ethyl ether (III, IV) gave crystals of the required complexes, which were filtered off, washed, and dried under vacuum.

Propionitrile (25 ml) was used as solvent instead of  $\text{CH}_2\text{Cl}_2$  for complex III. Complex VIII was extracted with acetone and crystallized by addition of ethyl ether. Yields ca. 50%.

*Preparation of complexes  $[\{\text{Co}(\eta^3\text{-}2\text{-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-L-L})]^{2+}$ ;  $\text{L-L} = \text{bipy}$  (VI),  $\text{dppm}$  (VII)*

The procedure was the same as that described above except that a 2/1 ratio of cobalt complex to L-L was used. The residue obtained from the reaction for complex VI was extracted into water and then precipitated by addition by  $\text{NH}_4\text{PF}_6$ . The yellow solid isolated was recrystallized from acetone/ethyl ether. The residue

obtained in the reaction for complex VII was extracted into acetone and crystallized by addition of ethyl ether to give orange-red crystals. Yields ca. 40%.

*Preparation of complexes  $\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{X}$ ; X = CN (IX),  $\text{CH}_3\text{COO}$  (X),  $\text{CF}_3\text{COO}$  (XI)*

A solution of  $\text{Co}(\eta^3\text{-2-MeC}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{I}$  (0.50 g, 1.6 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) was treated with solid  $\text{Ag}(\text{CH}_3\text{COO})$  or  $\text{Ag}(\text{CF}_3\text{COO})$  (1.6 mmol) and the mixture was stirred for 4 h at room temperature. A mixture of  $\text{CH}_2\text{Cl}_2$ /ethanol (15/15) and KCN was used for complex IX. After filtration, the solvent was removed under vacuum and the residue in the case of IX was extracted with  $\text{CH}_2\text{Cl}_2$ . Addition of petroleum ether and cooling gave IX as orange-red crystals. The residues for X and XI were extracted with petroleum ether, and dark, almost black, crystals were obtained on cooling of the extract to 0°C. Yields ca. 40%.

*Preparation of complexes  $[\text{Co}(\eta^3\text{-2Me-C}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{L}]^+$ ; L =  $\text{CNCy}$  (V),  $\text{CNMe}$  (XII),  $\text{CNEt}$  (XIII),  $\text{CNSiMe}_3$  (XIV),  $\text{CNPh}_2$  (XV)*

*Method A.* The procedure was the same as that described for complexes II–IV but with  $\text{CNCy}$  as the ligand [7]. After 0.5 h stirring at room temperature the solvent was removed under vacuum and the residue extracted with ethanol. Evaporation and cooling to 0°C gave red crystals of V.

*Method B.* An excess of  $\text{MeI}$ ,  $\text{SiMe}_3\text{Cl}$ , or  $\text{PPh}_2\text{Cl}$  (10/1) was added to a solution of complex IX (0.50 mmol) in acetonitrile (XIIa) or  $\text{CH}_2\text{Cl}_2$  (XIII–XV) (20 ml) and the mixture was stirred for 15–24 h at room temperature. An excess of  $\text{NH}_4\text{BPh}_4$  was added and the mixture was stirred for 15 min, then filtered, and the filtrate was evaporated to dryness under vacuum. The residue was extracted into  $\text{CH}_2\text{Cl}_2$ , and evaporation and addition of petroleum ether gave yellow crystals of the required complex.

*Method C.* An excess (10/1) of  $\text{OR}_3^+\text{BF}_4^-$ , R = Me, Et, was added to a solution of complex IX (0.50 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 ml) and the mixture was stirred for 12 h at room temperature. The solution was filtered then evaporated to dryness under vacuum. The residue was extracted with ethanol, and evaporation of the extract gave red-orange crystals of XII and XIII. Yields 30%.

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