Pseudotetrahedral Organocobalt(III) Compounds Containing Specific Coordination Sites for Brønsted Acids

Mario Roberto Meneghetti,[c] Mary Grellier,[a] Michel Pfeffer,*[a] André De Cian,[b] and Jean Fischer[b]

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Transmetallation of the lithiated derivative 2,6-bis[dimethyl(amino)methyl]phenyllithium with the cobalt(III) centre of the dimer bis[(η^5-cyclopentadienyl)cobalt(iodo)(μ-iodo)] has been found to afford the organocobalt compound [CoI{2-(Me_2NCH_2)-6-($Me_2NH^+CH_2$)C_6H_3}(η^5-C_5H_5)]I, **3**, in which the potentially terdentate (pincer) ligand is bound to Co through the formerly lithiated aryl carbon atom and one NMe_2 unit only, whilst the second NMe_2 group is protonated by HI. In the presence of aqueous KPF_6, **3** has been found to undergo both substitution of the iodide bound to Co by a water molecule and deprotonation of the Me_2NH group to afford [CoI{2,6-(Me_2NCH_2)$_2C_6H_3$}(η^5-C_5H_5)(H_2O)]PF_6, **4a**. It was found that the water ligand in **4a** could be substituted by neutral ligands such as PMe_2Ph as well as by Brønsted acids such as HCl, HI, HF, or HOAc to afford the compounds [CoX{2-(Me_2NCH_2)-6-($Me_2NH^+CH_2$)C_6H_3}(η^5-C_5H_5)]PF_6, **5a–d**, where X = Cl, I, F, or OAc, respectively. Crystal structure analyses of some representative examples of these compounds, including **4a**, have shown unambiguously that an intramolecular hydrogen bond is present between X and the proton of the Me_2NH^+ unit. ^{1}H-NMR evidence that this interaction persists in solution has been found for compounds **4a**, **5a**, **5c**, and **5d**.

Introduction

We have recently shown that organometallic compounds of Co^{III} containing a metallacyclic unit may readily be synthesized by transmetallation reactions of lithiated tertiary amines.[1] Such reactions have afforded a wide variety of stable pseudotetrahedral organocobalt compounds in which the cobalt is a stereogenic centre. While investigating the scope of this procedure, we became interested in ascertaining whether other lithiated polydentate amino derivatives could be used to extend the synthetic potential to other organocobalt compounds with a view to varying the nature of the resulting compounds. Thus, we first attempted to synthesize derivatives using the well-known “pincer” ligand [2,6-(Me_2NCH_2)$_2C_6H_3$]$^-$ = N^C^N, the chemistry of which with transition metals has been extensively studied by van Koten et al.[2]

This ligand usually bonds to a metal centre through an aryl−M σ bond, but it is also capable of donating a further two electron pairs to the metal through N coordination. The potentially terdentate “pincer” ligand has been shown to be extremely flexible in its coordination and bonding modes (see Figure 1). Its use has led to the isolation and characterization of bis(amino)aryl metal complexes of both main group and transition metals, which exhibit novel reactivities and structural features.[3] Consequently, although it was reasonable to assume that the lithiated derivative of the “pincer” ligand would interact with a Co^{III} centre, we could not predict a priori the type of structure that would be formed.

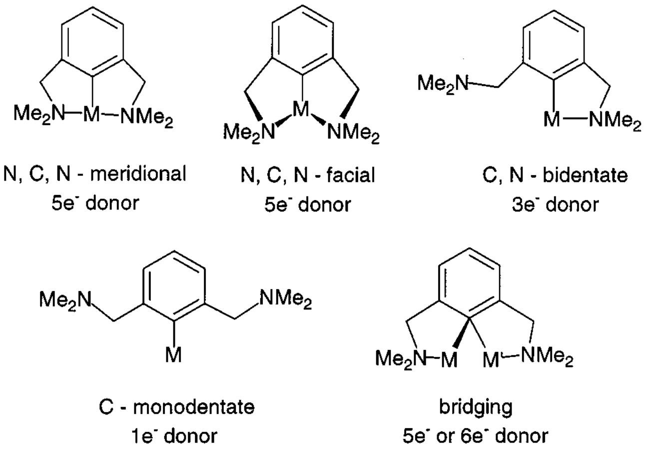

Figure 1. Encountered bonding modes of the pincer ligand

Prior to our work, we were aware of only one cobalt(II) complex, namely Co[2,6-(Me_2NCH_2)$_2C_6H_3$]X(L) (X = Cl, Br, I; L = py, PPh_3),[4] in which this “pincer” ligand is coordinated to Co through one aryl carbon and the two nitrogen atoms in a meridional geometry (see Figure 2). Its structure was deduced on the basis of ESR studies and it

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[a] Laboratoire de Synthèses Métallo-Induites,
UMR 7513 du CNRS,
4, rue Blaise Pascal, F-67000 Strasbourg, France
[b] Laboratoire de Cristallochimie et Chimie Structurale,
UMR 7513 du CNRS,
4, rue Blaise Pascal, F-67000 Strasbourg, France
[c] Address [a] or permanent address:
Laboratory of Molecular Catalysis, IQ/UFRGS,
Av. Bento Gonçalves, 9500 Porto Alegre, Brazil

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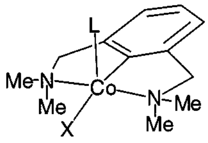


Figure 2. Proposed structure of $Co^{II}[C_6H_3(CH_2NMe_2)_2-2,6]XL$

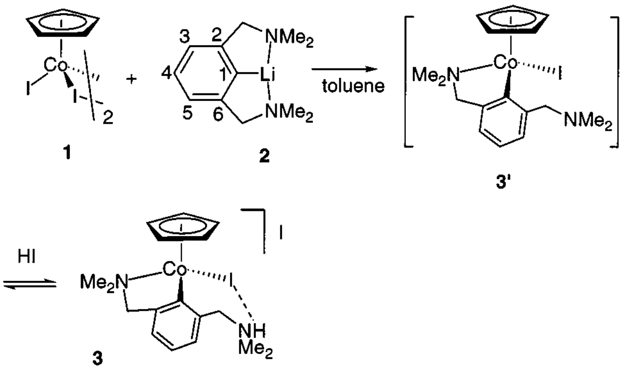
proved to be isostructural with the related Ni^{III} compound $Ni[C_6H_3(CH_2NMe_2)_2-2,6]Br_2$.[5]

We describe herein the synthesis of a number of novel aryl Co^{III} complexes in which the "pincer" ligand is coordinated to the cobalt centre through the carbon and one nitrogen atom while significant intramolecular H-bonding interactions are in evidence between the third anionic ligand and the protonated non-coordinated NMe_2 unit.

Results

1. Synthesis of the Organometallic Complexes

We have recently shown that *ortho*-lithiated N-containing ligands (LiC^N) can be readily transmetallated with $[CpCoI_2]_2$, thereby generating a series of stable organocobalt complexes of the type CpCo(C^N)I. However, we found that when any lithiated aryl compound substituted at its 2-position by CH_2NMe_2 and at its 6-position by another substituent (Me, OMe, or F) was used, the expected product was not obtained.[1] Nevertheless, in marked contrast, reaction of the lithiated "pincer" ligand **2** with $[CpCoI_2]_2$ (**1**) in toluene at room temperature afforded the organocobalt compound **3** as a green powder in good yield (see Scheme 1).



Scheme 1

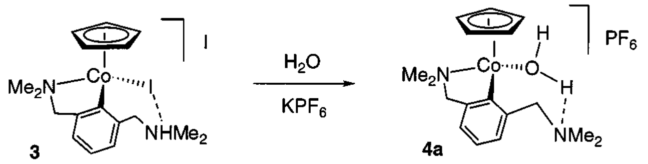
Complex **3** was found to be very soluble in acetone, THF, and chlorinated solvents, quite soluble in C_6H_6, sparingly soluble in Et_2O and MeOH, and insoluble in alkanes. Analytical samples of this complex were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution. It proved to be stable towards air, both in the solid-state and in solution (2 days in $CDCl_3$).

Compound **3** has been fully characterized by ^1H- and ^{13}C-NMR spectrometry, IR spectroscopy, and X-ray analysis (see below). The ^1H- and ^{13}C-NMR spectra in $CDCl_3$ feature resonances consistent with a diamagnetic Co^{III} complex associated with the relevant organic fragments. From the ^1H-NMR spectrum of **3**, it can be concluded that only one of the NMe_2 units is diastereotopic, giving rise to two signals at $\delta = 3.16$ and 2.31. A broad singlet at $\delta = 2.93$ can be assigned to the second NMe_2 unit. This latter chemical shift is at rather low field compared to the signals of non-coordinated NMe_2 groups in related molecules, which usually appear at around $\delta = 2.1-2.3$.[6,7]

Since both combustion analyses and ^1H-NMR spectra suggested that **3** was actually a 1:1 adduct of $[CoI\{C_6H_3(CH_2NMe_2)(CH_2NMe_2)-2,6\}(\eta^5-C_5H_5)]$, **3′**, and HI, we propose that some hydroiodic acid was produced during the synthesis of **3′**, which then protonated the non-coordinated NMe_2 group. Addition of an excess of HI to a $CDCl_3$ solution of **3** in an NMR tube led to splitting of the aforementioned broad signal resulting in two doublets at $\delta = 3.02$ and 2.82 with $^3J_{H-H} = 5.64$ Hz, as well as to the appearance of a well-defined broad singlet at $\delta = 10.0$. These signals can be assigned to the methyl groups and the acidic proton, respectively, of the protonated Me_2NH^+ group. Thus, it would seem that in solution **3** is in equilibrium with **3′** and HI according to Scheme 1; in the presence of excess of HI, this equilibrium is shifted completely towards **3**. The same phenomenon was evident from the ^{13}C-NMR spectra. On treatment of **3** with HI, a broad signal at $\delta = 42.03$ was transformed into two signals at $\delta = 44.17$ and 40.69, corresponding to the two diastereotopic methyl groups of the Me_2NH^+ unit.

2. Reaction of 3 with Water (Synthesis of 4a)

By washing a solution of **3** in CH_2Cl_2 several times with water and combining the aqueous extracts, a new complex, **4a**, was obtained (Scheme 2). This could be isolated as a red powder following the addition of KPF_6.



Scheme 2

IR spectroscopy confirmed the presence of a water molecule in the complex through the appearance of an intense, sharp absorption at 3575 cm^{-1}. Combustion analysis clearly revealed that one water molecule was present and, significantly, that hydroiodic acid was no longer incorporated. By NMR spectrometry, two distinct diastereotopic NMe_2 groups were observed in $CDCl_3$ solution. It is remarkable that the NMe_2 group coordinated to the cobalt centre displays chemical shifts separated by more than 2.0 ppm, whereas for the second NMe_2 group the chemical shift difference is just 0.65 ppm.

3. Reactions of 4a with Phosphanes and Brønsted Acids

3.1 Reaction with PMe_2Ph

It was found that the water ligand in **4a** could be substituted by a phosphane (PMe_2Ph) to quantitatively afford **4b** as a violet powder. The ^1H-NMR spectrum of **4b** features the expected signals with two singlets due to a coordinated NMe_2 unit at δ = 2.89 and 2.23 and a singlet at δ = 2.34 due to the "free" amine. Additionally, two discrete AB spin systems for the CH_2 groups are observed. In the presence of traces of hydrochloric acid, the "free" NMe_2 unit of **4b** is protonated to give **6**, which could be isolated as a red powder. In its ^1H-NMR spectrum, **6** exhibits a signal at δ = 9.25 attributable to the H^+ of the Me_2NH^+ group, and a broad unresolved peak due to the methyl groups of the Me_2NH^+ unit, which appears further downfield (δ = 3.37) compared to the corresponding signal of the unprotonated amine. Moreover, in the IR spectrum a typical absorption band for an $N-H^+$ unit is observed at 2704 cm^{-1}.

3.2 Reactions with Brønsted Acids

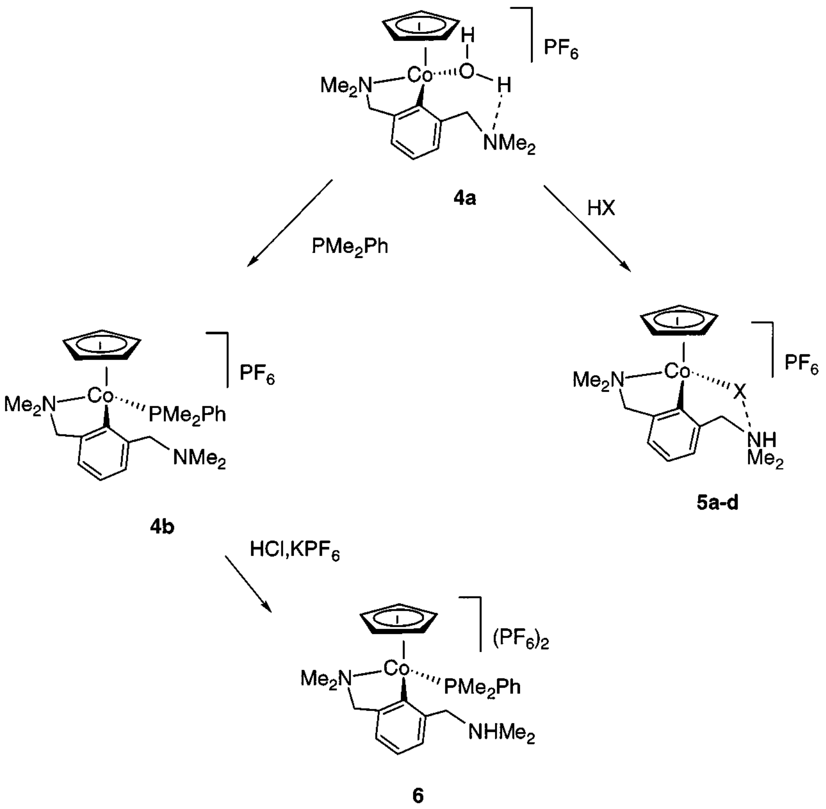
3.2.1 Reaction with HCl (Synthesis of 5a)

In order to find out why the aquo complex **4a** was obtained, we tried to expand this series of compounds by employing related ligands. We found that neither primary or secondary amines nor alcohols led to adducts analogous to **4a**, i.e. no products of substitution of the water molecule by these OH- or NH-containing ligands were obtained. However, we have found that a series of Brønsted acids are capable of substituting the water ligand in **4a** to afford stable organocobalt compounds, and that such reactions occur without any hydrolysis of the Co−C bond of the complex (see Scheme 3). Thus, treatment of **4a** with HCl afforded **5a** as a red-violet powder. This substitution was best achieved using ammonium chloride as a source of HCl with **4a** in methanol.

The ^1H-NMR spectrum of **5a** is similar to that of **4a** in that the large chemical shift difference (Δδ ≈ 2.0 ppm) for the NMe_2 unit coordinated to the cobalt is again apparent and the protonated NMe_2 group is also diastereotopic (Δδ ≈ 0.5 ppm). Furthermore, the effect of "HCl coordination" versus "H_2O coordination" on the cobalt centre can easily be detected. In **5a**, both the CH_2 and NMe_2 protons of the non-coordinating CH_2NMe_2 unit are very much deshielded as compared to those of the corresponding unit in **4a** (see Experimental Section). The coordinated hydrochloric acid gives rise to a broad signal at δ = 9.48. In the IR spectrum a typical absorption for the M_2N-H^+ group is seen at 2692 cm^{-1}.

3.2.2 Reaction with HI (Synthesis of 5b)

The reaction of **4a** with HI (derived from NH_4I) furnished **5b** as a green powder of a similar hue as **3**. The IR spectrum of **5b** confirmed the presence of an Me_2NH^+ group through the appearance of an absorption band at 2697 cm^{-1}. The ^1H-NMR spectrum of **5b** provides strong evidence that this compound has a different magnetic environment compared to **4a** and **5a**, with the Δδ of the diastereotopic Me groups of the NMe_2-Co unit being comparable to that in **3** (0.6 ppm). The acidic proton of the Me_2NH^+ group could be observed as a broad feature at δ = 9.33, but the J_{H-H} between H^+ and NMe_2 in this group was not detectable. It seems likely that the structure of **5b** is similar to that observed in **3**, i.e. with the same ligands about the cobalt centre, and most likely the same electronic interac-



Scheme 3

tion between the iodo ligand and the Me_2NH^+ unit (see below).

3.2.3 Reaction with HF (Synthesis of 5c)

Compound **5c** could easily be obtained in good yield by treatment of **4a** with 40% aq. HF. The IR spectrum of **5c** features a large, prominent absorption band at 2260 cm^{-1} due to the stretching vibration of an $N-H^+$ bond. In order to unambiguously confirm that this band was indeed due to a stretching mode of an $N-H^+$ unit, a H/D exchange experiment using D_2O was carried out. Under these conditions, a new absorption at 1800 cm^{-1} was observed, while the absorption at 2260 cm^{-1} disappeared, thus confirming our assignment. This significant shift to lower frequency for the ν_{sN-H} band of a tertiary ammonium salt[8] may be explained in terms of a hydrogen-bonding interaction between NH^+ and F, which would increase the $N-H^+$ bond length and consequently decrease the associated stretching frequency. Moreover, the ν_{sN-H}/ν_{sN-D} ratio (1.25) gives an additional indication of the existence of a strong hydrogen bond between N−H and F in **5c**.[9]

The ^{1}H-NMR spectrum of **5c** displays the same trends as observed for the previous complexes. This feature suggests that the structures are closely related, i.e. the water ligand in **4a** is merely replaced by HCl and HF to form **5a** and **5c**, respectively. The large $\Delta\delta$ chemical shift difference (2.43 ppm) for the NMe_2-Co unit is strongly indicative of interactions akin to those found in **4a** and **5a**. Some interesting features of the ^{1}H-NMR spectrum of **5c** arise from the presence of the F atom: (i) the signal of the NH^+ proton is located at $\delta = 11$ and shows a sizable J_{H-F} coupling constant (89 Hz);[10] (ii) the highfield resonating methyl group of the NMe_2 unit directly coordinated to the cobalt centre displays a $^4J_{H-F}$ coupling (6.90 Hz); (iii) the two methyl groups of the non-coordinated NMe_2 unit display a $^4J_{H-F}$ coupling ($\approx$ 4.1 Hz), proving the existence of bonding interactions between N−H and F−Co.

3.2.4 Reaction with CH_3COOH (Synthesis of 5d)

Treatment of **4a** with an excess of CH_3COOH in methanol led to the formation of **5d** in very good yield. The IR spectrum of **5d** features a series of overtones consistent with the presence of an Me_2NH^+ group (2700−2400 cm^{-1}) and a typical C=O absorption band at 1634 cm^{-1}. The ^{1}H-NMR spectrum of **5d** also shows a large $\Delta\delta$ chemical shift difference (2.24 ppm) for the NMe_2 unit coordinated to Co, as observed for **4a**, **5a**, and **5c**.

4. X-ray Crystal Structure Analysis of 3, 4a, 5a, and 5d

In order to obtain more structural information on this series of novel complexes, X-ray diffraction studies on some representative compounds have been undertaken. In Table 1, selected geometrical parameters for the complexes **3**, **4a**, **5a**, and **5d** are presented. ORTEP representations of the cationic parts of these salts are depicted in Figures 3−6, while crystallographic data is collected in Table 2. Despite the rather different ^{1}H-NMR data observed for these compounds, their molecular geometries display several analo-

Table 1. Selected bond distances and angles in complexes **3**, **4a**, **5a**, and **5d**

Bond lengths [Å]		Bond angles [°]	
	Compound **3**		
Co−Cp$^{\#[a]}$	1.731(2)	N1−Co−C14	83.2(2)
Co−C(Cp)$_{av}$	2.106(8)	N1−Co−I1	98.9(2)
Co−I1	2.598(1)	I1−Co−C14	97.0(2)
Co−N1	2.067(6)	Cp^a−Co−N1	127.8(5)
Co−C14	1.966(5)	Cp^a−Co−C14	122.7(5)
N1−C8	1.52(1)	Cp^a−Co−I1	118.6(6)
C8−C9	1.50(1)	Co−N1−C8	103.0(5)
C9−C14	1.387(8)	N1−C8−C9	106.6(6)
N2−HO1	0.88(1)	C8−C9−C14	118.1(6)
N2I1	3.43(1)	C9−C14−Co	110.4(4)
		C6−N1−Co−I1	19.1(5)
		N2−HO1−I1	170(1)
		C14−C13−C15−N2	92.6(6)
	4a		
Co−Cp$^{\#[a]}$	1.719(6)	N1−Co−C14	82.6(2)
Co−C(Cp)$_{av}$	2.090(6)	N1−Co−O1	94.1(2)
Co−O	1.977(4)	O−Co−C14	91.2(2)
Co−N1	2.029(4)	Cp^a−Co−N1	128.2(6)
Co−C14	1.951(5)	Cp^a−Co−C14	124.0(1)
N1−C8	1.494(8)	Cp^a−Co−O	124.6(3)
C8−C9	1.474(8)	Co−N1−C8	103.0(3)
C9−C14	1.404(8)	N1−C8−C9	107.9(8)
N2HO1	1.74(1)	C8−C9−C14	115.1(6)
N2O	2.588(8)	C9−C14−Co	110.7(6)
		C6−N1−Co−O	12.6(4)
		N2−HO1−O	168(1)
		C14−C13−C15−N2	−65.4(7)
	5a		
Co−Cp$^{\#}$	1.71(1)	N1−Co−C14	82.8(1)
Co−C(Cp)$_{av}$	2.089(4)	N1−Co−Cl	96.8(1)
Co−Cl	2.2832(9)	Cl−Co−C14	95.9(1)
Co−N1	2.074(3)	Cp^a−Co−N1	125.5(8)
Co−C14	1.964(3)	Cp^a−Co−C14	128.7(6)
N1−C8	1.487(5)	Cp^a−Co−Cl	120.9(2)
C8−C9	1.490(5)	Co−N1−C8	120.9(2)
C9−C14	1.406(5)	N1−C8−C9	107.5(3)
N2Cl	3.028(8)	C8−C9−C14	116.4(3)
N2−H01	1.08(7)	C9−C14−Co	110.7(2)
ClH01	1.99(2)	N2−H01Cl	158.1(4)
N2Cl	3.02(8)	C6−N1−Co−Cl	14.6(6)
		C14−C13−C15−N2	−77.5(4)
	5d		
Co−Cp$^{\#}$	1.71(8)	N1−Co−C14	82.5(3)
Co−C(Cp)$_{av}$	2.082(9)	N1−Co−O1	96.4(2)
Co−O1	1.992(5)	O1−Co−C14	93.3(3)
Co−N1	2.010(6)	Cp^a−Co−N1	131.0(2)
Co−C14	1.936(7)	Cp^a−Co−C14	122.9(5)
N1−C8	1.48(1)	Cp^a−Co−O1	119.9(4)
C8−C9	1.51(1)	Co−N1−C8	102.9(4)
C9−C14	1.37(1)	N1−C8−C9	105.7(6)
O1−C18	1.31(1)	C8−C9−C14	115.8(7)
O2−C18	1.20(1)	C9−C14−Co	110.3(5)
N2O1	2.72(2)	O1−C18−O2	123.8(9)
N2−H01	0.92(2)	O1−C18−C19	114.0(8)
O1H01	1.80(2)	O2−C18−C19	122.1(8)
		N2−H01O1	173.0(3)
		C7−N1−Co−O1	16.4(4)
		C14−C13−C15−N2	−67.9(7)

[a] Cp$^{\#}$ centroid of cyclopentadienyl ring.

gies, at least as far as the “CpCo(pincer)” fragments of the molecules are concerned.

In all cases, the cobalt atoms are found in a distorted octahedral (pseudotetrahedral) environment. The metal coordination sphere comprises a η^5-C_5H_5 ligand and the “pincer” coordinated through the central aryl carbon atom and the nitrogen atom of one NMe_2 unit only. The final coordination site at Co is occupied by an iodide, a water molecule, a chloride, or an acetate group coordinated through an oxygen atom, respectively (throughout this section these ligands will be denoted as “X”).

The bite angles of the five-membered chelated rings, N1−Co−C14, and the distances Co−centroid Cp, Co−C14, and Co−N1 are similar in all the complexes. The chelate ring (note that comparable distances and angles have recently been reported for related organocobalt species)[1,11] appears to display a somewhat unfavourable orientation of the N1−C6 bond with respect to the Co−X bonds, which are more or less eclipsed; the torsion angle C6−N1−Co−X is in the range 12.6° to 19.3°. This geometry leads to a puckering of the five-membered chelate ring, which may minimize the steric interactions of the CH_2NMe_2 unit, the N of which does not interact with the Co or the Cp ring (see Figures 3, 5, and 6). However, this NMe_2 unit is positioned in such a way that it resides at a suitable distance from the X groups.

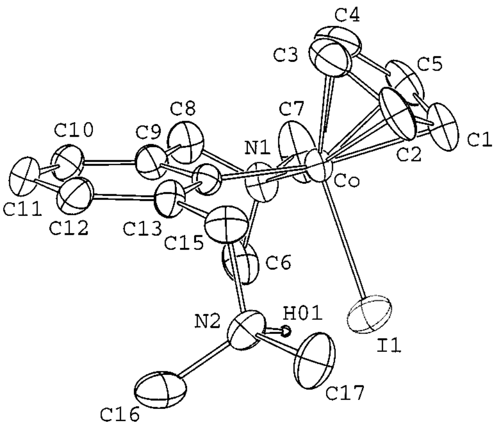


Figure 3. ORTEP view of the cation of **3** [CoI{$C_6H_3(CH_2NMe_2)(CH_2NMe_2H^+)$-2,6}($\eta^5$-$C_5H_5$)]I

In complexes **3** (Figure 3), **5a**, and **5d**, these nitrogen atoms are protonated and the N−H bond of the $NHMe_2^+$ unit points towards the group X. On the other hand, in compound **4a** the lone pair on the NMe_2 group is oriented towards one O−H vector of the water coordinated to Co. These interactions lead to rather short N···X distances in all four cases. In **3**, however, the N2···I1 distance amounts to 3.43 Å, which is 0.2 Å shorter than the sum of the relevant van der Waals radii and corresponds to the upper range for hydrogen bonds between I and NH^+.[12]

In **4a**, the N2···O distance measures 2.59 Å, which is indicative of significant hydrogen-bonding between the water coordinated to Co and the nitrogen lone pair (Figure 4). This N2···O distance falls at the short end of the range of distances reported for similar types of hydrogen bonds; the O···N distances in O−H···N systems are more typically in the range 2.68−2.79 Å.[13]

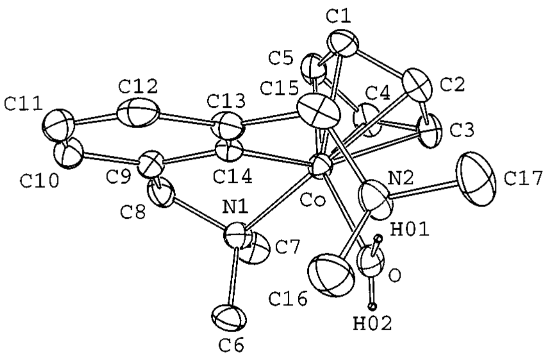


Figure 4. ORTEP view of the cationic part of **4a** [Co{C_6H_3-$(CH_2NMe_2)(CH_2NMe_2)$-2,6}(η^5-C_5H_5)(H_2O)]PF_6

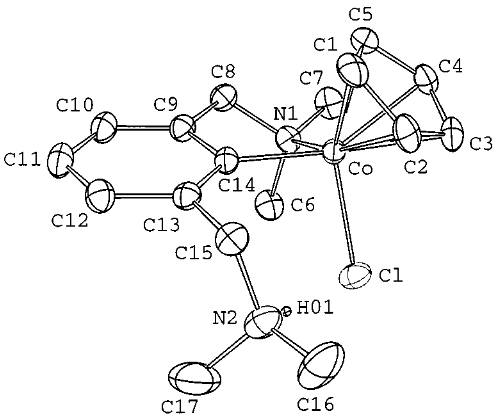


Figure 5. ORTEP view of the cationic part of **5a** [CoCl{C_6H_3-$(CH_2NMe_2)(CH_2NMe_2H^+)$-2,6}($\eta^5$-$C_5H_5$)]$PF_6$

In the crystal structure of compound **5a** (Figure 5), the N···Cl distance [3.02(8) Å] is also shorter than is typically found for related intermolecular interactions.[12] It is noteworthy that in this case the proton attached to the nitrogen atom could be located [(N2−H = 1.08(7) Å; N−H···Cl = 158.1(4)°].

Related intramolecular N−H···Cl interactions have recently been described for ruthenium compounds built-up from simple tridentate ligands bearing two distal pyridine bases uncoordinated to the Ru; such compounds, in which the pyridine ligands are protonated, display intramolecular N···Cl distances analogous to that reported here.[14]

Finally, the O···N distance in **5d** (Figure 6) amounts to 2.72 Å, at the short end of the range for N−H···O systems (2.81−3.04 Å).[12] Here, too, the hydrogen atom was successfully located (N2−H = 0.92 Å). These structural data are indicative of a significant hydrogen bond in this molecule as well, as the N2−H···O angle is very close to 180° [173.0(3)°].[12] Note that in this latter complex the N···O distance is significantly longer than in **4a** (see above), which

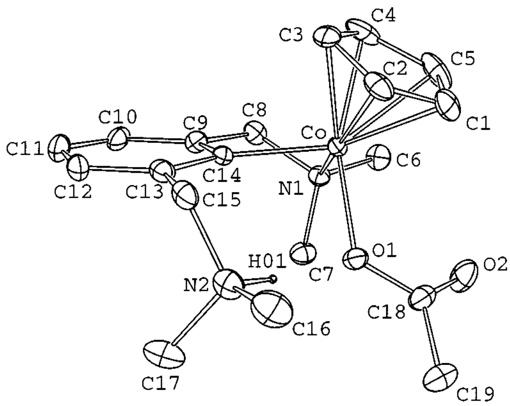
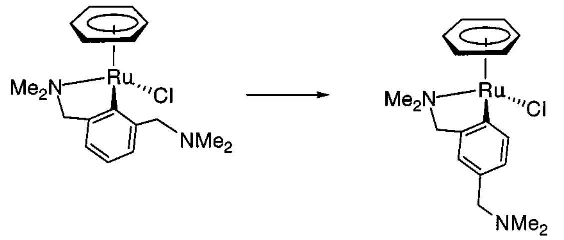


Figure 6. ORTEP view of the cationic part of **5d** [Co(CH$_3$COO)-{C$_6$H$_3$(CH$_2$NMe$_2$)(CH$_2$NMe$_2$H$^+$)-2,6}(η^5-C$_5$H$_5$)]PF$_6$



Scheme 4

rules out the possibility of considering the aquo complex as an association between OH$^-$ and an NH$^+$ unit.

It thus appears that the CH$_2$NMe$_2$ unit is remarkably flexible in adapting its orientation to the nature of the ligand attached to Co, although in all cases the nitrogen atom points towards the ligand X.

This latter behaviour is in marked contrast to that exhibited by some recently reported organoruthenium compounds incorporating the same pincer ligand. Indeed, Steenwinkel et al.[15] have shown that the pincer ligand in two such Ru^{II} compounds also interacts with Ru through the central carbon atom and just one nitrogen atom of an NMe$_2$ unit. However, in these compounds, in contrast to what we have seen in our cobalt complexes, the lone pair of the non-coordinated NMe$_2$ unit appears to be oriented away from the metal *and* from a chloride/phosphane ligand, respectively. In fact, these complexes proved to be unstable and isomerized to two compounds (see Scheme 4) in which the ruthenium atoms had migrated from the central carbon to carbons *ortho* and *para* to the two CH$_2$NMe$_2$ groups through a sequence of intramolecular C−H activation reactions. The driving force for this rearrangement most probably stems from the increased steric bulk of the non-coordinated CH$_2$NMe$_2$ moiety, which must interact with the arene ligand.

The stabilities of our complexes may thus be interpreted in terms of some extra stabilization of the organocobalt molecule owing to the presence of a hydrogen bond, a feature that is not possible in their ruthenium analogues. We have checked that treatment of the corresponding ruthenium complex by an acid such as HCl does not lead to any such intramolecular hydrogen bond; instead, we only observed extensive decomposition of the organoruthenium complex. We may thus view the cobalt complexes as dimetallacyclic species, in which five-membered and pseudo seven-membered chelated rings are present about the cobalt atom.

5. Behaviour of the Co-Pincer Compounds in Solution

A common feature of the structures of the four compounds is an intramolecular interaction between an NH$^+$ unit and X in **3**, **5a**, and **5d**, and between N and H−O in **4a**. In addition to these close contacts, puckering of the five-membered chelate rings of all complexes appears to result in an unfavourable orientation with respect to the Co−X vectors of the molecules. This latter phenomenon has also been observed in the related ruthenium compounds.[15] A reasonable explanation for this is that this ring puckering minimizes the steric interaction between the non-coordinated NMe$_2$ unit and the arene moiety of the Ru derivatives. A driving force behind adoption of the same conformation of the related organocobalt metallacycles in our compounds might also be a minimization of the steric interaction between the Cp ring and the NMe$_2$ group. However, it is evident from the chemical shifts of the NMe$_2$ unit of the five-membered chelate that we can unequivocally identify two different types of compounds.

The $\Delta\delta$ of the diastereotopic NMe$_2$ group coordinated to Co is very much dependent on the conformation of the five-membered chelate ring. We have seen previously in related metallacyclic compounds that when the conformation of this chelate ring is such that one N−Me bond and a Co−X bond are eclipsed (X = PR$_3$, for instance), then the $\Delta\delta$ of the two NMe$_2$ groups is usually greater than 1.6 ppm. Thus, in the ^{1}H-NMR spectrum of compound **3**, in which the hydrogen bond between N−H$^+$ and I is likely to be the weakest of the series studied, this $\Delta\delta$ is 0.85 ppm. A value of the same order of magnitude is observed for **4b**, **5b**, and **6**, for which no such hydrogen bond can be invoked. It is interesting to note that the Ru analogues of our compounds,[15] in which no hydrogen bonds are present, display analogous $\Delta\delta$ values (0.1−0.5 ppm). On the other hand, for the other compounds, $\Delta\delta$ is equal to or larger than 2.0 ppm, which can be taken as strong evidence that the conformation of the five-membered chelate is maintained in solution. Since this conformation is thermodynamically not the most stable, one may infer from these results that the strength of the intramolecular hydrogen bond[10] is sufficient to prevent a conformational change of the organocobalt chelate ring, which would lead to staggered N−Me and Co−X bonds in solution (see Figure 7).

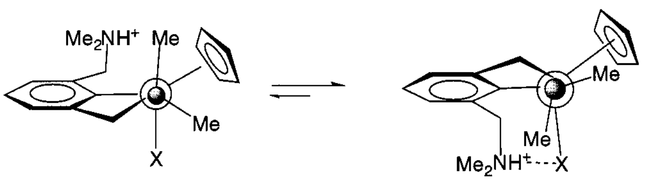


Figure 7. Newman projection along the N−Co vector of the complexes **5** showing the relationship between the intramolecular NHX interaction and the degree of ring puckering

Conclusion

We have synthesized an organometallic compound possessing a coordination site at which Brønsted acids can be accommodated. This behaviour is seemingly specific to Co-^{III} since analogous ruthenium(II) compounds, despite their close structural analogies, are not capable of similar interactions with acids. It would also seem to be a specific feature of the metallated ligand since our previous closely related organocobalt complexes consisting of N^C chelates do not display such behaviour. Further work is currently in progress with the aim of defining the scope of this behaviour with different acid derivatives and extending the range of pseudo terdentate ligands that may exhibit analogous behaviour.

Experimental Section

General: All reactions were performed in Schlenk flasks under oxygen-free, dry nitrogen. Solvents were dried and distilled under nitrogen, toluene from sodium and CH_2Cl_2 from P_2O_5. − IR spectra were recorded from samples in KBr on a Bruker IFS-66 spectrometer. − Elemental analyses were performed by the Service Central d'Analyse de l'Université Louis Pasteur (Strasbourg). − ^{1}H-NMR spectra were recorded at 300.13 MHz, $^{13}C\{^1H\}$-NMR spectra at 75.47 MHz, and $^{31}P\{^1H\}$-NMR spectra at 121.51 MHz on a Bruker FT instrument (AC-300) and were externally referenced to TMS. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively.

The starting materials $[CpCoI_2]_2$ [16] and $Li[C_6H_3(CH_2NMe_2)_2]$ [17] were prepared according to published methods.

$[CoI\{2\text{-}(Me_2NCH_2)\text{-}6\text{-}(Me_2NH^+CH_2)C_6H_3\}(\eta^5\text{-}C_5H_5)]I$ (3): To a stirred suspension of $[CpCoI_2]_2$ (1.511 g, 2.00 mmol) in toluene (100 mL) at 0 °C was slowly added 2,6-bis[dimethyl(amino)methyl]-phenyllithium (**2**) (0.79 g, 4.00 mmol). The resulting green suspension was stirred for 16 h at room temperature and then the volatiles were completely removed in vacuo. The residue was taken up in CH_2Cl_2/MeOH (98:2) and the resulting solution was stirred for 30 min and then filtered. The filtrate was concentrated to a volume of 30 mL and hexane was slowly added. The green solid thus formed was washed with hexane and dried in vacuo to give **3** as green crystals. Yield: 0.88 g (50%). − IR (KBr): $\tilde{\nu}$ = 2733 cm^{-1} (ν_s Me_2N-H^+). − ^{1}H NMR ($CDCl_3$): δ = 10.01 (br. s, 1 H, NH^+), 7.97 (d, $^3J_{H-H}$ = 7.44, 1 H, Ar), 7.08 (t, $^3J_{H-H}$ = 7.14, 1 H, Ar), 6.90 (d, 1 H, Ar), 5.07 (s, 5 H, C_5H_5), 5.09 and 4.98 (AB spin system, $^2J_{H-H}$ = 13.17, 2 H, CH_2N), 3.94 and 3.39 (AB spin system, $^2J_{H-H}$ = 13.20, 2 H, CH_2N-Co), 3.16 and 2.31 (2 s, 6 H, $Co-NMe_2$), 2.93 (br. s, 6 H, NMe_2H^+). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 153.9, 149.8, 142.1, 128.9, 125.2, 122.1 (C_6H_3), 85.1 (C_5H_5), 75.7 (CH_2N-Co), 64.1 (CH_2N), 58.9 and 58.5 ($Co-NMe_2$), 42.0 (br. s, NMe_2). − $C_{17}H_{25}CoI_2N_2$ (570.1): calcd. C 35.81, H 4.42, N 4.91; found C 33.67, H 4.23, N 4.38.

$[2,6\text{-}(Me_2NCH_2)_2Co\{C_6H_3(CH_2NMe_2)\}(\eta^5\text{-}C_5H_5)(H_2O)]PF_6$ (4a): A solution of **3′** (0.44 g, 1.00 mmol) in CH_2Cl_2 (20 mL) was washed several times with water (10 mL). The combined red aqueous solutions were then treated with excess KPF_6, which led to the immediate deposition of a red-brown solid. After stirring for 15 min, the solid was collected by filtration, washed with hexane, recrystallized from acetone/hexane, and dried in vacuo to give **4a** as brown-red crystals. Yield: 0.28 g (60%). − IR (KBr): $\tilde{\nu}$ = 3575 cm^{-1} (ν_s H−OH). − ^{1}H NMR ([D$_6$]acetone): δ = 7.25 (d, $^3J_{H-H}$ = 6.93, 1 H, Ar), 7.16 (t, $^3J_{H-H}$ = 7.32, 1 H, Ar), 7.09 (d, 1 H, Ar), 5.49 (s, 5 H, C_5H_5), 4.64 and 3.65 (AB spin system, $^2J_{H-H}$ = 12.24, 2 H, CH_2NMe_2), 4.40 and 3.69 (AB spin system $^2J_{H-H}$ = 13.90, 2 H, CH_2N-Co), 3.49 and 1.34 (2 s, 6 H, NMe_2-Co), 2.20 (br. s, 6 H, NMe_2).[18] − $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 158.0, 152.1, 130.2, 125.3, and 122.7 (C_6H_3), 85.4 (C_5H_5), 76.7 (CH_2N-Co), 67.7 (CH_2N), 58.4 and 49.2 (NMe_2-Co), 43.0 (NMe_2). − $C_{17}H_{26}CoF_6N_2OP$ (478.3): calcd. C 42.69, H 5.48, N 5.86; found C 43.02, H 5.43, N 5.84.

$[Co\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\eta^5\text{-}C_5H_5)(PMe_2Ph)]PF_6$ (4b): To a solution of **4a** (0.48 g, 1.00 mmol) in CH_2Cl_2 (10 mL) was added PMe_2Ph (0.17 mL, 1.20 mmol). After 3 h, *n*-hexane (100 mL) was added, which led to the deposition of a dark-violet solid. The solid was collected by filtration and dried in vacuo to give **4b** as a red-violet powder. Yield: 0.46 g (77%). − ^{1}H NMR ([D$_6$]acetone): δ = 7.70−7.40 (m, 5 H, PPh), 7.29 (d, $^3J_{H-H}$ = 7.32, 1 H, Ar), 7.08 (t, 1 H, Ar), 6.81 (d, $^3J_{H-H}$ = 7.08, 1 H, Ar), 5.91 (s, 5 H, C_5H_5), 3.44 and 3.33 (AB spin system, $^2J_{H-H}$ = 12.18, 2 H, CH_2N), 3.44 and 3.33 (AB spin system, $^2J_{H-H}$ = 14.40, 2 H, CH_2N), 2.89 and 2.23 (2 s, 6 H, NMe_2-Co), 2.34 (s, 6 H, NMe_2), 2.21 and 1.97 (2 d, $^2J_{H-P}$ = 9.51 and $^2J_{H-P}$ = 10.26, 6 H, PMe_2). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 12.8 (s, PMe_2Ph), −143.6 (sept., PF_6, $^1J_{P-F}$ = 707.0). − $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 151.4 (d, $^2J_{C-P}$ = 35.77), 150.1, 149.4, 131.2, 124.6, 122.9 (C_6H_3), 135.5 (d, $^1J_{C-P}$ = 60.98), 131.3, 129.6 (d, $^2J_{C-P}$ = 8.41) (PPh), 88.2 (C_5H_5), 74.3 (CH_2N-Co), 67.5 (CH_2N), 60.0 and 55.2 (NMe_2-Co), 45.0 (NMe_2), 22.2 and 15.3 (2 d, $^1J_{C-P}$ = 31.69 and $^1J_{C-P}$ = 33.67) (PMe_2). − $C_{25}H_{35}CoF_6N_2P_2$: (598.4): calcd. C 50.18, H 5.89, N 4.68; found C 50.62, H 5.75, N 4.38.

$[CoCl\{2\text{-}(Me_2NCH_2)\text{-}6\text{-}(Me_2NH^+CH_2)C_6H_3\}(\eta^5\text{-}C_5H_5)]PF_6$ (5a): To a solution of **4a** (0.48 g, 1.00 mmol) in MeOH (20 mL) was added excess NH_4Cl. After 7 h, the volatiles were removed. The residue was redissolved in CH_2Cl_2 and this solution was filtered. The brown filtrate was concentrated and the residue was recrystallized from acetone/hexane and dried in vacuo to give **5a** as dark, red-violet crystals. Yield: 0.40 g (81%). − IR (KBr): $\tilde{\nu}$ = 2692 cm^{-1} (ν_s Me_2N-H^+). − ^{1}H NMR ([D$_6$]acetone): δ = 9.48 (br. s, 1 H, NH^+), 7.41 (d, $^3J_{H-H}$ = 6.90, 1 H, Ar), 7.18 (t, $^3J_{H-H}$ = 7.14, 1 H, Ar), 7.12 (d, $^3J_{H-H}$ = 6.45, 1 H, Ar), 5.46 (s, 5 H, C_5H_5), 5.07 and 4.60 (AB spin system, $^2J_{H-H}$ = 12.63, 2 H, CH_2N), 4.60 and 3.72 (AB spin system, $^2J_{H-H}$ = 14.05, 2 H, CH_2N), 3.50 and 1.51 (2 s, 6 H, NMe_2-Co), 3.21 and 2.68 (2 br. s, 6 H, NMe_2). − $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 157.4, 152.6, 143.0, 132.2, 125.2, 123.4 (C_6H_3), 86.6 (C_5H_5), 76.7 (CH_2N-Co), 66.3 (CH_2N), 58.6 and 52.4 (NMe_2-Co), 43.4 and 39.8 (2 br. s, NMe_2). − $C_{17}H_{25}ClCoF_6N_2P$ (496.7): calcd. C 41.10, H 5.07, N 5.64; found C 42.10, H 5.00, N 5.40.

$[CoI\{2\text{-}(Me_2NCH_2)\text{-}6\text{-}(Me_2NH^+CH_2)C_6H_3\}(\eta^5\text{-}C_5H_5)]PF_6$ (5b): To a solution of **4a** (0.48 g, 1.00 mmol) in MeOH (20 mL) was added excess NH_4I. After 7 h, the volatiles were removed. The residue was redissolved in CH_2Cl_2 and this solution was filtered. The green filtrate was concentrated and the residue was recrystallized from CH_2Cl_2/hexane. The solid was collected by filtration, washed with hexane, further recrystallized from acetone/hexane, and dried in vacuo to give **5b** as a green powder. Yield: 0.46 g (78%). − IR (KBr): $\tilde{\nu}$ = 2697 cm^{-1} (ν_s Me_2N-H^+). − ^{1}H NMR ([D$_6$]acetone): δ = 9.33 (br. s, 1 H, NH^+), 7.92 (d, $^3J_{H-H}$ = 7.38, 1 H, Ar) 7.04 (t, 1 H, Ar), 6.97 (d, 1 H, Ar), 5.34 (s, 5 H, C_5H_5), 5.10 and 5.00 (AB spin system, $^2J_{H-H}$ = 13.11, 2 H, CH_2NH), 3.98 and 3.42 (AB spin system, $^2J_{H-H}$ = 13.32, 2 H, CH_2N-Co), 3.19 and 2.55 (2 s, 6 H, NMe$_2$−Co), 2.98 (br. s, 6 H, HNMe$_2$). − ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 156.0, 152.0, 142.9, 129.8, 124.7, 122.6 (C$_6$H$_3$), 86.0 (C$_5$H$_5$), 75.1 (CH$_2$N−Co), 66.5 (CH$_2$N), 58.6 and 57.9 (NMe$_2$−Co), 42.5 (br. s, NMe$_2$). − $C_{17}H_{25}CoF_6IN_2P$ (588.2): calcd. C 34.71, H 4.28, N 4.76; found C 33.91, H 4.16, N 4.96.

[CoF{2-(Me$_2$NCH$_2$)-6-(Me$_2$NH$^+$CH$_2$)C$_6$H$_3$}(η^5-C$_5$H$_5$)]PF$_6$ (5c): To a solution of **4a** (0.48 g, 1.00 mmol) in acetone (20 mL) was added 40% aq. HF (0.3 mL). After 3 h, the mixture was filtered, the filtrate was concentrated, and the residue was crystallized from hexane. The solid was collected by filtration, washed with hexane, recrystallized from acetone/hexane, and dried in vacuo to give **5c** as a brown powder. Yield: 0.39 g (82%). − IR (KBr): ṽ = 2260 cm^{-1} (ν_s Me$_2$N−H$^+$). − ^{1}H NMR ([D$_6$]acetone): δ = 11.00 (br. d, $^1J_{H-F}$ = 89.14, 1 H, NH$^+$), 7.37 (d, $^3J_{H-H}$ = 6.66, 1 H, Ar), 7.21 (t, $^3J_{H-H}$ = 7.17, 1 H, Ar), 7.17 (d, $^3J_{H-H}$ = 6.90, 1 H, Ar), 5.44 (s, 5 H, C$_5$H$_5$), 5.20 and 4.41 (AB spin system, $^2J_{H-H}$ = 12.87, 2 H, CH$_2$NH$^+$), 4.43 and 3.71 (AB spin system, $^2J_{H-H}$ = 14.07, 2 H, CH$_2$N−Co), 3.64 and 1.21 (s and d, $^4J_{H-F}$ = 6.90, 6 H, NMe$_2$−Co), 3.04 and 2.26 (2 d, $^4J_{H-F}$ = 4.05 and $^4J_{H-F}$ = 4.29, 6 H, NMe$_2$H$^+$). − ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 153.0, 143.7, 148.5, 130.7, 125.3, 123.4 (C$_6$H$_3$), 85.2 (C$_5$H$_5$), 76.4 (CH$_2$N−Co), 66.4 (CH$_2$NH$^+$), 58.4 and 47.9 (NMe$_2$−Co), 43.3 and 39.9 (NMe$_2$H$^+$). − $C_{17}H_{25}CoF_7N_2P$ (480.3): calcd. C 42.51, H 5.25, N 5.83; found C 42.09, H 5.74, N 5.72.

[Co(CH$_3$COO){2-(Me$_2$NCH$_2$)-6-(Me$_2$NH$^+$CH$_2$)C$_6$H$_3$}-(η^5-C$_5$H$_5$)]PF$_6$ (5d): To a solution of **4a** (0.48 g, 1.00 mmol) in acetone (20 mL) was added acetic acid (0.2 mL). After 3 h, the mixture was filtered, the filtrate was concentrated, and the residue was crystallized from hexane. The solid was collected by filtration, washed with hexane, recrystallized from acetone/hexane, and dried in vacuo to give **5d** as brown crystals. Yield 0.44 g (85%). − IR (KBr): ṽ = overtones between 2700−2400 cm^{-1} (ν_s Me$_2$N−H$^+$), 1638 cm^{-1} (ν_s C=O). − ^{1}H NMR ([D$_6$]acetone): δ = 10.70 (br. s, 1 H, NH$^+$), 7.42 (d, $^3J_{H-H}$ = 6.69, 1 H, Ar), 7.24 (t, $^3J_{H-H}$ = 7.38, 1 H, Ar), 7.16 (d, $^3J_{H-H}$ = 6.66, 1 H, Ar), 5.40 (s, 5 H, C$_5$H$_5$), 5.18 and 4.57 (AB spin system, $^2J_{H-H}$ = 12.87, 2 H, CH$_2$NH$^+$) 4.38 and 3.68 (AB spin system, $^2J_{H-H}$ = 13.83, 2 H, CH$_2$N−Co), 3.51 and 1.27 (2 s, 6 H, NMe$_2$−Co), 3.31 and 2.64 (2 s, 6 H, Me$_2$NH$^+$), 1.96 (s, 3 H, CH$_3$COO). − ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 178.0 (COO), 158.6, 153.2, 143.6, 131.3, 125.4, 123.6 (C$_6$H$_3$), 85.7 (C$_5$H$_5$), 76.7 (CH$_2$N−Co), 66.6 (CH$_2$NH$^+$), 57.5 and 48.6 (NMe$_2$−Co), 43.8 and 40.1 (NMe$_2$H$^+$), 24.0 (CH$_3$COO). − $C_{19}H_{28}CoF_6N_2O_2P$ (520.3): calcd. C 43.86, H 5.42, N 5.38; found C 43.05, H 4.99, N 5.27.

[Co{2-(Me$_2$NCH$_2$)-6-(Me$_2$NH$^+$CH$_2$)C$_6$H$_3$}(η^5-C$_5$H$_5$)(PMe$_2$Ph)]-(PF$_6$)$_2$ (6): To a solution of **4b** (0.48 g, 0.50 mmol) in CH$_2$Cl$_2$ (20 mL) was added 10% aq. HCl (0.3 mL), which led to the immediate separation of a light-red solid. After 3 h, this solid was col-

Table 2. X-ray diffraction data

Complex	**3**	**4a**	**5a**	**5d**
Crystal data				
Formula	$C_{17}H_{25}CoI_2N_2$	$C_{17}H_{26}CoN_2O\cdot PF_6$	$C_{17}H_{25}ClCoN_2\cdot PF_6$	$C_{19}H_{28}CoN_2O_2\cdot PF_6$
M_r	570.14	478.31	496.75	520.34
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1$	$Pbca$	$Pca2_1$	$Pna2_1$
a [Å]	11.1104(3)	12.542(1)	15.2698(3)	15.246(2)
b [Å]	7.1910(2)	15.172(1)	6.9796(1)	7.557(1)
c [Å]	12.7706(3)	21.880(1)	19.4307(2)	19.646(4)
β [°]	100.635(1)			
V [Å^3]	1002.78(8)	4163.5(8)	2070.87(9)	2263(1)
Z	2	8	4	4
Colour	green	orange	dark red	violet
Crystal dim. [mm]	0.20 × 0.15 × 0.10	0.16 × 0.12 × 0.10	0.20 × 0.20 × 0.15	0.40 × 0.40 × 0.20
$D_{calcd.}$ [gcm^{-3}]	1.89	1.53	1.59	1.53
F(000)	548	1968	1016	1072
μ [mm^{-1}]	3.933	0.963	1.093	0.896
Min. and max. trans.				0.8940/1.0000
Data collection				
T [K]	294	173	173	294
λ [Å]	0.71073	0.71073	0.71073	0.71073
Radiation	Mo-K_α graphite-monochromated	Mo-K_α graphite-monochromated	Mo-K_α graphite-monochromated	Mo-K_α graphite-monochromated
Diffractometer	CCD	CCD	CCD	Enraf Nonius MACH3
Scan mode	θ scans	θ scans	θ scans	θ/2θ
hkl limits	$-13 \le h \le 11$	$0 \le h \le 13$	$-9 \le h \le 9$	$0 \le h \le 9$
	$-8 \le k \le 8$	$0 \le k \le 16$	$-19 \le k \le 19$	$0 \le k \le 18$
	$-14 \le l \le 14$	$0 \le l \le 24$	$-23 \le l \le 23$	$0 \le l \le 24$
limits [°]	2.5/25.36	2.5/23.25	2.5/29.56	2.5/26.28
No. of data meas.	6291	22289	18396	2647
No. of data with $I > 3\sigma(I)$	1751	1986	2325	1481
Weighting scheme	$4F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$	$4F_o^2/[\sigma^2(F_o^2) + 0.0004\ F_o^4] + 1.0$	$4F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$	$4F_o^2/[\sigma^2(F_o^2) + 0.0036\ F_o^4]$
No. of variables	198	253	288	283
R	0.031	0.046	0.039	0.036
R_w	0.050	0.057	0.048	0.044
GoF	1.059	1.121	1.043	1.068
Largest peak in final difference [eÅ^{-3}]	0.803	0.476	0.328	0.290

lected by filtration and washed with hexane. It was then stirred with saturated aqueous KPF_6 solution for 1 h, filtered off, washed with hexane, recrystallized from acetone/hexane, and dried in vacuo to give **6** as a light-red powder. Yield 0.18 g (62%). − IR (KBr): $\tilde{\nu}$ = 2704 cm^{-1} (ν_s Me_2N-H^+). − ^1H NMR ([D$_6$]acetone): δ = 9.25 (br. s, 1 H, NH$^+$), 7.95−7.45 (m, 5 H, PPh), 7.63 (d, $^3J_{H-H}$ = 7.14, 1 H, Ar), 7.28 (t, 1 H, Ar), 7.03 (d, 1 H, Ar), 5.94 (s, 5 H, C_5H_5), 4.92 and 4.58 (AB spin system, $^2J_{H-H}$ = 14.02, 2 H, CH_2NH^+), 3.80 and 3.08 (AB spin system, $^2J_{H-H}$ = 14.56, 2 H, CH_2N-Co), 3.37 (ps. s, 6 H, Me_2NH^+), 2.86 and 2.02 (s and d, $^4J_{H-P}$ = 1.38, 6 H, NMe_2-Co), 2.25 and 1.58 (2 d, $^2J_{H-P}$ = 9.63 and $^2J_{H-P}$ = 10.17, 6 H, PMe_2). − $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 13.0 (s, PMe_2), −143.5 (sept., $^1J_{P-F}$ = 708.0). − $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 156.2 (d, $^2J_{C-P}$ = 25.82), 151.5, 144.0, 126.5, 126.0, 124.4 (C_6H_5), 134.8 (d, $^1J_{C-P}$ = 37.56), 131.5, 131.5 (d, $^2J_{C-P}$ = 16.43), 129.9 (d, $^3J_{C-P}$ = 9.38) (PPh), 89.1 (C_5H_5), 75.3 (CH_2N-Co), 64.8 (CH_2NH^+), 59.7 and 54.8 (NMe_2-Co), 44.2 (NMe_2H^+), 21.2 and 15.2 (2 d, $^2J_{C-P}$ = 32.86, PMe_2).

X-ray Data and Structure Determinations for 3, 4a, 5a, and 5d: Single crystals suitable for X-ray diffraction analysis were obtained as described above. In the case of **3**, **4a**, and **5a**, data were collected on a Nonius KappaCCD diffractometer, while for **5d** a Nonius MACH3 machine was used. All four data collections were performed using Mo-K_α graphite-monochromated radiation (λ = 0.7107 Å), φ and ω scans for **3**, **4a**, and **5a**, and $\theta/2\theta$ scans for **5d**. Absorption corrections were computed from the psi scans of 7 reflections for **5d**, while for **3**, **4a**, and **5a** these corrections were partially included in the data reduction procedure. The structures were solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced in structure factor calculations as fixed contributors by their computed coordinates [d(C−H) = 0.95 Å, B(H) = 1.3*Beqv Å^2 of the attached carbon atom] except for the NH protons of **3**, **5a**, and **5d** and the water protons of **4a**, which were located in difference Fourier maps. The absolute structures of **3**, **4a**, and **5d** were determined by refinement of Flack's x parameter. For all computations, the Nonius OpenMoLeN package[19] was used. Crystal data and results for all four compounds are given in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132438 (**3**), -132439 (**4a**), -132440 (**5a**), and -132441 (**5d**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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