

Synthesis, X-ray structure, and theoretical studies of novel cationic mono-cyclopentadienyl complexes of Co(III): the orthometalation of *trans*-azobenzene

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Abstract

New cationic mono-cyclopentadienyl complexes of Co(III) containing mono or bidentate nitrogen donor ligands of general formula $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2][\text{BF}_4]_2$ ($\text{L} = \text{NC-CH}_3$, **2**, and NC-Ph , **3**) or $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L-L})][\text{BF}_4]_2$, [$\text{L-L} = 2,2'$ -bisimidazole (H_2biim) (**4**) and dipyridylamine $[\text{HN}(\text{NC}_5\text{H}_5)_2]$ (**5**)] have been synthesised by the stoichiometric reaction of the Co(III) complex $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$ (**1**), with $\text{Ag}[\text{BF}_4]$ and the appropriate ligand in CH_2Cl_2 . Under the same conditions and using *trans*-azobenzene as a ligand, an orthometalation reaction took place, giving the new compound $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})][\text{BF}_4]$ (**6**) in high yield. The structural characterisation of compounds **4** and **6**, and of the starting compound $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$ (**1**) was done by single-crystal X-ray diffraction studies. DFT calculations (ADF program) were performed in order to understand the orthometallation reaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Co(III) complexes; Orthometallation; DFT calculations; X-ray structures

1. Introduction

Organometallic complexes are very interesting precursors as building blocks for the design of solids, owing to the variety of coordination environments and oxidation states, among others, which they can provide [1]. Cationic complexes allow the additional possibility of changing counter ions. A differently charged anion may lead to other stoichiometries of the salts and the presence of donor/acceptor groups may induce the formation of directional hydrogen bonds between ions. The synthesis of cationic monocyclopentadienyl cobalt(III) complexes has therefore been pursued, with

the aim of understanding the factors responsible for the structure of the solids, and mono or bidentate N-donor ligands were considered. Some of the ligands might also act as bridges between metals, leading to the formation of binuclear species. The complex $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$ (**1**), shown to be a good precursor for the synthesis of cationic species [2], was used for these studies, using silver salts in the presence of the appropriate ligand. The ligand 2,2'-bismidazole, for instance, may coordinate through two nitrogen atoms, leaving two N–H bonds available for donation towards hydrogen bond receptors. *Trans*-azobenzene has been known for a long time to undergo orthometallation reactions with transition metals [3], but, in the case of cobalt, the only reactions described involve Co(I) complexes [4]. In complex $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\eta^2\text{-PhN=NPh})$, *trans*-azobenzene is coordinated in a η^2 -mode [5]. The reac-

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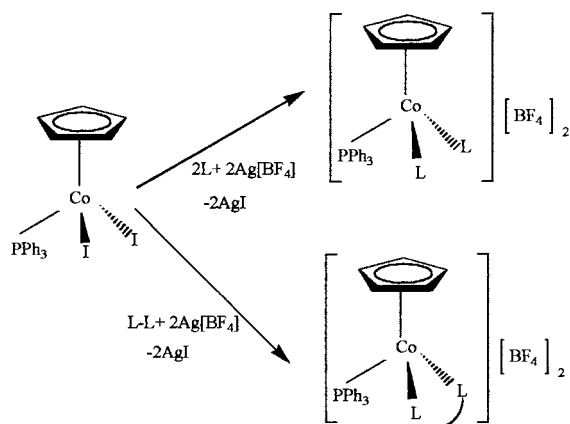
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tion of $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{I}_2$ with *trans*-azobenzene, using $\text{Ag}[\text{BF}_4]$ on the other hand, gave rise to an orthometallation reaction, the new complex $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})][\text{BF}_4]$ (**6**) being formed. It represents, to the best of our knowledge, the first example of an orthometallation reaction accomplished by a Co(III) complex. Both, this orthometalated complex, the 2,2'-bismidazole derivative, and the starting material were structurally characterised by single-crystal X-ray diffraction. Density functional theory calculations [6], using the ADF program [7], were performed in order to understand the driving force for the orthometallation reaction.

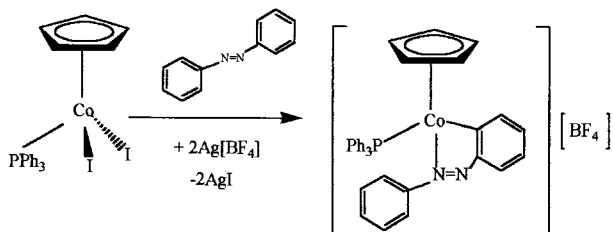
2. Results and discussion

2.1. Chemical studies

The reaction of $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{I}_2$ (**1**) with 2 mol of $\text{Ag}[\text{BF}_4]$ in CH_2Cl_2 and the stoichiometric amount of the appropriate mono or bidentate nitrogen donor ligand, at room temperature, yields crystalline red complexes of general formula $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{L}][\text{BF}_4]_2$, where $\text{L} = \text{NCCH}_3$ (**2**) and NCC_6H_5 (**3**), or $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{L-L})][\text{BF}_4]_2$, where $\text{L-L} = 2,2'$ -bisimidazole (H_2biim) (**4**) and dipyridylamine $[\text{HN}(\text{NC}_5\text{H}_5)_2]$ (**5**) in good yields (Scheme 1).



Scheme 1.



Scheme 2.

The nitrile derivatives **2** and **3** are very hygroscopic and it proves difficult to obtain crystals of good quality for single-crystal X-ray structure determination. The $^1\text{H-NMR}$ spectra of complexes **2** and **3** in CDCl_3 are in agreement with the proposed structures, as shown by the singlet observed for the Cp protons at δ 5.98, and 6.3 ppm, respectively. The $^1\text{H-NMR}$ of complexes **4** and **5** in d^6 acetone also exhibit a singlet for the Cp protons at δ 6.23, and 6.62 ppm, respectively, in accordance with the proposed structures. These spectra also show a series of complex peaks in the region for aromatic protons (protons of the N-donor ligands and of PPh_3), while the $^{31}\text{P-NMR}$ spectra show singlets at δ 43.54 and 41.15, respectively, for the PPh_3 phosphorus atom of complexes **4** and **5**. A crystal of **4**, $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{H}_2\text{biim})][\text{BF}_4]_2$, suitable for X-ray structure determination, was grown by slow vapour diffusion of diethylether into an acetone solution of the complex. Attempts to grow good quality crystals of **5** by the same procedure failed. Crystals of the starting material **1** were obtained from CH_2Cl_2 -petroleum ether.

When the reaction of $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{I}_2$ (**1**) with 2 mol of $\text{Ag}[\text{BF}_4]$ in CH_2Cl_2 is performed using *trans*-azobenzene as a ligand, an orthometallation reaction takes place, giving rise to the new compound $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})][\text{BF}_4]$ (**6**) in high yield (Scheme 2). Good quality crystals of **6** were obtained from CH_2Cl_2 -petroleum ether.

Complex **6** was also fully characterised by multinuclear NMR spectroscopy. The $^1\text{H-NMR}$ spectrum in CD_2Cl_2 show a singlet for the Cp protons at δ 5.47 ppm and a series of complex peaks in the aromatic region for the protons of the peaks in the aromatic region for the protons of the *trans*-azobenzene and of PPh_3 . In the ^{13}C spectrum, besides the expected peaks in the aromatic region (from δ 133.7 to 122.85 ppm) and the peak corresponding to the Cp carbons at δ 90.92 ppm, four isolated peaks are observed, namely one doublet at δ 173.06 ppm and 172.8 ppm ($J^{13}\text{C}-^{31}\text{P} = 26.83$ Hz) which can be assigned to the azobenzene carbon bound to Co [8], two peaks at δ 167.75 and 156.21 ppm assigned to the N-substituted phenyl carbons, and a fourth peak at δ 142.9 ppm, assigned to the *ipso*-carbons of PPh_3 . The $^{31}\text{P-NMR}$ spectrum shows a singlet at 45.21 ppm. The liquid secondary ion mass spectra (LSIMS+) shows the cation peak at m/z 567 $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})]^+$ (90%).

The IR spectra in Nujol mulls of compounds **2–6**, display strong absorption bands centered at ca. ν 1050 cm^{-1} characteristic of the counter ion $[\text{BF}_4]^-$.

Compounds $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{I}_2$ (**1**), $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{H}_2\text{biim})][\text{BF}_4]_2$ (**4**), and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})][\text{BF}_4]$ (**6**), were structurally characterised by single-crystal X-ray diffraction studies.

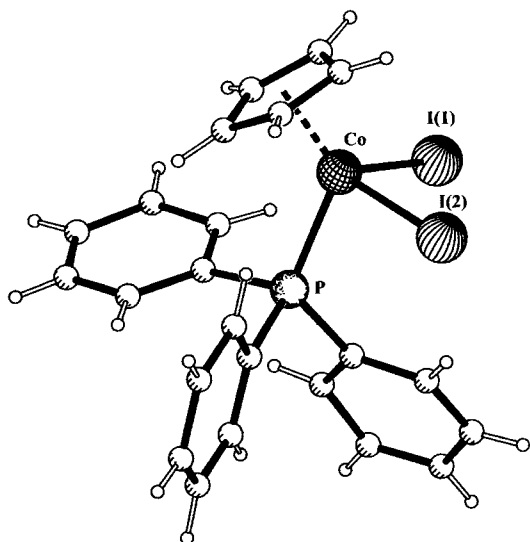


Fig. 1. A PLUTON view of $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{I}_2$ (**1**), showing the molecular geometry and the atomic notation scheme adopted. For clarity only the atomic notation for the quoted atoms in the text is included.

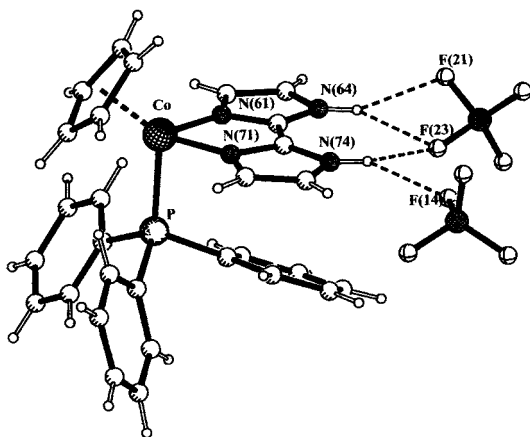


Fig. 2. A PLUTON view of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{H}_2\text{biim})][\text{BF}_4]_2$ (**4**), showing the molecular geometry, the hydrogen bonds $\text{N}\cdots\text{H}\cdots\text{F}$ to the BF_4^- anion, and the atomic notation scheme adopted. For clarity only the atomic notation for the quoted atoms in the text is included.

2.2. Crystallographic studies of $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{I}_2$ (**1**), $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{H}_2\text{biim})][\text{BF}_4]_2$ (**4**) and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})][\text{BF}_4]$ (**6**)

The solid state structures of metal complexes $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{I}_2$ (**1**), $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{H}_2\text{biim})][\text{BF}_4]_2$ (**4**), and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})][\text{BF}_4]$ (**6**), were determined by single-crystal X-ray diffraction. PLUTON style diagrams showing the overall geometry of the complexes **1**, **4**, and **6** and the atomic notation scheme used are presented in Figs. 1–3, respectively. Selected bond lengths and angles are given in Table 1.

In the three structures the cobalt centre displays a distorted pseudo tetrahedral co-ordination environment containing one $\eta^5\text{-C}_5\text{H}_5$ ring and one P from a PPh_3 ligand. The two remaining positions of the metal co-ordination sphere are occupied by two iodine atoms in **1**, two nitrogen atoms from H_2biim in **4**, and one nitrogen atom and one carbon atom from $\text{C}_6\text{H}_4\text{N=NPh}^-$ in **6**. The more significant distortion from the idealised tetrahedral geometry is reported for complexes **4** and **6** and arises from the small bite angles of the bidentate ligands. Thus the chelation of H_2biim in **4** and $\text{C}_6\text{H}_4\text{N=NPh}^-$ in **6** results in similar chelating angles N-Co-N and N-Co-C of $82.3(2)^\circ$ and $80.6(3)^\circ$, respectively. In contrast, in the complex **1**, where that steric constraint is absent, a wider I-Co-I angle of $95.05(4)^\circ$, closer to the ideal value for a tetrahedron, is observed. The remaining angles subtended at the cobalt(III) centre are comparable in the three complexes. On the other hand, the structural parameters reported in Table 1 for complex **1** agrees well with those found for related cobalt(III) pseudo tetrahedral neutral species $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_2\text{CH}_2\text{POPPh}_2)\text{I}_2]$ and $[\{\text{Co}(\eta^5\text{-C}_5\text{H}_5)\text{I}_2\}_2(\mu_2\text{-PPh}_2(\text{CH}_2)_5\text{PPh}_2)]$ [9], in which two $\text{Co}(\eta^5\text{-C}_5\text{H}_5)\text{I}_2$ moieties are bridged by the $\text{PPh}_2(\text{CH}_2)_5\text{PPh}_2$ ligand.

To the best of our knowledge, the structure of complex **4** represents the first X-ray determination of a cobalt complex containing the H_2biim ligand. In fact, no crystal structures of cobalt complexes with that ligand were found in the Cambridge Data Base (CSD) [10] and consequently it is not possible to establish any structural comparison of the structure reported for complex **4** with other related structures.

The two BF_4^- anions are close to the complex cation **4** leading to $\text{F}\cdots\text{H}\cdots\text{N}$ interactions between three fluorine atoms and the two N-H groups of H_2biim via

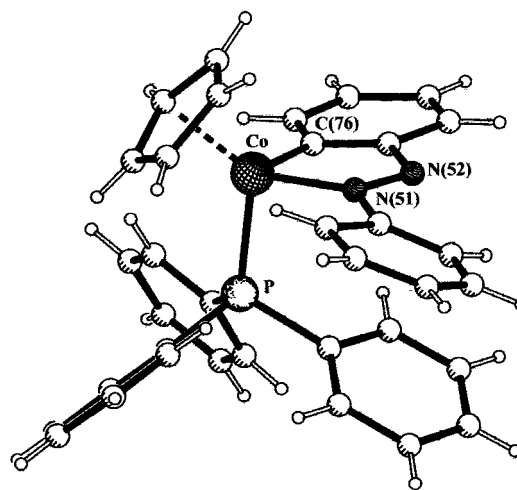


Fig. 3. A PLUTON view of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})]^+$ (**6**), showing the molecular geometry and the atomic notation scheme adopted. For clarity only the atomic notation for the quoted atoms in the text is included.

Table 1
Selected bond distances (Å) and bond angles (°) for complexes **1**, **4** and **6**^a

Complex 1			
Co–I(1)	2.584(3)	Co–I(2)	2.607(3)
Co–P	2.242(3)	Co–Cp	1.716
I(1)–Co–I(2)	95.05(4)		
P–Co–I(1)	92.04(6)	P–Co–I(2)	95.13(12)
Cp–Co–I(1)	119.2	Cp–Co–I(2)	120.7
P–Co–Cp	126.8		
Complex 4			
Co–N(61)	1.961(5)	Co–N(71)	1.946(6)
Co–P	2.270(2)	Co–Cp	1.707
N(71)–Co–N(61)	82.3(2)		
N(61)–Co–P	91.4(2)	N(71)–Co–P	91.1(2)
N(61)–Co–Cp	126.0	N(71)–Co–Cp	126.1
P–Co–Cp	126.9		
Complex 6			
Co–N(51)	1.925(6)	Co–C(76)	1.987(8)
Co–P	2.240(2)	Co–Cp	1.722
N(51)–C(61)	1.424(9)	N(52)–C(71)	1.476(9)
N(51)–N(52)	1.242(7)		
Cp–Co–N(51)	130.3	Co–Cp–N(76)	120.0
P–Co–Cp	126.8		
N(51)–Co–C(76)	80.7(3)		
N(51)–Co–P	94.4(2)	C(76)–Co–P	90.6(2)
N(51)–N(52)–C(71)	110.1(5)	C(76)–C(71)–N(52)	117.4(6)
C(75)–C(76)–Co	135.4(6)	C(71)–C(76)–Co	110.0(6)
C(61)–N(51)–Co	129.8(5)	N(52)–N(51)–Co	121.4(5)
N(52)–N(51)–C(61)	108.7(6)		

^a Cp represents the centroid of the η^5 -C₅H₅ ring.

two hydrogen bonding bifurcated arrangements (Fig. 2). One fluorine atom of one BF₄[−] anion interacts concomitantly with both nitrogen atoms of H₂bim [N(64)–H(64)⋯F(23) 2.284 Å, 146.0° (−1/2 + x, 1/2 − y, −1/2 + z) and N(74)–H(74)⋯F(23) 2.289 Å, 146.7° (−1/2 + x, 1/2 − y, −1/2 + z)] resulting in the formation of a seven member ring (counting the hydrogen atoms). The other two hydrogen bonds involving these donor atoms and fluorine atoms are N(64)–H(64)⋯F(21) 2.130 Å, 152.9° (−1/2 + x, 1/2 − y, −1/2 + z) and N(74)–H(74)⋯F(14) 2.960 Å, 126.2° (3/2 − x, −1/2 + y, 1/2 − z).

Complex **6** represents also the first X-ray determination of the structure of a cobalt(III) complex in which the *trans*-azobenzene ligand is orthometalated. Indeed, the structure of the neutral complex Co(η^5 -C₅H₅)(PMe₃)(η^2 -PhN=NPh) (**7**) [5] was the unique example of a cobalt complex containing the *trans*-azobenzene ligand retrieved from a search on the CSD. In this complex, the *trans*-azobenzene is co-ordinated to a Co(I) centre in a η^2 -fashion, with two Co–N bond distances of 1.965(5) and 1.913(6) Å. The orthometalation of PhN=NPh in **6** leads to Co–N and Co–C bond distances of 1.925(6) and 1.987(8) Å, respectively. The uncoordinated nitrogen donor N(52) in **6** is at a distance of 2.781(6) Å from the cobalt atom.

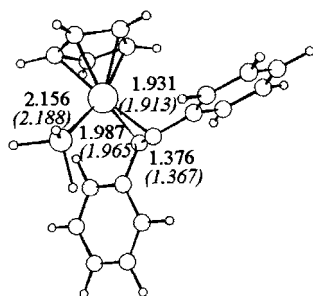
Complex **7** exhibits an acute N–Co–N chelating angle of 41.2(3)°, which is much narrower than the N–Co–C chelating angle of 80.7(3)° in complex **6**. This difference is expected, owing to the different bite angles of the five and three chelating member rings present in **6** and **7**, respectively.

The *N,N*-chelation of *trans*-azobenzene in **7** results in a distance of 1.367(9) Å between the two nitrogen donor atoms, which is much longer than that of 1.242(7) Å found for **6**, where the N=N bond retains a double character. Furthermore, in **7** the azobenzene ligand is far away from planarity, so that the C–N–N–C torsion angle is 138.3° and the dihedral angle between the two phenyl rings is 89.2°. These angles take the values of 175.1(5)° and 23.3(4)° in **6** (see Fig. 3).

2.3. DFT studies

DFT calculations [6] using the ADF program [7] (see Section 4 for details) were performed on models of complexes **6** and **7**, respectively [Co(η^5 -C₅H₅)(PH₃)(κ -C, κ -N–C₆H₄N=NPh)]⁺ and Co(η^5 -C₅H₅)(PH₃)(η^2 -PhN=NPh), where the phosphines were taken as PH₃. The geometries of the two complexes were fully optimised.

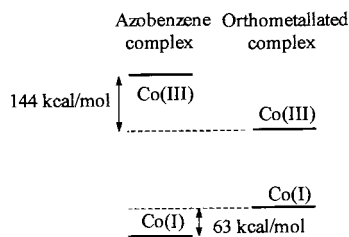
Some of the relevant distances are given in Scheme 3 for the η^2 -azobenzene complex **7**. The numbers in italics are those from the observed structure, while the others are calculated. The agreement is very good. The C–N–N–C torsion angle was calculated as 138° (138.3° in the structure), with the two phenyl groups moving away from the metal. The coordination of



Scheme 3.

Table 2
Relevant bond distances (Å) and bond angles ($^\circ$) calculated for the model complex $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PH}_3)(\kappa\text{-C},\kappa\text{-N-C}_6\text{H}_4\text{N=NPh})]^+$

Co–N(51)	1.966	Co–C(76)	1.940
Co–P	2.176		
N(51)–C(61)	1.433	N(52)–C(71)	1.368
N(51)–N(52)	1.276		
N(51)–Co–C(76)	81.9	C(76)–Co–P	89.2
N(51)–Co–P	92.0	C(76)–C(71)–N(52)	118.1
N(51)–N(52)–C(71)	114.0	C(71)–C(76)–Co	109.2
C(61)–N(51)–Co	129.3	N(52)–N(51)–Co	116.3



Scheme 4.

Table 3
The decomposition of the bonding energy (kcal mol^{-1}) for the possible complexes of Co(I) and Co(III)

	Co(III)		Co(I)	
	η^2 -Azo- benzene	Ortho- metallation	η^2 -Azo- benzene	Ortho- metallation
ΔE_{Pauli}	22626.4	22412.1	22262.4	21978.6
ΔE_{elec}	–4961.3	–4957.6	–4916.1	–4839.4
ΔE_{oi}	–23009.8	–22943.2	–23047.1	–22777.4
ΔE_{int}	–5344.7	–5488.7	–5700.8	–5638.2

azobenzene also leads to a weakening of the N=N bond, which becomes longer than in free *trans*-azobenzene, as a result of donation from the N–N π bond to the metal and back donation into the empty π^* . This value was calculated to be 1.261 Å by full optimisation of free *trans*-azobenzene, and the X-ray determination at 82 K showed two independent molecules with N=N distances of 1.252 and 1.259 Å [11].

The geometry of the orthometallated complex **6** was also optimised with the ADF program. Some relevant distances and angles are given in Table 2 and can be compared to those of the X-ray structure in Table 1 (same numbering scheme). The agreement between calculated (model) and experimental structures is also very good for this complex.

The next step consisted of calculating the complementary species, namely the η^2 -azobenzene complex of Co(III), $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PH}_3)(\eta^2\text{-PhN=NPh})]^2+$ (**8**), and the orthometallated derivative of Co(I), $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PH}_3)(\kappa\text{-C},\kappa\text{-C}_6\text{H}_4\text{N=NPh})]^-$ (**9**). Their geometries were also fully optimised, without any symmetry constraints. The relative energies are given in Scheme 4.

The immediate conclusion from these results is that Co(III) prefers to form the orthometallated complex (by 144 kcal mol^{-1} , while for Co(I) coordination of azobenzene is more favoured (by 63 kcal mol^{-1}). The bonding energy (ΔE_{int}) can be decomposed as the sum of several terms, namely Pauli repulsion (ΔE_{Pauli}), electrostatic (ΔE_{elec}) and orbital interactions (ΔE_{oi}), representing the Pauli repulsion between occupied orbitals of the fragments, the electrostatic interaction between fragments (an attractive term), and the two-electron stabilising interactions between occupied levels of one fragment and empty levels of the other [12] (Table 3).

The preference of the Co(III) fragment for orthometallation can be ascribed to the smaller Pauli repulsion accompanied by very similar electrostatic and orbital interactions. On the other hand, for Co(I), although the same trend is observed for the Pauli repulsion, the electrostatic and orbital interactions decrease considerably for orthometallation. In other words, the high charges on the $\text{CoCp}(\text{PH}_3)^{2+}$ and $\text{C}_6\text{H}_4\text{N=NPh}^-$ fragments with Co(III) lead to a favourable interaction, contrary to $\text{CoCp}(\text{PH}_3)$ and $\text{C}_6\text{H}_4\text{N=NPh}$ for Co(I). For Co(I), the stronger covalent bonds formed with azobenzene (the ΔE_{oi} term) mainly determine the preference.

3. Conclusions

Among the new Co(III) complexes synthesised, the first orthometallation reaction of *trans*-azobenzene in the presence of Co(III) was observed, although simple coordination takes place when this ligand reacts with

similar Co(I) fragments. DFT calculations showed that the experimental observations were consistent with the relative energies of the possible species. The H₂biim ligand coordinates to the CoCp(PPh₃) fragment, the N–H groups being involved in hydrogen bonds with fluorine atoms of the BF₄[−] counter ion in the solid.

4. Experimental

4.1. General procedures and materials

All reactions and manipulations of solutions were performed under an argon atmosphere using Schlenck techniques. Solvents were reagent grade and were dried according to literature methods. Co₂(CO)₈ was purchased from Fluka and Ag[BF₄] was purchased from Aldrich and they were used as supplied. The complexes Co(η⁵-C₅H₅)(CO)₂ [13], Co(η⁵-C₅H₅)(CO)I₂ and Co(η⁵-C₅H₅)(PPh₃)₂I₂ [14] were prepared as previously reported. The petroleum ether used has a b.p. of 40–60°C.

Infrared spectra were recorded as mulls on NaCl plates using an ATI Mattson Genesis FTIR spectrometer. Elemental analyses were performed at the microanalytical laboratory of the Universidade Técnica de Lisboa, Portugal.

Mass spectra were recorded on VG Autospec LSIMS Technique using 3-nitrobenzylalcohol as a matrix and a Caesium gun at the Instituto de Ciencias de Materiales de Aragon, Zaragoza, Spain. ¹H-, ¹³C- and ³¹P-NMR spectra were recorded on a Bruker ARX 400 spectrophotometer. ¹H-NMR spectra were recorded using TMS as internal reference, ³¹P shifts were measured with respect to external 85% H₃PO₄, and ¹³C-NMR spectra were referenced using the ¹³C resonance of the solvent as internal standard.

4.2. Synthesis of [Co(η⁵-C₅H₅)(PPh₃)(NCCH₃)₂][BF₄]₂ (2)

A solution of Co(η⁵-C₅H₅)(PPh₃)₂I₂ (0.6 g, 1.0 mmol) in CH₂Cl₂ (50 cm³) was added to a suspension of Ag[BF₄] (0.50 g, 2.5 mmol) and acetonitrile (2 cm³ of a 1 M solution in CH₂Cl₂, 2.0 mmol) in CH₂Cl₂ (20 cm³), magnetically stirred at room temperature (r.t.). A colour change of the initial solution from green to red was observed, and a precipitate formed. The mixture was left stirring for about 20 min, it was filtered, and the solvent was removed under vacuum. The oily residue was washed several times with petroleum ether (3 × 20 cm³), and it was recrystallised from CH₂Cl₂–petroleum ether, to give nice red crystals. They were recovered by filtration, washed with petroleum ether, and dried in vacuum to afford pure **2**. Yield ca. 70%. (Found: C, 50.74; H, 4.04; N, 4.19; Calc. for C₂₇H₂₆N₂PCoB₂F₈: C, 50.51; H, 4.05 N, 4.36%). ¹H-

NMR (400 MHz, CDCl₃): δ 7.56–7.38 (m, 15H, Ph), 5.98 (s, 5H, C₅H₅), 2.14 (s, 6H, NC–CH₃), IR (nujol, ν (cm^{−1})): broad band centred at 1050 cm^{−1}, BF₄[−].

4.3. Synthesis of

[Co(η⁵-C₅H₅)(PPh₃)(NC–Ph)₂][BF₄]₂·CH₂Cl₂ (3)

A solution of Co(η⁵-C₅H₅)(PPh₃)₂I₂ (0.39 g, 0.6 mmol) and benzonitrile (0.13 cm³, 1.26 mmol) in CH₂Cl₂ (20 cm³) was added to a suspension of Ag[BF₄] (0.30 g, 1.5 mmol) in CH₂Cl₂ (20 cm³), magnetically stirred at r.t. A colour change of the initial solution from green to red was observed, and a precipitate formed. The mixture was left stirring for about 20 min filtered and the solvent was removed under vacuum. The oily residue was washed several times with petroleum ether (3 × 20 cm³). It was recrystallised from CH₂Cl₂–toluene to give nice red crystals, which recovered by filtration, washed with petroleum ether, and dried in vacuum to give pure **3**. Yield ca. 70%. (Found: C, 53.53; H, 3.92; N, 3.18; Calc. for C₃₈H₃₂CoN₂PB₂F₈Cl₂: C, 53.6; H, 3.76; N, 3.29%). ¹H-NMR (400 MHz, CDCl₃): δ 7.64–7.43 (m, 25 H, Ph), 6.31 (s, 5H, C₅H₅), IR (nujol, ν (cm^{−1})): broad band centred at 1050 cm^{−1}, BF₄[−].

4.4. Synthesis of [Co(η⁵-C₅H₅)(PPh₃)(H₂biim)][BF₄]₂ (4)

A solution of Co(η⁵-C₅H₅)(PPh₃)₂I₂ (0.4 g, 0.62 mmol) in CH₂Cl₂ (20 cm³) was added to a suspension of Ag[BF₄] (0.60 g, 3.0 mmol) and 2,2'-bisimidazole (0.09 g, 0.62 mmol) in CH₂Cl₂ (30 cm³), magnetically stirred at r.t. A colour change of the initial solution from green to red was observed, and a precipitate formed. The mixture was left stirring over night, filtered, and the solvent was partially removed under vacuum. Petroleum ether was added and a precipitate was formed (a red crystalline powder together with some oil was formed). Extraction with acetone followed by addition of diethylether gave red crystals, which were recovered by filtration, washed with petroleum ether, and dried in vacuum to give pure **4**. Yield ca. 70%. (Found: C, 50.11; H, 3.73; N, 7.87; Calc. for C₂₉H₂₆CoN₄PB₂F₈: C, 50.0; H, 3.73; N, 8.04%). ¹H-NMR (400 MHz, d⁶-acetone): δ 11.79 (s, 2H, NH), 8.09–7.20 (m, 19 H, Ph), 6.23 (s, 5H, C₅H₅), ³¹P{¹H}-NMR (161.986 MHz, d⁶-acetone): δ 43.54(s). IR (nujol, ν (cm^{−1})): broad band centred at 1050 cm^{−1}, BF₄[−].

4.5. Synthesis of

[Co(η⁵-C₅H₅)(PPh₃){HN(NC₅H₅)₂}[BF₄]₂ (5)

A solution of Co(η⁵-C₅H₅)(PPh₃)₂I₂ (0.34 g, 0.53 mmol) in CH₂Cl₂ (20 cm³) was added to a suspension of Ag[BF₄] (0.58 g, 2.9 mmol) and dipyrilidamine (0.1

Table 4
Crystal data and refinement details for cobalt(III) complexes **1**, **4**, and **6**

Compound	1	4	6
Empirical formula	C ₂₃ H ₂₀ CoI ₂ P	C ₂₉ H ₂₆ B ₂ CoF ₈ N ₄ P	C ₃₅ H ₂₉ BCoF ₄ N ₂ P
<i>M</i>	640.09	694.06	654.31
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
Unit cell dimensions			
<i>a</i> (Å)	22.176(27)	13.315(16)	10.346(12)
<i>b</i> (Å)	14.253(17)	14.539(17)	13.350(15)
<i>c</i> (Å)	17.735(21)	15.713(19)	22.663(24)
β (°)	127.89(1)	98.24(1)	100.79(1)
<i>V</i> (Å ³)	4424(9)	3010(6)	3071(6)
<i>Z</i>	8	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.922	1.531	1.415
μ (mm ⁻¹)	3.645	0.701	0.663
<i>F</i> (000)	2448	1408	1344
θ Range (°)	1.84–92	2.58–26.19	2.38–26.03
Index ranges <i>hkl</i>	0 ≤ <i>h</i> ≤ 27, –17 ≤ <i>k</i> ≤ 17, –21 ≤ <i>l</i> ≤ 16	–16 ≤ <i>h</i> ≤ 0, –17 ≤ <i>k</i> ≤ 17, –19 ≤ <i>l</i> ≤ 19	–12 ≤ <i>h</i> ≤ 0, –15 ≤ <i>k</i> ≤ 16, –27 ≤ <i>l</i> ≤ 27
Reflections collected	5158	9815	10 370
Unique reflections	3312 (<i>R</i> _{int} = 0.0470)	5686 (<i>R</i> _{int} = 0.0745)	5835 (<i>R</i> _{int} = 0.0485)
Refined parameters	245	404	390
Goodness-of-fit on <i>F</i> ²	1.070	0.990	1.139
<i>R</i> and <i>R</i> _w [<i>I</i> > 2(<i>I</i>)]	0.0515, 0.1516	0.0832, 0.2137	0.0995, 0.2452
(all data)	0.0727, 0.1694	0.1729, 0.2598	0.1425, 0.2443
Largest difference peak and hole (e Å ⁻³)	0.991 and –1.624	0.774 and –0.656	1.107 and –0.525

g, 0.53 mmol) in CH₂Cl₂ (20 cm³), magnetically stirred at r.t. A colour change of the initial solution from green to red was observed, and a precipitate formed. The mixture was left stirring for about 20 min, it was filtered, concentrated and petroleum ether added. A precipitate was formed, it was washed several times with petroleum ether (3 × 20 cm³), and recrystallised from a mixture of acetone diethylether, to give nice red crystals, which were recovered by filtration, washed with petroleum ether, and dried in vacuum to give pure **5**. Yield ca. 70%. (Found: C, 52.27; H, 4.18; N, 4.92; Calc. for C₃₃H₃₁N₃PCoB₂F₈: C, 51.23; H, 4.01; N, 5.43%). ¹H-NMR (400 MHz, *d*⁶-acetone): δ 10.42 (s, 1H, NH), 8.20–6.62 (m, 23 H, Ph), 6.28 (s, 5H, C₅H₅), ³¹P{¹H}-NMR (161.986 MHz, *d*⁶-acetone): δ 41.15(s). IR (nujol, ν (cm⁻¹)): broad band centred at 1050 cm⁻¹, BF₄⁻.

4.6. Synthesis of

[Co(η^5 -C₅H₅)(PPh₃)(κ -C, κ -N-C₆H₄N=NPh)][BF₄] (**6**)

A solution of Co(η^5 -C₅H₅)(PPh₃)₂ (1.24 g, 1.94 mmol) and *trans*-azobenzene (0.36 g, 1.94 mmol) in CH₂Cl₂ (20 cm³) was added to a suspension of Ag[BF₄] (0.78 g, 3.9 mmol), magnetically stirred at r.t. A colour change of the initial solution from green to red was observed, and a precipitate formed. The mixture was left stirring for about 20 min, it was filtered, and the solvent was removed by vacuum. The oily residue was

washed several times with petroleum ether (3 × 20 cm³). This reaction was repeated a large number of times, and sometimes it was difficult to solidify the oil, that was achieved by washing the red oily residue with water, followed by petroleum ether. It was recrystallised from CH₂Cl₂–petroleum ether to give nice red crystals, which were recovered by filtration, washed with petroleum ether, and dried in vacuum to give pure **6**: 1.11 g (88%) (Found: C, 63.13; H, 4.41; N, 4.05; Calc. for C₃₅H₂₉N₂PCoBF₄: C, 64.24; H, 4.43; N, 4.28%). ¹H-NMR (400 MHz, CD₂Cl₂): δ 8.00–6.85 (m, 24 H, Ph), 5.47 (s, 5H, C₅H₅), ¹³C{¹H}-NMR (100.62 MHz, CD₂Cl₂): δ 173.06, 172.8(d, *J* ¹³C–³¹P = 26.83 Hz, C–Co) 167.75 (s, C–Co), 156.21 (s, C–N), 142.90 (s, C *ipso*, PPh₃), 133.70–122.85 (m, Ph), 90.92 (s, Cp), ³¹P{¹H}-NMR (161.986 MHz, CD₂Cl₂): δ 45.21(s) IR (nujol, ν (cm⁻¹)): broad band centred at 1050 cm⁻¹, BF₄⁻.

4.7. Crystallography

In the Table 4 are summarised the crystal data, pertinent data collection parameters and refinement details for complexes **1**, **4** and **6**.

The X-ray data for these three complexes were collected on a MAR research plate system using graphite Mo–K α radiation at Reading University. The crystals were positioned at 70 mm from the image plate. Ninety-five frames were measured at 2° intervals using

a counting time between 2 and 10 min appropriate to the crystal under study. Data analysis was carried out with the XDS program [15]. Only the intensities of the complex were corrected empirically for absorption effects, using a version of DIFABS modified for image plate geometry [16]. The structures were solved by a combination of the direct methods, Fourier-difference syntheses and subsequent full-matrix least-squares refinements on F^2 . All hydrogen atoms were introduced in the refinement at the geometric idealised positions. In complex **6** the BF_4^- anions were disordered. Two sets of tetrahedral fluorine atoms were found from difference Fourier maps and were refined with occupancy factors x and $1 - x$, being x refined to 0.56(1). All non-hydrogen atoms were refined with anisotropic thermal parameters except the fluorine atoms of **6**, which were refined with group isotropic ones. The hydrogen atoms were refined with isotropic thermal parameters equal to 1.2 times that of the parent atom.

The residual electronic density found for all complexes were within the expected values. All calculations required to solve and refine the structures were carried out with SHELXS and SHELXL from the SHELX-97 package [17]. Molecular diagrams and the analysis of hydrogen bonds were performed with the PLATON software [18].

4.8. DFT calculations

Density functional calculations [6] were carried out with the Amsterdam Density Functional (ADF) program [7] developed by Baerends and coworkers (release 2.3) [19]. Vosko and coworkers' local exchange correlation potential was used [20], with Becke's non-local exchange [21] and Perdew's correlation corrections [22]. The geometry optimisation procedure was based on the method developed by Versluis and Ziegler [23], using the non-local correction terms in the calculation of the gradients, together with non-local exchange and correlation corrections. The structures of the complexes described above and others referred in the text were used to prepare input files for the optimisation of the geometry of the model complexes. Full optimisations without symmetry constraints were always performed. In all the calculations, a triple- ζ Slater-type orbital (STO) basis set was used for Co 3s, 3p, 4s, 4p, 3d; triple- ζ STO augmented with a single- ζ polarisation function was used for P 3s and 3p, C 2s and 2p, N 2s and 2p, and H 1s. A frozen core approximation was used to treat the core electrons of C (1s), N (1s), P ([1–2]s, 2p) and Co ([1–2]s, 2p).

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge

Crystallographic Data Centre, CCDC no. 151552 for compound **1**, CCDC no. 151553 for compound **4** and CCDC no. 151554 for compound **6**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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