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New benzotriazole derivatives as multifunctional ligands

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Abstract

A series of new multifunctional ligands based on the benzotriazole unit has been synthesized by condensation of hydroximethylbenzotriazole with carboxylic acid derivatives of pyridine, triphenylphosphine, ferrocene and thiophene. The coordination properties of these ligands towards cobalt, rhodium and iridium have been studied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Phosphine ligands; Benzotriazole

1. Introduction

Nitrogen donor ligands are widely used in coordination chemistry [1]. Apart from the classical amine ligands such as ammonia and ethylene diamine, the most common nitrogen-containing ligand systems are heterocycles such as pyridine$^{(a)}$, pyrazine$^{(b)}$, bipyridine$^{(c)}$, oxazoline$^{(d)}$ (Scheme 1) and derivatives thereof [2–6]. Complexes of these ligands are known with almost all transition metals [7–11].

Surprisingly benzotriazole$^{(e)}$ and its derivatives are less frequently encountered in coordination chemistry: Only a few complexes were known so far [12]. Recently we reported the synthesis of thiophene-2,5-di(carboxylatomethylenebenzotriazole) as a new multifunctional ligand for the rhodium-catalysed carbonylation of methanol, from the reaction mixture the macrocyclic rhodium $[Rh_2(CO)_2I_6(C_6H_4N_3CH_2CO_2C_4H_2S\text{-}CO_2CH_2C_6H_4N_3)]_2$ complex was isolated and characterised [13]. We also found this ligand to react with cobalt iodide to give the polymeric complex $[CoI_2(C_6H_4N_3CH_2CO_2C_4H_2SCO_2CH_2C_6H_4N_3)]$ [14]. With the catalytic perspective in mind, we decided to synthesize new ester ligands based on the benzotriazole unit that can be used to improve the activity of late transition metal catalysts in the carbonylation of methanol. One important property of these potentially multidentate ligands is that they can stabilize metal ions in a variety of oxidation states and geometries.

2. Results

The new benzotriazole ligands **1**–**5** are easily accessible by classical condensation methods [15] from hydroximethylbenzotriazole and the corresponding mono- or diacids (Scheme 2). They can be isolated with good yields as micro-crystalline powders; **1** can be recrystallised from ethyl acetate–hexane to give colourless, air-stable crystals and **2** can be recrystallised from acetone–hexane to give orange–red, air-stable crystals.

The molecular structure of the ligand **1** is depicted in Fig. 1. The pyridine ring is almost planar, the ring atoms being formally sp^2 hybridised. In accordance with the aromaticity, the C–C and C–N distances in the pyridine ring are shorter [C(9)–C(10) 1.381(3), C(10)–C(11) 1.383(4), C(9)–N(4) 1.338(3) Å] than those in the benzotriazole ring [C(1)–C(2) 1.391(3), C(1)–C(6) 1.396(3), C(4)–C(5) 1.408(3), C(1)–N(1) 1.369(3) Å]. The two nitrogen–nitrogen distances of the benzotriazole unit are in line with the lengths of a single and a double bond [N(2)–N(3) 1.301(2), N(1)–N(2) 1.367(3) Å]. The C(8)–O(1) bond distance [1.203(2) Å] and the

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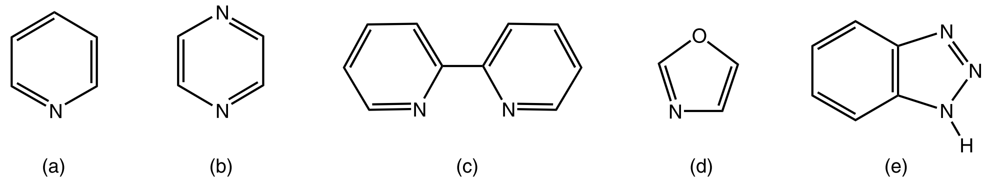


Scheme 1.

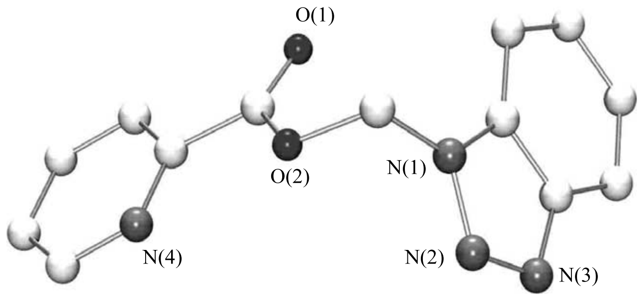


Fig. 1. Molecular structure of ($C_6H_4N_3CH_2CO_2C_5H_4N$) (**1**).

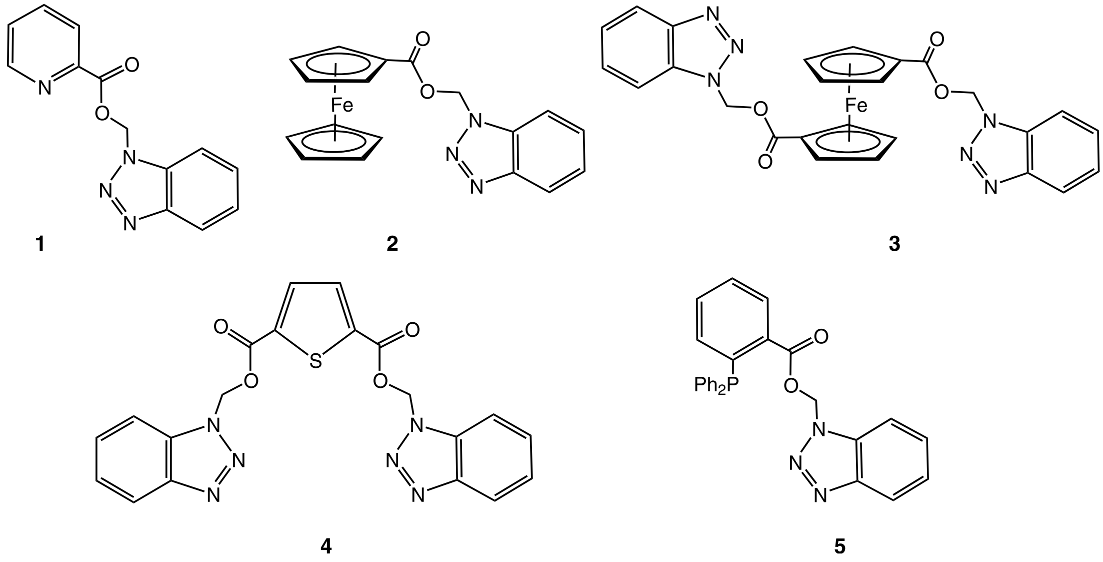
Table 1
Selected bond lengths (Å) for **1**

C(9)–C(10)	1.381(3)	N(2)–N(3)	1.301(2)
C(10)–C(11)	1.383(4)	N(1)–N(2)	1.367(3)
C(9)–N(4)	1.338(3)	C(8)–O(1)	1.203(2)
C(1)–C(2)	1.391(3)	C(8)–O(2)	1.346(2)
C(1)–C(6)	1.396(3)		
C(1)–N(1)	1.369(3)		

C(8)–O(2) bond distance [1.346(2) Å] are similar to those reported for other pyridine esters [16,17] (Table 1).

Selected bond distances and angles for **2** are given in Table 2. The molecular structure of ligand **2** is given in Fig. 2. The ferrocene moiety is in the eclipsed conformation. In each molecule, the Cp rings are almost parallel to each other (angle between the two Cp planes: 5.30°). The iron–carbon distances are as expected and compare well with those of other ferrocene structures [18]. Interestingly, the carbon–carbon bond distances in the substituted Cp ring [C(9)–C(13) 1.430(3), C(9)–C(10) 1.433(2) Å] are longer than those in the unsubstituted Cp ring [C(14)–C(18) 1.409(4), C(14)–C(15) 1.403(3) Å], as it has been observed in similar cases [18]. The carbon–carbon distance between the carbonyl function and the Cp ring [C(8)–C(9) 1.456(2) Å] corresponds to a C–C single bond.

The methylenebenzotriazole substituent is rotated out of the ester plane by 79.45°, allowing no efficient interaction between the π-system of the Cp ring and the benzotriazole moiety. A similar behavior has been observed for benzoylferrocene [19], where the solid state structure shows the phenyl ring rotated out of the Cp plane by 40.4°; steric interference does not allow coplanarity of the Cp and Ph groups [19]. Similar steric problems are most likely responsible for the arrangement of the benzotriazole substituent. The C(8)–O(1) bond of 1.211(2) Å is shorter than those observed for ferrocenecarboxylic acid [20] (1.261(15) Å) and ferrocenedicarboxylic acid (1.228(3) Å) [21]. However, it is also longer than those of other ferrocenecarboxylic esters, such as 2-(1-hydroxyethyl)-1-ferrocenecarboxylic acid



Scheme 2.

Table 2
Selected bond lengths (Å) for **2**

C(9)–C(13)	1.430(3)	C(8)–O(2)	1.363(2)
C(9)–C(10)	1.433(2)	C(8)–C(9)	1.456(2)
C(14)–C(18)	1.409(4)	C(8)–O(1)	1.211(2)
C(14)–C(15)	1.403(3)		

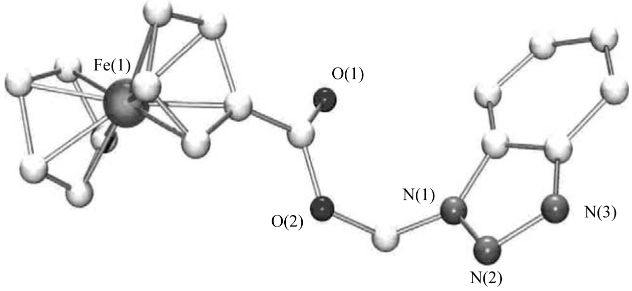
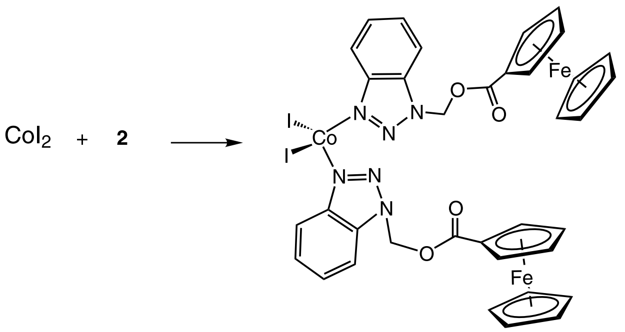


Fig. 2. Molecular structure of ($C_6H_4N_3CH_2CO_2C_5H_4FeC_5H_5$) (**2**).

methyl ester [C=O 1.205(4) Å] [22] and 3-(diphenylphosphino)-1-ferrocenecarboxylic acid methyl ester [C=O 1.204(3) Å] [23]. The C(8)–O(2) bond distance [1.363(2) Å] is about 0.06 Å shorter than that of ferrocenecarboxylic acid benzotriazole ester [1.427(2) Å], which is known to have a weak and reactive ester bond, facilitating the amidation in the peptide-coupling reactions [24]. These findings are in line with the stability of the ester bond observed for **2**.

Compound **2** was found to coordinate easily to cobalt through the 3-N atom of the triazole unit. The reaction of **2** with CoI_2 in dichloromethane at room temperature gives quantitatively the cobalt(II) complex [CoI_2(**2**)$_2$] (**6**) as an air-stable green solid (Scheme 3). This compound is moderately soluble in acetone and toluene, but only sparingly soluble in alcohols and insoluble in alkanes; **6** can be recrystallised from dichloromethane/hexane to give green, air-stable crystals.

The single-crystal X-ray structure analysis reveals that the cobalt(II) centre is tetrahedrally coordinated to two iodine atoms and to the 3-N nitrogen atoms of two triazole ligands. The angles N(23)–Co(1)–N(3), N(23)–Co(1)–I(1), N(23)–Co(1)–I(2), N(3)–Co(1)–I(1), N(3)–Co(1)–I(2), I(1)–Co(1)–I(2) (103.5(2), 106.99(17), 113.42(17), 104.65(15), 110.97(15), 116.20(4)°, respectively) are not far from the ideal tetrahedral angle. The two cobalt–nitrogen bonds [Co(1)–N(3) 2.033(5), Co(1)–N(23) 2.044(5) Å] and the two cobalt–iodine bonds [Co(1)–I(1) 2.5510(11), Co(1)–I(2) 2.5692(11) Å] are almost equal in length and are normal for this kind of complexes [25,26]. Some deviation from regular tetrahedral geometry is indicated by the relatively large I(1)–Co(1)–I(2) and corresponding small N(23)–Co(1)–N(3) angles. Interligand repulsions between the iodine presumably are responsible for the observed distortion [27]. The two C=O bond distances (C(8)–O(1) 1.197(8), C(28)–O(21) 1.195(8) Å) are shorter than this in the free ligand (1.211(2) Å). Selected bond distances and angles for **6** are given in Table 3. The molecular structure of ligand **6** is given in Fig. 3.



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Scheme 3.

Compound **4** was found to coordinate easily to iridium through the 3-N atom of the benzotriazole unit. The reaction of **4** with [Ir(μ-Cl)(cod)]$_2$ in toluene at 110 °C in a carbon monoxide atmosphere gives quantitatively the iridium(I) complex solid [IrCl(CO)(**4**)]$_2$ (**7**) as an air-stable orange solid (Scheme 4). Micro-analytical and NMR data are consistent with the composition proposed, the dimeric nature of the molecule clearly follows from the ESI mass spectrum which shows the molecular peak at m/z 1380. Complex **7** exhibits two strong ν(CO) absorptions at 2074 and 1994 cm^{-1} in the infrared spectrum, as expected for a *cisoid* arrangement of the two terminal carbonyl ligands [28].

The phosphine derivative **5** reacts with $[RhCl(CO)_2]_2$ to give the diphosphine complex $[C_6H_4N_3CH_2CO_2C_6H_4P(C_6H_5)_2]_2Rh(CO)Cl$ (**8**) in high yield (Scheme 5). The product is very easily isolated by evaporation of the solvent and washing of the residues with ether. Compound **8** exhibits, as expected, only one strong ν(CO) absorption in the infrared spectrum, the monomeric

Table 3
Selected bond lengths (Å) and angles (°) for complex **6**

Bond lengths	
Co(1)–N(3)	1.430(3)
Co(1)–N(23)	1.433(2)
Co(1)–I(1)	1.409(4)
Co(1)–I(2)	1.403(3)
C(8)–O(1)	1.197(8)
C(28)–O(21)	1.195(8)
Bond angles	
N(23)–Co(1)–N(3)	103.5(2)
N(23)–Co(1)–I(1)	106.99(17)
N(23)–Co(1)–I(2)	113.42(17)
N(3)–Co(1)–I(1)	104.65(15)
N(3)–Co(1)–I(2)	110.97(15)
I(1)–Co(1)–I(2)	116.20(4)

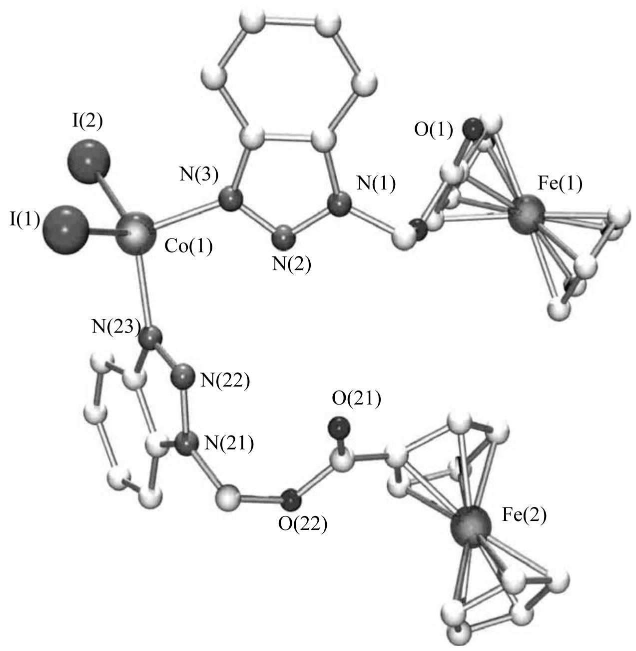
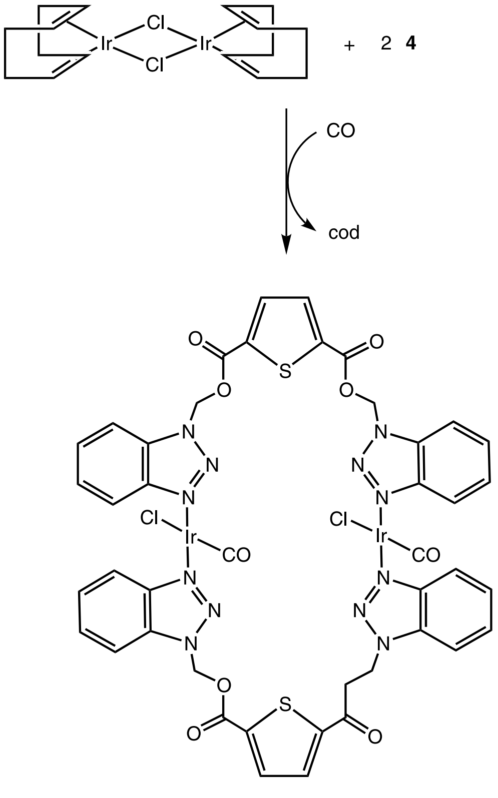


Fig. 3. Molecular structure of $CoI_2(C_6H_4N_3CH_2CO_2C_5H_4FeC_5H_5)$ (**6**).



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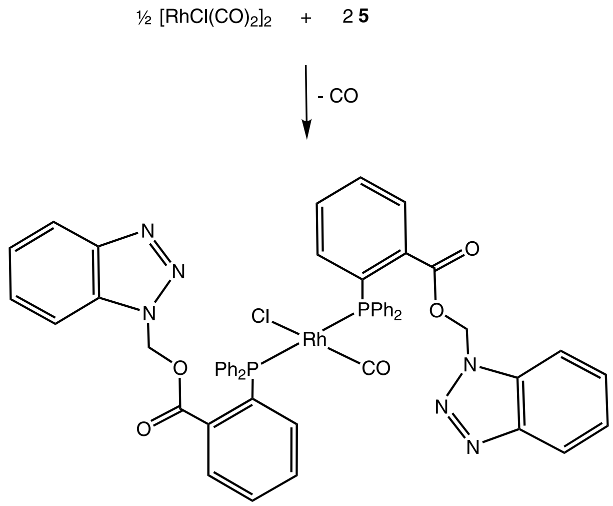
Scheme 4.

nature of these complexes can be deduced from the mass spectra. It shows only one resonance for the two equivalent phosphorus atoms in the $^{31}P\{^1H\}$-NMR spectrum (see Section 5), which appears as a doublet due to coupling of the phosphorus atoms to ^{103}Rh ($I=\frac{1}{2}$), in agreement with the *trans*-*P*,*P* coordination. This is in agreement with the NMR observations for similar β-ketophosphine complexes reported by Shaw and coworkers [29]. Final structural proof was obtained by a single-crystal X-ray structure analysis; the molecular structure of **8** is depicted in Fig. 4, important bond lengths and angles are given in Table 4.



8

Scheme 5.

The single-crystal X-ray structure analysis of **8** shows the rhodium atom carrying two phosphine ligands in *trans* position, one carbonyl ligand and one chloride. The metal atom is in a square-planar environment, the angles C(27)–Rh(1)–Cl(1), P(1a)–Rh(1)–C(27), C(27)–Rh(1)–P(1), P(1)–Rh(1)–Cl(1), Cl(1)–Rh(1)–P(1a) being 178.2(2), 91.1(3), 88.9(3), 88.62(7), 91.38(7)°, respectively. The two Rh–P lengths of 2.32 Å (Table 4) compare well with the analogous triphenylphosphine complex [30–32]. The least-square planes of the benzotriazole rings are tilted toward the Rh–P–CO–P–Cl least-square plane by about 71.2°.

3. Discussion

Of the five new ligands based on the benzotriazole unit synthesized, the phosphine ligand **5** is of particular interest with respect to its donor–acceptor properties, which can be studied in the case of the rhodium complex [Rh(**5**)$_2$(CO)Cl] (**8**). Since monocarbonyl complexes provide easy-to-interpret infrared spectra with a single carbonyl band, complexes of this type have found wide applications as probes for the electronic properties of donor ligands [33]. The extensive literature available [34–37] allows a rapid evaluation of the electronic properties of a new ligand. Thus, for **8** the CO band is detected at 1949 cm^{-1}, which is about 16 cm^{-1} lower in

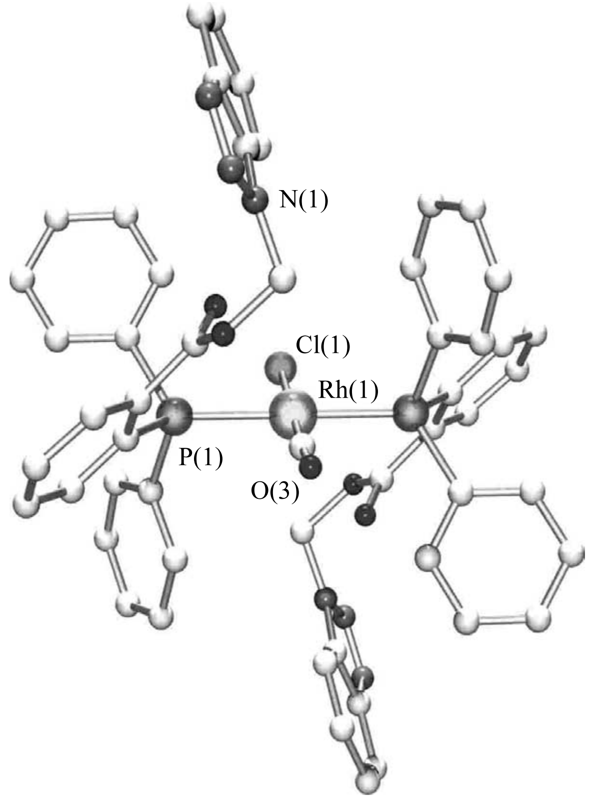


Fig. 4. Molecular structure of Rh(CO)Cl[$C_6H_4N_3CH_2$-$CO_2C_6H_4P(C_6H_5)_2$]$_2$ (**8**).

Table 4
Selected bond lengths (Å) and angles (°) for complex **8**

Bond lengths	
P(1)–Rh(1)	2.3223(6)
C(8)–O(1)	1.205(3)
C(27)–O(3)	1.190(7)
Bond angles	
C(27)–Rh(1)–Cl(1)	178.2(2)
P(1a)–Rh(1)–C(27)	91.1(3)
C(27)–Rh(1)–P(1)	88.9(3)
P(1)–Rh(1)–Cl(1)	88.62(7)
Cl(1)–Rh(1)–P(1a)	91.38(7)

energy than that of the triphenylphosphine complex [Rh(PPh_3)$_2$(CO)Cl] [34], but 7 cm^{-1} higher in energy than that of [Rh(PR_2R')$_2$(CO)Cl] (R = *N*-pyrrolidinyl, R′ = *tert*-butyl), containing a very electron-rich phosphine ligand [37]. The ν_{CO} value for **8** is significantly lower than those of most electron-rich alkylphosphine complexes [Rh(PR_3)$_2$(CO)Cl] (R = Me: ν_{CO} 1960, R = Et: ν_{CO} 1956) [37,38] which are often used in catalysis. Tri-*tert*-butylphosphine, which is generally thought of as one of the most electron-donating phosphines, actually forms a tetrahedral complex [Rh(P^tBu_3)$_2$-(CO)Cl] and cannot be directly compared [39]. Given this comparison, the phosphine **5** can be considered as a strong donor ligand.

Moreover, the overall structural features of **8** being as expected (square-planar coordination, *trans* diphosphine configuration), the bond lengths involving the rhodium atom are of particular interest. A comparison of bond lengths in **8** with those of other *trans*-Rh(PR_3)$_2$(CO)Cl structures [40] shows that **8** has the shortest Rh–C carbonyl bond [1.722(7) Å] observed for this type of complexes. Although the differences in bond lengths are small, these trends are consistent for all structurally characterized Rh(PR_3)$_2$(CO)Cl complexes.

The short Rh–C bond in **8** is consistent with the low-energy ν_{CO} absorption in the infrared spectrum. Since the phosphine ligand **5** is electron-rich and therefore a good σ-donor ligand, the structure of **8** suggests that the long Rh–P distance may result from a reduced π-back-bonding from rhodium to phosphorus. The good σ-donor and poor π-acceptor character of ligand **5** is also reflected in the rhodium–chlorine bond length. As the rhodium atom has a 16 electrons configuration, the reduced electron density at the metal is compensated in such complexes by enhanced donation of electrons from the chlorine lone pairs [41], which causes in general a shortening of the Rh–Cl bond. However, since **5** is a good σ-donor ligand, the Rh–Cl bond [2.391(2) Å] in **8** is longer than in Rh[P(*N*-pyrrolyl)$_3$]$_2$Cl(CO) [2.350(4) Å] and comparable to that of [P(^{t}Bu)$_3$]$_2$Rh(CO)Cl [2.389(2) Å]. The Rh–C distance [1.722(7) Å] in **8** is shortened due to enhanced π-back-bonding to the carbonyl, as demonstrated by the carbonyl stretching frequency at 1949 cm^{-1}. Hence, ligand **5** compares to tri-*tert*-butylphosphine and not to triphenylphosphine as far as its donor–acceptor properties are concerned.

4. Conclusion

The aim of this work was the synthesis of new nitrogen-donor ligands and to study their ability to coordinate as ligand to transition metals. A high-yield route was developed to synthesize different ester derivatives of benzotriazole. The coordination chemistry of these multifunctional ligands studied with Rh(I), Ir(I) and Co(II) centers shows that ligands **2** and **4** are modentate using the 3-N atom of the benzotriazole unit for coordination, while **5** coordinates through the phosphorus atom. Compounds **1** and **3** were not found to be useful as ligands for these metals.

5. Experimental

Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques. The compounds **4** [13], [IrCl(cod)]$_2$ [42], and [RhCl(CO)$_2$]$_2$ [43] were prepared as described previously. All other reagents were purchased (Fluka) and used as received. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200 BB instrument or a Bruker AMX 400 spectrometer and referenced by using the resonances of residual protons in the deuterated solvents. ^{1}H-NMR: internal standard solvent, external standard Me_4Si; ^{13}C-NMR: internal standard solvent, external standard Me_4Si; ^{31}P-NMR: external standard 85% H_3PO_4. Infrared spectra were recorded with a Perkin–Elmer 1720X FT-IR spectrometer. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

5.1. ($C_6H_4N_3CH_2CO_2C_5H_4N$) (**1**)

A solution of 2-pyridinecarboxylic acid (826 mg, 6.71 mmol), *N*,*N*-dicyclohexylcarbodiimide (2.7 g, 13.1 mmol), 4-(dimethylamino)pyridine (122 mg, 1 mmol), 4-pyrrolidinopyridine (148 mg, 1 mmol) and hydroxymethylbenzotriazole (1.1 g, 7.4 mmol) in CH_2Cl_2 (40 ml) was allowed to stand at room temperature (r.t.) under nitrogen, until the esterification was complete. The resulting solution was filtered through Celite to remove *N*,*N*-dicyclohexyl urea, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column (150 g), eluting with EtOAc–C_6H_{14} (1/1). The product was isolated from the third fraction by evaporation of the solvent, giving 1.1 g (65%) of **1** as a white solid. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 1:1 EtOAc–C_6H_{14} solution. Anal. Calc. for $C_{13}H_{10}N_4O_2$ (254.2): C, 61.4; H, 4.0. Found: C, 61.1; H, 4.3%; IR (KBr): 3283m, 3071vw, 3050vw, 3002vw, 2927s, 2852m, 2119vw, 1695vs (C=O ester), 1645s (C=O amide), 1584vw, 1519s, 1432m, 1349m, 1119m, 748m, 694m cm^{-1}; ESI-MS: *m*/*z*: 254 $[M]^+$; ^{1}H-NMR (200 MHz, d_6-C_3H_6O, 21 °C): δ 8.60 (d, 1H, ArH), 8.10 (d, 1H, ArH), 7.93 (d, 1H, ArH), 7.65 (t, 1H, ArH), 7.62 (t, 1H, ArH), 7.44 (t, 1H, ArH), 7.28 (t, 2H, ArH), 6.82 (s, 2H, $-CH_2$); ^{13}C-NMR (50 MHz, d_6-C_3H_6O, 21 °C): δ 164.40, 150.46, 146.63, 146.36, 137.48, 133.13, 128.81, 127.94, 126.11, 124.88, 120.26, 110.55, 69.11.

5.2. ($C_6H_4N_3CH_2CO_2C_5H_4FeC_5H_5$) (**2**)

A solution of ferrocenecarboxylic acid (1.4 g, 6.54 mmol), *N*,*N*-dicyclohexylcarbodiimide (2.7 g, 13.1 mmol), 4-(dimethylamino)pyridine (122 mg, 1 mmol), 4-pyrrolidinopyridine (148 mg, 1 mmol) and hydroxymethylbenzotriazole (1.04 g, 7.04 mmol) in CH_2Cl_2 (40 ml) was allowed to stand at r.t. under nitrogen, until the esterification was complete. The resulting solution was filtered through Celite to remove *N*,*N*-dicyclohexyl urea, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column (150 g), eluting with C_3H_6O–C_6H_{14} (1/4). The product was isolated from the third fraction by evaporation of the solvent, giving 1.3 g (58%) of **2** as an orange solid. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 1:1 C_3H_6O–C_6H_{14} solution. Anal. Calc. for $C_{18}H_{15}Fe_1N_3O_2$ (361.2): C, 59.9; H, 4.2. Found: C, 60.1; H, 4.3%; IR (KBr): 3118vw, 3040vw, 2928m, 1708vs (C=O ester), 1459s, 1276m, 1108s, 967m, 746m cm^{-1}; ESI-MS: *m*/*z*: 361 $[M]^+$; ^{1}H-NMR (200 MHz, d_6-C_3H_6O, 21 °C): δ 8.10 (d, 1H, ArH), 7.93 (d, 1H, ArH), 7.62 (t, 1H, ArH), 7.44 (t, 1H, ArH), 6.82 (s, 2H, $-CH_2$), 4.82 (t, 2H, CpH), 4.44 (t, 2H, CpH), 3.90 (s, 5H; CpH); ^{13}C-NMR (50 MHz, d_6-C_3H_6O, 21 °C): δ 171.30, 147.30, 146.39, 133.06, 133.03, 128.67, 124.93, 120.34, 110.74, 72.46, 72.43, 70.76, 70.16, 70.03, 70.00, 69.95, 69.01, 68.98, 67.62.

5.3. $(C_6H_4N_3CH_2CO_2C_5H_4Fe)_2$ (**3**)

A solution of ferrocenedicarboxylic acid (1.7 g, 6.59 mmol), *N*,*N*-dicyclohexylcarbodiimide (5.5 g, 26.6 mmol), 4-(dimethylamino)pyridine (122 mg, 1 mmol), 4-pyrrolidinopyridine (148 mg, 1 mmol) and hydroxymethylbenzotriazole (1.94 g, 13.04 mmol) in CH_2Cl_2 (40 ml) was allowed to stand at r.t. under nitrogen, until the esterification was complete. The resulting solution was filtered through Celite to remove *N*,*N*-dicyclohexyl urea, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column (150 g), eluting with C_3H_6O–C_6H_{14} (1/1). The product was isolated from the fourth fraction by evaporation of the solvent, giving 1.3 g (51%) of **3** as an orange solid. Anal. Calc. for $C_{26}H_{20}Fe_2N_6O_4$ (592.2): C, 52.7; H, 3.4. Found: C, 52.9; H, 3.5%; IR (KBr): 3100vw, 3050vw, 2927s, 1723vs (C=O ester), 1452m, 1270s, 1155m, 1102s, 968m cm^{-1}; ESI-MS: *m*/*z*: 592 $[M]^+$; ^{1}H-NMR (200 MHz, d_6-C_3H_6O, 21 °C): δ 8.10 (d, 4H, ArH), 7.71 (t, 2H, ArH), 7.51 (t, 2H, ArH), 6.89 (s, 4H, $-CH_2$), 4.66 (t, 4H, CpH), 4.19 (t, 4H, CpH); ^{13}C-NMR (50 MHz, d_6-C_3H_6O, 21 °C): δ 171.30, 147.30, 146.39, 133.06, 133.03, 128.67, 124.93, 120.34, 110.74, 72.46, 72.43, 70.76, 70.16, 70.03, 70.00, 69.95, 69.01, 68.98, 67.62.

5.4. $[C_6H_4N_3CH_2CO_2C_6H_4P(C_6H_5)_2]$ (**5**)

A solution of 2-diphenylphosphinobenzoic acid (1.4 g, 4.6 mmol), *N*,*N*-dicyclohexylcarbodiimide (1.3 g, 6.3 mmol), 4-(dimethylamino)pyridine (122 mg, 1 mmol), 4-pyrrolidinopyridine (148 mg, 1 mmol) and hydroxymethylbenzotriazole (750 mg, 5.0 mmol) in CH_2Cl_2 (40 ml) was allowed to stand at r.t. under nitrogen, until the esterification was complete. The resulting solution was filtered through Celite to remove *N*,*N*-dicyclohexyl urea, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on a silica gel column (150 g), eluting with $Et_2O–C_6H_{14}$ (1/1). The product was isolated from the third fraction by evaporation of the solvent, giving 1.3 g (65%) of **5** as a white solid. Anal. Calc. for $C_{26}H_{20}N_3O_2P_1$ (437.4): C, 71.4; H, 4.6. Found: C, 71.1; H, 4.3%; IR (KBr): 3051vw, 2927s, 2852m, 1723vs (C=O ester), 1584vw, 1434m, 1244s, 1049m, 984m, 695s cm^{-1}; ESI-MS: *m/z*: 437 $[M]^+$; ^{1}H-NMR (200 MHz, d_6-C_3H_6O, 21 °C): δ 8.06–7.46 (m, 1H; ArH), 6.94 (s, 2H, $–CH_2$); ^{13}C-NMR (50 MHz, d_6-C_3H_6O, 21 °C): δ 165.76, 146.36, 142.10 (d, $J_{C-P} = 28.1$ Hz), 137.58 (d, $J_{C-P} = 11.0$ Hz), 134.68, 134.13 (d, $J_{C-P} = 20.7$ Hz), 133.10 (d, $J_{C-P} = 14.6$ Hz), 132.19 (d, $J_{C-P} = 18.3$ Hz), 131.67, 131.62, 129.10, 128.80 (d, $J_{C-P} = 7.3$ Hz), 128.62, 124.73, 120.19, 110.48, 68.73; ^{31}P-NMR (81 MHz, d_6-C_3H_6O, 21 °C): −2.7 (s).

5.5. $CoI_2(C_6H_4N_3CH_2CO_2C_5H_4FeC_5H_5)_2$ (*6*)

A solution of CoI_2 (200 mg, 0.62 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of ferrocene(carboxylato-methylenebenzotriazole) (431 mg, 1.25 mmol) in the same solvent (10 ml). The resulting solution was stirred at room temperature for 1 h. The product precipitated as green solid, which was filtered off, washed with C_6H_{14} (20 ml) and dried in vacuo (174 mg, 75%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 1:3 $C_3H_6O–C_6H_{14}$ solution. Anal. Calc. for $C_{36}H_{30}Co_1Fe_2I_2N_6O_4$ (1035.1): C, 41.8; H, 2.9. Found: C, 41.5; H, 3.1%; IR (KBr): 3092m, 3030vw, 1723vs (C=O ester), 1455m, 1269s, 1199m, 782m, 481m cm^{-1}; ESI-MS: *m/z*: 1035 $[M]^+$.

5.6. $[Ir(CO)Cl(C_6H_4N_3CH_2CO_2C_4H_2SCO_2$-$CH_2C_6H_4N_3)]_2$ (7)

A solution of $[IrCl(cod)]_2$ (175 mg, 0.26 mmol) and thiophene-2,5-di(carboxylatomethylenebenzotriazole) (248 mg, 0.57 mmol) in $C_6H_5CH_3$ (20 ml) was stirred at reflux for 12 h under 1 bar of carbon monoxide. The solution was filtered then evaporated to dryness. The resulting yellow–orange solid was washed with ether (10 ml) and dried under vacuum (240 mg, 67%). Anal. Calc. for $C_{42}H_{28}Cl_2Ir_2N_{12}O_{10}S_2$ (1380.2): C, 36.6; H, 2.0. Found: C, 36.9; H, 2.2%; IR (KBr): 3324m, 3071vw, 2928s, 2852m, 2074s, 1990vs, 1727vs (C=O ester), 1584vw, 1527m, 1454m, 1234m, 1070m, 744m, 634m cm^{-1}; ESI-MS: *m/z*: 1380 $[M]^+$; ^{1}H-NMR (C_3H_6O): δ 8.17 (d, 4H), 7.86 (s, 4H), 7.81 (m, 4H), 7.6 (m, 4H), 7.05 (s, 8H); ^{13}C-NMR (C_3H_6O): δ 160.37, 145.36, 138.23, 135.14, 132.82, 129.73, 125.52, 120.52, 111.23, 69.82.

5.7. $Rh(CO)Cl[C_6H_4N_3CH_2CO_2C_6H_4P(C_6H_5)_2]_2$ (*8*)

A solution of $[RhCl(CO)_2]_2$ (50 mg, 0.13 mmol) and **5** (246 mg, 0.56 mmol) in MeCN (20 ml) was stirred at r.t. for 2 h. Then the solvent was removed under reduced pressure. The resulting yellow solid was washed with ether (10 ml) and dried under vacuum (210 mg, 0.20 mmol, 78%). Anal. Calc. for $C_{53}H_{40}Cl_1N_6O_5P_2Rh_1$ (1041.2): C, 61.1; H, 3.9. Found: C, 61.5; H, 4.1%; IR (KBr): 3058m, 2926m, 1949vs, 1730vs (C=O ester), 1480w, 1452vw, 1435s, 1275s, 1156m, 1096s, 1055m, 986m, 962m, 743s, 696s cm^{-1}; ESI-MS: *m/z*: 844 $[M-Cl]^+$; ^{1}H-NMR (200 MHz, d_6-C_3H_6O, 21 °C): δ 8.04 (m, 4H, ArH), 7.83 (m, 8H, ArH), 7.45 (m, 22H, ArH), 7.17 (m, 2H, ArH), 6.74 (s, 4H, $–CH_2$); ^{13}C-NMR (50 MHz, d_6-C_3H_6O, 21 °C): δ 188.20 (dt, $^1J_{P-Rh} = 65$ Hz d, $^2J_{C-P} = 22$ Hz, carbonyl ligand), 171.25, 153.62, 144.80, 144.42, 138.54–125.20, 68.62, 49.92; ^{31}P-NMR (81 MHz, d_6-C_3H_6O, 21 °C): 33.7 (d, $^1J(^{103}Rh-^{31}P) = 136$ Hz).

6. Supplementary material

Lists of atomic coordinates, anisotropic displacement parameters and crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 179635, 179636, 179637 and 179638 for compounds **1**, **2**, **6** and **8**. 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 www: http://www.ccdc.cam.ac.uk).

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