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New chelating nitrogen ligands and their application to the catalytic reduction of nitrobenzene to aniline. X-ray structure of [Rh(CO)$_2$(BBOM)] (HBBOM = bis(2-benzoxazolyl)methane)

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Abstract

The use of two novel chelating nitrogen ligands of the bis(azaheteroaryl)methane type is reported. Two complexes were synthesized: [Rh(CO)$_2$(BBOM)] and [Pd(HBBOM)$_2$](NO$_3$)$_2$ (HBBOM = bis(2-benzoxazolyl)methane), the first of which was completely characterized by X-ray crystallography. The dimethylated compound α,α-dimethyl-bis(2-benzothiazolyl)methane was also synthesized by an original procedure and used as a promoter in the [Ru$_3$(CO)$_{12}$]-catalyzed reduction of nitrobenzene to aniline. It gave much better conversions and selectivities with respect to the non-methylated HBBOM, probably due to the fact that the latter can be deprotonated when coordinated to the metal.

Keywords: Rhodium; Palladium; Carbonylation; Nitrobenzene; Aniline; Nitrogen base

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1. Introduction

The $-N=C-CH_2-C=N-$ fragment, present in the bis-*ortho*,*ortho'*-(azaheteroaryl)methane systems, is interesting because, in its deprotonated form and as a diimine analogue, it mimics the coordinating capacities of β-diketonate moieties. Heterocycles containing such a group could behave both as a neutral (HL) or anionic (L^-) ligands towards metal ions. Among the bis(azaheteroaryl)methanes with such a structural frame, the most studied are bis(2-quinolyl)methane [1] and bis(2-pyridyl)methane [2]. In recent years, much attention has been directed to the use of compounds belonging to the aforementioned class and having two five-membered rings linked to the central $-CH_2-$ group, such as semicorrins and bis(oxazolines) [3]. Examples are known [4] both of complex *salts* of the general formula [M(HL)$_n$]X$_m$ with divalent metal ions and of chelate complexes of the general formula [ML$_2$]. In a recent paper some of us showed that the formation of one kind of complex rather than the other depends critically on HL, the metal and the ancillary anion present in the starting metal salt [5].

The structure of the compounds HL discussed in this paper is also similar to that of bis(pyrazolyl)borates which have received a great attention in the last 30 years [6]. The ones here described are more chemically robust than the pyrazolylborate and their electronic properties are more easily finely tuned by appropriate modification of their structure.

In this paper, we report the synthesis of two new complexes of rhodium and palladium, containing the BBOM (HBBOM = bis-(2-benzoxazolyl)methane). Though the HBBOM molecule has been known for sometime [7], to the best of our knowledge it has never been used before in metal complex. We also report on the use of this and a similar methylated compound as co-catalysts in the reduction of nitrobenzene to aniline catalyzed by palladium and ruthenium complexes.

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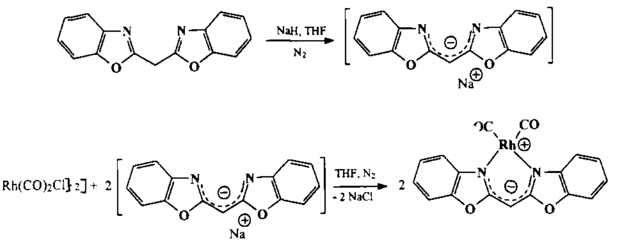
2. Results and discussion

2.1. Synthesis and reactivity of complexes containing BBOM

Addition of a THF solution of Na(BBOM), generated from HBBOM and NaH, to a THF solution of [{Rh(CO)$_2$Cl}$_2$] gave immediate formation of a complex which has been shown to be *cis*-[Rh(CO)$_2$(BBOM)] by means of IR, NMR and mass spectroscopies, and by X-ray crystallography.



No reaction was observed if neutral HBBOM was added to a solution of [{Rh(CO)$_2$Cl}$_2$], even in the presence of a base such as Et$_3$N or Li$_2$CO$_3$, indicating that the neutral base is too weak to break the dimeric structure of the starting material. [Rh(CO)$_2$(BBOM)] is a robust, air-stable orange complex and can be purified by chromatography on silica gel (96.2% purified yield).

The ν_{CO} frequencies in the IR spectrum of [Rh(CO)$_2$(BBOM)] (2069 (s), 2013 (s) in Nujol) compare to the values previously reported for [Rh(CO)$_2$(H$_2$BPz$_2$)] (Pz = 1-pyrazolyl) (2088 (s), 2022 (s)) [8] and [Rh(CO)$_2$(pentane-2,4-dionate)] (2083 (s), 2015 (s)) [9] but are significantly shifted to lower frequencies, indicating that the BBOM is more basic than both acetylacetonate and a bis(pyrazolyl)borate, despite the last molecule having two nitrogen atoms in each of the five-membered rings.

Evidence for the carbanionic nature of the BBOM in [Rh(CO)$_2$(BBOM)] is provided both by the ^{13}C NMR data and the crystallographic analysis (see Tables 1 and 2 and also later). As in previously reported chelate complexes [5], the ^{13}C NMR chemical shift of the bridging methine carbon (61.37 ppm) is displaced to low field in comparison with the methylene of the free base (28.58 ppm) due to its rehybridization sp^3 → sp^2. Accordingly, even the $^1J_{CH}$ coupling constant of the methine doublet is considerably increased (^1J = 169 Hz) in comparison with the neutral precursor (^1J = 133.8 Hz). The bridging methine chemical shift is at the same field as that of [Zn(BBOM)$_2$] (58.90 ppm) [5,10], suggesting a similar negative charge density on this carbon atom.

The solubility of [Rh(CO)$_2$(BBOM)] in most organic solvents is very temperature-dependent and this has allowed the growing of crystals of this compound by slow cooling of a hot saturated acetone solution. The [Rh(CO)$_2$(BBOM)] complex possesses C_s crystallographic symmetry, with atoms Rh, C(1) and H(1) lying on the mirror plane (see Fig. 1). The rhodium atom displays the expected square-planar coordination with the following displacements with respect to the average plane: Rh, 0.056(1) Å; C and C′, −0.015(6) Å; N(1) and N(1)′, −0.013(2) Å. The six-membered metallacycle has an envelope conformation; the N(1)–C(2)–C(1)–C(2)′–N(1)′ moiety is essentially planar (the largest deviation from the least-squares plane does not exceed six times its e.s.d.) and makes a dihedral angle with the coordination plane of 26.2(2)°. Selected interatomic distances and angles are reported in Table 3. The C(1)–C(2) bond is 1.378(4) Å and the C(2)–C(1)–

Table 1
Crystallographic data for [Rh(CO)$_2$(BBOM)]

Formula	$C_{17}H_9N_2O_4Rh$
Molecular weight	408.18
Crystal system	orthorhombic
Space group	*Cmc*2$_1$ (No. 36)
a (Å)	25.886(4)
b (Å)	8.314(1)
c (Å)	6.874(1)
V (Å^3)	1479.4(3)
Z	4
$D_{calc.}$ (g cm^{-3})	1.833
μ (cm^{-1})	11.6
Min. transmission factor	0.97
Scan mode	ω
ω-Scan width (°)	0.9 + 0.35 tan θ
θ-Range (°)	3–27
Reciprocal space explored	$+h, +k, -l$
Measured reflections	905
Unique observed reflections with $I > 3\sigma(I)$	837
Final R and R_w indices [a]	0.017, 0.023
No. of variables	111
GOF [b]	1.022

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$; $R_w = [\Sigma_w(F_o - k|F_c|)^2/\Sigma_w F_o^2]^{1/2}$.
[b] $\text{GOF} = [\Sigma_w(F_o - k|F_c|)^2/(N_{\text{observations}} - N_{\text{variables}})]^{1/2}$; $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_oLp$.

Table 2
Fractional atomic coordinates of non-hydrogen atoms for [Rh(CO)$_2$(BBOM)]

Atom	*x*	*y*	*z*
Rh	0.000	0.04400(2)	0.000
O	0.07762(8)	−0.2225(2)	0.0058(5)
O(1)	0.0908(1)	0.4475(2)	0.1516(4)
N(1)	0.05536(8)	0.2247(2)	0.0215(3)
C	0.0488(1)	−0.1203(3)	0.0000(8)
C(1)	0.000	0.4325(4)	0.1652(7)
C(2)	0.0463(1)	0.3640(3)	0.1112(4)
C(3)	0.1304(1)	0.3557(4)	0.0745(5)
C(4)	0.1827(2)	0.3890(5)	0.0777(7)
C(5)	0.2142(1)	0.2776(5)	−0.0136(9)
C(6)	0.1940(1)	0.1420(4)	−0.1016(7)
C(7)	0.1410(1)	0.1088(4)	−0.1024(5)
C(8)	0.10933(9)	0.2188(3)	−0.0093(6)

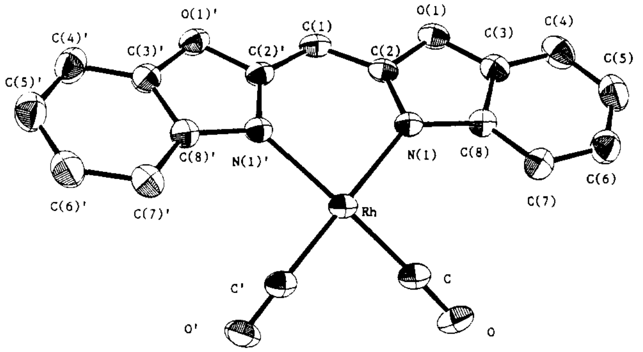


Fig. 1. ORTEP drawing of $[Rh(CO)_2(BBOM)]$. Thermal ellipsoids are drawn at 30% probability level.

C(2)' angle is 120.9(4)°. Both values indicate that the negative charge of the carbanion is removed from the C(1) atom, which is sp^2 hybridized by delocalization through the heteroaromatic system.

Reaction of $[Rh(CO)_2(BBOM)]$ with PPh_3 in toluene yielded a novel complex formulated as $[Rh(CO)(PPh_3)(BBOM)]$ on the basis of its ^1H NMR, ^{13}C NMR and mass spectra. However, other unidentified products also formed in large amounts and it was not possible to obtain this complex analytically pure. The double substitution product, $[Rh(PPh_3)_2(BBOM)]$, could not be obtained in this way, probably because it would be sterically very hindered. Even reaction of Na(BBOM) with $[RhCl(PPh_3)_3]$ led to a mixture of products.

Though $[\{Rh(CO)_2Cl\}_2]$ did not react with neutral HBBOM, palladium nitrate did, affording a complex, $[Pd(HBBOM)_2](NO_3)_2$, in which the HBBOM molecule is neutral. It is interesting to note that the identity of the counteranion plays an important role in this case. Indeed, reaction of $Pd(OAc)_2$ with HBBOM gave the neutral complex $[Pd(BBOM)_2]$ [5,10]. The acetate anion is thus sufficiently basic to deprotonate HBBOM coordinated to Pd^{II}, whereas the nitrate anion is not.

Table 3
Selected interatomic distances (Å) and angles (°) in $[Rh(CO)_2(BBOM)]$ [a]

Rh-N(1)	2.081(2)	Rh-C	1.861(3)
C-O	1.131(3)	C(1)-C(2)	1.378(4)
C(3)-C(4)	1.382(5)	C(3)-C(8)	1.387(5)
C(4)-C(5)	1.385(8)	O(1)-C(2)	1.373(4)
C(5)-C(6)	1.382(7)	O(1)-C(3)	1.383(4)
C(6)-C(7)	1.400(5)	N(1)-C(2)	1.333(4)
C(7)-C(8)	1.384(5)	N(1)-C(8)	1.414(4)
N(1)-Rh-N(1)'	87.0(1)	C-Rh-C'	85.5(2)
N(1)-Rh-C	93.6(1)	O(1)-C(2)-C(1)	117.8(3)
N(1)-Rh-C'	175.8(3)	N(1)-C(2)-C(1)	129.5(3)
O(1)-C(2)-N(1)	112.6(3)	O(1)-C(3)-C(4)	127.5(3)
O(1)-C(3)-C(8)	108.8(3)	C(4)-C(3)-C(8)	123.8(4)
C(3)-C(4)-C(5)	115.8(4)	C(2)-O(1)-C(3)	105.4(2)
C(4)-C(5)-C(6)	121.4(3)	Rh-C-O	177.5(6)
Rh-N(1)-C(2)	122.6(2)	C(5)-C(6)-C(7)	122.3(4)
Rh-N(1)-C(8)	130.1(2)	C(6)-C(7)-C(8)	116.6(3)
C(2)-N(1)-C(8)	105.9(3)	N(1)-C(8)-C(3)	107.3(3)
N(1)-C(8)-C(7)	132.6(3)	C(3)-C(8)-C(7)	120.1(3)
C(2)-C(1)-C(2)'	120.9(4)		

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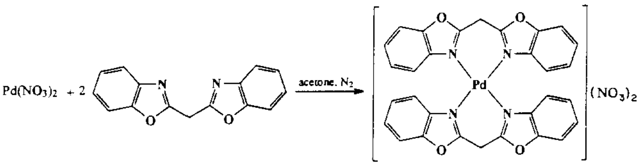
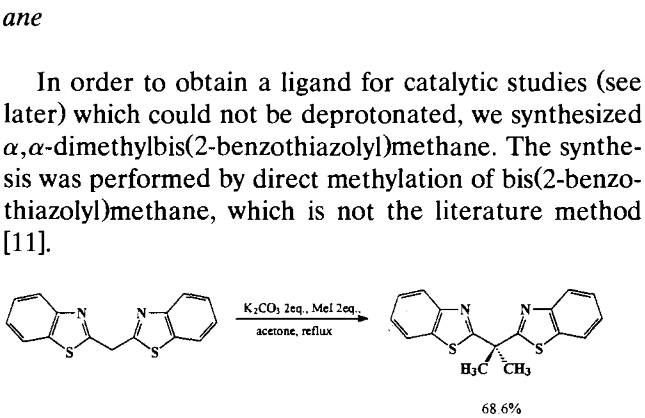
[a] Primed atoms are related to the unprimed ones by the operation: $-x, y, z$.



Similar complexes have been also obtained for cobalt and copper. They will be reported elsewhere.

2.2. Synthesis of α,α-dimethylbis(2-benzothiazolyl)methane

In order to obtain a ligand for catalytic studies (see later) which could not be deprotonated, we synthesized α,α-dimethylbis(2-benzothiazolyl)methane. The synthesis was performed by direct methylation of bis(2-benzothiazolyl)methane, which is not the literature method [11].



An attempt to generate the corresponding oxygenated compound from dimethylmalonic acid and 2-aminophenol, following a procedure for the synthesis of benzoazolylmethane derivatives reported in the literature [11], did not lead to the desired product. 2-Isopropylbenzoxazole was formed instead.

2.3. Catalytic reduction and carbonylation of nitrobenzene to aniline and methyl phenylcarbamate

Catalytic carbonylation and reduction of organic nitro compounds are topics of high current interest [12]. Chelating nitrogen ligands such as phenanthrolines are known to be active promoters of the palladium-catalyzed carbonylation of nitrobenzene to methyl phenylcarbamate and to phenyl isocyanate [13]. However, several chelating nitrogen ligands have also been shown to be promoters of the carbonylation of nitrobenzene to methyl phenylcarbamate [14] or its reduction to aniline [15] catalyzed by $[Ru_3(CO)_{12}]$.

We first attempted to effect the carbonylation of nitrobenzene to methyl phenylcarbamate using $[Pd(BBOM)_2]$ or the systems generated in situ from $[Pd(TMB)_2]$ (HTMB = 2,4,6-trimethylbenzoic acid), bis(2-benzoxazolyl)methane or α,α-dimethylbis(2-benzothiazolyl)methane, and HTMB. This kind of system has been shown previously by some of us to be very effi-

Table 4
Reduction of nitrobenzene to aniline catalyzed by $[Ru_3(CO)_{12}]/\alpha,\alpha$-dimethylbis(2-benzothiazolyl)methane [a]

T (°C)	P_{CO} (bar)	Base/$[Ru_3(CO)_{12}]$ ratio	Conv. (%) [b]	Select. aniline (%) [c]
165	30	1.5 [d]	31.7	25.4
165	30	1.5	97.8	73.5
165	30	1	30.7	49.5
165	30	2	95.4	75.7
180	30	1.5	95.4	77.8
200	30	1.5	90.2	73.9
150	30	1.5	35.2	78.8
165	50	1.5	32.3	78.0
165	10	1.5	39.7	71.5

[a] Experimental conditions: $[Ru_3(CO)_{12}]$ 10 mg (0.0156 mmol), $PhNO_2$ 1.92 g (15.6 mmol) in EtOH (23.5 ml) + H_2O (1.25 ml) for 1.5 h.
[b] Calculated with respect to the starting $PhNO_2$.
[c] Calculated with respect to the converted $PhNO_2$.
[d] Bis(2-benzoxazolyl)methane was used instead of α,α-dimethylbis(2-benzothiazolyl)methane.

cient when the nitrogen ligand is a phenanthroline derivative [13]. However, in the present case, only negative results were obtained. The conversions were somewhat better if the cationic $[Pd(HBBOM)_2](NO_3)_2$ or $[Pd(HBBOM)_2](BF_4)_2$ (derived by anion exchange from the corresponding nitrate) were used as catalysts, but the conversions and selectivities still remained low.

We then moved to catalytic systems based on $[Ru_3(CO)_{12}]$. Poor results were again obtained when the carbonylation to the carbamate was attempted, although the α,α-methylated ligand gave better conversions than HBBOM. However, good activities were found when the reduction of nitrobenzene to aniline was investigated.

$$PhNO_2 + 3CO + H_2O \xrightarrow[EtOH/H_2O,\ 150-200^{\circ}C]{[Ru_3(CO)_{12}],\ N\text{-base}} PhNH_2 + 3CO_2$$

The results of this study are reported in Table 4. Apart from aniline, azo- and azoxy-benzene were also always formed. However, it has been shown previously that these two products convert to aniline on a longer timescale in similar catalytic systems [15]. Again the dimethylated compound was found to be markedly superior to HBBOM (compare the first entry of the table with the others). Since these two bases are similar in basicity, it is evident that the much lower promoting capability of HBBOM is related to the possibility of its being deprotonated once coordinated to ruthenium. Under the same experimental conditions, $[Rh(CO)_2(BBOM)]$ was completely inactive as a catalyst for the reduction of nitrobenzene to aniline, a further evidence of the deactivating effect of deprotonation on these reactions.

The system employing α,α-dimethylbis(2-benzothiazolyl)methane was partly optimized with respect to the temperature, pressure and base $[Ru_3(CO)_{12}]$ ratio. As shown by the values reported in Table 4, the best results were obtained by working at $P_{CO} = 30$ bar and at temperatures between 165 and 180°C. Working at 200°C gave a somewhat lower conversion, probably due to partial decomposition of the catalytic system at this temperature, whereas at 150°C only a 35% conversion was obtained. Similar behaviour was observed for the pressure, with lower conversions obtained for values higher or lower than 30 bar. Base $[Ru_3(CO)_{12}]$ molar ratios of 1.5 and 2 gave similar results, but if the ratio was lowered to 1 a sharp decrease in conversion from 97.8 to 30.7 was observed. Overall the activity of the present catalytic system is very good, though even better results have been obtained previously by some of us using bases of the type DIAN-R (DIAN-R = acenaphtene quinone bis(*para*-R phenylimmino)) [15a].

3. Experimental details

All the syntheses were conducted under dinitrogen, using a standard Schlenk apparatus, but chromatographic separations were conducted in air. Solvents were dried by standard procedures. $[\{Rh(CO)_2Cl\}_2]$ [16], $[Ru_3(CO)_{12}]$ [17], bis(2-benzothiazolyl)methane [18] and bis(2-benzoxazolyl)methane [7] were synthesized by methods reported in the literature. Nitrobenzene was washed with 10% H_2SO_4, dried over $CaCl_2$, distilled under reduced pressure of dinitrogen and stored under dinitrogen. All other starting materials were commercial products and were used as received. IR spectra were recorded on a Bio-Rad FTS-7 FT-IR spectrophotometer; NMR spectra were recorded on either a Bruker AC-200 FT, a Bruker AC-300 FT or a Varian XL 300-FT spectrometer. Gas chromatographic analyses were performed on a Perkin-Elmer 8420 capillary gas chromatograph equipped with a PSS 255 column. Elemental analyses were performed in the analytical laboratories of the University of Milano.

3.1. Synthesis of $[Rh(CO)_2(BBOM)]$

To a solution of bis(2-benzoxazolyl)methane (0.10 g, 0.40 mmol) in THF (2 ml) was added an excess of NaH until a solid residue remained at the bottom of the flask. Dihydrogen was evolved during the addition. The solution was left to settle, after which it was added under stirring to a solution of $[\{Rh(CO)_2Cl\}_2]$ (78 mg, 0.20 mmol) in THF (1 ml). An orange suspension was immediately formed. Evaporation of the solvent led to an orange solid which was purified by filtration over a pad of silica gel (height, 5 cm; eluent CH_2Cl_2). Evaporation of the CH_2Cl_2 solution afforded the analytically pure product as an orange solid (197 mg, 0.38 mmol, 96.2% yield). In the solid state, the product is indefinitely stable in air.

IR (Nujol) (cm^{-1}): 2069 (s, ν_{CO}); 2013 (s, ν_{CO}); 1629 (s); 1583 (s); 1322 (m); 1254 (m); 1027 (m); 911 (w). ^1H NMR ($CDCl_3$)δ: 7.53 (d, 2H, $J_{7,6} = 7.6$ Hz, $J_{7,5} = 1.5$ Hz, H_7); 7.30 (d, 2H, $J_{4,5} = 8.0$ Hz, $J_{4,6} = 1.2$ Hz, H_4); 7.23 (t, 2H, $J_{5,6} = 7.8$ Hz, H_5); 7.13 (t, 2H, H_6); 5.34 (s, 1H, H_{bridge}) ppm. ^{13}C NMR ($CDCl_3$)δ: 185.53 (d, $J_{Rh-C} = 66.2$ Hz, C_{CO}); 166.70 (s, C_2); 148.34 (s, C_8); 142.17 (s, C_9); 124.00 (d, C_5); 122.55 (d, C_6); 114.66 (d, C_4); 109.48 (d, C_7); 61.37 (d, $J_{C-H} = 169.2$ Hz, C_{bridge}) ppm. Mass spectrum (E.I.)m/z: 408 (M, 36%); 380 (M – CO, 14%); 352 (M – 2CO, 65%); 276 (57%); 199 (100%); 122 (40%). Anal. Found: C, 49.57; H, 2.25; N, 6.66%. Calc.: $C_{17}H_9N_2O_4Rh$ requires: C, 50.02; H, 2.22; N, 6.86%. M.P. > 300°C.

3.2. Synthesis of $[Pd(HBBOM)](NO_3)_2$

To a solution of $Pd(NO_3)_2 \cdot 2H_2O$ (133 mg, 0.50 mmol) in acetone (30 ml) was added a solution of HBBOM (250 mg, 1.00 mmol) in acetone (3 ml). The red-orange suspension obtained was stirred for 2 h, after which was filtered and the orange solid obtained washed with further acetone (5 ml) and dried in vacuo at 70°C for 2 h (104 mg, 0.14 mmol, 28.5% yield). IR (Nujol) (cm^{-1}): 1716 (w); 1625 (w); 1602 (w); 1580 (w); 1562 (m); 1522 (w); 1500 (s); 1366 (s); 1256 (m); 1244 (w); 1169 (w); 1079 (w); 1034 (w); 760 (m); 745 (s); 722 (m). Anal. Found: C, 48.70; H, 2.28; N, 10.96%. Calc.: $C_{30}H_{20}N_6O_{10}Pd$. C, 49.29; H, 2.76; N, 10.96%, M.p. > 300°C.

3.3. Synthesis of α,α-dimethylbis(2-benzothiazolyl)-methane

K_2CO_3 (11.1 g, 80.0 mmol) was quickly grounded and then stored in a desiccator. Bis(2-benzothiazolyl)-methane (2.82 g, 10.0 mmol) was dissolved in acetone (200 ml) and half the $K_2(CO)_3$ added, affording a yellow solution. A solution of MeI (5.68 g, 40 mmol) in acetone (30 ml) was slowly dropped into the first solution under magnetic stirring and then heated under reflux for 4 h. After this time, the remaining portion of K_2CO_3 and further MeI (5.68 g, 40.0 mmol) were added, the solution stirred at room temperature overnight and then refluxed for 5 h. The suspension was filtered and the solid K_2CO_3 remained on the filter washed with acetone (15 ml). Evaporation of the clear yellow solution afforded a yellow solid which was crystallized from ethanol (2.13 g, 6.86 mmol, 68.6% yield). ^1H NMR ($CDCl_3$)δ: 8.05 (d, 2H, $J_{4,5} = 8.1$ Hz, H_4); 7.82 (d, 2H, $J_{7,6} = 7.9$ Hz, H_7); 7.46 (t, 2H, $J_{5,6} = 7.69$, $J_{5,7} = 1.0$ Hz, H_5); 7.35 (t, 2H, $J_{6,4} = 0.7$ Hz); 2.15 (s, 6H, CH_3)ppm. Anal. Found: C, 65.91; H, 4.40; N, 9.21%. Calc.: $C_{17}H_{14}N_2S_2$. C, 65.77; H, 4.55; N, 9.03%. M.p. = 137–138°C (The melting point reported in Ref. [11] is 157°C. However, given the excellent elemental analysis obtained by us, we consider the value reported here to be more reliable.)

3.4. Catalytic reactions

Catalytic reactions were performed in a glass liner placed inside an Hastelloy autoclave fitted with a magnetic stirrer. The base, $[Ru_3(CO)_{12}]$ and nitrobenzene were weighed inside the liner which was then placed in a large Schlenk tube under dinitrogen. The tube was frozen with dry ice–acetone, evacuated and filled three times with dinitrogen before the solvent was added. After the solvent had also been frozen, the liner was quickly transferred to the autoclave and air was immediately pumped off and replaced by dinitrogen. The autoclave was charged at the desired pressure at room temperature and placed in a thermoregulated oil bath, previously heated at the required temperature. At the end of the reaction, the autoclave was cooled with an ice bath, vented and the solution was analyzed by gas chromatography (using naphthalene as an internal standard).

3.5. X-ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 1. A prismatic crystal of approximate dimensions 0.15 × 0.08 × 0.25 mm was used. Diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The diffracted intensities were corrected for Lorentz, polarization and absorption (empirical corrections) [19] but not for extinction. Scattering factors for all the atomic species and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from Ref. [20]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\Sigma w(|F_o| - k|F_c|)^2$. An anisotropic thermal parameter was assigned to all non-hydrogen atoms. All hydrogen atoms were introduced in the structure model at calculated positions (C–H, 0.95 Å). The refinement of the two enantiomorphs was not significant for the choice of the correct one. The final difference Fourier synthesis showed maximal residuals of 0.4 e $Å^{-3}$. The final atomic coordinates are listed in Table 2. All the calculations were performed on a HP Vectra 486/33 computer using the Personal SDP Structure Determination Package [21]. Full lists of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

4. Conclusions

The use of ligands of the type described in this paper is a new interesting area with numerous potential applications. Accurate choice of the base and of the counteranion allows one to direct the synthesis of the complexes towards the formation of neutral or cationic complexes. The IR spectrum of [Rh(CO)$_2$-(BBOM)] complex indicates that, BBOM is a very strong base, whereas its basicity is probably much decreased when it is coordinated in the neutral form. The catalytic results reported indicate that this change in basicity can greatly affect the outcome of the reaction, representing an effective way to modify the electronic properties of the catalyst. Further studies are necessary to fully develop the potentialities of these bases.

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References

[1] (a) G. Sheibe and E. Daltrozzo, *Adv. Heterocycl. Chem., 7* (1966) 153; (b) A. Abbotto, S. Bradamante, G.A. Pagani, R. Rzepa and F. Stoppa, *Heterocycles*, in press; (c) H. Adolfsson, K. Warnmark and C. Moberg, *J. Org. Chem., 59* (1994) 2004.

[2] (a) D.St.C Black, *Aust. J. Chem., 20* (1967) 2101; (b) A.J. Canty and E.A. Stevens, *Inorg. Chim. Acta, 55* (1981) L57; (c) A.J. Canty, N.J. Minchin, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1986) 2205; (d) B.E. Fisher and H. Ieghel, *Inorg. Chem., 18* (1979) 425; (e) F.R. Keene, M.R. Snow, P.J. Stephenson and E.R.T. Tiekink, *Inorg. Chem., 27* (1988) 2040.

[3] A. Pfaltz, *Acc. Chem. Res., 26* (1993) 339, and references therein.

[4] A. Abbotto, V. Alanzo, S. Bradamante, G.A. Pagani, C. Rizzoli and G. Calestani, *Gazz. Chim. Ital., 121* (1991) 365, and references therein.

[5] A. Abbotto, *Ph.D. Thesis*, University of Milano, 1993.

[6] (a) F. Mani, *Coord. Chem. Rev., 120* (1992) 325; (b) S. Trofimenko, *Prog. Inorg. Chem., 34* (1986) 115; (c) E.C. Constable and P.J. Steel, *Coord. Chem. Rev., 93* (1989) 223; (d) P.J. Steel, *Coord. Chem. Rev., 106* (1990) 227.

[7] C. Ray and J.B. Braunwarth, U.S. Patent 3250780, 1966; [*Chem. Abs., 65* (1966) 7180g].

[8] (a) R.B. King and A. Bond, *J. Organomet. Chem., 73* (1974) 115; (b) F. Bonati, G. Minghetti and G. Banditelli, *J. Organomet. Chem., 87* (1975) 365.

[9] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 3156.

[10] A. Abbotto, G.A. Pagani, S. Bradamante et al., unpublished results.

[11] A.I. Kiprianov, L.P. Yakovleva and Yu.S. Rozum, *Zh. Obshchei. Khim., 22* (1952) 302; [*Chem. Abs., 46* (1952) 11181f].

[12] S. Cenini, M. Pizzotti and C. Crotti, in R. Ugo (Ed.), *Aspects of Homogeneous Catalysis*, Reidel, Dordrecht, 1988, Vol. 6, pp. 97–198.

[13] (a) S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni and E. Alessio, *J. Mol. Catal., 64* (1991) 179; (b) A. Bontempi, E. Alessio, G. Chanos and G. Mestroni, *J. Mol. Catal., 42* (1987) 67.

[14] S. Cenini, M. Pizzotti, C. Crotti, F. Ragaini and F. Porta, *J. Mol. Catal., 49* (1989) 67.

[15] (a) F. Ragaini, S. Cenini and S. Tollari, *J. Mol. Catal., 85* (1993) L1; (b) E. Alessio, G. Clauti, F. Vinzi and G. Mestroni, *J. Mol. Catal., 29* (1985) 117.

[16] J.A. McCleverty and G. Wilkinson, *Inorg. Synth., 28* (1990) 84.

[17] M.I. Bruce, C.M. Jensen and N.L. Jones, *Inorg. Synth., 28* (1990) 216.

[18] (a) C. Ray and J.B. Braunwarth, *J. Org. Chem., 26* (1961) 3434; (b) C. Avedaño, M.T. Ramos, J. Elguero, M.L. Jimeno, J. Bellanato and F. Florencio, *Can. J. Chem., 66* (1988) 1467.

[19] A.C. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr., A24* (1968) 351.

[20] *International Tables for X-ray Crystallography*, Kynoch, Birmingham, UK, 1974, Vol. IV.

[21] (a) B.A. Frenz, *Comput. Phys., 2* (1988) 42; (b) B.A. Frenz, *Crystallographic Computing 5*, Oxford University Press, Oxford, 1991, Ch. 11, p. 126.