Stepwise Construction of Polynuclear Complexes of Rhodium and Iridium Assisted by Benzimidazole-2-thiol. NMR and X-ray Diffraction Studies

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Reactions of $[M_2(\mu\text{-Cl})_2(cod)_2]$ (cod = 1,5-cyclooctadiene, M = Rh, Ir) with benzimidazole-2-thiol (H_2Bzimt) afford the mononuclear complexes $[MCl(H_2Bzimt)(cod)]$ (M = Rh (**1**), Ir (**2**)) for which a S-coordination of the ligand is proposed based on their spectroscopic data. The dinuclear complexes $[M_2(\mu\text{-HBzimt})_2(cod)_2]$ (M = Rh (**3**), Ir (**4**)) are isolated from the reaction of [M(acac)(cod)] and benzimidazole-2-thiol. They contain the monodeprotonated ligand ($HBzimt^-$) bridging the two metals in a μ_2-(1κN,2κS) coordination mode and in a relative *cis*,*cis*-HT arrangement. Complexes **3** and **4** react with the appropriate species $[M(cod)(Me_2CO)_2]^+$ to afford the trinuclear cationic aggregates $[M_3(\mu\text{-HBzimt})_2(cod)_3]^+$ (M = Rh (**5**), Ir (**6**)) and with the $[M'_2(\mu\text{-OMe})_2(cod)_2]$ compounds to give the homo- and heterotetranuclear complexes $[MM'(\mu\text{-Bzimt})(cod)_2]_2$ (M = M′ = Rh (**7**), Ir (**8**); M = Ir, M′ = Rh (**9**)) containing the dideprotonated ligand ($Bzimt^{2-}$). The trinuclear neutral complexes $[M_3(\mu\text{-Bzimt})(\mu\text{-HBzimt})(cod)_3]$ are intermediates detected in the synthesis of the tetranuclear complexes. Protonation of **9** with HBF_4 gives the unsymmetrical complex $[Ir_2Rh(\mu\text{-HBzimt})_2(cod)_3]BF_4$ (**10**). This reaction involves the protonation of the bridging ligands followed by the removal of one "Rh(cod)" moiety to give a single isomer. The molecular structure of $[Rh_2(\mu\text{-Bzimt})(cod)_2]_2$ (**7**) has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$, a = 20.173(5) Å, b = 42.076(8) Å, c = 10.983(3) Å, β = 93.32(2)°, Z = 8, 7145 reflections, R = 0.0622, and R_w = 0.0779. The complete assignment of the resonances of the ^{1}H NMR spectra of the complexes **3**, **4**, and **7**−**9** was carried out by selective decoupling, NOE, and H,H-COSY experiments. The differences in the chemical shifts of the olefinic protons are discussed on the basis of steric and magnetic anisotropy effects.

Introduction

The design of a molecular architecture in coordination compounds by ligand assisted reactions have aroused increased interest over the past few years.[1] Most of the ligands used with this aim have P-donor atoms and are neutral of the type P⌒P[1,2] or P⌒N[3] while our approach has taken into account the use of anionic ligands of the N⌒X (X = N, O, S) type. Trinuclear linear[4a] and tetranuclear planar[4b,c] complexes with unusual structures have been obtained for N⌒N and N⌒O ligands. Also unusual reactivites[4d,e] and structures[4f,g] have been found for complexes having N⌒S bridges. An additional interest arises when the polydentate bridging ligands are molecules of relevant importance in biological processes, because their coordination to metals serves as model of reference in bioinorganic chemistry. In this context, the imidazole-thiol derivatives, structurally analogous to the thionucleosides, have potential pharmacological activity as found for H1-Meimt (methimazole[5]) and they are used as biomimetic models for cysteine proteases.[6] We have decided to investigate the coordination ability of one of them, benzimidazole-2-thiol (H_2Bzimt) which contains an imidazole ring together with a thiol group (Figure 1A) or alternatively two donor entities HN−C═S (Figure 1B), that should be useful for the construction of polynuclear complexes.

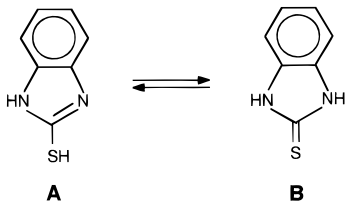

Figure 1. Tautomers for benzimidazole-2-thiol.

The imidazole ring is an ubiquitous ligand in chemical and biological systems as it appears in proteins, in the nucleic acids DNA and RNA, and in the vitamin B_{12} coenzyme. In these systems, the imidazole ring plays different roles; for example, the imidazolate ion acts as a bridging ligand between Cu(II)

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and Zn(II) in the BESOD (bovine erythrocyte superoxide dismutase).[7] From this point of view, spectroscopic and structural studies to characterise the bonding between imidazole and transition metal ions are of considerable interest.[8] Although the orientation of the donor orbitals on the nitrogen atoms forces to a large separation between the metallic centers, it also favors high nuclearities as found in $[Rh_4(\mu\text{-}2\text{-MeIm})_4(CO)_8]$[9] or in $[Cu_4(\mu\text{-Im})_4(L)_4](ClO_4)_4\cdot 2H_2O$[10] (L = 1,4,7-triazacyclononane). In addition, the other tautomer of benzimidazole-2-thiol (Figure 1B) can be considered as a thioamide or thiourea derivative. The versatility of the N⁀S ligands such as pyridine-2-thiol (HPyt), benzothiazole-2-thiol (HBztzt), and thiazolidine-2-thiol (HTzdt) and, in particular, their deprotonated forms is demonstrated by the variety of coordination modes that they may adopt in their coordination compounds. In particular, complexes with platinum group metals have received significant current attention.[11]

The ligand of our interest, benzimidazole-2-thiol (H_2Bzimt), and its analogs such as imidazole-2-thiol (H_2Imdt), 1-methylimidazole-2-thiol (H1-MeImt), and imidazolidine-2-thiol (H_2Imdt) show the characteristics of both imidazole and thioamide systems. Many complexes of the neutral ligands with transition metals,[5] palladium,[12] iron,[13] nickel,[14] tin,[15] and especially copper,[16] have been obtained and the copper ones were shown to be mono-,[17] di-,[18] tetra-,[19] or polynuclear[20] by their X-ray structures. The deprotonation of these imidazole-2-thiol derivatives would lead to the corresponding mono- or dianions in which the presence of one electron pair on the heterocyclic nitrogen/s and three electron pairs on the sulfur atom could generate a considerable coordination potential.

The monoanions, similar to the well-known Pyt^-, $Bztzt^-$ or $Tzdt^-$ can act as monodentate ligands through the sulfur atom as found in the mononuclear $[HgMe(1\text{-MeImt})]$,[21] $[Au(1\text{-MeImt})(PCy_3)]$,[22] and $(N(PPh_3)_2)[Au(HBzimt)_2]$[23] complexes and as chelating ligands through both N and S atoms as found in $(NBu_4)[Ni(C_6F_5)_2(HBzimt)]$.[24] They are also able to act as bridging ligands in a μ_2-($1\kappa N,2\kappa S$) coordination mode in dinuclear complexes of Pd,[25] Ru,[26] or Ga[27] and as chelating and bridging ligands of the type μ_2-($1\kappa N,1{:}2\kappa S$) in $[Ru_2(\mu\text{-H4,5-Ph}_2\text{Imt})(\mu\text{-Cl})Cl(\eta^6\text{-p-MeC}_6\text{H}_4\text{CHMe}_2)_2]$.[28] An alternative coordination mode to three metal centers of the type μ_3-($1\kappa N,2{:}3\kappa S$) has been found in the tetranuclear complex $[Cu_4(1\text{-MeImt})_4]$.[29] Finally, the sulfur atoms form double, triple, and quadruple bridges between the copper atoms in the cluster $[Cu^{I}_{10}Cu^{II}_2(\mu\text{-1-MeImt})_{12}(MeCN)_4]^{2+}$.[30]

Complexes containing the dianions are rare and have been reported only recently. Sheldrick[28] has described the trinuclear C-metallated complex $[Ru_3(\mu\text{-4,5-Ph}_2\text{Imt}_{-1})(\mu\text{-Cl})Cl_2(\eta^6\text{-p-MeC}_6\text{H}_4\text{CHMe}_2)_3]$ and Armstrong[31] the tetranuclear complex $[Li_4(Bzimt)_2(hmpa)_6]$ (hmpa = hexamethylphosphoramide). It is noteworthy that these are the only two complexes with a dianionic thioamide derivative. These dianions can behave as imidazolates to generate polynuclear species and, because of the narrow bite typical of the N⁀S ligands,[4,11,32] can act also as bridges between metal atoms with and without formation of metal−metal bonds. The combination of both these features with the potential pharmacological activity can generate a wide range of interesting compounds. In this paper we describe an exploratory study on the coordination modes of the benzimidazole-2-thiol as well as of its mono- and dianions that has led to the preparation of new mono-, di-, tri-, and tetranuclear complexes.

Experimental Section

Starting Materials and Physical Methods. The benzimidazole-2-thiol (H_2Bzimt) ligand was obtained from Janssen Chimica and recrystallized from warm methanol before use. Standard literature procedures were used to prepare the starting materials $[M_2(\mu\text{-Cl})_2(cod)_2]$,[33] $[M_2(\mu\text{-OMe})_2(cod)_2]$,[34] and [M(acac)(cod)].[35] All solvents were dried and distilled before use by standard methods. Iridium

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complexes were prepared under an argon atmosphere using Schlenk techniques. Molecular weights were determined with a Knauer osmometer using chloroform solutions. Carbon, hydrogen, nitrogen, and sulfur analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet-IR 550 (4000−400 cm^{-1}) spectrophotometer with the bands calibrated against the sharp peak (1601.4 cm^{-1}) of a polystyrene film. Mass spectra were recorded in a VG Autospec double-focousing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at *ca.* 30 kV; 3-nitrobenzyl alcohol (NBA) or sulfolene was used as the matrix. ^1H and $^{13}C\{^1H\}$ spectra were recorded on Varian UNITY 300 and Bruker ARX 300 spectrometers operating at 299.95 and 300.13 MHz for ^1H. Chemical shifts are referenced to $SiMe_4$. *J* values are given in Hz. NOE experiments on complex **4** were carried out at 273 K to eliminate the negative enhancements due to the chemical exchange processes that occur at higher temperatures using the standard NOE 1d pulse sequence on the Varian spectrometer. H,H-COSY spectra were recorded with the cosygr pulse program on the Bruker spectrometer using 256 individual FID's with four acquisitions per FID. For the cod ligand, the olefinic protons are labeled with single figures from 1 to 8. The exo and endo protons contiguous (coupled) to a given olefinic proton (*i*) are labeled as 1*i* and 2*i*, respectively.

Preparation of the Complexes. [RhCl(H_2Bzimt)(cod)] (1). Solid [$Rh_2(\mu$-Cl)$_2$(cod)$_2$] (74 mg, 0.15 mmol) was added to a suspension of H_2Bzimt (45 mg, 0.3 mmol) in diethyl ether (10 mL) to give a yellow suspension after 1 h. The crystallization was completed by concentration under vacuum to *ca.* 3 mL and further addition of hexane (5 mL). The yellow microcrystalline solid was collected by filtration, washed with hexane, and dried under vacuum. Yield: 95 mg (80%). IR (Nujol, cm^{-1}): ν_{NH} 3269, 3154. ^1H NMR ($CDCl_3$, 298 K): δ 11.56 (s, 2H, NH), 7.22 (m, 4H, HC) (H_2Bzimt), 4.26 (m, 4H, HC═), 2.43 (m, 4H, CH_2), 1.81 (m, 4H, CH_2) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 328 K): δ 165.7 (CS), 131.1 (CN), 124.1 and 111.1 (HC) (H_2Bzimt), 81.3 (HC═), 31.0 (CH_2) (cod). Anal. Calcd for $C_{15}H_{18}ClN_2SRh$: C, 45.41; H, 4.57; N, 7.06; S, 8.06. Found: C, 45.04; H, 4.28; N, 7.07; S, 8.03. Molecular weight: calcd for [RhCl(H_2Bzimt)(cod)], 397; found, 376.

[IrCl(H_2Bzimt)(cod)] (2) was prepared from [$Ir_2(\mu$-Cl)$_2$(cod)$_2$] (100.7 mg, 0.15 mmol) and H_2Bzimt (45 mg, 0.3 mmol) by the method described above for **1** using THF as solvent. Yield: 111 mg (76%). IR (Nujol, cm^{-1}): ν_{NH} 3250, 3151. ^1H NMR ($CDCl_3$, 298 K): δ 11.51 (s, 2H, NH), 7.30 (m, 4H, HC) (H_2Bzimt), 4.28 (m, 2H, HC═), 3.64 (m, 2H, HC═), 2.34 (m, 4H, CH_2), 1.66 (m, 4H, CH_2) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 166.7 (CS), 130.8 (CN), 124.2 and 111.4 (HC) (H_2Bzimt), 71.7 (HC═), 31.2 (CH_2) (cod). Anal. Calcd for $C_{15}H_{18}ClN_2SIr$: C, 37.07; H, 3.73; N, 5.76; S, 6.60. Found: C, 36.80; H, 3.53; N, 5.67; S, 6.23.

[$Rh_2(\mu$-HBzimt)$_2$(cod)$_2$] (3). A yellow solution of [Rh(acac)(cod)] (62 mg, 0.2 mmol) in acetone (5 mL) was added dropwise to a solution of H_2Bzimt (30 mg, 0.2 mmol) in 5 mL of the same solvent. The resulting orange solution was stirred for 30 min and then was concentrated to *ca.* 2 mL. Slow addition of pentane gave **3** as an orange microcrystalline solid which was filtered, washed with pentane, and vacuum-dried. Yield: 62 mg (85%). IR (Nujol, cm^{-1}): ν_{NH} 3180. ^1H NMR ($CDCl_3$, 293 K): δ 8.01 (d, $^3J_{HH}$ = 8.2, 2H, H^3), 7.98 (s, 2H, NH), 7.11 (t, $^3J_{HH}$ = 7.6, 2H, H^4), 6.88 (t, $^3J_{HH}$ = 7.6, 2H, H^5), 6.53 (d, $^3J_{HH}$ = 7.9, 2H, H^6) ($HBzimt^-$), 4.96 (m, 2H, 1), 4.44 (m, 2H, 2), 4.17 (m, 2H, 3), 3.90 (m, 2H, 4), 2.80 (m, 4H, 11, 12), 2.50 (m, 4H, 13, 14), 2.09 (m, 2H, 21), 1.95 (m, 4H, 22, 23), 1.81 (m, 2H, 24) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 328 K): δ 162.7 (CS), 142.5 and 133.1 (CN), 121.5, 121.3, 115.8 and 109.0 (HC) ($HBzimt^-$), 79.4 (HC═), 31.2 (CH_2) (cod). Anal. Calcd for $C_{30}H_{34}N_4S_2Rh_2$: C, 50.01; H, 4.76; N, 7.77; S, 8.90. Found: C, 50.21; H, 4.64; N, 7.94; S, 8.49. MS (FAB^+): *m/e* 720 (M^+, 73%) 612 (M − cod^+, 22%), 571 (M − $HBzimt^+$, 100%), 360 ($M/2^+$, 62%), 931 (M + $Rh(cod)^+$, 15%).

[$Ir_2(\mu$-HBzimt)$_2$(cod)$_2$] (4) was prepared, as a red microcrystalline solid, from [Ir(acac)(cod)] (80 mg, 0.2 mmol) and H_2Bzimt (30 mg, 0.2 mmol) by the method described above for **3**. Yield: 76.5 mg (85%). IR (Nujol, cm^{-1}): ν_{NH} 3190. ^1H NMR ($CDCl_3$, 293 K): δ 8.17 (s, 2H, NH), 7.59 (d, $^3J_{HH}$ = 8.0, 2H, H^3), 7.10 (t, $^3J_{HH}$ = 7.7, 2H, H^4), 6.93 (t, $^3J_{HH}$ = 7.6, 2H, H^5), 6.66 (d, $^3J_{HH}$ = 7.9, 2H, H^6) ($HBzimt^-$), 4.59 (m, 2H, 1), 4.00 (m, 2H, 2), 3.85 (m, 2H, 3), 3.33 (m, 2H, 4), 2.56 (m, 2H, 11), 2.52 (m, 2H, 12), 2.27 (m, 2H, 13), 2.18 (m, 2H, 14), 1.81 (m, 2H, 21), 1.64 (m, 4H, 22, 23), 1.45 (m, 2H, 24) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 161.3 (CS), 141.6 and 132.5 (CN), 122.1, 121.8, 116.0, and 109.3 (HC) ($HBzimt^-$), 64.2, 63.3 and 63.0 (2C) (HC═), 32.0, 31.9, 31.5, and 31.4 (CH_2) (cod). Anal. Calcd for $C_{30}H_{34}N_4S_2Ir_2$: C, 40.07; H, 3.81; N, 6.23; S, 7.13. Found: C, 39.92; H, 3.93 N, 6.15; S, 6.54. MS (FAB^+): *m/e* 900 (M^+, 100%), 791 (M − cod^+, 20%), 749 (M − $HBzimt^+$, 22%), 449 ($M/2^+$, 51%), 1199 (M + $Ir(cod)^+$, 7%).

[$Rh_3(\mu$-HBzimt)$_2$(cod)$_3$]BF_4 (5). An acetone solution of [Rh(cod)-(Me_2CO)$_2$]BF_4 (prepared by treating [$Rh_2(\mu$-Cl)$_2$(cod)$_2$] (24.6 mg, 0.05 mmol) with $AgBF_4$ (19.5 mg, 0.1 mmol) in acetone (5 mL) for 30 min and filtering off the AgCl formed) was added slowly to a solution of [$Rh_2(\mu$-HBzimt)$_2$(cod)$_2$] (72 mg, 0.1 mmol) in acetone (10 mL). The orange solution quickly turned to red, and a dark red microcrystalline precipitate began to form almost inmediately. The mixture was stirred for 20 min and was maintained at −20 °C overnight. The dark red microcrystalline product was collected by filtration, washed with 10 mL of diethyl ether, and vacuum dried. Yield: 87.5 mg (86%). IR (Nujol, cm^{-1}): ν_{NH} 3270. ^1H NMR (CD_3OD, 293 K): δ 7.72 (d, $^3J_{HH}$ = 8.2, 2H, H^3), 6.87 (t, $^3J_{HH}$ = 8.2, 2H, H^4), 6.62 (t, $^3J_{HH}$ = 7.3, 2H, H^5), 6.52 (d, $^3J_{HH}$ = 8.1, 2H, H^6) ($HBzimt^-$), 5.62 (m, 2H, HC═), 5.36 (m, 2H, HC═), 4.45 (m, 2H, HC═), 4.31 (m, 2H, HC═), 3.92 (m, 2H, HC═), 3.66 (m, 2H, HC═), 3.17 (m, 4H, CH_2), 2.98 (m, 2H, CH_2), 2.50 (m, 4H, CH_2), 2.35 (m, 4H, CH_2), 2.24 (m, 4H, CH_2), 2.02 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.70 (m, 2H, CH_2) (cod). Anal. Calcd for $C_{38}H_{46}N_4S_2Rh_3BF_4$: C, 44.81; H, 4.55; N, 5.50; S, 6.30. Found: C, 44.69; H, 4.75; N, 5.60; S, 6.24. MS (FAB^+): 931 (M^+, 100%), 823 (M − cod^+, 10%), 571 (M − Rh(HBzimt)$(cod)^+$, 80%).

[$Ir_3(\mu$-HBzimt)$_2$(cod)$_3$]ClO_4 (6) was prepared, as a dark green microcrystalline solid, from [$Ir_2(\mu$-Cl)$_2$(cod)$_2$] (33.6 mg, 0.05 mmol), $AgClO_4$ (21 mg, 0.1 mmol), and [$Ir_2(\mu$-HBzimt)$_2$(cod)$_2$] (90 mg, 0.1 mmol) by the method described above for **5**. Yield: 114 mg (88%). IR (Nujol, cm^{-1}): ν_{NH} 3170. Anal. Calcd for $C_{38}H_{46}N_4S_2Ir_3ClO_4$: C, 35.14; H, 3.57; N, 4.31; S, 4.94. Found: C, 35.19; H, 3.11 N, 4.34; S, 5.26. MS (FAB^+): *m/e* 1199 (M^+, 100%), 1091 (M − cod^+, 16%), 750 (M − Ir(HBzimt)$(cod)^+$, 11%). The low solubility of this complex prevented the determination of its ^1H and $^{13}C\{^1H\}$ NMR spectra.

[$Rh_2(\mu$-Bzimt)(cod)$_2$]$_2$ (7). Method A. Solid [$Rh_2(\mu$-HBzimt)$_2$-(cod)$_2$] (72 mg, 0.1 mmol) was added to a yellow solution of [$Rh_2(\mu$-OMe)$_2$(cod)$_2$] (48.5 mg, 0.1 mmol) in acetone (10 mL) to give a yellow solution. The resulting solution was allowed to stand overnight at −40 °C to give orange crystals, which were collected by filtration, washed with a small quantity of cold acetone, and vacuum-dried. Yield: 114 mg (75%).

Method B. To a solution of lithium benzimidazole-2-thiolate in diethyl ether (prepared by reaction of *n*-butyllithium (0.25 mL, 1.6 mol L^{-1}, 0.4 mmol) with a suspension of benzimidazole-2-thiol (30 mg, 0.2 mmol) in diethyl ether (10 mL) for 1 h), solid [$Rh_2(\mu$-Cl)$_2$(cod)$_2$] (98.6 mg, 0.2 mmol) was added and allowed to react for 30 min. The solvent was pumped off and the residue washed with 10 mL of methanol to give a yellow microcrystalline solid which was separated by filtration, washed with methanol, and vacuum-dried. Yield: 104 mg (91%). ^1H NMR ($CDCl_3$, 293 K): δ 8.53 (d, $^3J_{HH}$ = 7.8, 2H, H^3), 7.08 (t, $^3J_{HH}$ = 8.0, 2H, H^4), 6.63 (t, $^3J_{HH}$ = 7.6, 2H, H^5), 6.07 (d, $^3J_{HH}$ = 7.9 2H, H^6) ($Bzimt^{2-}$), 5.19 (m, 2H, 5), 4.81 (m, 2H, 1), 4.68 (m, 2H, 8), 4.37 (m, 4H, 6, 7), 4.32 (m, 2H, 4), 4.11 (m, 2H, 2), 3.35 (m, 2H, 3), 2.98 (m, 2H, 15), 2.78 (m, 2H, 11), 2.71 (m, 2H, 16), 2.62 (m, 2H, 14), 2.42 (m, 2H, 12), 2.36 (m, 2H, 17), 2.31 (m, 2H, 18), 2.20 (m, 2H, 13), 2.08 (m, 2H, 21), 2.01 (m, 2H, 25), 1.86 (m, 2H, 24), 1.80 (m, 10H, 23, 27, 28, 22, 26) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 162.8 (CS), 141.5 and 140.3 (CN), 119.7, 118.8, 115.6 and 111.9 (HC) ($Bzimt^{2-}$), 83.7 (d, $^1J_{CRh}$ = 16, HC═), 82.3 (d, $^1J_{CRh}$ = 12, 2 HC═), 78.4 (d, $^1J_{CRh}$ = 13, HC═), 77.4 (d, $^1J_{CRh}$ = 12, HC═), 76.8 (d, $^1J_{CRh}$ = 13, HC═), 76.6 (d, $^1J_{CRh}$ = 12, HC═), 76.1 (d, $^1J_{CRh}$ = 12, HC═), 32.6, 32.1, 32.0, 31.2, 30.7, 30.6, 30.4, and 30.2 (CH_2) (cod). Anal. Calcd for $C_{46}H_{56}N_4S_2Rh_4$: C, 48.43; H, 4.77; N, 4.57; S, 5.23. Found: C, 48.95; H, 4.95 N, 4.91; S, 5.62. MS (FAB^+): *m/e* 1141 (M^+, 31%), 931 (M − Rh$(cod)^+$, 58%), 571 ($M/2^+$, 100%). Molecular weight: Calcd for [Rh_2(Bzimt)(cod)$_2$]$_2$: 1140. Found: 1124.

[$Ir_2(\mu$-Bzimt)(cod)$_2$]$_2$ (8) was prepared, as an orange microcrystalline solid, from benzimidazole-2-thiol (22.5 mg, 0.15 mmol), *n*-butyllithium (0.19 mL, 1.6 mol L^{-1}, 0.3 mmol), and [$Ir_2(\mu$-Cl)$_2$(cod)$_2$] (101 mg, 0.15 mmol) by the Method B described above for **8**. Yield: 98 mg (88%). ^1H NMR ($CDCl_3$, 293 K): δ 8.29 (d, $^3J_{HH}$ = 7.9, 2H, H^3),

7.04 (t, $^3J_{HH}$ = 8.0, 2H, H^4), 6.66 (t, $^3J_{HH}$ = 8.1, 2H, H^5), 6.20 (d, $^3J_{HH}$ = 7.8, 2H, H^6) (Bzimt^{2-}), 4.99 (m, 2H, 5), 4.55 (m, 2H, 1), 4.41 (m, 2H, 8), 4.28 (m, 2H, 7), 4.23 (m, 2H, 6), 3.91 (m, 2H, 4), 3.63 (m, 2H, 2), 3.11 (m, 2H, 3), 2.62 (m, 2H, 15), 2.53 (m, 2H, 16), 2.48 (m, 2H, 11), 2.42 (m, 2H, 14), 2.31 (m, 2H, 17), 2.19 (m, 2H, 12), 2.15 (m, 2H, 13, 18), 2.03 (m, 2H, 21), 1.80 (m, 2H, 24), 1.73 (m, 2H, 25), 1.63 (m, 2H, 27), 1.56 (m, 2H, 26), 1.46 (m, 2H, 22), 1.44 (m, 2H, 23), 1.38 (m, 2H, 28) (cod). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 164.6 (CS), 141.1 and 139.8 (CN), 122.0, 119.7, 116.1, and 112.5 (HC) (Bzimt^{2-}), 68.9, 68.7, 67.8, 62.7, 61.9, 61.2, 61.1, and 60.5 (HC═), 33.8, 33.1, 32.4, 32.0, 31.8, 31.6, 30.3, and 29.9 (CH_2). Anal. Calcd for $C_{46}H_{56}N_4S_2Ir_4$: C, 36.88; H, 3.77; N, 3.74; S, 4.28. Found: C, 37.22; H, 4.02 N, 3.70; S, 4.17. MS (FAB$^+$): *m/e* 1497 (M$^+$, 9%), 1199 (M − Ir(cod)$^+$, 100%), 748 (M/2$^+$, 34%).

[IrRh(μ-Bzimt)(cod)$_2$]$_2$ (9) was prepared, as a yellow microcrystalline solid, from [Ir$_2$(μ-HBzimt)$_2$(cod)$_2$] (89.9 mg, 0.10 mmol) and [Rh$_2$(μ-OMe)$_2$(cod)$_2$] (48.4 mg, 0.10 mmol) by Method A described above for **7**. Yield: 99 mg (75%). ^{1}H NMR ($CDCl_3$, 293 K): δ 8.51 (d, $^3J_{HH}$ = 7.5, 2H, H^3), 7.09 (t, $^3J_{HH}$ = 7.3, 2H, H^4), 6.65 (t, $^3J_{HH}$ = 7.3, 2H, H^5), 6.12 (d, $^3J_{HH}$ = 7.9, 2H, H^6) (Bzimt^{2-}), 5.13 (m, 2H, 5), 4.73 (m, 2H, 8), 4.47 (m, 2H, 1), 4.41 (m, 2H, 6, 7), 3.88 (m, 2H, 4), 3.60 (m, 2H, 2), 2.98 (m, 2H, 3), 2.83 (m, 2H, 15), 2.72 (m, 2H, 16), 2.48 (m, 2H, 11), 2.40 (m, 2H, 14), 2.43 (m, 2H, 17), 2.11 (m, 2H, 12), 2.10 (m, 2H, 13), 2.34 (m, 2H, 18), 1.96 (m, 2H, 21), 1.75 (m, 2H, 24, 28), 1.98 (m, 2H, 25), 1.78 (m, 2H, 27), 1.85 (m, 2H, 26), 1.50 (m, 2H, 22), 1.44 (m, 2H, 23) (cod). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 161.0 (CS), 141.1 and 139.8 (CN), 122.0, 118.9, 115.4, and 112.1 (HC) (Bzimt^{2-}), 78.3 (d, J_{CRh} = 14, HC═), 78.2 (d, J_{CRh} = 12, HC═), 77.21 (d, J_{CRh} = 12, HC═), 76.7 (d, J_{CRh} = 14, HC═), 67.7, 67.2, 66.6, and 59.8 (HC═), 33.5, 33.0, 31.8, 31.0, 30.7 (2C), 30.4, and 30.2 (CH_2) (cod). Anal. Calcd for $C_{46}H_{56}N_4S_2Ir_2Rh_2$: C, 41.88; H, 4.28; N, 4.25; S, 4.86. Found: C, 41.52; H, 3.89 N, 3.90; S, 4.55. MS (FAB$^+$): *m/e* 1318 (M$^+$, 48%), 1107 (M − Ir(cod)$^+$, 36%).

Reaction of 9 with HBF_4. To a solution of **9** (120 mg, 0.09 mmol) in dichlorometane−diethyl ether (1:1, 10 mL) was added HBF_4 (25 μL, 7.3 mol L^{-1}, 0.18 mmol). The yellow solution quickly turned green, and a dark green microcrystalline precipitate began to form almost inmediately. The mixture was stirred for 20 min and was maintained overnight at −20 °C. The dark green microcrystalline product [Ir$_2$Rh(μ-HBzimt)$_2$(cod)$_3$]BF_4 (**10**) was collected by filtration, washed with 10 mL of acetone diethyl ether (1:1), and vacuum-dried. Yield: 90 mg (83%). IR (Nujol, cm^{-1}): ν_{NH} 3240. ^{1}H NMR (CD_3OH, 293 K): δ 7.79 (d, $^3J_{HH}$ = 8.4, 1H), 7.57 (d, $^3J_{HH}$ = 8.3, 1H), 6.93 (t, $^3J_{HH}$ = 8.2, 1H), 6.87 (t, $^3J_{HH}$ = 7.7, 1H), 6.67 (t, $^3J_{HH}$ = 8.1, 1H), 6.66 (t, $^3J_{HH}$ = 8.1, 1H), 6.57 (d, $^3J_{HH}$ = 8.0, 1H), 6.53 (d, $^3J_{HH}$ = 8.0, 1H) (HBzimt$^-$), 5.35 (m, 2H, HC═), 5.20 (m, 1H, HC═), 5.05 (m, 1H, HC═), 4.84 (m, 2H, HC═), 4.35 (m, 1H, HC═), 4.20 (m, 1H, HC═), 4.05 (m, 1H, HC═), 3.95 (m, 2H, HC═), 3.45 (m, 1H, HC═), 2.85−1.95 (m, 18H, CH_2), 1.70 (m, 4H, CH_2), 1.35 (m, 2H, CH_2) (cod). Anal. Calcd for $C_{38}H_{46}N_4S_2IrRh_2BF_4$: C, 38.13; H, 3.87; N, 4.68; S, 5.36. Found: C, 37.64; H, 3.41; N, 4.55; S, 5.40. MS (FAB$^+$): *m/e* 1109 (M$^+$, 100%), 1001 (M − cod$^+$, 28%).

Crystal Structure Determination of Complex 7·CH_2Cl_2. Selected crystallographic data for the dichloromethane solvate of complex **7** are listed in Table 1. Data were collected at room temperature (22 °C) on a Siemens AED single-crystal diffractometer using graphite-monochromated Cu Kα radiation. All reflections with θ in the range 3−70° were measured; of 17 662 independent reflections, 7145, having $I > 2\sigma(I)$, were considered observed and used in the analysis. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.0 and 0.7629).[36]

The structure was solved by Patterson and Fourier methods and refined by blocked full-matrix least-squares methods first with isotropic thermal parameters and then with anisotropic thermal parameters for the non-hydrogen atoms excepting the carbon atoms of the cod ligands. All hydrogen atoms were placed at their geometrically calculated positions (C−H = 0.96 Å) and refined "riding" on the corresponding carbon atoms (with isotropic thermal parameters). The final cycles of refinement were carried out on the basis of 721 variables; after the last cycles, no parameters shifted by more than 0.6 esd. The highest remaining peak in the final difference map was equivalent to about 1.09 e/Å^3. In the final cycles of refinement a weighting scheme $w = K[\sigma^2(Fo) + gFo^2]^{-1}$ was used; at convergence the K and g values were 0.509 and 0.0010. Final R and R_w values were 0.0622 and 0.0779, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 37. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[38] The final atomic coordinates for the non-hydrogen atoms are given in the Supporting Information.

Table 1. Experimental Data for the X-ray Diffraction Studies of Complex **7**

formula	$C_{46}H_{56}N_4Rh_4S_2{\cdot}CH_2Cl_2$
mol wt	1225.65
cryst syst	monoclinic
space group	$P2_1/n$
radiation (λ Å)	graphite-monochromated (Cu Kα, 1.541 838)
a, Å	20.173(5)
b, Å	42.076(8)
c, Å	10.983(3)
β, deg	93.32(2)
V, Å^3	9307(4)
Z	8
D_{calcd}, g cm^{-3}	1.750
F(000)	4912
cryst size, mm	0.12 × 0.18 × 0.21
μ, cm^{-1}	134.59 (Cu Kα)
diffractometer	Siemens
scan type	$\theta/2\theta$
scan speed, deg/min	3−9
θ range, deg	3−70
std reflcn	one measd after 100 reflcns
no. of reflcns measd	$\pm h,k,l$
no. of unique tot. data	17662
no. of unique obsd data [$I > 2\sigma(I)$]	7145
R^a	0.0622
$R_w{}^b$	0.0779

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Results and Discussion

Scheme 1 shows the synthetic approaches used in the preparation of the new rhodium and iridium complexes. Two special features of the precursor of the ligand, namely the presence of two acidic protons and lone electron pairs on the sulfur atom, have been the central guide for the stepwise building of the new compounds.

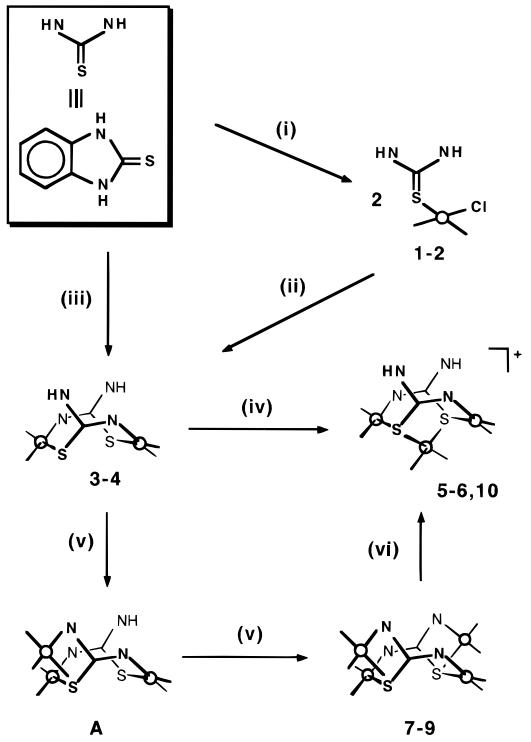
Mononuclear Complexes. The bridge-splitting reaction in [M$_2$(μ-Cl)$_2$(cod)$_2$] (M = Rh, Ir; cod = 1,5-cyclooctadiene) by benzimidazole-2-thiol (H_2Bzimt) affords the mononuclear complexes of the type [MCl(H_2Bzimt)(cod)] (M = Rh (**1**), Ir (**2**)) in good yield. They are isolated as yellow microcrystalline solids; elemental analysis and molecular weight measurement for complex **1** confirm the proposed stoichiometry and the mononuclear nature. Due to the bifunctionality of the H_2Bzimt ligand, either a N- or a S-coordination could be expected; however, the following spectroscopic data unequivocally confirm the S-coordination mode of the ligand in the thiourea tautomeric form: (i) the lack of a ν_{SH} band around 2500 cm^{-1}; (ii) the presence of two ν_{NH} bands at *ca*. 3260 and 3150 cm^{-1}

(36) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158. Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

(37) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.

(38) Sheldrick, G. M. SHELX-76 Program for crystal structure determination. University of Cambridge, England, 1976; SHELXS-86 Program for the solution of crystal structures. University of Göttingen, 1986.

Scheme 1[a]



[a] Key: (i) $[M_2(\mu\text{-Cl})_2(\text{cod})_2]$; (ii) KOH; (iii) 2[M(acac)(cod)]; (iv) $[M(\text{cod})(Me_2CO)_2]^+$; (v) $^1/_2[M_2(\mu\text{-OMe})_2(\text{cod})_2]$; (vi) HBF_4. ⊂ represents the "M(cod)" moiety.

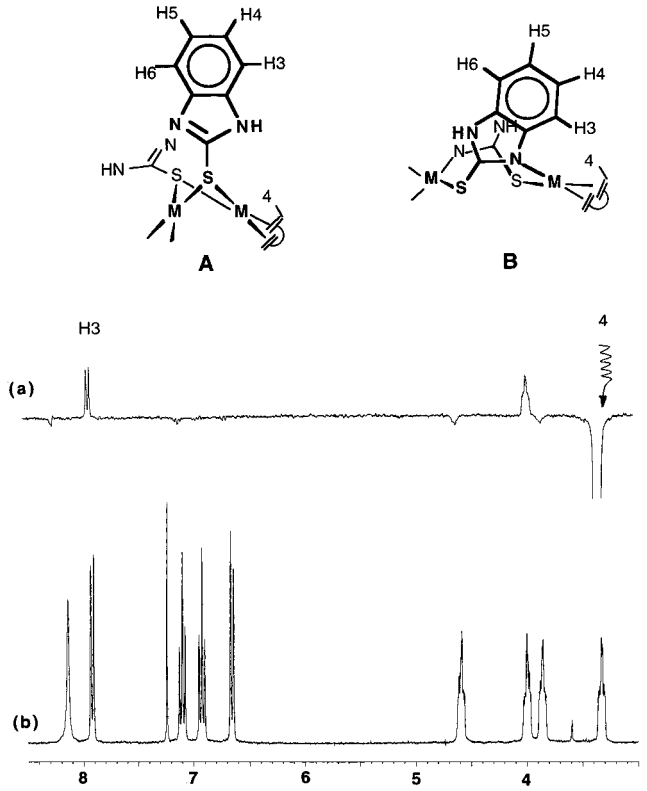


Figure 2. Possible structures (A and B) for complexes **3** and **4**. (a) NOE difference spectrum on saturation of the resonance at δ 3.33 ppm for **4**. (b) Normal spectrum.

and of a resonance for the two NH protons at δ 11.5 ppm in their IR and ^{1}H NMR spectra, respectively. Moreover, the equivalence between the two NH protons and the AA′BB′ spin system observed for the aromatic protons of H_2Bzimt suggest a very fast inversion at the sulfur atom. Although neutral thioureas are able to bridge two metal atoms through the sulfur in di- or polynuclear complexes,[18,19] the presence of cationic complexes of the type μ_2-(1:2κS)-$[M_2(\mu\text{-}H_2\text{Bzimt})_2(\text{cod})_2]Cl_2$ can be excluded because the molecular weight measurement and because of the very low value of the conductivity of the solutions of **1** and **2** in chloroform. A further evidence of our proposal comes from their $^{13}C\{^1H\}$ NMR spectra that show four resonances for the carbons of H_2Bzimt instead of the seven expected for a N-coordination and for a static S-coordination of the ligand. Interestingly, the C═S resonance is shifted 5 ppm upfield relative to the free ligand upon coordination to the metal. Such a shift corresponds probably to a reduction in the π-character of the C═S bond.

Dinuclear Complexes. Complexes **1** and **2** react with stoichiometric amounts of KOH in methanol to give the new dinuclear rhodium and iridium compounds of general formula $[M_2(\mu\text{-HBzimt})_2(\text{cod})_2]$ (M = Rh (**3**), Ir (**4**)). These compounds are also straightforwardly obtained by protonation of [M(acac)-(cod)] by H_2Bzimt. One of the acidic protons of H_2Bzimt ligand is abstracted by the acac complexes with the concomitant release of acetylacetone. Complexes **3** and **4** were isolated as microcrystalline solids and identified by elemental analyses and ^{1}H and $^{13}C\{^1H\}$ NMR, MS (FAB^+), and IR spectra. Their dinuclear nature in solution was confirmed by the presence of the expected molecular ions in their MS (FAB^+) spectra, in which at least two effective primary ionization processes, involving the breaking of the metal−ligand bond, seem to appear: first the loss of an H_2Bzimt ligand to generate the $[M_2(\mu\text{-Bzimt})(\text{cod})_2]^+$ species and then the loss of one $M(\text{cod})^+$ fragment to give the mononuclear entities $[M(\text{HBzimt})(\text{cod})]^+$. As a consequence of the presence of these $M(\text{cod})^+$ fragments in the mass spectrometer, weak peaks, whose isotopic profile corresponds to the very stable trinuclear cations $[M_3(\mu\text{-HBzimt})_2(\text{cod})_3]^+$ (see below), are also observed.

Although the $HBzimt^-$ anion may coordinate two metal centers in a variety of modes, only one isomer is formed in both synthetic approaches. Information concerning the structure of the investigated dinuclear complexes, as well as the coordination mode of the ligands, can be provided on the basis of NMR data. The ^{1}H NMR spectra show an identical pattern for the two complexes: one resonance due to the NH proton, whose integral confirms the monodeprotonation of the ligand, four separated resonances for the aromatic protons of the two equivalent $HBzimt^-$ ligands, and 12 resonances for the cod protons. The equivalence between the two bridging ligands as well as the dinuclear nature of the complexes support the coordination of the $HBzimt^-$ either as bridging thiolate μ_2-(1:2κS) or in a μ_2-(1κN,2κS) fashion through the N and S atoms. As shown in Figure 2, the useful major difference between the two possibilities is the distance between one of the protons of the $HBzimt^-$ (namely H^3) and one of the olefinic cod protons (namely 4). This provides a way to make a clear-cut distinction between them because a NOE effect between these protons should be observed for the μ_2-(1κN,2κS) isomer but not for the thiolate. Indeed, saturation of the transition due to the H^3 proton produces an enhancement of the olefinic resonance at δ 3.33 ppm and, conversely, saturation of this transition enhances the resonance corresponding to the H^3 proton (Figure 2). This firmly reveals the proximity between one olefinic proton (4) and the H^3 proton, possible only for a μ_2-(1κN,2κS) coordination mode.

Because there are two different donor atoms in the bridging ligands, complexes **3**-**4** can exist as two geometrical isomers, the head-to-head (HH, C_s symmetry) and the head-to-tail (HT, C_2 symmetry). Analysis of their HH-COSY spectra confirms unequivocally that these compounds have the HT configuration. Thus, the presence of four cross-peaks for each endo (21−24) and exo (11−14) protons exclude the presence of any mirror

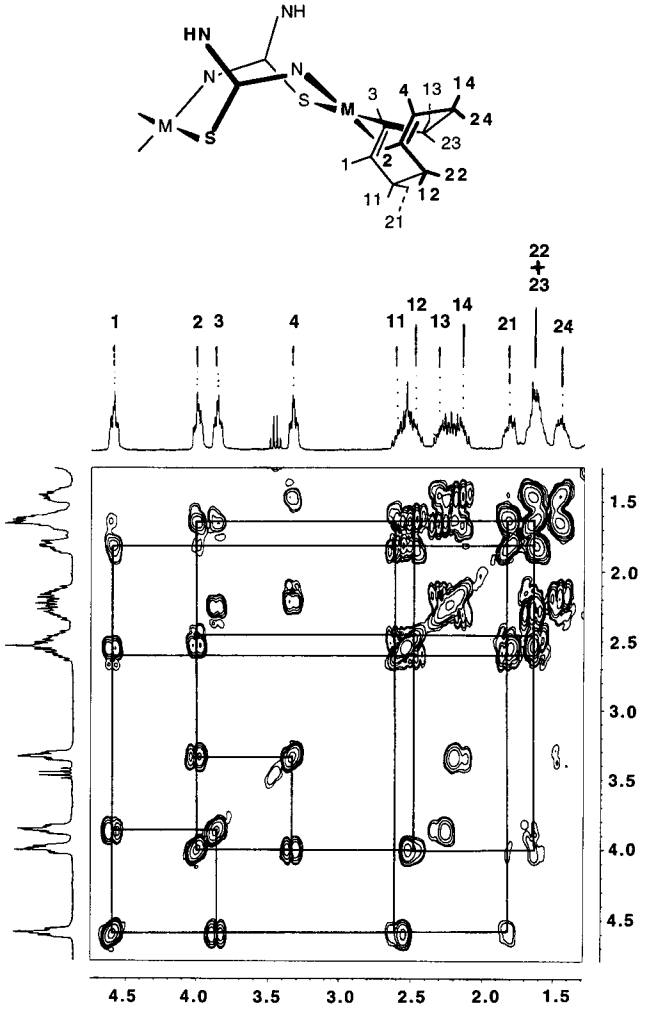


Figure 3. H,H-COSY spectrum of the diolefin for complex **4**, showing the protons labeling.

plane in the molecule, as shown in Figure 3 for complex **4**. Moreover, no appreciable isomerization into HH isomers is observed in $CDCl_3$ solution.

Trinuclear Complexes. The synthetic route to the trinuclear complexes consists in the addition of the species $[M(cod)(Me_2CO)_2]^+$, having two easily accessible *cis* coordination positions, to the dinuclear complexes $[M_2(\mu\text{-HBzimt})_2(cod)_2]$, which act as metalloligands providing two lone pairs in the required orientations. In this way, the trinuclear aggregates $[M_3(\mu\text{-HBzimt})_2(cod)_3]^+$ (M = Rh (**5**), Ir (**6**)) are immediately formed and isolated as the BF_4^- or ClO_4^- salts (Scheme 1). They are microcrystalline dark-red and green solids, respectively, and their analytical data are in accordance with the proposed stoichiometry. The high stability of these trinuclear cations is confirmed by the appearance of the molecular ion M^+ with relative abundance 100% in their MS (FAB^+) spectra. The IR spectra of both complexes show the expected ν_{NH} at *ca.* 3200 cm^{-1} and the ^1H NMR spectrum of the more soluble complex **5** is consistent with the proposed structure with the simple "$M_3(\mu\text{-HBzimt})_2$" framework. It shows four sharp resonances for the two equivalent $HBzimt^-$ anions related by a C_2 symmetry axis passing through the central metal atom. This C_2 axis also groups the olefinic cod protons in six sets of equivalent nuclei. The proposed C_2 symmetry of these complexes is based on the analogy of their spectroscopic data with those of the related trinuclear rhodium complexes with benzothiazole-2-thiolate, for which the structures have been confirmed by NMR and X-ray studies.[4f,11e]

Tetranuclear Complexes. The above-described dinuclear complexes **3** and **4** have two further acidic protons which are

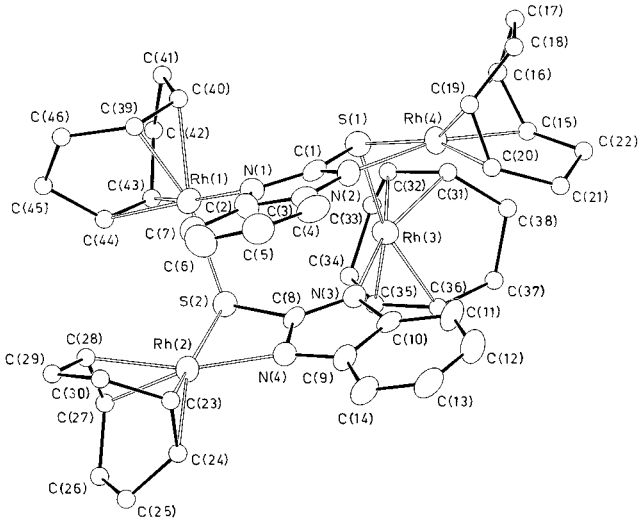


Figure 4. View of the molecular structure of one of the two independent complexes $[Rh_2(\mu\text{-Bzimt})(cod)_2]_2$ (**7**).

removed by the complexes $[M_2(\mu\text{-OMe})_2(cod)_2]$ to give the tetranuclear complexes $[M_2(\mu\text{-Bzimt})(cod)_2]_2$ (M = Rh (**7**), Ir (**8**)). They are isolated as orange crystalline solids and identified by elemental analyses and spectroscopic studies and by an X-ray diffraction study for the rhodium derivative **7**. A more direct synthetic route to these tetranuclear compounds is the reaction between the dilithium derivative Li_2Bzimt and the chloro-bridged compounds $[M_2(\mu\text{-Cl})_2(cod)_2]$ in 1:1 molar ratio. It is noteworthy that the dinuclear complexes [(cod)M(μ-Bzimt)M-(cod)] similar to those described by Armstrong[31] $[Li_2(Bzimt)(HMPA)_3]_2$, with $Bzimt^{2-}$ acting as chelating and bridging ligand, are detected in the mass spectra only.

Crystal Structure of the Complex $[Rh_2(\mu\text{-Bzimt})(cod)_2]_2 \cdot CH_2Cl_2$ ($7\cdot CH_2Cl_2$). Two crystallographically independent tetranuclear complexes **7** and dichloromethane molecules of crystallization are present in the crystals. The structure of one of the two independent, but very similar, complexes **7** is shown in Figure 4, together with the atom numbering scheme. Selected bond distances and angles in the two independent complexes are given in Table 2. The complex **7** shows a pseudosymmetry C_2 with the 2-fold axis passing through the midpoints of the two Rh(1)−Rh(3) and Rh(2)−Rh(4) lines. Taking into account that the complex does not display any symmetry element of the type S_n, it is chiral. Even in the crystals both enantiomers are present due to the centrosymmetric space group.

Each Rh atom of the tetranuclear complex is bound to a cod molecule through the two olefinic double bonds. The four metal atoms are connected through two $Bzimt^{2-}$ anions; each of them acts as N,S-chelating to one Rh atom and as N,S-bridging two Rh atoms. If the midpoints of the two double bonds of each cod molecule are considered as coordination sites, each Rh atom displays a distorted square planar coordination. The four Rh environments can be considered of two types: the former shows a S,N-chelating coordination from one $Bzimt^{2-}$ anion, the latter a S,N-coordination, involving the sulfur atom and the second imidazole nitrogen atom, from two $Bzimt^{2-}$ anions. In the S,N-chelating Rh environments the values of the Rh−S bond distances, 2.447(4) [2.450(4)] and 2.450(4) [2.439(4)] Å (heretoafter the values in brackets refer to the second independent molecule), are much longer than those in the S,N-bridging Rh environments, 2.357(4) [2.355(4)] and 2.355(4) [2.357(4)] Å, whereas the values of the Rh−N bond distances in the S,N-chelating Rh environments, 2.079(11) [2.074(11)] and 2.049-(12) [2.061(11)] Å, are shorter than those in the S,N-bridging Rh environments, 2.096(11) [2.101(11)] and 2.099(12) [2.114-(13)] Å. The values of the Rh−S and Rh−N bond distances

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **7**

molecule 1		molecule 2		molecule 1		molecule 2	
Rh(11)−S(21)	2.357(4)	Rh(12)−S(22)	2.355(4)	Rh(31)−S(11)	2.355(4)	Rh(32)−S(12)	2.357(4)
Rh(11)−N(11)	2.099(12)	Rh(12)−N(12)	2.114(13)	Rh(31)−N(31)	2.096(11)	Rh(32)−N(32)	2.101(11)
Rh(11)−C(391)	2.130(18)	Rh(12)−C(392)	2.12(2)	Rh(31)−C(311)	2.140(19)	Rh(32)−C(312)	2.139(18)
Rh(11)−C(401)	2.180(19)	Rh(12)−C(402)	2.17(2)	Rh(31)−C(321)	2.129(19)	Rh(32)−C(322)	2.126(18)
Rh(11)−C(431)	2.10(2)	Rh(12)−C(432)	2.14(2)	Rh(31)−C(351)	2.132(17)	Rh(32)−C(352)	2.134(17)
Rh(11)−C(441)	2.12(2)	Rh(12)−C(442)	2.13(2)	Rh(31)−C(361)	2.158(15)	Rh(32)−C(362)	2.130(16)
Rh(21)−S(21)	2.450(4)	Rh(22)−S(22)	2.439(4)	Rh(41)−S(11)	2.447(4)	Rh(42)−S(12)	2.450(4)
Rh(21)−N(41)	2.079(11)	Rh(22)−N(42)	2.074(11)	Rh(41)−N(21)	2.049(12)	Rh(42)−N(22)	2.061(11)
Rh(21)−C(231)	2.142(15)	Rh(22)−C(232)	2.123(16)	Rh(41)−C(151)	2.112(16)	Rh(42)−C(152)	2.160(16)
Rh(21)−C(241)	2.113(16)	Rh(22)−C(242)	2.129(16)	Rh(41)−C(161)	2.092(19)	Rh(42)−C(162)	2.080(17)
Rh(21)−C(271)	2.073(18)	Rh(22)−C(272)	2.115(19)	Rh(41)−C(191)	2.112(16)	Rh(42)−C(192)	2.145(15)
Rh(21)−C(281)	2.152(17)	Rh(22)−C(282)	2.137(17)	Rh(41)−C(201)	2.128(17)	Rh(42)−C(202)	2.131(16)
S(11)−C(11)	1.755(14)	S(12)−C(12)	1.763(14)	C(21)−C(31)	1.36(2)	C(22)−C(32)	1.38(2)
S(21)−C(81)	1.747(14)	S(22)−C(82)	1.742(14)	C(91)−C(101)	1.43(2)	C(92)−C(102)	1.43(2)
N(11)−C(11)	1.357(18)	N(12)−C(12)	1.298(18)	C(151)−C(161)	1.35(2)	C(152)−C(162)	1.35(2)
N(11)−C(21)	1.40(2)	N(12)−C(22)	1.429(19)	C(191)−C(201)	1.39(2)	C(192)−C(202)	1.41(2)
N(21)−C(11)	1.302(18)	N(22)−C(12)	1.367(19)	C(231)−C(241)	1.39(2)	C(232)−C(242)	1.37(2)
N(21)−C(31)	1.41(2)	N(22)−C(32)	1.385(19)	C(271)−C(281)	1.34(2)	C(272)−C(282)	1.35(2)
N(31)−C(81)	1.334(17)	N(32)−C(82)	1.351(18)	C(311)−C(321)	1.35(3)	C(312)−C(322)	1.35(2)
N(31)−C(101)	1.416(17)	N(32)−C(102)	1.401(17)	C(351)−C(361)	1.39(2)	C(352)−C(362)	1.39(2)
N(41)−C(81)	1.350(18)	N(42)−C(82)	1.350(18)	C(391)−C(401)	1.39(3)	C(392)−C(402)	1.36(3)
N(41)−C(91)	1.383(18)	N(42)−C(92)	1.371(18)	C(431)−C(441)	1.31(3)	C(432)−C(442)	1.31(3)
S(21)−Rh(11)−N(11)	93.1(3)	S(22)−Rh(12)−N(12)	93.1(3)	Rh(41)−N(21)−C(11)	101.7(9)	Rh(42)−N(22)−C(12)	100.6(8)
S(21)−Rh(21)−N(41)	69.8(3)	S(22)−Rh(22)−N(42)	69.9(3)	C(11)−N(21)−C(31)	102.5(12)	C(12)−N(22)−C(32)	102.7(11)
S(11)−Rh(31)−N(31)	92.3(3)	S(12)−Rh(32)−N(32)	91.8(3)	Rh(31)−N(31)−C(101)	128.6(9)	Rh(32)−N(32)−C(102)	130.1(9)
S(11)−Rh(41)−N(21)	69.0(3)	S(12)−Rh(42)−N(22)	70.1(3)	Rh(31)−N(31)−C(81)	126.8(9)	Rh(32)−N(32)−C(82)	124.8(9)
Rh(31)−S(11)−Rh(41)	106.7(2)	Rh(32)−S(12)−Rh(42)	106.5(2)	C(81)−N(31)−C(101)	104.4(11)	C(82)−N(32)−C(102)	104.9(11)
Rh(41)−S(11)−C(11)	75.9(5)	Rh(42)−S(12)−C(12)	76.9(5)	Rh(21)−N(41)−C(91)	155.4(9)	Rh(22)−N(42)−C(92)	155.9(9)
Rh(31)−S(11)−C(11)	108.9(5)	Rh(32)−S(12)−C(12)	107.5(5)	Rh(21)−N(41)−C(81)	99.4(8)	Rh(22)−N(42)−C(82)	99.3(9)
Rh(11)−S(21)−Rh(21)	104.3(2)	Rh(12)−S(22)−Rh(22)	105.2(2)	C(81)−N(41)−C(91)	105.1(11)	C(82)−N(42)−C(92)	104.8(11)
Rh(21)−S(21)−C(81)	76.5(5)	Rh(22)−S(22)−C(82)	76.7(5)	N(11)−C(11)−N(21)	117.1(12)	N(12)−C(12)−N(22)	116.7(12)
Rh(11)−S(21)−C(81)	107.9(5)	Rh(12)−S(22)−C(82)	107.3(5)	S(11)−C(11)−N(21)	113.4(10)	S(12)−C(12)−N(22)	112.4(10)
Rh(11)−N(11)−C(21)	130.9(10)	Rh(12)−N(12)−C(22)	130.1(10)	S(11)−C(11)−N(11)	129.4(10)	S(12)−C(12)−N(12)	130.9(11)
Rh(11)−N(11)−C(11)	126.4(9)	Rh(12)−N(12)−C(12)	125.6(10)	N(31)−C(81)−N(41)	115.6(11)	N(32)−C(82)−N(42)	114.7(12)
C(11)−N(11)−C(21)	102.4(11)	C(12)−N(12)−C(22)	103.9(11)	S(21)−C(81)−N(41)	114.3(10)	S(22)−C(82)−N(42)	114.1(10)
Rh(41)−N(21)−C(31)	155.8(10)	Rh(42)−N(22)−C(32)	156.7(10)	S(21)−C(81)−N(31)	130.1(10)	S(22)−C(82)−N(32)	131.2(11)

in the S,N-bridging Rh environments are strictly comparable to those found in the structure of the dinuclear $[Rh_2(\mu\text{-Bztzt})_2(CO)_3(PPh_3)]$ complex, 2.370(1) and 2.376(1) Å and 2.100(3) and 2.107(2) Å, respectively,[11d] in which the benzothiazole-2-thiolate ligand (Bztzt) bridges two Rh atoms thorough a N−C−S fragment very similar to that of the $Bzimt^{2-}$ anions.

It is noteworthy the remarkable difference for the values of the S−Rh−N angles in the two types of Rh environments, 93.1(3) and 92.3(3) [93.1(3) and 91.8(3)]° in the S,N-bridging ones, against 69.8(3) and 69.0(3) [69.9(3) and 70.1(3)]° in the S,N-chelating ones where the $Bzimt^{2-}$ ligand is compelled to present a very narrow bite angle in order to form a four-atom chelation ring.

In spite of the very complicated bonding mode, the $Bzimt^{2-}$ tridentate ligands are planar with the Rh atoms almost coplanar (maximum deviation 0.150(1) Å). The two planar ligands, connected through the Rh-S-bridging bonds, form an angle of 24.5 [24.3(1)]°.

In solution, both complexes **7** and **8** show the structure described for **7** in the solid state, as deduced from their NOE and H,H-COSY spectra. The key for the unambiguous assignment of all olefinic protons is the space position of the olefinic proton 6 (Figure 5). Molecular models and the X-ray structure of **7** show that it is very close to the H^6 proton of one $Bzimt^{2-}$ ligand and to the H^3 proton of the other $Bzimt^{2-}$ ligand, the average nonbonding 6-H^6 and 6-H^3 distances being 2.80 and 3.27 Å respectively. Indeed, NOE experiments confirm this situation. Saturation of the upfield doublet of the ligand (H^6) leads to an equal enhancement of the resonances corresponding to 6 and 8 (Figure 5b), the two protons of the C═C bond *trans* to S in the N,S-Rh chelate system; the nonbonding 8-H^6 distance being 3.02 Å. In addition, saturation of the downfield doublet of the ligand (H^3) leads to a strong enhancement for 4 and a weak for 5 and 6 (Figure 5a). The average nonbonding H^3-4 and H^3-5 distances are 2.63 and 2.91 Å respectively. From this,

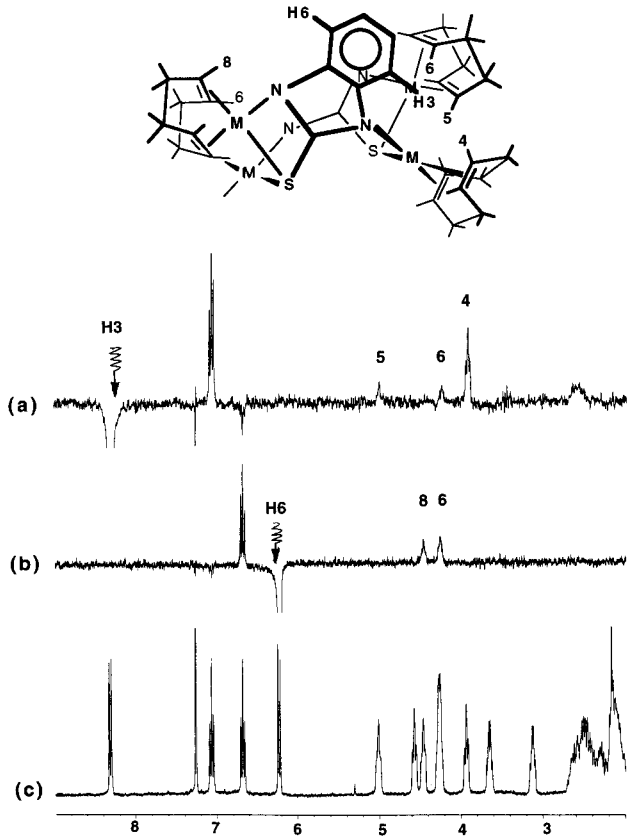


Figure 5. NOE difference spectra on saturation of the resonances at δ 8.29 ppm (a) and at δ 6.20 ppm (b) for **8**. (c) Normal spectrum.

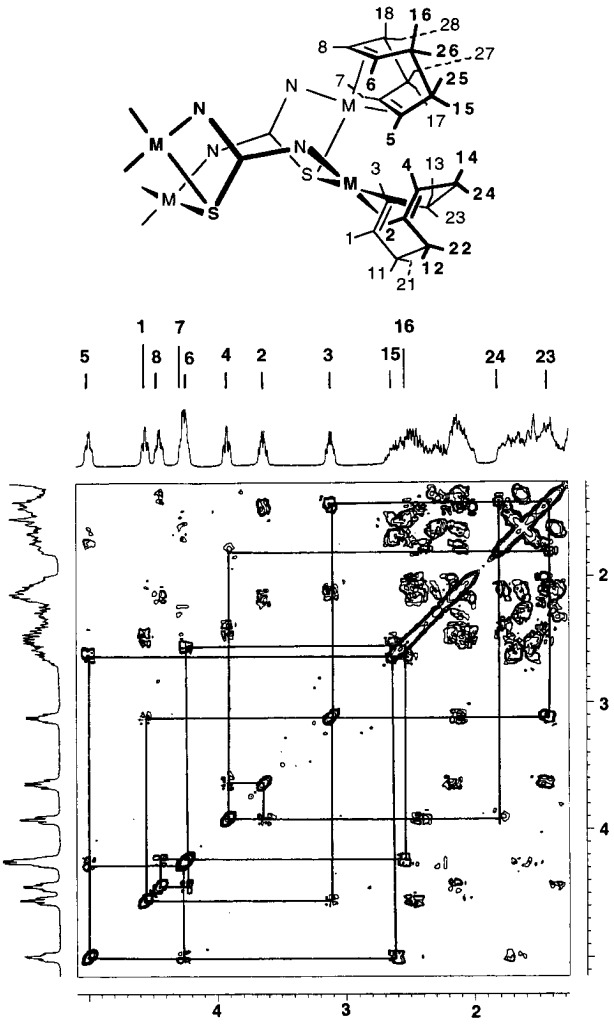


Figure 6. H,H-COSY spectrum of the diolefins for complex **8**, showing the protons labeling.

5 and 6 are the olefinic protons of cod in the N,S-Rh chelate system inside the "$M_2(\mu$-Bzimt$)_2$" metallacycle and 4 is the olefinic proton of the other cod *trans* to S and outside of the pocket of the complex.

Once the 4, 5, 6, and 8 protons are identified, the complete assignment of the 24 diolefinic protons is easily achieved from their H,H-COSY spectra. Figure 6 shows the H,H-COSY spectrum for complex **8** as a representative example together with some connections. Again, the presence of four cross-peaks for each one of the methylenic protons excludes the presence of any mirror plane in the molecule and confirms the *cis*,*cis*-HT arrangement of the bridging ligands as found in the solid state for **7**.

Formation and Relationships between the Polynuclear Complexes. The synthesis of the tetranuclear complexes from $[M_2(\mu$-HBzimt$)_2$(cod$)_2]$ and $[M_2(\mu$-OMe$)_2$(cod$)_2]$ consists in the deprotonation of the former by the methoxo-bridging complex giving methanol and generating two "M(cod)" fragments that chelate through the deprotonated nitrogen and the lone pair of the closest sulfur. As the formation of these tetranuclear complexes is accomplished by two deprotonations, they run probably in two steps. The first should lead to the neutral trinuclear complexes $[M_3(\mu$-HBzimt$)(\mu$-Bzimt$)$(cod$)_3]$ (**A**, Scheme 1). This hypothesis is confirmed by monitoring the reactions in a 1:0.5 molar ratio by ^{1}H NMR spectroscopy. A mixture of three compounds is observed among them the starting $[M_2(\mu$-HBzimt$)_2$(cod$)_2]$ (**3**, **4**) complexes and the tetranuclear $[M_2(\mu$-Bzimt$)$(cod$)_2]_2$ (**7**, **8**) complexes were easily identified, whereas the trinuclear $[M_3(\mu$-HBzimt$)(\mu$-Bzimt$)$(cod$)_3]$ complexes were identified by subtraction of the spectra of the known complexes from those of the reaction mixtures. They show nine resonances of the same intensity in the aromatic region: four doublets, four triplets, and one broad singlet according with the presence of one HBzimt$^-$ and one Bzimt^{2-} bridging ligand. A further addition of 0.5 mol of $[M_2(\mu$-OMe$)_2$(cod$)_2]$ to the reaction mixtures leads to the tetranuclear complexes quantitatively. The trinuclear neutral complexes are in the following equilibrium with the di- and tetranuclear ones:

$$2[M_2(\mu\text{-HBzimt})_2(\text{cod})_2] + [M_2(\mu\text{-OMe})_2(\text{cod})_2] \rightarrow 2[M_3(\mu\text{-HBzimt})(\mu\text{-Bzimt})(\text{cod})_3] \rightleftharpoons [M_2(\mu\text{-HBzimt})_2(\text{cod})_2] + [M_2(\mu\text{-Bzimt})(\text{cod})_2]_2$$

Thus, this equilibrium is also reached by preparing mixtures of equimolecular amounts of the di- and tetranuclear complexes. Indeed, the equilibrium is an acid−base comproportionation reaction. The equilibrium constant (K_c) at 293 K for the rhodium complexes is 2.35 ± 0.02; i.e., it is large enough to observe the three species in solution but too low to drive the equilibrium to the trinuclear complex. The value of this constant associated with the solubility of the trinuclear complexes, intermediate between those of the di- and tetranuclear ones, make it difficult to isolate them in a pure state.

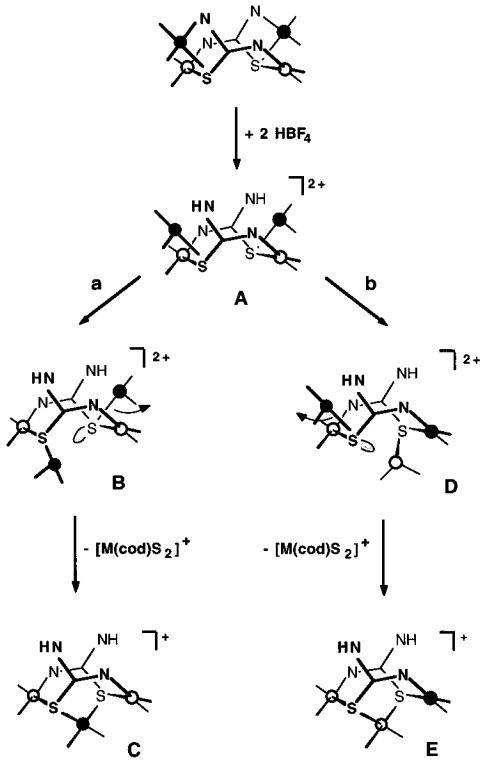
Nevertheless, the protonation of the tetranuclear complex **7** with 2 equiv of HBF_4 leads to the formation of the very stable and slightly soluble cationic trinuclear complex $[Rh_3(\mu$-HBzimt$)_2$-(cod$)_3]BF_4$ (**5**) described above and to the solvated species $[Rh(cod)(S)_x]^+$. In this reaction the "Rh(cod)" fragment is removed either from the "$Rh_2(\mu$-NCS$)_2$" metallacycle or from the "N,S−Rh" chelate. To address this point it would be necessary that the two metal environments were different. With this aim, we have prepared the heterotetranuclear complex $[IrRh(\mu$-Bzimt$)$-(cod$)_2]_2$ (**9**) by reacting $[Ir_2(\mu$-HBzimt$)_2$(cod$)_2]$ (**4**) and $[Rh_2(\mu$-OMe$)_2$(cod$)_2]$. The reaction takes place cleanly giving a single isomer: just that having the basic "$Ir_2(\mu$-NCS$)_2$" core of the starting dinuclear complex **4** (as deduced from analytical and spectroscopic data, see Experimental Section).

The heterotetranuclear complex $[IrRh(\mu$-Bzimt$)$(cod$)_2]_2$ (**9**) reacts with 2 equiv of HBF_4 giving the heterotrinuclear complex $[Ir_2Rh(\mu$-HBzimt$)_2$(cod$)_3]BF_4$ (**10**), which was isolated as a single isomer. Analytical data and a mass spectrum for **10** confirm the presence of two iridium and one rhodium atoms. Moreover, the ^{1}H NMR spectrum of **10** shows two inequivalent bridging ligands and hence it corresponds to a "unsymmetrical" trinuclear complex (**E**, Scheme 2). Therefore the protonation reactions of the tetranuclear complexes with HBF_4 lead to the release of one of the chelated metals.

A plausible mechanism for this process is shown in Scheme 2: protonation of the two nitrogen atoms of **9** involves the breaking of two N−Rh bonds to give the dicationic complex **A**. Now, two pathways are possible: a subsequent inversion of the configuration at one of the two sulfur atoms (complex **B**) drives one of the $Rh(cod)^+$ fragments to be close to the lone pair on the other sulfur atom; the formation of this Rh−S bond with the concomitant release of $[Rh(cod)S_x]^+$ would give the "symmetrical" trinuclear complex **C** (path *a*). Alternatively (path *b*), the breaking of a Ir−N bond in the intermediate **A** and the formation of a Rh−N bond (complex **D**), would drive the iridium atom to link the nearest sulfur with release of the solvated species $[Rh(cod)S_x]^+$ to give the "unsymmetrical" complex **E**. Formation of **E** instead of **C** clearly reveals that path *b* is followed in this protonation reaction.

Further Comments. Table 3 shows the chemical shifts for the olefinic protons in complexes **3**, **4**, $[Ir_2(\mu$-Opy$)_2$(cod$)_2]$,[39] and $[Ir_2(\mu$-aza$)_2$(cod$)_2]$.[40] In the latter complexes, the olefinic

Scheme 2. Possible Mechanisms for the Protonation Reaction of Complex **9** Leading to the "Unsymmetrical" Trinuclear Complex **10**[a]



[a] Key: ○< and ●< represent the "Ir(cod)" and "Rh(cod)" moieties respectively.

Table 3. ^{1}H NMR Resonances (δ) of Rh(I) and Ir(I) cod Complexes in the Olefin Region for the cod Ligands that Constitute the "$M_2(\mu$-NCX$)_2$" Metallocycle

complex	*trans*-N^{in}	*trans*-X^{in}	*trans*-N^{out}	*trans*-X^{out}
[$Rh_2(\mu$-HBzimt$)_2$(cod)$_2$] (**3**)	4.96	4.44	4.17	3.90
[$Ir_2(\mu$-HBzimt$)_2$(cod)$_2$] (**4**)	4.59	4.00	3.85	3.33
[$Ir_2(\mu$-Opy$)_2$(cod)$_2$]	4.42	3.56	4.63	2.87
[$Ir_2(\mu$-aza$)_2$(cod)$_2$]	4.50 (Py)	3.50	4.75 (Py)	3.25
[$Rh_2(\mu$-Bzimt)(cod)$_2]_2$ (**7**)	4.81	4.11	3.35	4.32
[$Ir_2(\mu$-Bzimt)(cod)$_2]_2$ (**8**)	4.55	3.63	3.11	3.91
[IrRh(μ-Bzimt)(cod)$_2]_2$ (**9**)	4.47	3.60	2.98	3.88

protons *trans* to the pyridine nitrogen are more deshielded than those *trans* to the oxygen or the pyrrolic nitrogen atom; i.e., the more relevant influence on the chemical shifts for these olefinic protons is given by the atom *trans* to the C═C bond. These chemical shifts are less influenced on whether these protons are inside or outside the "pocket" of the complex. However, for complexes **3** and **4** this relative position seems to be as influent on their chemical shifts as the atoms *trans* to them. In consequence, an accurate assignment of the olefinic protons in "open-book" dinuclear complexes requires a particular study. Moreover, comparison of the chemical shifts of the olefinic protons (1−4) in complexes **7**-**9** with their counterparts in the dinuclear complexes **3** and **4** (Table 3) reveals the influence of unaccounted anisotropic effects on the chemical shifts. Going from the dinuclear to the tetranuclear complexes, the resonances for the protons 2 and 3 are shifted upfield in *ca.* 0.35 and 0.8 ppm, respectively, while for proton 4 is shifted downfield in *ca.* 0.5 ppm and that for proton 1 remains unchanged. A close examination of the X-ray structure of **7** and molecular models for the dinuclear complexes shows that proton 4 is very close and, more important, in the same plane as the aromatic ring of one bridging ligand. Therefore, this proton undergoes a deshielding due to the ring current in the aromatic ring; this effect is more pronounced in complexes **7**-**9** than in **3** and **4** because of their close proximity in the former. In addition, as a consequence of the steric crowding in the tetranuclear complexes, the olefinic proton 3 lies very close to the C═C double bond *trans* to N of the cod in the N,S−Rh chelate system; i.e., it is in the shielding cone due to the electronic circulation on the double bond. This neighboring anisotropic effect is probably the origin of the relative shift for this proton in *ca.* 0.8 ppm in complexes **7**-**9**. Finally, the coordination of the additional Rh(cod) fragments in **7**-**9** causes a separation of 2 from the lone pairs on the sulfur atom relative to **3** and **4**, leading to an upfield shift. In consequence, the chemical shifts of the olefinic protons 1−4 of the cod ligands associated to the "$M_2(\mu$-NCS$)_2$" metallacycle in complexes **3** and **4** and **7**-**9** are also influenced by anisotropic effects. These are mostly due to the ring currents of the aromatic and C═C double bonds since the magnetic anisotropy from the d^8-d^8 metal-metal interaction of the distal metal is probably unimportant in these systems, as pointed out by Mann.[39]

Table 4. $^{13}C\{^1H\}$ NMR Resonances (δ) of CS and CN Carbons for H_2Bzimt, HBzimt$^-$, and Bzimt^{2-} Ligands

	H_2Bzimt	**1**	**2**	**3**	**4**	**7**	**8**	**9**
C═S	170.7	165.7	166.7	162.7	161.3	162.8	164.6	161.0
C−N−H	133.4	131.1	130.8	133.1	132.5			
C−N−M				142.5	141.6	140.3	139.8	139.8
						141.5	141.1	141.1

Table 4 collects the $^{13}C\{^1H\}$ NMR resonances due to the carbons of the five-membered ring of the bridging ligands. Upon coordination to a metal, through the sulfur atom (complexes **1**-**2**), the C═S resonance is shifted upfield by 5 ppm relative to the free ligand due probably to a reduction in the π-character of the C═S bond. A further reduction occurs on deprotonation of the H_2Bzimt ligand. In addition, the chemical shift of the quaternary bridgehead carbons also provides information about the coordination mode of the benzimidazole bridging ligand. Complexes **1** and **2**, for which two NH groups are present, have one resonance for this carbon at *ca.* δ 131 ppm as in the free ligand. Coordination of the HBzimt$^-$ ligand as binucleating in a μ_2-(1κN,2κS) fashion causes a shift downfield for the carbon nearest to the N−metal group of *ca.* 9 ppm. In fact, complexes **3** and **4** show two different resonances for the two quaternary bridgehead carbons, where one of them remains at *ca.* δ 131 ppm. On coordination through both nitrogen atoms, the quaternary bridgehead carbons of Bzimt^{2-} give resonances at *ca.* δ 140 ppm as found in complexes **7**-**9**.

Finally, it is convenient to remark that all di- and polynuclear complexes here reported lack any symmetry plane and, therefore, they are chiral. This expectation is clearly proved by the presence of both enantiomers in the crystals of complex **7**.

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Supporting Information Available: Fractional atomic coordinates of non-H atoms of **7** (Table SI), fractional atomic coordinates of H atoms of **7** (Table SII), anisotropic coefficients of non-H atoms of **7** (Table SIII), and bond lengths and angles (Table SIV) (14 pages). Ordering information is given on any current masthead page.

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