Heterobi- and Heterotetranuclear RuRh and RuIr Complexes with 2,2'-Biimidazolate and 2,2'-Bibenzimidazolate Anions as Bridging Ligands

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The reaction of the dimer [$\{\eta^6$ -p-cymene)RuCl $_2(\mu$ -Cl $_2$] (p-cymene = p-isopropylmethylbenzene) with 2,2'-biimidazole (H₂Bim) afforded the chloride complex $[(\eta^6-p-cymene)Ru (H_2Bim)Cl]Cl(1)$ which has also been isolated as the tetrafluoroborate salt $[(\eta^6-p-cymene)Ru(H_2-tyme)Ru(H_2 Bim)Cl]BF_4$ (2) by metathesis with NaBF₄. Complex 1 underwent reaction with [M(acac)- L_2] yielding the corresponding heterobinuclear species [(η^6 -p-cymene)ClRu(μ -HBim)MClL₂] $(M = Rh; L_2 = cis, cis-1, 5$ -cyclooctadiene (COD) (3), (CO)₂ (4); $M = Ir, L_2 = COD$ (5)]. Complexes 3-5 exhibit a dynamic behavior which equilibrates the two imidazole rings of the HBim bridging ligand. The reaction of 4 with KOH led to two tetranuclear isomers $[(\eta^6 - p - \text{cymene}) \text{ClRu}(\mu - \text{Bim}) \text{Rh}(\text{CO})_2]_2$ (6) which in solution reached an equilibrium with a K value for the process $6b - 6a \le 0.11$. Reaction of $[(\eta^6 - p - cymene)Ru(acac)Cl]$ with [Rh(HBim) - bcacce + bcacee(COD)] afforded the heterobinuclear complex $[(\eta^6-p-cymene)Ru(acac)(\mu-HBim)Rh(COD)]A$ $(A = Cl(7), BF_4(8))$. At room temperature the Rh(HBim)(COD) moiety of complexes 7 and 8 rotates rapidly around the Ru–N bond, but this process stops at 223 K. [$(\eta^{6}$ -p-cymene)-Ru(acac)Cl] and $[(\eta^6-p-cymene)Ru(acac)(PPh_3)]BF_4$ reacted with 2,2'-bibenzimidazole (H₂-Bbzim) rendering $[(\eta^6-p-cymene)Ru(HBbzim)Cl]$ (9) and $[(\eta^6-p-cymene)Ru(HBbzim)(PPh_3)]BF_4$ (10), respectively. Complex 9 undergoes reaction with $[M(acac)L_2]$ yielding $[(\eta^6-p-cymene) ClRu(\mu-Bbzim)ML_2]_n$ (M = Rh; L₂ = COD (n = 1) (11), norborna-2,5-diene (NBD) (n = 2) (12), $(CO)_2 (n = 2)$ (13). $M = Ir; L_2 = COD (n = 1)$ (14)). The molecular structure of complex 12 has been determined. Crystals are triclinic, space group $P\overline{1}$, with cell parameters a =12.998(1) Å, b = 14.035(1) Å, c = 18.081(2) Å, $\alpha = 79.864(4)^{\circ}$, $\beta = 78.046(5)^{\circ}$, $\gamma = 73.326(7)^{\circ}$, and Z = 2. The compound is tetranuclear with two Bbzim²⁻ ligands bridging the metal atoms. Each Bbzim²⁻ coordinates to the metals in an unsymmetrical tetradentate manner through its four nitrogen atoms, chelated to the Ru atoms and bonded in an unidentate manner to the two Rh atoms. The cationic complex 10 undergo reaction with the acetylacetonates [M(acac)L₂] yielding the cationic binuclear complexes [$(\eta^6$ -p-cymene)(PPh₃)- $Ru(\mu-Bbzim)ML_2]BF_4$ (M = Rh; $L_2 = COD$ (15), NBD (16), (CO)₂ (17). M = Ir; $L_2 = COD$ (18)). Carbonylation of 18 afforded $[(\eta^6-p-\text{cymene})(\text{PPh}_3)\text{Ru}(\mu-\text{Bbzim})\text{Ir}(\text{CO})_2]\text{BF}_4$ (19) and complex 17 could analogously be obtained from complexes 15 or 16. The molecular structure of complex 19 has been determined by diffractometric methods. Crystals are monoclinic, space group $P2_1/c$, with cell parameters a = 11.586(2) Å, b = 20.489(2) Å, c = 17.225(1) Å, $\beta = 95.34(1)^{\circ}$, and Z = 4. In the solid state, two complex cations $[(\eta^{6}-p-\text{cymene})(\text{PPh}_{3})\text{Ru}$ - $(\mu$ -Bbzim)Ir(CO)₂] related by an inversion center are joined by an intermetallic Ir-Ir interaction (3.0808(5) Å). The cation consists of a Ru and an Ir atom connected by a Bbzim²⁻ anion that chelates both metals through four nitrogen atoms. Complexes 11, 14, and 15-**19** are active catalysts for the homogeneous hydrogenation of cyclohexene. Kinetic studies showed that the reduction catalyzed by 14 is first-order in catalyst concentration and secondorder in hydrogen concentration.

Introduction

The coordination of 2,2'-biimidazole (H₂Bim), 2,2'bibenzimidazole (H₂Bbzim), and their related anions to

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transition metal ions has attracted much attention since Rasmussen et al. published the first examples of binuclear complexes containing the tetracoordinate dianion $Bim^{2-.1}$ The presence of an imidazole moiety in important biological molecules has encouraged the preparative studies of discrete H₂Bim- and H₂Bbzimcontaining transition metal complexes. Thus, for example, H₂Bim has been used as ligand in pentacoordinate zinc complexes relevant for the discussion of the active sites in enzymes such as carboxypeptidase.² Several chelates resulting from the reaction of H₂Bim and H₂Bbzim with a variety of ferrous salts have been synthesized and studied owing to the interest of such ferrous complexes as models of the ferrous ion of mononuclear non-heme-containing proteins.³

Haga and co-workers have extensively studied the synthesis, electrochemical, and spectral properties of mono- and binuclear complexes of Ru, Os, Co, and Ni in various oxidation states with H₂Bim and H₂Bbzim or their derived mono- and dianions as ligands.⁴ In particular, the spectroscopic and electrochemical properties of multimetallic ruthenium(II) complexes containing H_2Bim and H_2Bbzim in their protonated and deprotonated forms have been investigated with the ultimate goal of effecting multiple-electron-transfer events from excited-state species.⁵ Anionic bridging ligands derived from 2,2'-biimidazole have been employed in order to prepare bimetallic ruthenium complexes for use in solar energy utilization studies.⁶ Very recently, the molecular structure and photophysical properties of di- and tetranuclear gold(I) complexes with the Bbzim²⁻ anion acting as bridging ligand have been described.⁷ Indirect cooperative effects leading to synergism in bimetallic homogeneous hydrogenation reactions have been found for Ru–Ir based catalysts containing Bim^{2–} as bridging ligand.⁸

However, 2,2'-biimidazole and 2,2'-bibenziimidazole and their derived anions have unique properties as coordinating ligands. They can complex as bidentate chelates. The dianions can also act as bis-bidentatechelate toward a pair of metal ions. Additionally, monoand bidentate nonchelate coordination modes can be achieved through the uncoordinated remaining nitrogens. Furthermore, the resulting complexes can be homo- or heterometallic, increasing the synthetic possibilities of this type of ligands. Compounds belonging to most of these coordination types have been described.4d,7,9

Pursuing our work in the study of the chemistry of transition metal ions with azole ligands,⁸⁻¹⁰ we now report the preparation and characterization of several RuRh and RuIr complexes, with the mono- and dianions

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derived from H₂Bim and H₂Bbzim as bridging ligands, of stoichiometries $[(\eta^6-p-cymene)ClRu(\mu-HBim)MClL_2]$ $(M = Rh; L_2 = COD (3), (CO)_2 (4).$ $M = Ir; L_2 = COD$ (5)), $[(\eta^6-p-\text{cymene})\text{ClRu}(\mu-\text{Bim})\text{Rh}(\text{CO})_2]_2$ (6), $[(\eta^6-p$ cymene)Ru(acac)(μ -HBim)Rh(COD)]A (A = Cl, (7) BF₄ (8)), $[(\eta^6\text{-}p\text{-}cymene)ClRu(\mu\text{-}Bbzim)ML_2]_n$ (M = Rh; L₂ = COD (n = 1) (11), NBD (n = 2) (12), (CO)₂ (n = 2) (13). M = Ir; L₂ = COD (n = 1) (14)) and $[(\eta^6-p-cymene) (PPh_3)Ru(\mu-Bbzim)ML_2]BF_4 (M = Rh; L_2 = COD (15),$ NBD (16), (CO)₂ (17). $M = Ir; L_2 = COD (18), (CO)_2$ (19)). The fluxional behavior in solution of complexes 3-5, 7, and 8 is studied as well as an unexpected isomerization process that exhibits the carbonyl compound 6. The molecular structures of $[(\eta^6-p-\text{cymene}) ClRu(\mu$ -Bbzim)Rh(NBD)]₂·2CH₂Cl₂ ((12)·2CH₂Cl₂) and $[(\eta^6-p\text{-cymene})(\text{PPh}_3)\text{Ru}(\mu\text{-Bbzim})\text{Ir}(\text{CO})_2]\text{BF}_4$ (19) are also reported.

Results and Discussion

Complexes with 2,2'-Biimidazole. Reaction of the binuclear complex¹¹ [{ $(\eta^6-p-cymene)RuCl$ }₂(μ -Cl)₂] with 1 equiv of 2,2'-biimidazole (H_2Bim) afforded the yellow mononuclear compound $[(\eta^6-p-cymene)Ru(H_2Bim)Cl]Cl$ (1). The tetrafluoroborate derivative $[(\eta^6-p-cymene) Ru(H_2Bim)Cl]BF_4(2)$ can be prepared by adding equimolar amounts of $NaBF_4$ to 1 in methanol. Both complexes have been characterized by elemental analyses and spectroscopic methods (see Experimental Section). Their IR spectra showed (i) a strong and very broad $\nu(NH)$ band in the $3650-2250 \text{ cm}^{-1}$ region which suggested that a strong N-H-X association is operating, 10c, f, k (ii) a band at ca. 300 cm^{-1} attributable to the stretching vibration $\nu(\text{RuCl})^{12}$ and, (iii) bands of the H₂Bim ligand.^{3,13} Complex 2 showed two bands at ca. 1100 and 520 cm⁻¹ characteristic of the uncoordinated $BF_4^$ anion.¹⁴ The molar conductivity of 1 in methanol, that corresponds to 1:1 electrolytes,¹⁵ along with the easy displacement of one chlorine atom by NaBF₄ strongly indicated that one of the chlorines in 1 is not covalently bonded to the ruthenium. Consequently, the FAB mass

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Figure 1. Proposed static structure for complexes 3-5.

spectrum showed a peak at m/z 405 with an isotopic distribution that matches the calculated for the $[(\eta^6 p - cymene)Ru(H_2Bim)Cl]^+$ fragment. The ¹H spectra were consistent with the proposed formulations. They showed two signals at 7.15 and 7.41 ppm for 1, and at 7.17 and 7.45 ppm for 2 corresponding to the CH protons of the 2,2'-biimidazole¹⁶ and the *p*-cymene and NH resonances with the expected relative intensities and multiplicities.

Attempts to prepare the neutral complex $[(\eta^6-p-cymene)Ru(HBim)Cl]$ from the reaction of 1 with a base (KOH, NEt₃ or 'BuOK) have been unsuccessful. The reactions gave complex mixtures of *p*-cymene-containing complexes that we have not been able to resolve. Similar mixtures were obtained when the acetylacetonate complex $[(\eta^6-p-cymene)Ru(acac)Cl]^{10f}$ was allowed to react with 2,2'-biimidazole.

Complex 1 has two NH groups that, potentially, could be used in ulterior coordination to afford bi- or polynuclear complexes. Thus, 1 reacted with $[M(acac)L_2]$ $(M = Rh; L_2 = COD,^{17} (CO)_2.^{18} M = Ir; L_2 = COD^{19})$ yielding the corresponding yellow heterobinuclear complexes $[(\eta^6-p\text{-cymene})CIRu(\mu\text{-HBim})MCIL_2] (M = Rh; L_2 = COD (3), (CO)_2 (4). M = Ir; L_2 = COD (5)).$ Complex 4 could also be prepared by bubbling carbon monoxide through dichloromethane solutions of 3. The new heterobinuclear complexes 3-5 were characterized on the basis of elemental analyses, IR and NMR spectroscopies (see Experimental Section). Their IR spectra in Nujol showed vibration bands at ca. 3300 and 300 cm⁻¹ attributable to N-H and M-Cl bonds, respectively, and the disappearance of the acac vibrations. The carbonyl complex 4 showed two strong $\nu(CO)$ bands characteristic of a *cis*-dicarbonyl structure.²⁰ The proposed structure for these complexes is schematically drawn in Figure 1. However, their ¹H NMR spectra at room temperature showed less bands than expected for a static structure as the proposed. The spectra exhibited only one doublet and one AB system assigned to the isopropyl methyl and aromatic protons of the p-cymene ligand, respectively. These data indicated that a fluxional process was occurring. In particular, the spectrum of 3 (Table 1), only showed two signals at 7.20 and 7.55 ppm for the CH protons of the biimidazolate ligand. By lowering the temperature to 193 K. four sharp separate singlets at 7.02, 7.39, 7.54 and 7.72 ppm appeared, and the broadening of the doublet and the AB system of the *p*-cymene ligand was observed. Consistently, while the ${}^{13}C{}^{1}H$ MR spectrum of 3 at room temperature (Table 2) only exhibited one signal for the 2 and 2' carbons and a broad resonance for the 4, 4', 5, and 5' carbon nuclei of the biimidazolate ligand, at 223 K there were six separate signals for these nuclei. Furthermore, at this temperature, it showed several overlapped signals for the diolefinic carbon nuclei of the cyclooctadiene ligand, while at room temperature only two broad resonances centered at 79.9 and 30.0 ppm were observed for this group.

All these observations were consistent with the existence, at low temperature, of the static structure shown in Figure 1. When the temperature was increased, a fluxional process operated, which rendered equivalent the two halves of the biimidazolate ligand and the two L groups. For this process, we suggest a dissociative mechanism via deprotonation of the NH group, loss of the chlorine atom attached to M. and formation of a new M-N bond to give the symmetric intermediate $[(\eta^6-p$ cymene)ClRu(μ -Bim)ML₂] followed by rupture of the former M-N bond and recoordination of the chloride and proton. A comparable mechanism has been previously reported by Dixon et al. for the palladium complex cis-[PdCl(PEt₃)₂(4-Br-3,5-Me₂Hpz)]ClO₄.²¹ Interestingly, the estimated energy barrier ΔG^{\ddagger} for the fluxional process in complex 3, according to the coalescence temperature of the biimidazolate protons, is 54 kJ

Table 1. ¹H NMR Spectroscopic Data^a at Different Temperatures for Complexes 3, 7, and 8

complex		<i>p</i> -cymene			HBim		COD	acetylace	tonate
(<i>T</i> , K)	Me	ⁱ Pr	AA'BB'	NH	СН	vinylic	aliphatic	Me	Н
3 ^b (293)	2.14 (s)	1.06 (d, J = 7.0)	5.62 (d, J = 6.1) 5.83 (d, J = 6.1)	_	7.55 (s), 7.20 (br s)	3.93 (m), 3.01 (m)	2.33 (m), 1.75 (m)		-
(193)	2.20 (br s)	1.02 (br)	5.75 (br), 5.86 (br)	12.20 (s)	7.72 (s), 7.54 (s), 7.39 (s), 7.02 (s)	4.25 (m), 3.60 (m)	2.20 (m), 1.80 (m)	-	-
7 (323)	1.74 (s)	1.19 (d, $J = 7.0$), 2.81 (sp)	5.55 (br s)		7.75 (s), 6.67 (s), 6.46 (s), 6.44 (s)	4.41 (m)	2.46 (m), 1.93 (m)	1.87 (s)	4.97 (s)
(293)	1.71 (s)	1.17 (br d), 2.79 (sp. $J = 6.4$)	5.21 (br s), 5.55 (br s), 5.77 (br s), 6.65 (br s)	11.76 (br s)	7.71 (s), 6.66 (s), 6.45 (s), 6.43 (s)	4.38 (m)	2.43 (m), 1.94 (m)	1.85 (s)	4.95 (s)
(223)	1.68 (s)	1.18 (d, $J = 6.4$), 1.11 (d, $J = 6.2$), 2.82 (sp)	5.17 (d, J = 5.9), 5.19(d, J = 5.9), 5.65(d, J = 6.0),6.60 (d, J = 6.0)	11.70 (s)	7.67 (s), 6.63 (s), 6.44 (s), 6.42 (s)	4.49 (m), 4.38 (m)	2.45 (m), 1.95 (m)	1.82 (s), 1.80 (s)	4.29 (s)
8 (323)	1.70 (s)	1.21 (d, $J = 6.8$, 2.73 (sp)	5.1-6.3 (br)	11.42 (br s)	7.49 (s), 6.70 (s), 6.50 (s), 6.48 (s)	4.43 (m)	2.47 (m), 1.96 (m)	1.89 (s)	5.02 (s)
(293)	1.69 (s)	1.20 (br s). 2.75 (sp)	5.12 (br s), 5.43 (br s), 5.54 (br s), 6.16 (br s)	11.45 (br s)	7.47 (s), 6.69 (s), 6.50 (s), 6.47 (s)	4.41 (m)	2.46 (m), 1.95 (m)	1.88 (s)	5.01 (s)
(223)	1.67 (s)	1.14 (d, $J = 6.8$), 1.19 (d, $J = 6.8$), 2.73 (sp)	5.12 (d, J = 5.8), 5.32 (d, J = 5.8), 5.51 (d, J = 5.9), 6.12 (d, J = 5.9)	11.44 (s)	7.43 (s), 6.66 (s), 6.49 (s), 6.46 (s)	4.51 (m), 4.41 (m)	2.45 (m), 1.90 (m)	1.87 (s), 1.84 (s)	4.98 (s)

"Measured in CDCl₃; J in hertz; d = doublet, sp = septet, m = multiplet; br = broad." In CD₃COCD₃.

Table 2. ¹³C{¹H} NMR Spectroscopic Data^{*a*} at Different Temperatures for Complexes 3 and 7

complex		p-cymene ^b	,				HBim ^{//} COD		acetylacetonate		onate		
(<i>T</i> , K)	C _{1/4}	C _{2.6/3,5}	C ₇	C _{8/9}	C ₁₀	C _{2/2'}	C _{4/4′}	C _{5/5′}	C(sp ³)	C(sp ²)	C _{1/3}	$\overline{C_2}$	C _{4/5}
3 ^c (293)	102.2, 99.8	83.6, 81.8	-	22.0	18.6	145.1	130.9)	30.0	79.9		_	-
(223)	101.8, 99.0	d	-	22.1	18.5	143.6	131.8, 12	9.9,	32.4, 31.4,	76.9 (d, $J = 14.2$),	-		_
							129.6,	118.6	31.0	76.3 (d, $J = 13.5$) ^d			
7 e (293)	102.0, 100.0	86.7	30.6	22.4	18.0	-	129.8, 125.7	123.7,	30.6	79.8	187.0	99.4	27.0
								120.8					
(223)	101.5, 99.3	86.1, 84.9,	30.1	22.4	17.9	147.1	129.4, 125.5	123.6,	30.7, 30.6,	79.3 (d, $J = 11.0$),	187.1,	99.0	27.1, 26.7
		78.3, 78.0		21.9		142.9		120.0	29.8	78.8 (d, J = 12.0), 80.6	186.1		

" J in hertz; d = doublet." The p-cymene and biimidazolate carbon atoms are numbered as follows:



^c In CD₃COCD₃. ^d There are five resonances at 84.1, 84.0, 83.9, 82.8, and 82.0 ppm for the two remaining sp² diolefinic carbon atoms and for the C_{2.6/3.5} carbons of the p-cymene ligand. e In CDCl₃.

mol⁻¹, similar to the ΔG^{\ddagger} value of 60 kJ mol⁻¹ found in the above mentioned palladium complex.²¹

The formation of the heterobinuclear complexes 3-5containing the monoanion HBim⁻ coordinated as a bridging tridentate ligand could be considered as an intermediate step in the preparation of $[(\eta^6-p-\text{cymene}) ClRu(\mu$ -Bim)ML₂]_n complexes, in which the tetradentate dianion Bim^{2-} is present. Thus, the reaction of 4 with stoichiometric amounts of KOH in methanol led to the formation of the new neutral red-orange complex [$(\eta^{6}$ p-cymene)ClRu(μ -Bim)Rh(CO)₂]_n (6). Nevertheless, starting from the diolefinic complexes 3 and 5, untreatable mixtures of reaction products were obtained. The IR spectrum of 6 in dichloromethane showed three strong ν (CO) bands at 2080, 2060, and 2010 cm⁻¹, a characteristic pattern for folded binuclear structures with four carbonyl groups coordinated to two adjacent metals.1c,10b,22 The mass spectrum showed an envelope of peaks at m/z1124 with the isotopic distribution calculated for the tetranuclear $[(\eta^6-p-cymene)ClRu(\mu-Bim)Rh(CO)_2]_2^+$ fragment. These data were consistent with a tetranuclear formulation $[(\eta^6-p-\text{cymene})ClRu(\mu-Bim)Rh(CO)_2]_2$ for complex 6. A similar increment of the nuclearity in biimidazolate complexes was found in the carbonylation of the binuclear complexes $[Rh_2(\mu-Bim)(COD)_2]^{1c}$ and $[Rh_2(\mu\text{-TcBim})(COD)_2]$ (TcBim = 4,4',5,5'-tetracyano-2,2'-biimidazolate)²³ to give the tetranuclear species $[Rh_4(\mu-tetraazolate)(CO)_8]$. Although we have only observed the above-mentioned three- $\nu(CO)$ -band pattern. analytical and ¹H NMR data showed the presence of two isomers in solution which were obtained in different ratios from one preparation to another. One isomer had only one type of *p*-cymene ligand and only two proton NMR signals were observed for its two biimidazolate ligands, while the other showed two different kind of p-cymene ligands and four biimidazolate proton resonances. Three possible structures for these isomers (6a-c) are schematically shown in Figure 2. Assuming free rotation of the *p*-cymene groups around the Ruarene axis, the spectrum with only one type of *p*-cymene had to be assigned to **6a** or **6c**, rigid tetranuclear structures with C_{2v} symmetry. The other spectrum was attributed to the C_s isomer **6b**. We could not conclude



Figure 2. Possible structures for the isomers of complex ß

if the obtained isomer was **6a** or **6c**, but only one of them was detected. Furthermore, we have been able to isolate isomer 6a or 6c pure and establish that an isomerization process between 6a or 6c and 6b takes place. This process was monitored by ¹H NMR spectroscopy in CDCl₃ at room temperature. Starting from a solution mixture 40/60 of 6b/6a (or 6c), the ratio was 90/10 after 4 h and remained constant (within the ± 2 error limit) over a 4-day period. Consequently, the equilibrium constant $6b \rightarrow 6a$ (or 6c) will be ≤ 0.11 .

Looking for an alternative route to prepare polynuclear compounds with the Bim²⁻ anion, the neutral acetylacetonate complex $[(\eta^6-p-\text{cymene})\text{Ru}(\text{acac})\text{Cl}]^{10\text{f}}$ was allowed to react with the mononuclear rhodium(I)

⁽¹⁴⁾ See for example: Lehner, H.; Matt, D.; Togni, A.; Thouvenot, R.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1984**, *23*, 4254. (15) Geary, J. *Coord. Chem. Rev.* **1981**, *7*, 81.

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Figure 3. Proposed structure for the cation of 7 and 8 at 223 K.

compound [Rh(HBim)(COD)],^{1b} in methanol. The ruthenium-rhodium complex $[(\eta^6-p-\text{cymene})\text{Ru}(\text{acac})(\mu-$ HBim)Rh(COD)]Cl (7) was obtained in 75% yield. The displacement of the chlorine atom of 7 by NaBF₄ gave $[(\eta^{6}-p\text{-cymene})\text{Ru}(\text{acac})(\mu\text{-HBim})\text{Rh}(\text{COD})]BF_{4}(\mathbf{8}).$ Both complexes were characterized on the basis of elemental analysis, conductivity measurements, mass spectrometry, and IR and NMR spectroscopies (see Experimental Section and Tables 1 and 2). Their molar conductivities in acetone were characteristic of 1:1 electrolytes.¹⁵ The FAB mass spectra showed a peak at m/z 679 due to the fragment $[(\eta^6-p-cymene)Ru(acac)(\mu-HBim)Rh(COD)]^+$ for both complexes. Surprisingly, the IR spectra of the resulting products showed that the acac group (two strong bands at ca. 1580 and 1520 cm⁻¹) and the NH proton of the biimidazolate ligand (one very broad band centered at ca. 3300 cm^{-1}) were simultaneously present, while the chloride ligand had been displaced from the coordination sphere of the ruthenium. Complex 8 exhibited the two characteristic bands at ca. 1100 and 520 cm⁻¹ corresponding to the uncoordinated tetrafluoroborate anion.

The NMR data were consistent with the heterobinuclear structure shown in Figure 3. Thus, the ¹H NMR spectra of both complexes in $CDCl_3$ at room temperature (Table 1) showed broad signals for the AB aromatic systems and for the isopropyl methyl protons of the *p*-cymene ligand and only one singlet for the two methyls of the acetylacetonate ligand. At 223 K the spectra exhibited two AB systems and two doublets for the four aromatic protons and for the two inequivalent methyls of each isopropyl group of the *p*-cymene ligand,

respectively, and two different methyl groups for the acetylacetonate ligand. At 323 K, the spectra showed only one doublet for the isopropyl methyl groups, one type of acetylacetonate methyl and one very broad resonance for the aromatic protons of the *p*-cymene ligand. Consistently, the ¹³C NMR spectrum of 7 in CDCl₃ at 223 K (Table 2) showed two types of carbonyl and methyl carbons for the acetylacetonate group and four resonances for the four CH aromatic carbon nuclei of the *p*-cymene ligand as well as two singlets for the two methyls of the isopropyl group, while at room temperature only one signal for each type of carbon was observed. Assuming, again, free rotation of the pcymene ligand around the Ru-arene axis, a fluxional process that satisfies the experimental data implies the rotation of the Rh(HBim)(COD) unit around the Ru-N bond. This process should be fast at room temperature or above, but it collapses at 223 K. Most probably N-H-O interactions between the NH group of the HBim⁻ anion and one of the carbonyl groups of the acetylacetonate are operating in the ground state and would be responsible for the proposed static structure. Similar solution interactions between NH protons and oxygen acac groups have been established for the palladium complex $[Pd(acac)(Et_2NH)_2](acac).^{24}$

Complexes with 2,2'-Bibenzimidazole. Following a comparable synthetic strategy we have studied the chemistry of the 2,2'-bibenzimidazole (H_2Bbzim) ligand with $(\eta^6$ -p-cymene)Ru units, the results being considerably different. Thus, the addition of an equimolar amount of H₂Bbzim over a suspension of [{ $(\eta^6-p-cy$ mene)RuCl $_2(\mu$ -Cl $_2$] in acetone afforded a mixture of the mononuclear complex $[(\eta^6-p-cymene)Ru(H_2Bbzim)Cl]Cl$, the binuclear derivative $[{(\eta^6-p-cymene)RuCl}_2(\mu-$ Bbzim)] where the dianionic ligand Bbzim²⁻ acts as a bis-bidentate chelate, and unreacted starting dimer. When an excess of H₂Bbzim was used the yield of $[(\eta^6$ p-cymene)Ru(H₂Bbzim)Cl]Cl increased, but we have not been able to prepare this compound pure nor to purify it efficiently from the reaction mixture. These results can be rationalized in terms of greater acid dissociation constants for coordinated H₂Bbzim than for H₂Bim. In fact, Haga has measured these constants for the $[(bipyridine)_2Ru(azole)]^{2+}$ (azole = H₂Bbzim or H₂Bim)



complexes and found that the constant corresponding to the bibenzimidazole system is about 2 orders of magnitude greater.^{4a,b}

The synthesis of bi- or polynuclear bibenzimidazolate complexes was attempted by alternative routes. The reaction of the acetylacetonate complex [(η^6 -p-cymene)-Ru(acac)Cl]^{10f} with H₂Bbzim led to the neutral complex $[(\eta^{6}\text{-}p\text{-}cymene)Ru(HBbzim)Cl]$ (9). Similarly, the acetylacetonate group can be removed from the cationic compound $[(\eta^{6}-p-\text{cymene})\text{Ru}(\text{acac})(\text{PPh}_{3})]\text{BF}_{4}^{10f}$ by reaction with H₂Bbzim yielding [$(\eta^6$ -p-cymene)Ru(HBbzim)- (PPh_3)]BF₄ (10). Long reaction times, 24 h and 7 days, respectively, were necessary to achieve greater than 70% yields, most probably due to the coordinative saturation of the parent ruthenium(II) complexes. An alternative route to 10 was the reaction of 9 with stoichiometric amounts of AgBF₄ and PPh₃. Both compounds have been characterized by elemental analyses and spectroscopic methods (see Experimental Section). Their IR spectra, in the solid state, showed a strong and very broad absorption in the 3200-2200 cm^{-1} region, a band at 290 cm^{-1} attributable to ν (RuCl) for 9, and the characteristic bands of the tetrafluoroborate anion and of the PPh_3 ligand for 10. These observations indicated the presence of a remaining N-H bond in the coordinated heterocycle and suggested a strong N-H-X association in the solid state. The ¹H NMR data were as expected for an endobidentate coordination of the HBbzim⁻ anion and, interestingly, showed only one type of p-cymene ligand in the molecule. These spectroscopic observations could be accounted for by assuming that, at room temperature, a prototropic exchange of the remaining NH proton between the two uncoordinated nitrogens is operating fast in the ¹H NMR time-scale. Related prototropic processes have been recently described for pyrazolate $ligands.^{10d,f,k}$

Furthermore, this NH group is capable of ulterior coordination rendering polynuclear compounds. Thus, **9** reacted with $[Rh(acac)L_2]$ (L₂ = COD, NBD,²⁵ (CO)₂) in methanol with displacement of the acetylacetonate group and formation of the corresponding complexes $[(\eta^{6}-p\text{-cymene})ClRu(\mu\text{-Bbzim})RhL_{2}]_{n} (L_{2} = COD (11),$ NBD (12), (CO)₂ (13)). The related RuIr complex [$(\eta^6$ p-cymene)ClRu(μ -Bbzim)Ir(COD)]_n (14) was similarly prepared but in acetone because in methanol a mixture of the homobinuclear complexes [$\{(\eta^6-p-cymene)ClRu\}_2$ - $(\mu$ -Bbzim)] and $[Ir_2(\mu$ -Bbzim)(COD)₂] was obtained. Again, in this process, the acidic character of coordinated HBbzim⁻ groups was manifested. Thus, they displaced acac coordinated anions while related HBim⁻ compounds did not. Carbonylation of 11 readily gave 13.



Figure 4. Proposed structure for complexes 11 and 14.

The IR spectra of these complexes showed the characteristic bands of the bibenzimidazolate anion^{3,13} and one band in the $285-300 \text{ cm}^{-1}$ region assignable to v-(RuCl).¹² The mass spectra of **11** and **14** showed molecular ions at m/z 714 and 804, respectively, and the peaks corresponding to the loss of the chlorine ligand from them. These values pointed to a binuclear formulation for these complexes (n = 1). The ¹H NMR data (see Experimental Section) showed one type of *p*-cymene and 2,2'-bibenzimidazolate ligand in a 1/1 ratio. From these data, we propose for complexes 11 and 14 a binuclear structure with the Bbzim²⁻ anion acting as a tetradentate bis-chelate bridging ligand between two $(\eta^6$ -p-cymene)ClRu fragments (Figure 4).

However, the IR spectrum of 13 in a dichloromethane solution showed three strong absorptions due to $\nu(CO)$ at 2090, 2070, and 2020 cm^{-1} , characteristic of four carbonyl groups coordinated to two adjacent metals.^{1c,10b,22} Its mass spectrum showed peaks at m/z 1324 and 1289 that we assign to the molecular ion and to the loss of one chlorine ligand from a tetranuclear structure (n =2). The spectroscopic data of the bibenzimidazolate complex 13, closely resembled those previously found for the C_{2v} biimidazolate isomers **6a** or **6c**, but no isomerization was detected in this case. According to all these spectroscopic data, we propose a tetranuclear C_{2v} structure of the **6a** or **6c** type for complex **13**.

The ¹H NMR spectrum of **12** (Experimental Section) showed the expected signals for one *p*-cymene ligand that has lost its plane of symmetry,^{10j,26} eight signals for eight inequivalent CH bibenzimidazolate protons and eight resonances for the protons of the NBD (C_7H_8) ligand.²⁷ These experimental data exclude structural assignment of 12 according to related heteronuclear compounds previously described in this paper: a binuclear geometry with a tetradentate azolate anion (complexes 11 and 14) or a tetranuclear structure with C_{2v} or C_s symmetries (compounds 6 and 13). Thus, in order to ascertain the molecular structure of complex 12, an X-ray diffraction study was undertaken.

Molecular Structure of $[(\eta^6-p-Cymene)ClRu(\mu-$ Bbzim)Rh(NBD)]2.2CH2Cl2 (12.2CH2Cl2). Figure 5 shows a view of the complex, together with the atom

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⁽²⁷⁾ Solutions of 12 spontaneously evolved to the homobinuclear species $[{\eta^6-p-cymene}ClRu}_2(\mu-Bbzim)]$ and $[Rh_2(\mu-Bbzim)(NBD)_2]$ which precludes to take more time demanding spectroscopic measurements. An authentic sample of the later was prepared by reacting H_2Bbzim with [Rh(acac)(NBD)] in methanol.



Figure 5. ORTEP view of the molecule $[(\eta^6-p-\text{cymene})ClRu(\mu-Bbzim)Rh(NBD)]_2$ (12) showing the atom-labeling scheme.

Table 3.	Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Rh and Ru Atoms) and Equivalent Isotropic Displacement Coefficients
	$(Å^2 \times 10^4)$ for $[(\eta^6-p-Cymene)ClRu(\mu-Bbzim)Rh(NBD)]_2 CH_2Cl_2$

atom	x/a	x/b	y/z	$U_{ m eq}{}^{\prime\prime}$	atom	x/a	x/b	y/z	$U_{eq}{}^a$
Rh(1)	58069(3)	18277(3)	38249(2)	272(1)	C(30)	6076(4)	714(4)	16(3)	416(21)
Rh(2)	56191(3)	40250(3)	28460(2)	276(1)	C(31)	7004(4)	-104(4)	-41(3)	423(21)
Ru(1)	72052(3)	9674(3)	6293(2)	316(1)	C(32)	8043(5)	58(4)	-326(3)	458(22)
Ru(2)	11003(3)	36271(3)	35130(2)	312(1)	C(33)	8130(4)	1055(4)	-545(3)	437(21)
Cl(1)	8480(1)	-79(1)	1423(1)	509(5)	C(34)	7188(4)	1864(4)	-462(3)	396(20)
Cl(2)	1310(1)	5157(1)	3815(1)	530(6)	C(35)	5146(4)	2613(4)	-130(3)	471(22)
N(1)	6083(3)	1021(3)	1627(2)	320(15)	C(36)	4160(5)	2399(5)	432(4)	596(26)
N(2)	7363(3)	2146(3)	1114(2)	287(14)	C(37)	4855(5)	3049(5)	-921(4)	675(29)
N(3)	5466(3)	1569(3)	2787(2)	272(13)	C(38)	9025(5)	-816(4)	-359(3)	575(25)
N(4)	6777(3)	3208(3)	2016(2)	269(13)	C(39)	596(4)	2434(4)	3149(3)	399(20)
N(5)	4130(3)	2389(3)	4238(2)	285(14)	C(40)	287(4)	3345(4)	2671(3)	415(20)
N(6)	4307(3)	3631(3)	2564(2)	279(13)	C(41)	-341(4)	4242(4)	2961(3)	435(21)
N(7)	2334(3)	2928(3)	4145(2)	320(14)	C(42)	-693(4)	4261(4)	3756(3)	458(22)
N(8)	2519(3)	3658(3)	2740(2)	328(14)	C(43)	-393(4)	3373(4)	4245(3)	424(21)
C (1)	6042(3)	1693(3)	2091(3)	285(16)	C(44)	263(4)	2472(4)	3949(3)	416(20)
C(2)	5455(4)	416(3)	2052(3)	335(18)	C(45)	1240(5)	1474(5)	2833(3)	560(25)
C(3)	5192(4)	-417(4)	1889(3)	424(21)	C(46)	2125(5)	1600(5)	2152(4)	697(30)
C(4)	4508(5)	-858(4)	2441(3)	505(24)	C(47)	482(6)	958(7)	2619(5)	1117(48)
C(5)	4084(4)	-489(4)	3139(3)	452(22)	C(48)	-1309(5)	5213(5)	4071(4)	664(28)
C(6)	4357(4)	317(4)	3316(3)	359(18)	C(49)	6357(4)	970(4)	4807(3)	343(18)
C(7)	5056(3)	767(3)	2766(3)	300(17)	C(50)	6432(4)	1941(4)	4787(3)	340(18)
C(8)	6687(3)	2395(3)	1760(2)	260(16)	C(51)	7592(4)	1949(4)	4371(3)	411(20)
C(9)	8001(3)	2815(3)	945(2)	279(16)	C(52)	7501(4)	1819(4)	3567(3)	390(19)
C(10)	8900(3)	2865(3)	363(3)	321(17)	C(53)	7407(4)	851(4)	3607(3)	389(19)
C(11)	9438(4)	3576(4)	371(3)	374(18)	C(54)	7457(4)	375(4)	4431(3)	394(19)
C(12)	9097(4)	4225(4)	924(3)	370(19)	C(55)	8224(4)	879(4)	4648(3)	464(21)
C(13)	8214(4)	4183(4)	1491(3)	332(18)	C(56)	4933(4)	4486(4)	3945(3)	374(19)
C(14)	7656(3)	3469(3)	1506(2)	285(16)	C(57)	4468(4)	5213(4)	3401(3)	420(20)
C(15)	3372(3)	2856(3)	3801(2)	277(16)	C(58)	5166(4)	5965(4)	3183(3)	456(21)
C(16)	3516(3)	2182(3)	4951(3)	288(16)	C(59)	6199(4)	5309(4)	2754(3)	381(19)
C(17)	3826(4)	1773(4)	5660(3)	357(18)	C(60)	6687(4)	4573(4)	3300(3)	342(18)
C(18)	3015(4)	1677(4)	6277(3)	392(19)	C(61)	5939(4)	4783(4)	4066(3)	395(20)
C(19)	1913(4)	1982(4)	6210(3)	412(20)	C(62)	5533(5)	5928(4)	3944(3)	505(23)
C(20)	1590(4)	2412(4)	5515(3)	373(18)	C(1S)	8324(6)	7421(5)	1863(4)	768(33)
C(21)	2404(4)	2503(3)	4893(2)	309(17)	Cl(3)	9737(2)	6882(2)	1785(1)	1002(11)
C(22)	3468(3)	3355(3)	3028(3)	282(16)	Cl(4)	7785(2)	7080(2)	1181(1)	954(10)
C(23)	3882(4)	4135(3)	1918(3)	290(16)	$C(2Sa)^b$	1416(8)	7477(10)	3069(5)	518(32)
C(24)	4378(4)	4579(4)	1248(3)	362(18)	Cl(5a) ^b	2458(5)	7173(6)	2326(3)	1189(22)
C(25)	3751(4)	5044(4)	697(3)	421(20)	$Cl(6a)^b$	2018(6)	7639(5)	3808(3)	1247(25)
C(26)	2642(4)	5079(4)	815(3)	468(21)	$C(2Sb)^b$	1052(10)	7977(18)	2886(7)	1269(74)
C(27)	2131(4)	4648(4)	1477(3)	437(20)	Cl(5b) ^b	1166(5)	8204(5)	3778(3)	1299(25)
C(28)	2774(4)	4158(4)	2034(3)	333(17)	Cl(6b) ^b	2341(5)	7788(6)	2371(3)	1351(23)
C(29)	6139(4)	1723(4)	-198(3)	409(20)	· ·				. ,

^{*a*} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{*b*} These groups of atoms, involved in disorder, were refined with isotropic displacement parameters. The refined occupancy factors were 0.485(7) for a-labeled atoms and 0.515(7) for b-labeled ones.

Table 4. Selected Bond Distances (Å) and Angles (deg) for the Complex [(n⁶-p-Cymene)ClRu(*u*-Bbzim)Rh(NBD)]₂·2CH₂Cl₂^a

			12012
Ru(1) - N(1)	2.069(3)	Ru(2) - N(7)	2.074(4)
Ru(1) - N(2)	2.080(4)	Ru(2) - N(8)	2.077(3)
Ru(1)-Cl(1)	2.411(2)	Ru(2)-Cl(2)	2.406(2)
Ru(1) - G(1)	1.669(6)	Ru(2)-G(2)	1.669(6)
Ru(1) - C(29)	2.177(5)	Ru(2) - C(39)	2.205(7)
Ru(1) - C(30)	2.151(6)	Ru(1) - C(40)	2.171(6)
Ru(1) - C(31)	2.191(6)	Ru(2) - C(41)	2.190(5)
Ru(1) - C(32)	2.236(5)	Ru(2) - C(42)	2.222(5)
Ru(1) - C(33)	2.214(5)	Ru(1) - C(43)	2.194(5)
Ru(1) - C(34)	2.147(5)	Ru(2) - C(44)	2.155(6)
Rh(1)- $Rh(2)$	3.2448(6)		
Rh(1) - N(3)	2.128(4)	Rh(2) - N(4)	2.124(3)
Rh(1) - N(5)	2.116(3)	Rh(2)-N(6)	2.115(4)
Rh(1)-G(3)	1.988(5)	Rh(2)-G(5)	2.019(5)
Rh(1)-G(4)	2.030(4)	Rh(2)-G(6)	1.997(6)
Rh(1) - C(49)	2.097(5)	Rh(2) - C(56)	2.133(5)
Rh(1) - C(50)	2.114(5)	Rh(2)~C(57)	2.135(5)
Rh(1) - C(52)	2.151(5)	Rh(2) - C(59)	2.113(6)
Rh(1) - C(53)	2.139(4)	Rh(2) - C(60)	2.121(6)
N(1) - Ru(1) - N(2)	75.6(2)	N(7) - Ru(2) - N(8)	76.0(2)
N(1) - Ru(1) - Cl(1)	84.8(1)	N(7) - Ru(2) - Cl(2)	84.8(1)
N(2)-Ru(1)-Cl(1)	85.2(1)	N(8) - Ru(2) - Cl(2)	83.4(1)
N(1)-Ru(1)-G(1)	131.4(2)	N(7) - Ru(2) - G(2)	132.5(2)
N(2) - Ru(1) - G(1)	131.1(2)	N(8) - Ru(2) - G(2)	132.8(2)
Cl(1) - Ru(1) - G(1)	129.8(2)	Cl(2) - Ru(2) - G(2)	128.2(2)
N(3)-Rh(1)-N(5)	91.6(2)	N(4) - Rh(2) - N(6)	92.9(2)
N(3) - Rh(1) - G(4)	97.5(2)	N(4) - Rh(2) - G(6)	100.7(2)
G(3) - Rh(1) - G(4)	71.1(2)	G(5) - Rh(2) - G(6)	71.7(2)
N(5)-Rh(1)-G(3)	100.5(2)	N(6) - Rh(2) - G(5)	95.3(2)

^{*a*} G1 and G2 represent the centroids of the Ru(1) and Ru(2) *p*-cymene rings, respectively, and G3, G4, G5, and G6 the midpoints of the olefinic bonds C49-C50, C52-C53, C56-C57, and C59-C60, respectively.

labeling used. Atomic positional parameters and selected bond lengths and angles are presented in Tables 3 and 4, respectively. The molecule consists of two independent (η^6 -p-cymene)ClRu(μ -Bbzim)Rh(NBD) units related to each other by a pseudo C_2 axis which accounts for the observed ¹H NMR data. Each Bbzim²⁻ anion coordinates to the metals in an unsymmetrical quadridentate manner through the four nitrogen atoms of the two imidazolate rings, chelating to one Ru atom through two nitrogens and bonding in a unidentate manner to the two rhodiums through the other two nitrogens. The ruthenium atoms complete their pseudooctahedral coordination by an η^6 -p-cymene ligand and a chloride anion. The chelate N-Ru-N angles (N(1)-Ru(1)-N(2))75.6(2), N(7)-Ru(2)-N(8) $76.0(2)^{\circ}$) compare well with those found in the related tetranuclear biimidazolate complex $[(\eta^5-C_5Me_5){P(OEt)_3}Rh(\mu-Bim)Rh(NBD)]_2[ClO_4]_2$ in which the Ru(III) atom also displays a pseudooctahedral coordination,^{10c} and the Bim²⁻ anion coordinates in a similar way to $Bbzim^{2-}$ in 12. However, these values are slightly lower than the N-Ru-N bond angle found in the RuIr complex $[(\eta^6-p-\text{cymene})(\text{PPh}_3)\text{Ru}(\mu Bbzim)Ir(CO)_2]_2[BF_4]_2$ (19) in which, although the Ru atom is also pseudooctahedral, the Bbzim²⁻ anion chelates both metals (see below).

As a consequence of the asymmetry of coordination about the metal, both *p*-cymene rings show significantly different Ru–C bond distances ranging from 2.147(5) to 2.236(5) Å. The two distances of the Ru metals to the least-squares plane through the six-membered carbocyclic ring are 1.669(4) Å comparable to those found in related *p*-cymene ruthenium complexes with azolatetype ligands.^{10f,i,28} The Ru–N bond distances (mean value 2.075(2) Å) are significantly shorter than those found in the related bibenzimidazolate complex **19** (mean value 2.163(2) Å) (see below) and in the binuclear biimidazolate complex $[(Ph_3P)_2(CO)HRu(\mu-Bim)Rh-(COD)]$, 2.283(5) and 2.180(5) Å.^{8a} The Ru-Cl distances 2.411(2) and 2.406(2) Å are in the range of usual Ru-(II)-Cl bond distances.²⁹

The coordination of the rhodiums, besides the two N atoms from the two Bbzim²⁻ ligands, involves a NBD molecule interacting through the two double bonds. The geometry around the rhodiums is approximately square planar with the plane defined by the two N atoms and the midpoints of the two olefinic bonds of the norborna-2,5-diene ligand. The rhodium atoms are out of these planes by $\pm 0.1803(5)$ (Rh(1)) ad $\pm 0.1599(5)$ (Rh(2)) A. These slight deviations of the metals from square planar coordination toward the other metal suggest some interaction between them, in spite of the relatively long Rh(1)-Rh(2) separation (3.2448(6) Å). The Rh-N bond distances (mean value 2.121(2) Å) are comparable to those found in related biimidazolate complexes in which the Bim²⁻ anion displays the same type of coordination.^{10c} The two C₇H₄N₂ moieties of each Bbzim²⁻ ligand are essentially planar, making dihedral angles of 14.8(1)° and $14.6(1)^{\circ}$ with each other. This twist is probably due to the ligand behaving as both chelating and bridging. Consequenty, in Bim²⁻ and Bbzim²⁻ compounds with this type of coordination dihedral angles ranging from 4.0 to 17.6° have been found.^{1c,9,10a,c}

The cationic complex 10 underwent reaction with the acetylacetonates $[M(acac)L_2]$ (M = Rh; L₂ = COD, NBD, $(CO)_2$. M = Ir; L₂ = COD) yielding the cationic polynuclear complexes $[(\eta^{6}-p\text{-cymene})(PPh_{3})Ru(\mu\text{-Bbzim})$ - $ML_2]_n[BF_4]_n (M = Rh; L_2 = COD (15), NBD (16), (CO)_2$ (17). $M = Ir; L_2 = COD$ (18)). Carbonylation of 18 afforded $[(\eta^6-p-cymene)(PPh_3)Ru(\mu-Bbzim)Ir(CO)_2]_n[BF_4]_n$ (19) and, analogously, complex 17 could be obtained by carbonylation of complexes 15 or 16 (Scheme 2). Compounds 15-19 have been characterized by elemental analyses, IR, and ¹H and ³¹P{¹H} NMR spectroscopies (see Experimental Section). All these complexes showed, in the IR spectra bands assignable to the Bbzim²⁻ ligand, BF_4^- anion under T_d symmetry and the triphenylphosphine group. The FAB mass spectra for complexes 15, 16, and 18 showed peaks assignable to the dinuclear $[(\eta^6-p-\text{cymene})(\text{PPh}_3)\text{Ru}(\mu-\text{Bbzim})M(\text{diole}$ fin)]⁺ fragment and their NMR data were consistent with a binuclear structure (n = 1). Analogously, solution IR spectra for the carbonylated compounds 17 and 19 exhibited two ν (CO) bands in the 2080-2000 cm⁻¹ region characteristic of cis-dicarbonyl species, suggesting a binuclear structure. Interestingly, solid 19 is violet but it gives yellow solutions. This behavior could be indicative of important structural differences between the solid state and solution, and in order to unequivocally know the crystal structure of 19, an X-ray diffraction study was undertaken.

Molecular Structure of $[(\eta^6\text{-}p\text{-}Cymene)(PPh_3)Ru-(\mu\text{-}Bbzim)Ir(CO)_2]BF_4$ (19). A view of the complex cation is shown in Figure 6 and atomic positional parameters and selected bond lengths and angles are presented in Tables 5 and 6, respectively. The cation is binuclear with a tetradentate bridging Bbzim ligand. In the solid state, a clear intermetallic interaction is established between two adjacent, symmetry related

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Figure 6. ORTEP view of two $[(\eta^6-p\text{-cymene})(PPh_3)Ru(\mu\text{-Bbzim})Ir(CO)_2]^+$ cations showing the atom-labeling scheme and the intermetallic Ir-Ir interaction.

iridium centers (Ir-Ir 3.0808(5) Å). This distance is longer than those reported among the very scarcely represented unsopported Ir-Ir bonds (range 2.717– 2.891 Å).³⁰ It has been stated that the nonbridged Ir-Ir single bond (2.857(1) Å) present in the $[Ir_8(CO)_{22}]^{2-}$ anion is readily cleaved by a variety of reagents.^{30b} Probably, in solution, the weaker metal-metal interaction present in **19** is broken and the resulting binuclear species accounted for the observed IR spectral data.

The bibenzimidazolate dianion coordinates as an essentially planar ligand in a symmetrical tetradentate manner through its four nitrogens to the ruthenium and iridium atoms. An η^{6} -p-cymene ring, with Ru-C bond distances ranging from 2.172(8) to 2.264(8) Å, and the phosphorus atom of the PPh₃ ligand complete the pseudooctahedral coordination of the ruthenium atom.

The two $C_7H_4N_2$ moieties of the Bbzim²⁻ ligand make a dihedral angle of 9.2(1)° with each other. The chelate N(2)-Ru(1)-N(4) angle (79.8(2)°) compares well with that found in the related binuclear biimidazolate complex [(PPh₃)₂(CO)HRu(μ -Bim)Rh(COD)], 79.2(2)°, in which the Ru atom displays a distorted-octahedral geometry,^{8a} and the Bim²⁻ anion coordinates in the same way than Bbzim²⁻ does in **19**. However, the Ru-N bond distances 2.150(6) and 2.175(6) Å for **19** are significantly shorter than those found for the RuRh complex above mentioned, 2.283(5) and 2.180(5) Å.^{8a}

The iridium atom is four-coordinated, having a squareplanar geometry being bonded to two nitrogens of the Bbzim²⁻ ligand and two carbonyl groups. The chelate N(1)-Ir-N(3) angle (81.0(2)°) falls in the range found for 2,2'-biimidazolate complexes.^{1b,c,8a,10a,c,31} The Ir-N



Table 5. Atomic Coordinates $(\times 10^4; \times 10^5$ for Ir and Ru Atoms) and Equivalent Isotropic Displacement Coefficients $(\mathring{A}^2 \times 10^3; \times 10^4$ for Ir, Ru, and P atoms) for $[(\eta^6-p-Cymene)(PPh_3)Ru(\mu-Bbzim)Ir(CO)_2]BF_4$

		•		· · · ·
atom	x/a	y/b	z/c	$U_{eq}{}^{a}$
ir(1)	-6553(2)	51156(2)	41920(2)	387(1)
Ru(1)	31836(1)	43818(3)	26951(3)	312(2)
P	1980(2)	4682(1)	1562(1)	351(7)
N(1)	83(5)	4268(3)	3737(3)	37(2)
N(2)	1672(5)	3965(3)	3135(3)	33(2)
N(3)	910(5)	5529(3)	3862(3)	35(2)
N(4)	2487(4)	5238(3)	3235(3)	31(2)
$\mathbf{O}(1)$	-1550(5)	6373(3)	4755(4)	51(2) 64(2)
O(2)	-2833(5)	4416(3)	4471(4)	70(3)
C(1)	-1200(7)	5808(5)	4536(5)	70(3) 48(3)
C(1)	-1000(8)	4601(5)	4330(3)	40(3)
C(2)	1105(6)	4091(3)	2499(4)	31(3)
C(3)	-52(6)	3620(3)	2524(4)	33(3)
C(4)	-32(0)	3125(4)	3524(4)	59(3)
C(3)	-939(7)	3163(4)	2214(6)	50(5)
C(0)	-870(8)	2370(3)	3314(0)	08(4)
C(7)	90(8)	2380(4)	2932(3)	50(3)
C(8)	1001(7)	2800(4)	2849(5)	46(3)
C(9)	919(6)	3424(3)	3140(4)	35(3)
C(10)	1528(6)	5066(3)	3555(4)	34(3)
C(11)	1530(6)	6097(4)	3756(4)	35(3)
C(12)	1335(7)	6730(4)	3960(4)	48(3)
C(13)	2123(8)	7189(4)	3761(5)	57(4)
C(14)	3127(7)	7021(4)	3399(5)	55(3)
C(15)	3339(7)	6388(4)	3207(4)	43(3)
C (16)	2527(6)	5915(3)	3380(4)	32(3)
C(17)	4377(6)	3848(4)	3598(5)	38(3)
C(18)	4066(6)	3457(4)	2923(5)	43(3)
C(19)	4280(6)	3654(4)	2180(5)	47(3)
C(20)	4779(6)	4268(4)	2042(5)	46(3)
C(21)	5016(6)	4682(4)	2695(5)	44(3)
C(22)	4829(6)	4465(4)	3453(5)	39(3)
C(23)	4165(7)	3595(4)	4385(5)	51(3)
C(24)	5007(8)	3027(5)	4621(6)	73(4)
C(25)	4247(7)	4113(5)	5012(5)	66(4)
C(26)	5075(7)	4457(5)	1240(5)	71(4)
C(27)	2289(7)	5466(4)	1129(4)	40(3)
C(28)	1488(7)	5750(4)	562(5)	51(3)
C(29)	1764(8)	6344(4)	241(5)	59(4)
C(30)	2802(8)	6652(4)	452(5)	61(4)
C(31)	3558(9)	6385(4)	1008(5)	67(4)
C(32)	3315(7)	5796(4)	1360(5)	53(3)
C(33)	2020(6)	4080(4)	786(5)	42(3)
C(34)	2217(8)	4246(5)	21(5)	62(4)
C(35)	2304(10)	3759(6)	-512(5)	92(5)
C(36)	2166(11)	3121(6)	-327(7)	100(6)
C(37)	1971(9)	2954(5)	424(7)	85(5)
C(38)	1918(7)	3432(4)	964(6)	58(4)
C(39)	443(6)	4767(4)	1724(4)	37(3)
C(40)	-320(7)	4243(4)	1624(5)	51(3)
C(41)	-1448(7)	4319(5)	1814(6)	63(4)
C(42)	-1812(8)	4892(6)	2102(6)	73(4)
C(43)	-1061(7)	5413(5)	2195(5)	58(3)
C(44)	73(6)	5350(4)	2010(4)	46(3)
B	3505(9)	1655(6)	2233(8)	64(5)
F(1)	2345(6)	1688(3)	2028(5)	125(4)
F(2)	3832(6)	1050(3)	2131(6)	163(5)
F(3)	4048(6)	2076(3)	1816(5)	128(4)
F(4)	3623(8)	1844(5)	2964(4)	167(5)
• (• /	2022(0)	10 19(0)		101(0)

"Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

bond distances (2.118(6) and 2.126(6) Å) are of the same order as those found in the Ir(III) complex $[(\eta^5-C_5-Me_5)Ir(H_2Bim)Cl]Cl,^{32}$ although slightly longer bonds lengths might be anticipated for Ir(I)-N due to the larger Ir(I) ionic radius. The geometry about the *cis*-Ir(CO)₂ moiety closely resembles that found in related *cis*-dicarbonyl azolate iridium complexes.^{10i,33}

Catalytic Hydrogenation. The homogeneous catalytic activity of the heteronuclear complexes 11, 14, and 15-19 for the hydrogenation of cyclohexene with molecular hydrogen was explored. Preliminary hydrogenation runs were performed in methanol at different H₂

Table 6. Selected Bond Distances (Å) and Angles (deg) for the Complex $[(\eta^6-p-\text{Cymene})(\text{PPh}_3)\text{Ru}(\mu-\text{Bbzim})\text{Ir}(\text{CO})_2]\text{BF}_4^a$

		•	
Ir(1)-Ir(1')	3.081(1)	Ir(1) - N(1)	2.118(6)
Ir(1) - N(3)	2.126(6)	Ir(1) - C(1)	1.841(9)
Ir(1) - C(2)	1.836(9)	O(1) - C(1)	1.137(11)
O(2) - C(2)	1.144(11)	Ru(1) - N(4)	2.175(6)
Ru(1) - N(2)	2.150(6)	Ru(1)-P	2.371(2)
Ru(1) - C(17)	2.263(7)	Ru(1) - C(18)	2.172(8)
Ru(1) - C(19)	2.198(8)	Ru(1) - C(20)	2.264(8)
Ru(1) - C(21)	2.210(7)	Ru(1) - C(22)	2.215(7)
Ru(1)-G	1.716(7)		
N(1) - Ir(1) - N(3)	81.0(2)	N(3) - Ir(1) - C(1)	93 8(3)
N(1) - Ir(1) - C(2)	93.0(3)	C(1) - Ir(1) - C(2)	92.1(4)
P - Ru(1) - N(2)	87.6(2)	P - Ru(1) - N(4)	86.0(1)
N(2) - Ru(1) - N(4)	79.8(2)	P-Ru(1)-G	131.7(3)
N(2) - Ru(1) - G	125.7(3)	N(4) - Ru(1) - G	129.3(3)
N(1) - Ir(1) - Ir(1')	91.5(2)	N(3) - Ir(1) - Ir(1')	86.7(1)
C(1) - Ir(1) - Ir(1')	89.9(2)	C(2) - Ir(1) - Ir(1')	97.3(3)

" G represents the centroid of the p-cymene ring.

Table 7. Catalytic Hydrogenation of Cyclohexene^a

0%

catalyst	P(H ₂) (atm)	Т (К)	time (min)	cyclo- hexane
[$(\eta^{b}-p-\text{cymene})ClRu(\mu-Bbzim)Rh(COD)$] (11)	2	313	105	98.0
	2.5	293	105	36.2
	3	313	90	100.0
	3	323	25	100.0
$[(\eta^{6}-p\text{-cymene})ClRu(\mu\text{-Bbzim})lr(COD)]$ (14)	2	293	90	37.4
	2	313	90	100.0
	3	313	30	70.0
$[(\eta^{6}\text{-}p\text{-}cymene)(PPh_{3})Ru(\mu\text{-}Bbzim)\text{-}Rh(COD)]BF_{4} (15)$	2	293	75	14.9
$[(\eta^{6}\text{-}p\text{-}cymene)(PPh_{3})Ru(\mu\text{-}Bbzim)\text{-}Rh(NBD)]BF_{4}(16)$	2.6	293	120	5.1
	3	313	90	19.0
	3	323	120	62.3
$[(\eta^{6}-p-cymene)(PPh_{3})Ru(\mu-Bbzim)-Rh(CO)_{2}]BF_{4} (17)$	2.5	293	105	8.5
$[(\eta^{6}\text{-}p\text{-}cymene)(PPh_{3})Ru(\mu\text{-}Bbzim)-Ir(COD)]BF_{4}(18)$	2	293	90	7.6
	3	313	60	8.0
	3	323	120	43.0
$[(\eta^6-p\text{-}cymene)(PPh_3)Ru(\mu\text{-}Bbzim)-Ir(CO)_2]BF_4$ (19)	2	293	2400	67.9

" [catalyst] = 5.6×10^{-4} M; [cyclohexene]/[catalyst] = 100; preactivation period: 30 min.

pressure and temperature and the data are collected in Table 7. No reduction of cyclohexene was observed either at atmospheric pressure, or under a N_2 atmosphere, the last fact showing that hydrogen transfer from methanol does not represent an important mechanistic pathway in the processes. According to the data of Table 7, the neutral compounds 11 and 14 are more active than the cationic complexes 15-19, the best results being obtained with complex 14. We then studied the catalytic activity of 14 in some detail.

The reaction shows an induction period that disappears by treating the solution of 14 with hydrogen during 30 min at 313 K. The reaction profiles do not change significantly when this period is increased from 30 to 90 min. Figure 7 summarizes the course of a typical reaction catalyzed by hydrogen-pretreated 14 at different hydrogen pressures (see Experimental Section).

The reaction was followed by measuring the cyclohexane formed as a function of time. Although no deactivation was observed up to ca. 70-80% conversion, the data correspond to cyclohexane percentages below 30% in order to perform a kinetic analysis based on the initial rates method. Values for initial rates under different reaction conditions are collected in Table 8. The results of varying the concentration of the substrate while all the other concentrations were kept constant showed that the rate of the catalytic process is independent of the substrate concentration. However, plots of the $\log(-d[cyclohexene]/dt)$ versus $\log[14]$ and $\log[H_2]$ yielded straight lines of slope 0.95 and 1.96, respectively, showing that the reduction of cyclohexene is first-order in catalyst concentration and second-order in hydrogen pressure. The catalytic rate law therefore is

$$-d[cyclohexene]/dt = k_{cat}[14][H_2]^2$$

The value of the catalytic rate constant at 313 K was calculated from this rate law as 2.3 \pm 0.2 s^{-1} M^{-2}.

We also proved that in the presence of variable concentrations of chloride ions the hydrogenation rate does not change significantly. The effect of temperature on the rate constant was studied in the range 313–333 K for concentrations of cyclohexene at 5.6×10^{-2} M, catalyst at 5.6×10^{-4} M, and at 2 atm of hydrogen pressure. Within the range of temperatures used, the variation of the hydrogen solubility in methanol is negligible.³⁴ An Arrhenius plot allowed us to evaluate the activation energy E_a , 59.8 kJ/mol, and the values of ΔH^{\ddagger} , 58.5 kJ/mol, and ΔS^{\ddagger} , -3.1 eu, and free energy of activation, ΔG^{\ddagger} , 62.7 kJ/mol.

The ¹H NMR spectrum in CD₃OD of a sample of 14 treated with hydrogen (2 atm, 313 K, 30 min) showed the presence of hydrogenated *p*-cymene and COD groups, and no high field NMR signals were detected from 213 K (the limiting solubility temperature) to room temperature. Thus, during the preactivation period the pcymene and COD ligands are hydrogenated and displaced from the coordination sphere of the metals rendering quantitatively unsaturated species without chloride dissociation (RuIr). Most probably, these species reacted with hydrogen leading to the true catalyst (RuIrH₂). The fact that the rate of hydrogenation is independent of the cyclohexene concentration indicates that the olefin is not involved in either the ratedetermining step of the catalytic cycle or in a previous step. Consequently, we propose the reaction with hydrogen as the initial step of the catalytic cycle. From these considerations, the following set of reactions could be operating in the catalytic cycle:

$$RuIr + H_2 \stackrel{K_1}{\longleftarrow} RuIrH_2$$
(1)

$$\operatorname{RuIrH}_{2} + \operatorname{H}_{2} \xrightarrow{k_{2}} \operatorname{RuIrH}_{4}$$
(2)

 $RuIrH_4 + cyclohexene \xrightarrow{fast} RuIrH_2 + cyclohexane$ (3)

If the rate-determining step of the catalytic cycle is reaction 2, the rate of formation of cyclohexane will be

 $d[cyclohexane]/dt = d[RuIrH_4]/dt = k_2[RuIrH_2][H_2]$

$$d[cyclohexane]/dt = k_2 K_1 [14] [H_2]^2$$

in good agreement with the kinetic measurements.

Very recently, one of us has reported that the biimidazolate bridged RuIr compound $[H(CO)(PPh_3)_2Ru(\mu-Bim)Ir(COD)]$ catalyzes the reduction of cyclohexene by molecular hydrogen and, on the basis of kinetic and spectroscopic data, it has been proposed that the reduc-



Figure 7. Hydrogenation of cyclohexene by complex 14 at different pressures: (O) 1.8 atm, (D) 2.0 atm, (\diamond) 2.2 atm, (\times) 2.6 atm, (+) 3.0 atm. [14] = 5.6 \times 10⁻⁴ M. [Cyclohexene] = 5.6 \times 10⁻² M. Solvent: methanol. V_{tot} = 15 mL. T = 313 K.

Table 8. Kinetic Data for the Hydrogenation of Cyclohexene Catalyzed by $[(\eta^6-p\text{-cymene})\text{CIRu}$ $(\mu\text{-Bbzim})\text{Ir}(\text{COD})]$ (14)^a

10 ⁴ [14]	10 ² [cyclohexene]	$10^{3}[H_{2}]$	$P(H_2)$	10 ³ [Cl ⁻]	$10^{7}r_{i}$	Т
(M)	(M)	(M)	(atm)	(M)	$(M s^{-1})$	(K)
5.6	5.6	8.5	2.0		0.98	313
8.3	5.6	8.5	2.0	-	1.39	313
9.7	5.6	8.5	2.0		1.62	313
11.1	5.6	8.5	2.0	-	1.93	313
5.6	5.6	7.7	1.8	_	0.84	313
5.6	5.6	9.4	2.2		1.23	313
5.6	5.6	11.1	2.6		1.70	313
5.6	5.6	12.7	3.0	-	2.25	313
5.6	11.1	8.5	2.0	-	0.81	313
5.6	16.6	8.5	2.0	-	1.01	313
5.6	22.2	8.5	2.0	-	0.85	313
5.6	11.1	12.7	3.0	-	2.19	313
5.6	16.6	12.7	3.0	_	2.41	313
5.6	22.2	12.7	3.0	-	2.02	313
5.6	5.6	8.5	2.0	0.17	0.85	313
5.6	5.6	8.5	2.0	0.33	0.83	313
5.6	5.6	8.5	2.0	0.50	0.94	313
5.6	5.6	8.5	2.0	1.20	0.98	313
5.6	5.6	8.7	2.0		1.43	318
5.6	5.6	9.0	2.0	_	2.28	323
5.6	5.6	9.4	2.0	-	4.49	333
$a r_{i} =$	initial rates.					

tion mainly proceeds via the ruthenium atom, while the same process catalyzed by $[H(CO)(PPh_3)_2Ru(\mu-pz)_2-Ir(TFB)]$ (TFB = tetrafluoro[5.6]bicyclo[2.2.2]octan-2,5,7-triene), under similar conditions, operates through the iridium.^{8b} Interestingly, the results that we now report

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are indicative that in the RuIr complex 14 both metals could be active for the hydrogenation process. In this context, it is therefore of interest to mention that the parent complexes [$(\eta^6$ -p-cymene)RuCl(HBbzim)] and [Ir-(HBbzim)(COD)] are inactive for the hydrogenation of cyclohexene even under forcing conditions.

Conclusions

In this paper we report the preparation and characterization of a family of bi- and tetranuclear RuRh or RuIr complexes with biimidazolate or bibenzimidazolate anions, as bridging ligands. We have isolated and elucidated the structure of the heterobinuclear species $[(\eta^6-p-\text{cymene})\text{ClRu}(\mu-\text{HBim})\text{MClL}_2]$ (3-5) and $[(\eta^6-p$ cymene) $Ru(acac)(\mu-HBim)Rh(COD)$]⁺ (7, 8) that could be considered as intermediates in the synthesis of μ -Bim²⁻ derivatives as has been demonstrated by preparing 6 from 4. Complexes 3-5 showed a dynamic behavior for which we suggest a dissociative mechanism via deprotonation of the NH group and loss of the chlorine atom attached to M. From NMR measurements, we have calculated the energy barrier for this process, 54 kJ mol⁻¹, for complex **3**. We have spectroscopically characterized two isomers of the tetracarbonyl complex 6 and studied an isomerization process between them, unprecedented in the chemistry of biimidazolate complexes. In solution, at room temperature, the Rh-(HBim)(COD) unit of complexes 7 and 8 rotates fast around the Ru-N bond but this process collapses at 223 K. It is remarkable that H_2Bim and H_2Bbzim (free or coordinated) react differently with (p-cymene)Ru compounds. The greater acidity of H₂Bbzim or its derivatives accounts for the observed results. The factors that govern the nuclearity of heteronuclear bi- or bibenziimidazolate compounds remain unclear. Even, in some cases, intermetallic interactions could be responsible for the increase in nuclearity, in the solid state, as has been observed in complex 19. Finally, complexes 11, 14, and 15–19 are active catalysts for the homogeneous hydrogenation of cyclohexene by molecular hydrogen at low pressures. Kinetic and spectroscopic studies conclude that the hydrogenation catalyzed by complex 14 operates through the hydride route and follows the kinetic rate law: $-d[cyclohexene]/dt = k_{cat}[14][H_2]^2$.

Experimental Section

General Considerations. All solvents were dried over appropriate drying agents, distilled under nitrogen, and degassed prior to use. All preparations have been carried out under nitrogen. Cyclohexene (Merck) was passed through an alumina column.

Physical Measurements. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Varian UNITY 300 (299.949 (¹H), 75.4 (¹³C) and 121.421 (³¹P) MHz) and a Varian XL-200 (200.0 (¹H), 50.3 (¹³C) and 80.9 (³¹P) MHz) using SiMe₄ (¹H, ¹³C) and 85% H₃-PO₄ in D₂O (³¹P) as external standards. Chemical shifts are expressed in ppm up field from SiMe₄ (¹H, ¹³C) or H₃PO₄ (³¹P).

Preparation of $[(\eta^{e}-p-Cymene)Ru(H_{2}Bim)Cl]Cl (1)$. To a red suspension of $[\{(\eta^{e}-p-cymene)RuCl\}_{2}(\mu-Cl)_{2}]$ (306.2 mg, 0.50 mmol) in acetone (30 mL) was added H₂Bim (134.2 mg, 1.00 mmol). The resulting yellow solution was stirred during 4 h and then vacuum-concentrated to 5 mL. The slow precipitation of a yellow solid was observed. The precipitation was completed by addition of diethyl ether (20 mL). The solid was collected, washed with diethyl ether, and dried under vacuum. Yield: 94%. $\Lambda_{M}(CH_{3}COCH_{3}) = 2.15 \text{ ohm}^{-1} \text{ cm}^{2} \text{ mol}^{-1}$, $\Lambda_{M}(MeOH) = 87.2 \text{ ohm}^{-1} \text{ cm}^{2} \text{ mol}^{-1}$. IR (Nujol): $\nu(NH)$ 3300-2250 (br); ν(RuCl) 300(m) cm⁻¹. Anal. Calcd for C₁₆H₂₀N₄Cl₂Ru: C, 43.6; H, 4.5; N, 12.7. Found: C, 43.7; H, 4.6; N, 12.85. ¹H NMR (CD₃COCD₃, δ) 13.89 (2H, br s, NH), 7.41, 7.15 (2H each, s, CH's of H₂bim), 5.64, 5.46 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 6.1$ Hz), 2.69 (1H, sp, ³J_{HH} = 6.8 Hz, CH of ⁱPr), 2.15 (3H, s, Me), 1.08 (6H, d, Me of ⁱPr). ¹³C NMR (CD₃COCD₃, δ) 138.8 (t, $J_{CH} = 8.0$ Hz, $C_{2/2}$ of H₂-Bim), 130.3 (ddd, ¹J_{CH} = 194.7 Hz, ²J_{CH} = 10.8 Hz, ²J_{CH} = 4.8 Hz, C_{4/4'} of H₂Bim), 119.7 (dd, ¹J_{CH} = 197.2 Hz, ²J_{CH} = 13.5 Hz, C_{5/5'} of H₂Bim), 103.0, 100.0 (s, C_{1/4} of *p*-cymene), 82.9 (d, ¹J_{CH} = 173.1 Hz, C_{2/6} or C_{3/5} of *p*-cymene), 81.2 (d, ¹J_{CH} = 167.5 Hz, C_{3/5} or C_{2/6} of *p*-cymene), 31.0 (d, ¹J_{CH} = 130.7 Hz, C₇ of *p*-cymene), 22.1 (q, ¹J_{CH} = 127.9 Hz, C_{8/9} of *p*-cymene), 18.9 (q, ¹J_{CH} = 130.1 Hz, C₁₀ of *p*-cymene). FAB MS *m/z* (*m*-nitrobenzyl alcohol) 405 (M⁺, 30%), 369 (M⁺ - Cl, 100%).

Preparation of $[(\eta^{6}-p-Cymene)Ru(H_{2}Bim)Cl]BF_{4}$ (2). To a solution of 1 (174.0 mg, 0.39 mmol) in methanol (30 mL) was added $NaBF_4$ (93.3 mg, 0.78 mmol). The solution was stirred during 13 h and then evaporated to dryness. The residue was dissolved in dichloromethane $(3 \times 20 \text{ mL})$ and filtered. The filtrate was concentrated under reduced pressure to ca. 2 mL and the slow addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and dried under vacuum. Yield 85%. $\Lambda_M(CH_3COCH_3) = 58.2$ $ohm^{-1} cm^2 mol^{-1}$, $\Lambda_M(MeOH) = 79.0 ohm^{-1} cm^2 mol^{-1}$. IR (Nujol): ν (NH) 3650–2450 (br); ν (RuCl) 300 (m); BF₄⁻ 1100 (vs), 520 (s) cm⁻¹. Anal. Calcd for $C_{16}H_{20}N_4BF_4ClRu$: C, 39.1; H, 4.1; N, 11.4. Found: C, 39.9; H, 4.5; N, 11.6. ¹H NMR (CD₃COCD₃, δ) 7.45, 7.17 (2H each, s, CH's of H₂bim), 6-8 (2H, br, NH), 5.68, 5.46 (AA'BB' system of p-cymene, $J_{AB} =$ $J_{A'B'} = 6.0$ Hz), 2.71 (1H, sp. ${}^{3}J_{HH} = 6.9$ Hz, CH of ${}^{i}Pr$), 2.16 (3H, s, Me), 1.10 (6H, d, Me of ⁱPr).

Preparation of [(η^{6} -*p*-Cymene)ClRu(μ -HBim)RhCl-(COD)] (3). To a solution of 1 (150.0 mg, 0.34 mmol) in methanol (30 mL) was added [Rh(acac)(COD)] (106.0 mg, 0.34 mmol). The resulting yellow solution was stirred during 4 h. The precipitation of a yellow solution was completed by addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and dried under vacuum. Yield 87%. $\Lambda_{\rm M}$ (CH₃COCH₃) = 4.45 ohm⁻¹ cm² mol⁻¹. IR (Nujol): ν (NH) 3350 (s); ν (MCl) 280 (m); cm⁻¹. Anal. Calcd for C₂₄H₃₁N₄Cl₂RhRu: C, 44.4; H, 4.8; N, 8.6. Found: C, 44.1; H, 4.8; N, 8.6.

Complexes 4 and 5 were similarly prepared. Complex 4: Yellow-orange solid, yield: 69%. $\Lambda_{M}(CH_{3}COCH_{3}) = 2.54$ ohm⁻¹ cm² mol⁻¹. IR (Nujol): ν (NH) 3220 (s); ν (MCl) 290 (m), 320 (m); ν (CO) (CH₂Cl₂) 2075 (s), 2001 (s) cm⁻¹. Anal. Calcd for C₁₈H₁₉N₄Cl₂O₂RhRu: C, 36.1; H, 3.2; N, 9.4. Found: C, 35.8; H, 3.1; N, 9.1. ¹H NMR (CDCl₃, δ) 7.40, 7.35, 7.18, 7.04 (1H each, br s, CH's of HBim), 5.58, 5.38 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 6.1$ Hz), 2.74 (1H, sp, ³J_{HH} = 6.8 Hz, CH of ⁱPr), 2.19 (3H, s, Me), 1.14 (6H, d, Me of ⁱPr).

Compound 4 can be alternatively prepared by bubbling carbon monoxide for 2 h through dichloromethane solutions of 3. The resulting solution was filtered and then concentrated under reduced pressure to ca. 2 mL. Slow addition of diethyl ether gave the yellow-orange solid 4. Yield: 60%.

Complex 5: yellow solid, yield: 79%. $\Lambda_{M}(CH_{3}COCH_{3}) =$ 17.95 ohm⁻¹ cm² mol⁻¹. IR (Nujol): ν (NH) 3330 (s); ν (MCl) 285 (m) cm⁻¹. Anal. Calcd for C₂₄H₃₁N₄Cl₂IrRu: C, 39.0; H, 4.2; N, 7.6. Found: C, 38.2; H, 4.1; N, 7.6. ¹H NMR (CD₃-COCD₃, δ) 11.52 (1H, br, NH), 7.63, 7.2, 7.1 (4H, br, CH's of HBim), 5.83, 5.62 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} =$ 6.4 Hz), 2.64 (1H, sp, ³J_{HH} = 6.9 Hz, CH of ⁱPr), 2.15 (3H, s, Me), 1.06 (6H, d, Me of ⁱPr).

Preparation of $[(\eta^6 \cdot p \cdot Cymene)ClRu(\mu \cdot Bim)Rh(CO)_2]_2$ (6). To a suspension of 4 (200.0 mg, 0.33 mmol) in methanol (30 mL) was added KOH (1.18 mL, 0.286 mol L⁻¹, 0.33 mmol). Within a few seconds the suspension became a red solution which was stirred for 30 min and vacuum evaporated to dryness. The residue was extracted with dichloromethane (3 × 20 mL) and then filtered. The filtrate was concentrated under reduced pressure to ca. 2 mL. Addition of diethyl ether led to the precipitation of a red-orange solid which was filtered off, washed with diethyl ether, and vacuum dried. Yield: 82%. IR (CH₂Cl₂): ν (CO) 2080 (s), 2060 (s), 2010 (s) cm⁻¹. Anal. Calcd for C₁₈H₁₈N₄ClO₂RhRu: C, 38.5; H, 3.2; N, 10.0. Found: C, 38.4; H, 3.2; N, 10.2. ¹H NMR (CDCl₃, δ) **6a** or **6c**: 7.24, 6.85 (4H each, s, CH's of Bim), 5.39, 5.25 (4H each, AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 5.9$ Hz), 2.55 (2H, sp. ³ $J_{HH} = 7.0$ Hz, CH of ⁱPr), 2.08 (6H, s, Me), 0.94 (12H, d, Me of ⁱPr). **6b**: 7.21, 7.19, 6.86, 6.80 (2H each, s, CH's of Bim), 5.43, 5.37, 5.29, 5.15, (two AA'BB' systems of *p*-cymene, $J_{AB} = J_{A'B'} = 6.8$ Hz), 2.78, 2.59 (1H each, sp. ³ $J_{HH} = 6.8$ Hz, CH of ⁱPr). 2.19, 1.65 (3H each, s, Me), 1.11, 1.02 (6H each, d, Me of ⁱPr). FAB MS *m/z* (*m*-nitrobenzyl alcohol) 1124 (M⁺, 10%), 1088 (M⁺ - Cl, 95%), 527 (¹/₂M⁺ - Cl, 100%), 471 (¹/₂M⁺ - Cl - 2CO, 50%).

Preparation of $[(\eta^6 p-Cymene)Ru(acac)(\mu-HBim)Rh-(COD)]Cl (7).$ To a suspension of $[(\eta^6 p-cymene)Ru(acac)Cl]$ (150.0 mg, 0.40 mmol) in methanol (30 mL) was added [Rh-(HBim)(COD)] (140.0 mg, 0.40 mmol). The resulting yellow solution was stirred during 3 h and then filtered. The filtrate was worked up as above and a yellow solid was collected. Yield: 75%. $\Lambda_M(CH_3COCH_3) = 90.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (Nujol): $\nu(NH)$ 3320 (ν br); $\nu(CO)$ 1580 (s), 1520 (s) cm⁻¹. Anal. Calcd for C₂₉H₃₈N₄ClO₂RhRu: C, 48.8; H, 5.4; N, 7.9. Found: C, 48.1; H, 6.2; N, 7.7. FAB MS m/z (m-nitrobenzyl alcohol) 679 (M⁺, 55%), 335 (M⁺ - COD - Rh - Bim, 100%).

Preparation of $[(\eta^6-p$ -Cymene)Ru(acac)(μ -HBim)Rh-(COD)]BF₄ (8). To a solution of 7 (125.0 mg, 0.17 mmol) in methanol (30 mL) was added NaBF₄ (62.0 mg, 0.51 mmol). The solution was stirred during 17 h and vacuum evaporated to dryness. The residue was extracted with dichloromethane (3 × 20 mL), filtered, and worked up as above and a yellow solid was collected. Yield: 56%. $\Lambda_{\rm M}(\rm CH_3COCH_3) = 129.8$ ohm⁻¹ cm² mol⁻¹. IR (Nujol): $\nu(\rm NH)$ 3280 (ν br); $\nu(\rm CO)$ 1575 (s), 1520 (s); BF₄⁻¹ 1100 (v s), 520 (s) cm⁻¹. Anal. Calcd for C₂₉H₃₈N₄O₂BF₄RhRu: C, 45.5; H, 5.0; N, 7.3. Found: C, 45.7; H, 4.9; N, 7.3. FAB MS *m/z* (*m*-nitrobenzyl alcohol) 679 (M⁺, 100%).

Preparation of $[(\eta^{e}-p-Cymene)Ru(HBbzim)Cl]$ (9). To a red suspension of $[(\eta^{e}-p-cymene)Ru(acac)Cl]$ (200.0 mg, 0.53 mmol) in acetone was added H₂Bbzim (126.8 mg, 0.53 mmol). After stirring for 24 h the solvent was vacuum-evaporated to dryness. The residue was extracted with chloroform and filtered. The filtrate was worked up as above and an orange solid was collected. Yield: 89%. IR (Nujol): ν (NH) 3200– 2200 (ν br); ν (RuCl) 290 (m) cm⁻¹. Anal. Calcd for C₂₄H₂₃N₄-ClRu: C, 57.2; H, 4.6; N, 11.1. Found: C, 56.7 H, 4.5; N, 11.2. ¹H NMR (CDCl₃, δ) 7.78 pd, 7.60 pd, 7.39 pt, 7.29 pt (2H each, CH's of HBbzim), 6.03, 5.86 (AA'BB' system of *p*-cymene, J_{AB} = $J_{A'B'}$ = 4.8 Hz), 5.8–4.6 (1H, br, NH), 2.42 (1H, sp, ³J_{HH} = 6.6 Hz, CH of ⁱPr), 2.33 (3H, s, Me), 0.87 (6H, d, Me of ⁱPr).

Preparation of $[(\eta^6$ -*p*-**Cymene)Ru**(**HBbzim**)(**PPh**₃)]**BF**₄ (10). **Method A.** To a solution of $[(\eta^6$ -*p*-cymene)**Ru**(acac)-(PPh₃)]**BF**₄ (273.4 mg, 0.40 mmol) in methanol (30 mL) H₂-Bbzim (187.4 mg, 0.80 mmol) was added. The orange mixture became yellow after stirring for a week. Excess H₂Bbzim was filtered off, and the resulting solution was concentrated at reduced pressure to ca. 2 mL. Addition of Et₂O completed the precipitation of a yellow solid which was filtered off, washed with Et₂O, and vacuum-dried. Yield: 73%.

Method B. To a suspension of **9** (206.0 mg, 0.40 mmol) in methanol (30 mL) was added AgBF₄ (79.5 mg, 0.40 mmol). The mixture was stirred during 1 h and the AgCl formed filtered off. Solid PPh₃ (107.2 mg, 0.40 mmol) was added to the red solution which was stirred during 24 h. The resulting yellow solution was worked up as above and a yellow solid was collected. Yield: 81%. IR (Nujol): ν (OH) 3610 (m), 3440 (m); ν (NH) 3150–2300 (br); ν (RuCl) 290 (m) cm⁻¹. Anal. Calcd for C₄₂H₃₈N₄BF₄PRu: C, 61.7; H, 4.7; N, 6.85. Found: C, 60.0; H, 4.75; N, 6.9. ³¹P{¹H} NMR (CDCl₃, δ) 41.3 (s). ¹H NMR

 (CDCl_3, δ) 8.04 pd, 7.62 pt (2H each, CH's of HBbzim), 7.5– 6.9 m (4H, CH's of HBbzim and 15H of PPh₃), 6.64, 6.25 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 6.2$ Hz), 3.8–2.6 (1H, br, NH), 2.14 (1H, sp. ${}^{3}J_{HH} = 6.6$ Hz, CH of ⁱPr), 1.68 (3H, s, Me), 0.55 (6H, d, Me of ⁱPr).

Preparation of $[(\eta^{6}-p-Cymene)ClRu(\mu-Bbzim)Rh(COD)]$ (11). To a suspension of 9 (100.8 mg, 0.20 mmol) in methanol (30 mL) was added [Rh(acac)(COD)] (62.0 mg, 0.20 mmol). Within a few seconds, the suspension became a yellow solution, and after 30 min the precipitation of a yellow solid was observed. The mixture was stirred during 4 h and then vacuum-concentrated to ca. 2 mL. Addition of Et₂O completed the precipitation of the yellow solid which was filtered off, washed with Et₂O, and dried under vacuum. Yield: 71%. IR (Nujol): ν (RuCl) 295 (m) cm⁻¹. Anal. Calcd for C₃₂H₃₄N₄-ClRhRu: C, 53.8; H, 4.8; N, 7.85. Found: C, 53.7; H, 5.0; N, 8.0. ¹H NMR (CDCl₃, δ) 7.59 (2H, pd, 2CH's of Bbzim), 7.26-7.14 (6H, m, 6CH's of Bbzim), 5.86, 5.70 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 5.6$ Hz), 4.96 (4H, m, vinylic CH of COD), 2.78 (1H, sp, ${}^{3}J_{HH} = 6.9$ Hz, CH of ${}^{i}Pr$), 2.49, 1.87 (4H each, m, aliphatic CH2 of COD), 2.21 (3H, s, Me), 1.12 (6H, d, Me of ⁱPr). FAB MS m/z (*m*-nitrobenzyl alcohol) 714 (M⁺, 20%), $679 (M^+ - Cl, 65\%), 469 (M^+ - Cl - COD - Rh, 100\%).$

Complexes 12 and 13 were similarly prepared. Complex 12: red solid, yield: 50%. Anal. Calcd for $C_{62}H_{60}N_8Cl_2Rh_2$ -Ru₂: C, 53.3; H, 4.3; N, 8.0. Found: C, 53.5; H, 4.2; N, 8.3. ¹H NMR (CDCl₃, δ) 7.62, 7.4–7.2, 7.14, 6.99, and 6.82 (16H, CH's of Bbzim), 5.87, 5.83, 5.67, 5.28 (two AA'BB' systems of *p*-cymene, $J_{AB} = J_{A'B'} = 5.8$ Hz), 5.59, 4.82, 4.76, 4.32 (8H, vinylic CH of NBD), 3.62, 2.71, 1.36, 1.13 (8H, aliphatic CH of NBD), 1.95 (2H, sp. ³ $J_{HH} = 6.8$ Hz, CH of ⁱPr), 1.55 (6H, s, 2Me), 0.77, 0.23 (6H each, d, Me of ⁱPr).

Complex 13: yellow solid, yield: 76%. IR (Nujol): ν (RuCl) 300 (m); (CH₂Cl₂): ν (CO) 2090 (s), 2070 (s) 2020 (s) cm⁻¹. Anal. Calcd for C₅₂H₄₄N₈Cl₂O₄Rh₂Ru₂: C, 47.2; H, 3.3; N, 8.5. Found: C, 47.15; H, 3.5; N, 8.45. ¹H NMR (CDCl₃, δ) 7.26–7.12 (16H, m, 16CH's of Bbzim), 5.80, 5.58 (two AA'BB' systems of *p*-cymene, $J_{AB} = J_{A'B'} = 5.8$ Hz), 1.86 (6H, s, Me), 1.82 (2H, sp, $^{3}J_{HH} = 6.7$ Hz, CH of ⁱPr), 0.26 (12H, d, Me of ⁱPr). FAB MS *m/z* (*m*-nitrobenzyl alcohol) 1324 (M⁺, 30%), 1289 (M⁺ - Cl, 95%).

Compound 13 can be alternatively prepared by bubbling carbon monoxide for 2 h through yellow dichloromethane solutions of 11. The resulting orange solution was filtered and then concentrated under reduced pressure to ca. 2 mL. Slow addition of *n*-hexane gave an orange solid, which was collected, washed with *n*-hexane, and dried under vacuum. Yield: 69%.

Complex 14 was prepared as complex 11 but in acetone: yellow solid, yield 70%. IR (Nujol): ν (RuCl) 285 (m) cm⁻¹. Anal. Calcd for C₃₂H₃₄N₄ClIrRu: C, 47.8; H, 4.3; N, 7.0. Found: C, 47.7; H, 4.4; N, 7.1. ¹H NMR (CDCl₃, δ) 7.61–7.06 (8H, m, CH's of Bbzim), 5.85, 5.69 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 5.5$ Hz), 4.72 (4H, m, vinylic CH of COD), 2.82 (1H, sp, ³J_{HH} = 6.9 Hz, CH of ⁱPr), 2.30, 1.56 (4H each, m, aliphatic CH₂ of COD), 2.18 (3H, s, Me), 1.16 (6H, d, Me of ⁱPr). FAB MS *m/z* (*m*-nitrobenzyl alcohol) 804 (M⁺, 20%), 769 (M⁺ - Cl, 45%), 469 (M⁺ - Cl - COD - Ir, 100%).

Preparation of [(η⁸-*p*-Cymene)(**PPh₃**)**Ru**(μ-Bbzim)**Rh**-(**COD**)]**BF**₄ (**15**). The same procedure described for **11**, but starting from **10** (163.5 mg, 0.20 mmol) and [Rh(acac)(COD)] (62.0 mg, 0.20 mmol) gave **15** as an orange solid. Yield: 72%. Anal. Calcd for C₅₀H₄₉N₄BF₄PRhRu: C, 58.4; H, 4.8; N, 5.5. Found: C, 57.6; H, 4.8; N, 5.4. ³¹P{¹H} NMR (CDCl₃, δ) 42.6 (s). ¹H NMR (CDCl₃, δ) 7.82 (2H, pd, 2CH's of Bbzim), 7.5– 6.9 (6H, 6CH's of Bbzim and 15H of PPh₃), 6.42, 5.89 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 5.8$ Hz), 4.85, 4.65 (2H each, m, vinylic CH of COD), 2.49, 1.84 (4H each, m, aliphatic CH₂ of COD), 2.28 (1H, sp, ³J_{HH} = 6.8 Hz, CH of ⁱPr), 1.65 (3H, s, Me), 0.76 (6H, d, Me of ⁱPr), FAB MS *m/z* (*m*-nitrobenzyl alcohol) 941 (M⁺, 20%), 731 (M⁺ - COD - Rh, 60%).

Complexes 16-18 were similarly prepared. Complex 16: yellow solid, yield: 78%. Anal. Calcd for $C_{49}H_{45}N_4BF_4$ -PRhRu: C, 58.2; H, 4.5; N, 5.5. Found: C, 57.9; H, 4.5; N,

Table 9. Crystal Data and Refinement Details for $[(\eta^6-p-Cymene)ClRu(\mu-Bbzim)Rh(NBD)]_2$ (12) and $[(\eta^{6}-p-Cymene)(PPh_{3})Ru(\mu-Bbzim)Ir(CO)_{2}]BF_{4}$ (19)

12.2CH2Cl2	19
C62H60Cl2N8Rh2Ru22CH2Cl2	C44H37BF4IrN4O2PRu
1565.9	1064.9
triclinic, PI	monoclinic, $P2_1/c$
12.998(1)	11.586(2)
14.035(1)	20.489(2)
18.081(2)	17.225(1)
79.864(4)	
78.046(5)	95.34(1)
73.326(7)	
3067.3(5), 2	4071.2(9), 4
1.695	1.737
Mo K_{α} ($\lambda = 0.71073 \text{ Å}$)	Mo $K\alpha$ ($\lambda = 0.71073$ Å)
$\omega/2\theta$ scan	$\omega/2\theta$ scan
$(3 \le 2\theta \le 50^\circ)$	$(3 \le 2\theta \le 45^\circ)$
12264 (h; -1515; k; -116; l; -2121)	6745 (h; -12 12; k; 0.22; l; -18 3)
8941 ($F_0 \ge 4.0 \ \sigma(F_0)$	$4242 \ (F_0 \ge 4.0 \ \sigma(F_0))$
13.0	37.2
$1.66 \text{ e}/\text{Å}^3$, close to disordered solvent	0.73 e/Å^3 , close to the BF ₄ anion
0.0375 0.0434	0.0359.0.0388
1.61	1.16
12.1:1	8.1:1
	12·2CH ₂ Cl ₂ $C_{62}H_{60}Cl_2N_8Rh_2Ru_2·2CH_2Cl_2$ 1565.9 triclinic, $P\bar{1}$ 12.998(1) 14.035(1) 18.081(2) 79.864(4) 78.046(5) 73.326(7) 3067.3(5), 2 1.695 Mo $K_{\alpha} (\lambda = 0.71073 \text{ Å})$ $\omega/2\theta$ scan ($3 \le 2\theta \le 50^{\circ}$) 12264 (h: -15 15; k: -1 16; l: -21 21) 8941 ($F_{\circ} \ge 4.0 \sigma(F_{\circ})$ 13.0 1.66 e/Å ³ , close to disordered solvent 0.0375, 0.0434 1.61 12.1:1

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|/\sum |F_{o}|, {}^{b}R_{w} = \{\sum w(|F_{o}| - |F_{c}|)^{2}/\sum w|F_{o}|^{2}\}^{1/2}, w^{-1} = \sigma^{2}(F) + 0.0002F^{2}(\mathbf{12}), w^{-1} = \sigma^{2}(F) + 0.0003F^{2}(\mathbf{13}), {}^{c}S = \{\sum w(|F_{o}| - |F_{c}|)^{2}/\sum w|F_{o}|^{2}\}^{1/2}, w^{-1} = \sigma^{2}(F) + 0.0002F^{2}(\mathbf{12}), w^{-1} = \sigma^{2}(F) + 0.0003F^{2}(\mathbf{13}), w^{-1} = \sigma^{2}(F) + 0.0003F^{2}(\mathbf{13$ $|F_c|^{2/(M-N)}$, where M and N denote the number of data and variables, respectively.

5.5. ³¹P{¹H} NMR (CDCl₃, δ) 42.5 (s). ¹H NMR (CDCl₃, δ) 7.74 pd, 7.55 pt, 7.10 pt, 6.86 pd (2H each, CH's of Bbzim), 7.5-6.9 (15H, m, PPh₃), 6.38, 5.85 (AA'BB' system of p-cymene, $J_{AB} = J_{A'B'} = 6.2$ Hz), 4.32, 4.18 (2H each, m, vinylic CH of NBD), 4.01, 1.29 (2H each, m, aliphatic CH of NBD), 2.28 (1H, $sp, {}^{3}J_{HH} = 6.8 Hz, CH of {}^{i}Pr), 1.61 (3H, s, Me), 0.73 (6H, d, Me)$ of ⁱPr). FAB MS m/z (m-nitrobenzyl alcohol) 925 (M⁺, 10%), 731 ($M^+ - NBD - Rh$, 60%), 469 ($M^+ - NBD - Rh - PPh_3$, 100%).

Complex 17: orange solid, yield: 79%. IR (CH₂Cl₂): ν (CO) 2080 (s), 2020 (s) cm⁻¹. Anal. Calcd for $C_{44}H_{37}N_4BF_4O_2$ -PRhRu: C, 54.2; H, 3.8; N, 5.7. Found: C, 53.65; H, 3.6; N, 5.6. $^{31}P\{^1H\}$ NMR (CDCl₃, $\delta)$ 42.7 (s). 1H NMR (CDCl₃, $\delta)$ 7.78 (2H, pd, 2CH of Bbzim), 7.5-6.9 (6H, 6CH's of Bbzim and 15H of PPh₃), 6.39, 5.72 (AA'BB' system of *p*-cymene, $J_{AB} =$ $J_{A'B'} = 6.0$ Hz), 2.35 (1H, sp. ${}^{3}J_{HH} = 7.0$ Hz, CH of ${}^{i}Pr$), 1.67 (3H, s, Me), 0.74 (6H, d, Me of ⁱPr).

Complex 17 was also prepared by bubbling carbon monoxide during 2 h through dichloromethane solutions of 15 or 16. The resulting orange solution was worked up as above and an orange solid was collected. Yield: 69%.

Complex 18: yellow solid, yield: 82%. Anal. Calcd for C₅₀H₄₉N₄BF₄IrPRu: C, 53.8; H, 4.4; N, 5.0. Found: C, 53.8; H, 4.7; N, 5.1. ${}^{31}P{}^{1}H{}$ NMR (CDCl₃, δ) 42.6 (s). ${}^{1}H$ NMR (CDCl₃, δ) 7.87 (2H, pd, 2CH of Bbzim), 7.5–6.9 (6H, 6CH's of Bbzim and 15H of PPh₃), 6.45, 5.89 (AA'BB' system of *p*-cymene, $J_{AB} = J_{A'B'} = 6.1$ Hz), 4.63, 4.47 (2H each, m, vinylic CH of COD), 2.28 (5H, m, CH of ⁱPr and aliphatic CH₂ of COD), 1.66 (3H, s, Me), 1.58, 1.52 (2H each, m, aliphatic CH₂ of COD), 0.79 (6H, d, ${}^{3}J_{HH} = 6.8$ Hz, Me of ${}^{i}Pr$). FAB MS m/z $(m-nitrobenzyl alcohol) 1031 (M^+, 30\%), 769 (M^+ - PPh_3, 30\%),$ 731 (M⁺ - COD - Ir, 70%), 469 (M⁺ - COD - Ir - PPh₃, 100%).

Preparation of $[(\eta^{\theta}-p-Cymene)(PPh_3)Ru(\mu-Bbzim)Ir (CO)_2$]BF₄ (19). Carbon monoxide was bubbled through a solution of 18 in dichloromethane (40 mL) during 30 min. The resulting yellow solution was filtered and vacuum-concentrated to ca. 2 mL. The slow addition of Et₂O (10 mL) gave a dark violet solid which was filtered off, washed with Et₂O, and vacuum-dried. Yield: 86%. IR (CH2Cl2): v(CO) 2070 (s), 2000 (s) cm⁻¹. Anal. Calcd for $C_{44}H_{37}N_4BF_4O_2PIrRu$: C, 49.6; H, 3.5; N, 5.3. Found: C, 50.0; H, 3.7; N, 5.1. ³¹P{¹H} NMR (CD₃-COCD₃/CH₃COCH₃, 1/4 v/v, δ) 42.9 (s). ¹H NMR (CD₂Cl₂, δ) 7.87 (2H, pd, 2CH's of Bbzim), 7.53-6.90 (6H, 6CH's of Bbzim

and 15H of PPh₃), 6.46, 5.88 (AA'BB' system of p-cymene, J_{AB} $= J_{A'B'} = 6.1$ Hz), 2.32 (1H, sp, ${}^{3}J_{HH} = 7.1$ Hz, CH of ⁱPr), 1.67 $(3H, s, Me), 0.76 (6H, Me of {}^{i}Pr).$

Catalytic Reactions. In a typical experiment, a degassed solution of the catalyst in methanol (10 mL) was placed into a 100 mL flask attached to a hydrogen reservoir through a threeway valve. The system was evacuated and flushed with hydrogen four times and then hydrogen was admitted to the system at the desired pressure. The flask was then immersed in a thermostated bath, at a preestablished temperaure and, prior to the introduction of the substrate dissolved in methanol (5 mL), it was shaken for 30 min. Solutions of tetrabutylammonium chloride in methanol were added with the substrate for the study of the influence of the chloride anions. The reaction was followed by measuring, by GC, the percentage of the formed cyclohexane as a function of time. Starting time corresponds to the addition of the substrate. All straight lines were fitted by use of conventional linear regression software to $r^2 > 0.98$. Concentrations of dissolved hydrogen were calculated using solubility data reported by Katayama et al.³⁴

X-ray Measurements and Structure Determinations for 12·2CH₂Cl₂ and 19. Red crystals of 12·2CH₂Cl₂ and dark red crystals of 19 were grown by slow diffusion of Et₂O into solutions of 12 and 19 in CH₂Cl₂. Prismatic blocks of dimensions 0.20 \times 0.14 \times 0.48 mm (12·2CH₂Cl₂) and 0.17 \times 0.23 \times 0.34 mm (19) were glued to the end of glass fibers. In each case, it was mounted on a four-circle Siemens AED diffractometer working with graphite-monochromated Mo K_{α} radiation and operating at 230 K for 12.2CH₂Cl₂ or 273 K for 19. Selected crystallographic data are collected in Table 9. Precise lattice parameters were determined by least-squares fit from $68 (12 \cdot 2 CH_2 Cl_2)$ and 58 (19) centered reflections in the region $20 \leq 2\theta \leq 42^{\circ}$. Three standard reflections were monitored every 55 min to check crystal and instrument stability. There were no significant fluctuations of the intensities. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction³⁵ based on ψ scans was also applied (min and max trans. fact. 0.156 and 0.186 for 12.2CH2- Cl_2 and 0.725 and 0.777 for 19). The structures were solved by the heavy-atom method followed by difference Fourier calculations using the SHELXTL-PLUS package.³⁶ All non-

⁽³⁵⁾ North, A. C. T.; Phillips, D. C.; Mathews, F. S. Acta Crystallogr. 1968, A24, 351.

⁽³⁶⁾ Sheldrick, G. M. SHELXTL-PLUS, Siemens Analytical X-ray Instruments, Madison, WI, 1990. (37) International Tables For Crystallography; Kynoch Press: Bir-

mingham, England, 1974; Vol. IV.

H-atoms were anisotropically refined except those of the disordered CH_2Cl_2 solvent molecule of compound 12 which were refined with isotropic displacement parameters. This disorder was modeled with two molecules each of them with a refined occupancy factor of ca. $^{1}/_{2}$. Hydrogen atoms were included in the last cycles in calculated (for 12·2CH₂Cl₂) and found (for 19) positions. All H-atoms were refined with a common thermal parameter using the riding method. The scattering factors, with anomalous dispersion correction for heavy-atoms, were taken from ref 37. All calculations were carried out on a μ -VAX 3400 computer.

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Supplementary Material Available: Tables SI-SVI with full details of crystallographic and experimental data, hydrogen positional parameters, anisotropic displacement parameters, and a full list of bond distances and angles for $12\cdot 2CH_2Cl_2$ and 19, respectively (11 pages). Ordering information is given on any current masthead page.

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