

Dinuclear Rhodium and Iridium Complexes with Mixed Amido/Methoxo and Amido/Hydroxo Bridges

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The reactions of $[\{M(\mu\text{-OME})(\text{cod})\}_2]$ ($M = \text{Rh}, \text{Ir}$; $\text{cod} = 1,5\text{-cyclooctadiene}$) with *p*-tolylamine, α -naphthylamine, and *p*-nitroaniline gave complexes with mixed-bridging ligands, $[\{M(\text{cod})\}_2(\mu\text{-NHAr})(\mu\text{-OME})]$. Similarly, the related complexes $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-NHAr})(\mu\text{-OH})]$ were prepared from the reactions of $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$ with *p*-tolylamine, α -naphthylamine, and *p*-nitroaniline. The reactions of $[\{\text{Rh}(\mu\text{-OR})(\text{cod})\}_2]$ ($R = \text{H}, \text{Me}$) with *o*-nitroaniline gave the mononuclear complex $[\text{Rh}(\text{o-NO}_2\text{C}_6\text{H}_4\text{NH})(\text{cod})]$. The syntheses of the amido complexes involve a proton exchange reaction from the amines to the methoxo or hydroxo ligands and the coordination of the amide ligand. These reactions were found to be reversible for the dinuclear complexes. The structure of $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-NH}\{\text{p-NO}_2\text{C}_6\text{H}_4\})\text{-}(\mu\text{-OME})]$ shows two edge-shared square-planar rhodium centers folded at the edge with an *anti* configuration of the bridging ligands. The complex $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-NH}\{\alpha\text{-naphthyl}\})\text{-}(\mu\text{-OH})]$ cocrystallizes with $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$ and THF, forming a supramolecular aggregate supported by five hydrogen bridges in the solid state. In the mononuclear $[\text{Rh}(\text{o-NO}_2\text{C}_6\text{H}_4\text{NH})(\text{cod})]$ complex the *o*-nitroamido ligand chelates the rhodium center through the amido nitrogen and an oxygen of the nitro group.

Introduction

Late-transition-metal compounds with anionic nitrogen (amido) and oxygen (alkoxo and hydroxo) ligands are becoming of increasing interest because of their remarkable reactivity¹ and their potential relevance to catalytic reactions.² While there is a large body of early-transition-metal chemistry based on these groups with applications in organo-

metallic chemistry and catalysis,³ the relative paucity of their homologues of late-transition-metals causes the factors controlling the nature of their M–N and M–O bonds to still not be well understood.⁴ A number of palladium amido and alkoxo complexes have recently been prepared;⁵ some of them undergo very unusual reductive elimination reactions with formation of C–N and C–O bonds.^{5b,e,6} As a consequence of this type of study, the palladium- and nickel-catalyzed amination of aryl halides has begun to be mecha-

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nistically understood.^{2b,7} Moreover, palladium and platinum hydroxide and amido complexes are related by simple acid–base chemistry with amines and water, which has provided an easy preparative entry into families of mixed μ -amido/ μ -hydroxo and bis(μ -amido) complexes of these metals.^{5b,8} Furthermore, this acid–base chemistry has been proved to be involved in the generation of the active species for the conversion of aryl halides to arylamido complexes.⁹

Although there are examples of alkoxy,¹⁰ hydroxy,^{1b,e,11} and amido^{1b,12} complexes of rhodium, their reactions with amines and water, similar to those reported for palladium and platinum, have scarcely been studied.¹³ As rhodium compounds of this kind could be of interest for new catalytic processes such as the amination of olefins,¹⁴ we have studied the reactions of rhodium(I) bis(μ -hydroxo) and bis(μ -methoxo) complexes with amines. We report herein our results on this subject leading to a new class of dinuclear rhodium complexes with mixed-bridging ligands, as well as on a study of the equilibria involved in their formation.

Results and Discussion

Syntheses of the Complexes. The methoxo-bridged complexes $\{[M(\mu\text{-OMe})(\text{cod})]_2\}$ ($M = \text{Rh, Ir}$; $\text{cod} = 1,5$ -cyclooctadiene) have been shown to be useful starting materials for the synthesis of a wide range of di- and polynuclear compounds¹⁵ when treated with polydentate

ligands containing an acidic proton. A rationalization of these reactions under conventional proton exchange reactions and coordination of the anionic polydentate ligand accounts for the preparative results. However, we have found that primary arylamines (ArNH_2), a class of compounds less acidic than methanol, protonate the methoxo groups in $\{[M(\mu\text{-OMe})(\text{cod})]_2\}$ to give the complexes $\{[M(\text{cod})]_2(\mu\text{-NHAr})(\mu\text{-OMe})\}$ ($M = \text{Rh}$, $\text{Ar} = p\text{-tolyl}$ (**1**), $p\text{-NO}_2\text{C}_6\text{H}_4$ (**2**), α -naphthyl (**3**); $M = \text{Ir}$, $\text{Ar} = p\text{-tolyl}$ (**4**)) with mixed-bridging ligands. Complexes **1–4** were obtained pure and in good yields using diethyl ether as the solvent, in which the products crystallized out as formed. However, mixtures of complexes were isolated if the reactions were carried out in solvents such as dichloromethane or benzene. The new complexes were characterized by analytical and NMR and mass spectroscopic methods and an X-ray diffraction analysis of complex **2** (see below).

Analogously, the related μ -hydroxo/ μ -amido complexes $\{[\text{Rh}(\text{cod})]_2(\mu\text{-NHAr})(\mu\text{-OH})\}$ ($\text{Ar} = p\text{-tolyl}$ (**5**), $p\text{-NO}_2\text{C}_6\text{H}_4$ (**6**), α -naphthyl (**7**)) were prepared by reacting equimolar amounts of $\{[\text{Rh}(\mu\text{-OH})(\text{cod})]_2\}$ with the corresponding amines in diethyl ether. Compounds **5** and **6** were isolated as yellow and red crystalline solids, respectively, whose elemental analyses agreed with the proposed formulation. However, attempts to obtain pure samples of complex **7** were unsuccessful, since it was always contaminated with $\{[\text{Rh}(\mu\text{-OH})(\text{cod})]_2\}$. In fact, the elemental analyses of the solid isolated from the reaction corresponded to the formulation $[\text{Rh}_3(\text{cod})_3(\text{NH}\{\alpha\text{-naphthyl}\})(\text{OH})_2] \cdot \text{THF}$. The complete characterization of this solid as the supramolecular entity $\{[\text{Rh}(\text{cod})]_2(\mu\text{-NH}\{\alpha\text{-naphthyl}\})(\mu\text{-OH})\}_2 \cdot \{[\text{Rh}(\mu\text{-OH})(\text{cod})]_2\} \cdot 2\text{THF}$ (**7'**) was achieved by a crystallographic X-ray diffraction study (see below).

A markedly different outcome was observed on treating $\{[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2\}$ and $\{[\text{Rh}(\mu\text{-OH})(\text{cod})]_2\}$ with *o*-nitroaniline, since 2 molar equiv of the amine was required to achieve the complete consumption of the dinuclear rhodium precursors. The new complex formed in both cases, $[\text{Rh}(\text{o-NO}_2\text{C}_6\text{H}_4\text{NH})(\text{cod})]$ (**8**), was isolated as purple needles for which the mass spectrum indicated a mononuclear nature. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[\text{Rh}(\text{o-NO}_2\text{C}_6\text{H}_4\text{NH})(\text{cod})]$ indicated that the *o*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH}$ ligand chelates the rhodium center through the amido nitrogen and one oxygen from the nitro group. To confirm this unusual coordination of the nitro group, complex **8** was definitively characterized by an X-ray diffraction study.

Crystal Structures of Complexes 2, 7', and 8. A view of the molecular structure of **2** is shown in Figure 1; selected bond distances and angles are given in Table 1. Complex **2** has an imposed crystallographic C_s symmetry, with all the atoms of the methoxo and *p*-nitrophenylamido bridging ligands situated on the crystallographic mirror plane. The

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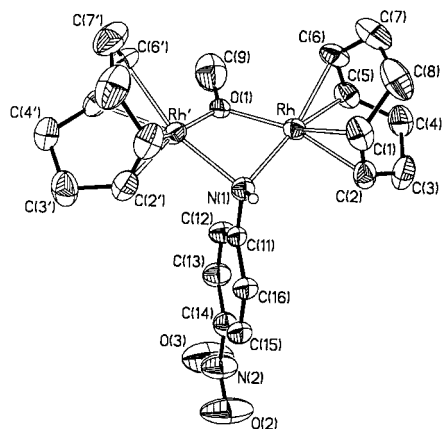


Figure 1. A representation of the molecular structure of complex **2** showing the atomic numbering scheme used.

Chart 1

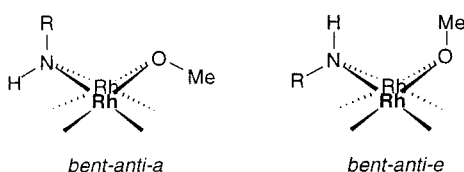


Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**^a

Rh...Rh'	3.0147(8)	N(1)–C(11)	1.414(7)
Rh–O(1)	2.152(3)	C(11)–C(12)	1.404(8)
Rh–N(1)	2.116(3)	C(11)–C(16)	1.400(7)
Rh–C(1)	2.101(4)	C(12)–C(13)	1.356(8)
Rh–C(2)	2.094(4)	C(13)–C(14)	1.396(9)
Rh–C(5)	2.130(4)	C(14)–C(15)	1.393(8)
Rh–C(6)	2.133(4)	C(15)–C(16)	1.373(8)
N(2)–O(2)	1.233(8)	N(2)–O(3)	1.219(7)
N(2)–C(14)	1.452(7)	O(1)–C(9)	1.214(9)
O(1)–Rh–N(1)	80.65(14)	M(1) ^b –Rh–M(2) ^b	88.2(2)
O(1)–Rh–M(1) ^b	173.88(14)	N(1)–Rh–M(1) ^b	93.01(14)
O(1)–Rh–M(2) ^b	97.89(14)	N(1)–Rh–M(2) ^b	178.00(14)
Rh–O(1)–Rh'	88.92(17)	Rh–N(1)–Rh'	90.85(17)
C(9)–O(1)–Rh	128.9(2)	C(11)–N(1)–Rh	

^a Primed atoms are related to the unprimed ones by a mirror plane. ^b M(1) and M(2) are the midpoints between C(1)–C(2) and C(5)–C(6), respectively.

coordinated oxygen atom of the methoxy group and the nitrogen atom of the bridging amido, together with a 1,5-cyclooctadiene ligand on each metal, complete distorted square-planar coordination for the metal centers. The four-membered ring “RhNRhO” shows a folded conformation: the dihedral angle between the coordination planes defined by O(1)–Rh–N(1) and O(1)–Rh'–N(1) was found to be 135.86(13)°. Accordingly, a relatively short intermetallic distance (3.0147(9) Å) was observed. While the Rh–N bond distance, 2.116(3) Å, compares well with those values observed in other square-planar rhodium cyclooctadiene complexes (range 2.066–2.200 Å, mean 2.12(3) Å), the Rh–O bond length, 2.152(3) Å, is in the upper end of those of related alkoxy-bridged rhodium(I) complexes (range 2.042–2.137 Å, mean 2.08(3) Å).¹⁶ The HN–C^{ipso} distance (N(1)–C(11) = 1.414(7) Å) indicates a N–C single bond. The methyl of the methoxy group and the proton of the

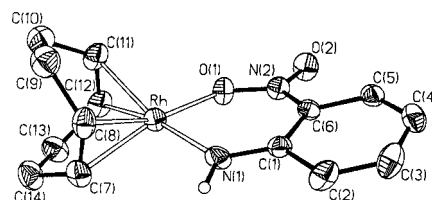


Figure 2. A representation of the molecular structure of the mononuclear complex **8**.

Chart 2

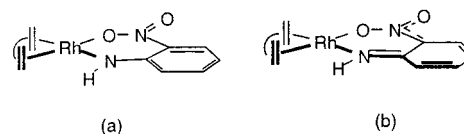


Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **8**

Rh–N(1)	1.989(5)	N(1)–C(1)	1.310(7)
Rh–O(1)	2.048(4)	N(2)–C(6)	1.389(7)
Rh–C(7)	2.107(6)	C(1)–C(2)	1.444(8)
Rh–C(8)	2.094(6)	C(1)–C(6)	1.435(7)
Rh–C(11)	2.155(6)	C(2)–C(3)	1.341(8)
Rh–C(12)	2.150(6)	C(3)–C(4)	1.423(8)
O(1)–N(2)	1.290(6)	C(4)–C(5)	1.347(8)
O(2)–N(2)	1.254(5)	C(5)–C(6)	1.415(7)
N(1)–Rh–O(1)	87.5(2)	M(1) ^a –Rh–M(2) ^a	88.1(3)
O(1)–Rh–M(1) ^a	178.9(2)	N(1)–Rh–M(1) ^a	92.7(2)
O(1)–Rh–M(2) ^a	91.6(2)	N(1)–Rh–M(2) ^a	177.6(2)
Rh–N(1)–C(1)	127.8(4)	Rh–O(1)–N(2)	129.0(3)
O(1)–N(2)–O(2)	116.1(5)	O(1)–N(2)–C(6)	124.5(5)

^a M(1) and M(2) are the midpoints between C(7)–C(8) and C(11)–C(12), respectively.

amido ligand were found in equatorial positions on the open-book skeleton, while the aryl group was in an axial position. Therefore, complex **2** showed an *anti* configuration that we have labeled *bent-anti-a* (Chart 1) to indicate the axial position of the aryl group. Within this convention, the *anti* conformer with the aryl group at the equatorial position would be that labeled *bent-anti-e* in Chart 1.

Although dinuclear complexes containing mixed methoxy and amido bridging ligands are unknown for the late-transition-metals, this *bent-anti-a* stereochemistry is similar to those reported for the related μ -hydroxo/ μ -amido complexes [Pt(PPh₃)₂]₂(μ -NH{*p*-tolyl})(μ -OH)(BF₄)₂,^{8b} *cis*-[Pd(C₆H₅)(PPh₃)₂]₂(μ -NHBU¹)(μ -OH),⁹ and *trans*-[Pd(C₆H₅)(PPh₃)₂]₂(μ -NH{*p*-OMeC₆H₄})(μ -OH),^{8d} which also showed folded structures.

The molecular structure of the square-planar complex **8** is shown in Figure 2. Selected bond distances and angles are given in Table 2. The more striking feature of the structure involves the inhomogeneous distribution of bond distances within the amido ligand. Thus, the benzenic ring of the *o*-NO₂C₆H₄NH ligand shows two significantly shorter distances (C(2)–C(3) = 1.341(8) Å, C(4)–C(5) = 1.347(8) Å) than the remaining four C–C bonds (range 1.415(7)–1.448(8) Å). In addition, the HN–C^{ipso} and O₂N–C^{ipso} distances (N(1)–C(1) = 1.310(7) Å and N(2)–C(6) = 1.389(7) Å) are clearly shorter than those expected for a single C–N bond (1.468(14) Å), or than distances reported for a noncoordinated *o*-nitroaniline (1.442(7) Å).¹⁷ Therefore, the

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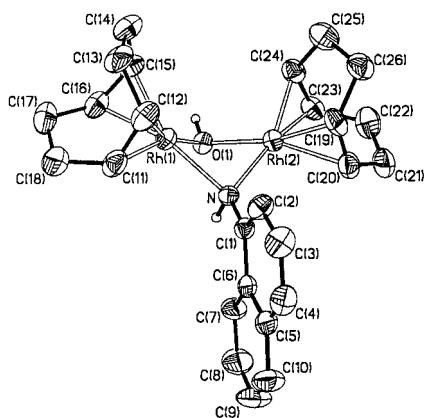


Figure 3. A drawing of the molecular structure of the heterobridged complex **7** together with the labeling scheme used.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **7**

Rh(1)···Rh(2)	2.8602(8)	Rh(2)–O(1)	2.068(4)
Rh(1)–O(1)	2.078(4)	Rh(2)–N	2.109(5)
Rh(1)–N	2.128(5)	Rh(2)–C(19)	2.088(6)
Rh(1)–C(11)	2.089(6)	Rh(2)–C(20)	2.098(7)
Rh(1)–C(12)	2.117(6)	Rh(2)–C(23)	2.107(7)
Rh(1)–C(15)	2.096(7)	Rh(2)–C(24)	2.097(7)
Rh(1)–C(16)	2.089(7)		
O(1)–Rh(1)–N	74.55(18)	O(1)–Rh(2)–N	75.15(18)
O(1)–Rh(1)–M(1) ^a	175.5(3)	O(1)–Rh(2)–M(3) ^a	174.7(3)
O(1)–Rh(1)–M(2) ^a	97.0(3)	O(1)–Rh(2)–M(4) ^a	96.7(2)
N–Rh(1)–M(1) ^a	100.9(3)	N–Rh(2)–M(3) ^a	99.8(3)
N–Rh(1)–M(2) ^a	171.6(3)	N–Rh(2)–M(4) ^a	171.9(2)
M(1)–Rh(1)–M(2) ^a	87.4(3)	M(3)–Rh(2)–M(4) ^a	88.4(3)
Rh(1)–O(1)–Rh(2)	87.26(15)	Rh(1)–N–Rh(2)	84.91(18)

^a M(1), M(2), M(3), and M(4) are the midpoints of the olefinic bonds C(11)–C(12), C(15)–C(16), C(19)–C(20), and C(23)–C(24), respectively.

o-NO₂C₆H₄NH ligand is better represented as a quinodiimide (b, Chart 2) rather than as an amide ligand (a, Chart 2). It is interesting to remark that, as a consequence of chelate coordination of the *o*-NO₂C₆H₄NH ligand to rhodium in **8**, the benzene ring loses aromaticity. We cannot comment on the generality of this situation, since complex **8** is the first example where the *o*-NO₂C₆H₄NH ligand coordinates in a chelate fashion. In contrast, the related *p*-NO₂C₆H₄NH ligand in **2** appeared close to the amide form. The major difference between the nitroanilide ligands in complexes **2** and **8** arises from the presence or absence of a lone electron pair on the amide nitrogen. In complex **2**, this pair is involved in the formation of a Rh–N dative bond, and the amide nitrogen was found to be tetrahedral, while the benzene ring was found almost aromatic. In complex **8**, this pair is not involved in a Rh–N bond; on the contrary, it is supposed to be delocalized on the benzene ring due to the –I and –M effect of the nitro group at the *ortho* position. This bonding situation leads to the observed short and long distances into the nitroanilide ligand.

The molecular structure of the dinuclear complex **7** is shown in Figure 3 together with the atom-numbering scheme. Selected bond distances and angles are given in Table 3. In **7**, an α -naphthylamido and a hydroxo group bridge both rhodium atoms, which complete an approximately square-

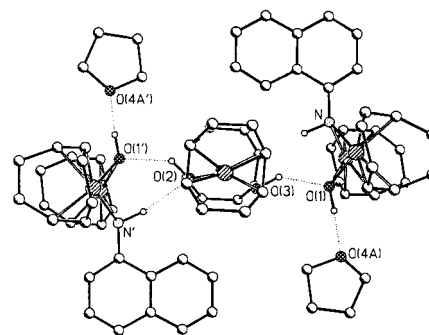


Figure 4. Hydrogen-bonding scheme established between the two different dinuclear complexes and the THF solvent molecule in the crystalline structure of **7'** (see Table 4 for structural parameters).

Table 4. Bond Lengths (Å) and Angles (deg) for the Hydrogen-Bonding System in **7'**

	A–H	H···B	A···B	A–H···B
O(1)–H···O(4a)	0.98	1.83	2.803(14)	171.4
O(1)–H···O(4b)	0.98	1.80	2.75(2)	162.5
N'∠H···O(2) ^a	1.08	2.24	3.305(10)	168.1
O(2)–H···O(1') ^b			2.888(10)	
O(3)–H···O(1') ^b			2.847(13)	

^a Primed atoms are related to the unprimed ones by the symmetry operation $-x + 1, -y, -z$. ^b Hydrogens atoms of O(2) and O(3) were not located in the X-ray structural analysis.

planar coordination with a 1,5-cyclooctadiene ligand. The four-membered ring RhNRhO also shows a folded conformation, with a dihedral angle between the O(1)–Rh(1)–N and O(1)–Rh(2)–N planes of 118.53(15)°, leading to a shorter intermetallic distance (2.8602(8) Å) than that observed in **2**. The stereochemistry around the central RhNRhO ring was found to be *syn-endo* with the aryl group and the proton of the OH ligand at equatorial positions. This stereochemistry of the bridging ligands, unusual for related μ -amido/ μ -hydroxo complexes, is probably due to the H-bonding network established at a supramolecular level in the crystalline structure of **7'**. Figure 4 shows the structure of this aggregate in which two molecules of **7** and two THF solvent molecules encapsulate a dinuclear di- μ -hydroxo complex, $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$. Five hydrogen bonds involving the strong H-bond acceptor/donor μ -hydroxo and μ -amido groups¹⁸ (see Table 4) are involved in the H-bonding network established. The hydroxo groups of the two (symmetry-related) molecules of **7** behave as H-donors toward the oxygens of the two THF molecules and H-acceptors for the two OH groups of the homobridged dinuclear $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$ complex. Additionally, the amido NH group acts as a H-donor toward one bridging hydroxo ligand of $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$ (Figure 4). However, this hydrogen-bonding system was found to be completely broken on dissolving the solid, since the individual components, **7**, $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$, and THF, were observed in the ¹H NMR spectrum of **7'**.

Characterization of Complexes 1–7 in Solution. Thermodynamic and Reactivity Considerations. Complexes

(17) Huang, S. D.; Lewandowski, B. J.; Liu, C.; Shan, Y. *Acta Crystallogr.* **1999**, C55, 2016.

(18) (a) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, 40, 2382. (b) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.

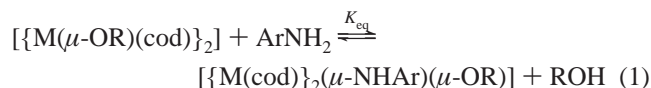
Table 5. K_{eq} Values for the Equilibria Shown in Eq 1

complex	amine	K_{eq}	ΔG_{298} (kcal/mol)
$[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$	<i>p</i> -tolylamine	1.01, ^a 9.0 ^b	-5.9×10^{-3} , -1.30
$[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$	<i>a</i> -naphthylamine	0.71 ^a	0.2×10^{-3}
$[\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2]$	<i>p</i> -tolylamine	1.03, ^a 8.5 ^b	-17.5×10^{-3} , -1.27
$[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$	<i>p</i> -tolylamine	5.44 ^a	-1.0

^a In CDCl_3 . ^b In benzene-*d*₆.

1–7 were found to be dinuclear by observation of the molecular ions (M^+) via mass spectra (FAB⁺). A general trend in these mass spectra was the detection of the “[$\{\text{Rh}(\text{cod})\}_2(\mu\text{-NHR})$]⁺” ions coming from the loss of the methoxo or hydroxo groups. The ¹H NMR data indicated that complexes **1–7** were single species in solution with a C_s symmetry plane, as found for **2** in the solid state. The structure of the complexes is evident from the number of resonances (i.e., four for the olefinic protons of the cod ligand), and was confirmed by the ¹H,¹H-COSY spectra of **1–7** (see the Supporting Information). A rapid rotation of the aryl groups around the $\text{HN}-\text{C}^{\text{ipso}}$ bond was found to be operative for complexes **1**, **2**, and **4–6** even at 193 K, since the *ortho* and *meta* protons of the amido ligands remained equivalent even at this temperature in CD_2Cl_2 . It is interesting to note that the possible interconversion of the *bent-anti-e* into the *bent-anti-a* conformation, through an inversion of the four-membered RhNRhO ring, was not detected by NMR spectroscopy.

The reactions of complexes $[\{\text{M}(\mu\text{-OR})(\text{cod})\}_2]$ (R = Me, H) with *p*-tolylamine, α -naphthylamine, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$ stop at the complexes with mixed-bridging ligands, **1–7**. Thus, the bis(amido) compounds $[\{\text{M}(\mu\text{-NHAr})(\text{cod})\}_2]$ were not detected upon addition of 1 molar equiv of the respective amine to **1–7**. However, we have observed the formation of the complexes $[\{\text{M}(\mu\text{-NH}\{p\text{-tolyl}\})(\text{CO})_2\}_2]$ (M = Rh, Ir)^{12g} by adding *p*-tolylamine to complexes **1**, **4**, and **5** under an atmosphere of carbon monoxide, which indicates the strong influence of the ancillary ligands on the products of these reactions. In addition, the reactions leading to complexes **1–7** were found to be reversible. Thus, addition of methanol to solutions of **1–4** in CDCl_3 gave $[\{\text{M}(\mu\text{-OMe})(\text{cod})\}_2]$ and free amine, while the addition of water to solutions of **5–7** in CDCl_3 resulted in the formation of $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$ and free amine. The equilibrium shown in eq 1



was established by mixing equimolar amounts of $[\{\text{M}(\mu\text{-OR})(\text{cod})\}_2]$ (R = Me, H) and the amines in solvents such as CDCl_3 or benzene-*d*₆ for which different K_{eq} values were observed. After the reaction reached equilibrium, the concentrations of the complexes were measured by ¹H NMR spectroscopy. Table 5 summarizes the equilibrium constant (K_{eq}) and the corresponding free enthalpy (ΔG_{298}) for the reactions amenable to study.

The reactions of the rhodium and iridium (M) complexes $[\{\text{M}(\mu\text{-OMe})(\text{cod})\}_2]$ with *p*-tolylamine gave similar K_{eq}

values, which indicate a small influence of the metal in these reactions. In addition, the larger K_{eq} value for the reactions of $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ with *p*-tolylamine versus α -naphthylamine is in marked contrast to the reactivity predicted only by the $\text{p}K_{\text{a}}$ values of the amines (5.08 and 3.92, respectively). Since methanol was formed in both reactions, the observed K_{eq} values indicate a larger affinity of metal for the *p*-tolylamido ligand than for the α -naphthylamido ligand. Moreover, since water is more acidic than methanol, larger K_{eq} values could be expected for the equilibria of *p*-tolylamine with $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ versus $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$ under a perspective based only on the $\text{p}K_{\text{a}}$ values of water and methanol. However, the results were again opposite to those anticipated, which indicated that the involved equilibria seem to be much more complex.

From a kinetic point of view, the reaction of $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ with α -naphthylamine was found to go slowly since 17 h was required to reach equilibrium at room temperature. In contrast, only 2 h was needed to attain equilibrium with the less hindered *p*-tolylamine under identical conditions.

To test the relative proton-acceptor characteristics of the coordinated methoxo and amido ligands in **1**, we have studied the reaction of this compound with *m*-nitrobenzyl alcohol (HNBA). Just after mixing, the products methanol and the new complex $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-NH}\{p\text{-tolyl}\})(\mu\text{-NBA})]$ along with the starting materials were observed by ¹H NMR spectroscopy. The concentration of the products increased with time, but $[\{\text{Rh}(\mu\text{-NBA})(\text{cod})\}_2]$ and free *p*-tolylamine along with unidentified compounds were observed 12 h after the reaction was started. Therefore, the results at the beginning of the reaction indicate that HNBA protonates the methoxo ligand faster than the *p*-tolylamido ligand in **1**. At first glance, one would expect that *p*-tolylamine was formed instead of methanol, assuming that the amido group is a better proton acceptor than the methoxo group. However, since the OMe ligand contains lone electron pairs in **1** while the amido ligand lacks them, the latter is less likely to be protonated. In other words, the proton easily finds an active site on the methoxo ligand, while the dissociation of the bridging amido group is a prerequisite to produce the proton transfer to the nitrogen.

Finally, the deprotonation reactions of *o*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$ by $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ and by $[\{\text{Rh}(\mu\text{-OH})(\text{cod})\}_2]$ leading to the mononuclear **8** rather than complexes with mixed-bridging ligands are easily explained considering the chelating effect. Assuming that the hypothetical intermediates $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-NH}\{o\text{-NO}_2\text{C}_6\text{H}_4\})(\mu\text{-OR})]$, analogous to $[\{\text{Rh}(\text{cod})\}_2(\mu\text{-NH}\{p\text{-NO}_2\text{C}_6\text{H}_4\})(\mu\text{-OR})]$ (**2**, **6**), were formed in the first steps of the reaction, the interaction of an oxygen atom of the nitro group with one of the metal centers provides an easy pathway to split the bridges in these intermediates to give **8**.

Experimental Section

Starting Materials and Physical Methods. All reactions were carried out under argon using standard Schlenk techniques. The complexes $[\{\text{M}(\mu\text{-OMe})(\text{cod})\}_2]$ ^{1b} (M = Rh, Ir,) and $[\{\text{Rh}(\mu\text{-OH})-$

(cod)}₂]^{11b} were prepared according to literature methods. *p*-Tolylamine, α -naphthylamine, *p*-NO₂C₆H₄NH₂, and *o*-NO₂C₆H₄NH₂ were purified by sublimation prior to use. Solvents were dried and distilled under argon before use by standard methods. Carbon, hydrogen, and nitrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB⁺ mode. Ions were produced with the standard Cs⁺ gun at ca. 30 kV; 2-nitrophenyl octyl ether (NPOE) was used as matrix. ¹H and ¹³C-{¹H} NMR spectra were recorded on Bruker ARX 300 and Varian UNITY 300 spectrometers operating at 299.95 and 300.13 MHz for ¹H, respectively. Chemical shifts are reported in parts per million and referenced to SiMe₄ using the residual signal of the deuterated solvent as reference.

Equilibrium Constants. Solutions (0.0066 mol·L⁻¹) of the complexes [{M(μ -OMe)(cod)}₂] (M = Rh, Ir) or [{Rh(μ -OH)(cod)}₂] with an equimolar amount of the amine (*p*-tolylamine, α -naphthylamine) were prepared in CDCl₃ and in C₆D₆. The evolution of the reactions was monitored by ¹H NMR spectroscopy until no changes in the concentrations were observed for 1 h. At this stage, the equilibrium was considered to be reached.

Synthesis of Complexes. [{Rh(cod)}₂(μ -NH{*p*-tolyl})(μ -OMe)] (1). Solid *p*-tolylamine (15.5 mg, 0.14 mmol) was added to a yellow solution of [{Rh(μ -OMe)(cod)}₂] (70.0 mg, 0.14 mmol) in diethyl ether (10 mL). After 4 h, the yellow solution was concentrated to ca. 5 mL, carefully layered with pentane (10 mL), and left for 3 days at room temperature to give yellow microcrystals. The liquid phase was decanted, and the solid was washed with pentane (5 mL) and vacuum-dried. Yield: 49.0 mg (61%). Anal. Calcd for C₂₄H₃₅NORh₂: C, 51.53; H, 6.31; N, 2.50. Found: C, 51.51; H, 6.11; N, 2.43. ¹H NMR (298 K, benzene-*d*₆): δ 6.80 (δ_A , 4H), 6.66 (δ_B , J_{AB} = 8.4 Hz, 4H) (*p*-MeC₆H₄); 3.93 (m, 2H), 3.80 (m, 2H), 3.69 (m, 2H), 3.24 (m, 2H) (=CH cod); 3.07 (s, 3H, OMe); 2.66 (m, 2H), 2.36 (m, 2H), 2.03 (m, 4H) (CH₂^{exo} cod); 2.10 (s, 3H, *p*-MeC₆H₄); 1.74 (s, 1H, NH); 1.92 (m, 2H), 1.67 (m, 2H), 1.30 (m, 4H) (CH₂^{endo} cod). ¹³C{¹H} NMR (298 K, benzene-*d*₆): δ 150.7, 129.5, 122.0, 121.0 (*p*-MeC₆H₄); 80.1 (d, J_{C-Rh} = 12 Hz), 78.6 (d, J_{C-Rh} = 13 Hz), 73.9 (d, J_{C-Rh} = 14 Hz), 70.2 (d, J_{C-Rh} = 15 Hz) (=CH cod); 53.7 (OMe); 32.7, 32.2, 29.4, 29.0 (CH₂ cod); 20.4 (*p*-MeC₆H₄). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)): 559 (52) (M⁺); 528 (100) (M⁺ - OMe).

[[Rh(cod)]₂(μ -NH{*p*-NO₂C₆H₄})(μ -OMe)] (2). A diethyl ether solution (10 mL) of [{Rh(μ -OMe)(cod)}₂] (70.0 mg, 0.14 mmol) was allowed to diffuse into a solution of *p*-NO₂C₆H₄NH₂ (20.0 mg, 0.14 mmol) in the same solvent (5 mL). Red crystals suitable for diffraction studies formed after 3 days. The solution was decanted, and the solid was washed with 2 \times 5 mL of pentane and vacuum-dried. Yield: 65.0 mg (76%). Anal. Calcd for C₂₃H₃₂N₂O₃Rh₂: C, 46.80; H, 5.46; N, 4.74. Found: 46.40; H, 4.81; N, 4.69. ¹H NMR (298 K, CDCl₃): δ 7.88 (δ_A , 4H), 6.78 (δ_B , J_{A-B} = 9.0 Hz, 4H) (*p*-NO₂C₆H₄); 3.90 (m, 4H), 3.27 (m, 2H), 3.05 (m, 2H) (=CH cod); 2.92 (s, 3H, OMe); 2.41 (m, 8H, CH₂^{exo} cod); 2.15 (m, 8H, CH₂^{endo} cod). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)): 590 (40) (M⁺); 559 (100) (M⁺ - OMe).

[[Rh(cod)]₂(μ -NH{ α -naphthyl})(μ -OMe)] (3). Solid α -naphthylamine (17.7 mg, 0.12 mmol) was added to a diethyl ether solution (10 mL) of [{Rh(μ -OMe)(cod)}₂] (60.0 mg, 0.12 mmol). After being stirred for 1 h, the yellow suspension was concentrated to ca. 2 mL and left in the freezer. The yellow microcrystalline solid was isolated by filtration, washed with 5 mL of cold diethyl ether, and vacuum-dried. Yield: 40.0 mg (54%). Anal. Calcd for C₂₇H₃₅NORh₂: C, 54.47; H, 5.92; N, 2.35. Found: C, 54.32; H,

6.01; N, 2.20. ¹H NMR (298 K, benzene-*d*₆): δ 8.77 (m, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.39 (m, 1H), 7.21 (m, 3H), 6.93 (m, 1H) (C₁₀H₇NH); 3.95 (m, 2H), 3.84 (m, 2H), 3.30 (m, 2H), 2.84 (m, 2H) (=CH cod); 3.07 (s, 3H, OMe); 2.62 (m, 2H), 2.33 (m, 2H), 1.99 (m, 2H), 1.87 (m, 2H) (CH₂^{exo} cod); 2.39 (s, 1H, NH); 1.81 (m, 2H), 1.53 (m, 2H), 1.29 (m, 2H), 1.08 (m, 2H) (CH₂^{endo} cod). ¹³C{¹H} NMR (298 K, benzene-*d*₆): δ 149.8, 135.0, 129.1, 128.6, 125.8, 124.6, 122.6, 120.3, 116.8, 109.8 (C₁₀H₇NH); 80.1 (d, J_{C-Rh} = 12 Hz), 78.8 (d, J_{C-Rh} = 13 Hz), 74.1 (d, J_{C-Rh} = 14 Hz), 71.5 (d, J_{C-Rh} = 14 Hz) (=CH cod); 53.6 (OMe); 32.7, 32.2, 29.6, 29.1 (CH₂ cod). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)): 595 (32) (M⁺); 564 (100) (M⁺ - OMe).

[[Ir(cod)]₂(μ -NH{*p*-tolyl})(μ -OMe)] (4). Solid *p*-tolylamine (12.9 mg, 0.12 mmol) was added to a yellow suspension of [{Ir(μ -OMe)(cod)}₂] (80.0 mg; 0.12 mmol) in diethyl ether (10 mL). After being stirred for 2 h, the yellow solution was concentrated to ca. 2 mL, carefully layered with pentane (10 mL), and left in the freezer for 3 days. The resulting yellow microcrystals were isolated by filtration, washed with 5 mL of pentane, and vacuum-dried. Yield: 52.0 mg (58%). Anal. Calcd for C₂₄H₃₅NOIr₂: C, 39.06; H, 4.78; N, 1.90. Found: C, 39.09; H, 4.76; N, 1.85. ¹H NMR (298 K, benzene-*d*₆): δ 6.80 (δ_A , 4H), 6.58 (δ_B , J_{A-B} = 7.8 Hz, 4H) (*p*-MeC₆H₄); 3.90 (m, 2H), 3.69 (m, 4H), 3.24 (m, 2H) (=CH cod); 3.47 (s, 3H, OMe); 2.85 (s, 1H, NH); 2.52 (m, 2H), 2.26 (m, 2H), 1.97 (m, 4H) (CH₂^{exo} cod); 2.08 (s, 3H, *p*-MeC₆H₄); 1.97 (m, 2H), 1.80 (m, 2H), 1.11 (m, 2H), 0.98 (m, 2H) (CH₂^{endo} cod). ¹³C{¹H} NMR (298 K, benzene-*d*₆): δ 147.3, 130.8, 128.7, 121.5 (*p*-MeC₆H₄); 63.5, 61.6, 57.5, 52.2 (=CH cod); 55.2 (OMe); 34.2, 33.8, 29.4, 29.2 (CH₂ cod); 20.3 (*p*-MeC₆H₄). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)): 738 (15) (M⁺); 707 (100) (M⁺ - OMe).

[[Rh(cod)]₂(μ -NH{*p*-tolyl})(μ -OH)] (5). Solid *p*-tolylamine (23.5 mg, 0.22 mmol) was added to a yellow suspension of [{Rh(μ -OH)(cod)}₂] (100.0 mg, 0.22 mmol) in diethyl ether (8 mL). After being stirred for 2 h, the yellow suspension was concentrated to ca. 2 mL, carefully layered with pentane (20 mL), and left in the refrigerator for 2 days. The liquid phase was decanted, and the solid was washed with pentane (5 mL) and vacuum-dried. Yield: 80.0 mg (67%). Anal. Calcd for C₂₃H₃₃NORh₂: C, 50.66; H, 6.10; N, 2.57. Found: 49.93; H, 5.63; N, 2.64. ¹H NMR (298 K, benzene-*d*₆): δ 6.82 (δ_A , 2H), 6.70 (δ_B , J_{A-B} = 8.1 Hz, 2H) (*p*-MeC₆H₄); 3.75 (m, 6H), 3.26 (m, 2H) (=CH cod); 2.61 (m, 2H), 2.40 (m, 2H), 2.10 (m, 4H) (CH₂^{exo} cod); 2.07 (s, 3H, *p*-MeC₆H₄); 1.86 (s, 1H, NH); 1.80 (m, 2H), 1.75 (m, 2H), 1.36 (m, 4H) (CH₂^{endo} cod); -0.90 (s, 1H, OH). ¹³C{¹H} NMR (298 K, benzene-*d*₆): δ 151.0, 129.9, 129.1, 120.8 (MeC₆H₄); 78.4 (d, J_{C-Rh} = 12 Hz), 77.1 (J_{C-Rh} = 13 Hz), 74.0 (J_{C-Rh} = 14 Hz), 71.1 (J_{C-Rh} = 14 Hz) (=CH cod); 33.0, 32.0, 30.0, 29.1 (CH₂ cod); 20.6 (*p*-MeC₆H₄). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)): 545 (90) (M⁺); 528 (100) (M⁺ - OH).

[[Rh(cod)]₂(μ -NH{*p*-NO₂C₆H₄})(μ -OH)] (6). The addition of solid *p*-NO₂C₆H₄NH₂ (15.2 mg, 0.11 mmol) to a suspension of [{Rh(μ -OH)(cod)}₂] (50.0 mg, 0.11 mmol) in diethyl ether (10 mL) gave a red microcrystalline solid. After being stirred for 30 min, the suspension was left in the refrigerator overnight. The solution was decanted, and the solid was washed with diethyl ether (5 mL) and vacuum-dried. Yield: 45.0 mg (71%). Anal. Calcd for C₂₂H₃₀N₂O₃Rh₂: C, 45.85; H, 5.25; N, 4.86. Found: 45.37; H, 4.82; N, 4.49. ¹H NMR (298 K, CDCl₃): δ 7.89 (δ_A , 2H), 6.82 (δ_B , J_{A-B} = 9.0 Hz, 2H) (*p*-NO₂C₆H₄); 3.84 (m, 4H), 3.35 (m, 2H), 3.16 (m, 2H) (=CH cod); 2.50 (m, 4H), 2.30 (m, 4H) (CH₂^{exo} cod); 1.83 (m, 2H), 1.58 (m, 6H) (CH₂^{endo} cod); 1.82 (s, 1H, NH); -0.89 (s, 1H, OH). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)): 576 (40) (M⁺); 559 (100) (M⁺ - OH).

Table 6. Crystallographic Data for the Structural Analyses of Complexes **2**, **7'**, and **8**

	2	7'	8
empirical formula	C ₂₃ H ₃₂ N ₂ O ₃ Rh ₂	C ₃₈ H ₅₄ NO ₃ Rh ₃	C ₁₄ H ₁₇ N ₂ O ₂ Rh
fw	590.33	881.55	348.21
temp, K	293(2)	173(2)	173(2)
space group	<i>Pnma</i> (no. 62)	<i>P1</i> (no. 2)	<i>P2₁/n</i> (no. 14)
<i>a</i> , Å	12.639(2)	10.1587(11)	9.4419(14)
<i>b</i> , Å	15.733(3)	11.4766(12)	12.0801(17)
<i>c</i> , Å	11.309(2)	16.4380(17)	12.2334(17)
α , deg		105.480(2)	
β , deg		90.307(2)	110.573(3)
γ , deg		109.288(2)	
<i>V</i> , Å ³	2248.8(7)	1734.0(3)	1306.3(3)
<i>Z</i>	4	2	4
ρ (calcd), g cm ⁻³	1.744	1.688	1.770
μ (Mo K α), mm ⁻¹	1.494	1.448	1.306
<i>R</i> (<i>F</i>) [<i>F</i> ² > 2 σ (<i>F</i> ²)] ^a	0.0288	0.0546	0.0533
<i>R</i> _w (<i>F</i> ²) (all data) ^b	0.0615	0.1143	0.1063

^a $R(F) = \sum[|F_o| - |F_c|]/\sum|F_o|$, for 1476, 4438, and 1829 observed reflections for **2**, **7'**, and **8**, respectively. ^b $R_w(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

[{Rh(cod)}₂(μ -NH(α -naphthyl))(μ -OH)]₂·[Rh(μ -OH)(cod)]₂·2THF (7'**). Solid α -naphthylamine (18.8 mg, 0.13 mmol) was added to a yellow suspension of [Rh(μ -OH)(cod)]₂ (60.0 mg, 0.13 mmol) in diethyl ether (5 mL). After being stirred for 1 h, the suspension was evaporated to dryness. The residue was dissolved in THF (3 mL), and the solution was carefully layered with pentane (15 mL). Cubic yellow crystals suitable for diffraction studies were formed after 4 days. The solution was decanted, and the solid was washed with pentane (2 mL) and vacuum-dried. Yield: 83.0 mg (72%). Anal. Calcd for C₃₈H₅₄NO₃Rh₃: C, 51.77; H, 6.17; N, 1.59. Found C, 51.46; H, 6.43; N, 1.70. ¹H NMR (298 K, benzene-*d*₆) for **7'**: δ 8.65 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.20 (m, 2H), 7.15 (m, 1H), 7.05 (d, *J* = 6.9 Hz, 1H) (C₁₀H₇NH); 3.83 (m, 2H), 3.73 (m, 2H), 3.10 (m, 2H), 2.66 (m, 2H) (=CH cod); 2.00 (m, 6H), 1.83 (m, 2H) (CH₂^{exo} cod); 1.50 (m, 2H), 1.34 (m, 4H), 1.11 (m, 2H) (CH₂^{endo} cod); 2.58 (s, 1H, NH); -1.01 (s, 1H, OH). ¹³C{¹H} NMR (298 K, benzene-*d*₆) for **7'**: δ 150.2, 153.1, 129.1, 128.0, 125.9, 125.8, 124.8, 122.6, 120.2, 116.6 (C₁₀H₇NH); 78.4 (d, *J*_{C-Rh} = 11 Hz), 77.2 (d, *J*_{C-Rh} = 9 Hz), 74.1 (d, *J*_{C-Rh} = 15 Hz), 72.1 (d, *J*_{C-Rh} = 11 Hz) (=CH cod); 32.9, 31.9, 29.8, 29.0 (CH₂ cod). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)) for **7'**: 581 (100) (M⁺); 564 (85) (M⁺ - OH).**

[Rh(*o*-NO₂C₆H₄NH)(cod)] (8**). The addition of solid *o*-NO₂C₆H₄NH₂ (57.1 mg, 0.42 mmol) to a solution of [Rh(μ -OMe)(cod)]₂ (100.0 mg, 0.21 mmol) in THF (10 mL) produced immediately a purple solution. This solution was concentrated to ca. 2 mL, carefully layered with pentane (20 mL), and left undisturbed for 3 days at room temperature. The resulting dark-purple needles were separated by decantation, washed with pentane (2 \times 5 mL), and vacuum-dried. Yield: 132.0 mg (92%). Anal. Calcd for C₁₄H₁₇N₂O₂Rh: C, 48.29; H, 4.92; N, 8.04. Found C, 47.89; H, 5.00; N, 7.89. ¹H NMR (298 K, CDCl₃): δ 7.87 (d, *J* = 9.1 Hz, 1H), 7.00 (m, 1H), 6.58 (d, *J* = 9.0 Hz, 1H), 6.39 (m, 1H) (*o*-NO₂C₆H₄); 6.08 (s, 1H, NH); 4.46 (m, 2H), 3.87 (m, 2H) (=CH cod); 2.44 (m, 4H, CH₂^{exo} cod), 2.00 (m, 4H, CH₂^{endo} cod). ¹³C{¹H} NMR (298 K, CDCl₃): δ 155.4, 135.6, 133.0, 126.5, 126.0 (d, *J*_{C-Rh} = 2 Hz), 117.6 (*o*-NO₂C₆H₄); 84.4 (d, *J*_{C-Rh} = 11 Hz), 71.8 (d, *J*_{C-Rh} = 11 Hz) (=CH cod); 31.1, 29.4 (CH₂ cod). MS (FAB⁺, CH₂Cl₂; *m/z* (rel intens, %)) for **7'**: 348 (100) (M⁺).**

Crystal Structure Determination of Compounds **2**, **7'**, and **8**.

A summary of crystal data and refinement parameters is given in Table 6. Data were collected on a Siemens P4 diffractometer at room temperature (**2**) or on a Bruker Smart APEX at 173 K (**7'**,

8), with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Corrections for Lorentz and polarization effects were applied. The structures were solved by the Patterson method (SHELXS97)¹⁹ and difference Fourier techniques and refined by full-matrix least-squares on *F*² (SHELXL97).¹⁹ Scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

Crystal Data for [Rh(cod)]₂(μ -NH(*p*-NO₂C₆H₄))(μ -OMe)] (2**). A red irregular block of approximate dimensions 0.09 \times 0.14 \times 0.34 mm was used for data collection. Of 4734 measured reflections in the range 2θ = 4–50° ($\omega/2\theta$ scans), 2056 were unique (*R*_{int} = 0.0318); a ψ scan absorption correction was applied,²⁰ with minimum/maximum transmission factors of 0.617/0.843. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens of the sp³ carbons were calculated and refined riding on the corresponding atoms; those bonded to the nitrogen or to sp² carbons were located in a difference Fourier map and refined with free positional and isotropic displacement parameters. Final agreement factors were obtained (Table 6) for 185 parameters with no restraints; GOF = 1.005. The largest peak and hole in the final difference map were 0.46 and -0.66 e Å⁻³.**

Crystal Data for [Rh(cod)]₂(μ -NH(α -naphthyl))(μ -OH)]₂·[Rh(μ -OH)(cod)]₂·2THF (7'**). A yellow irregular block of approximate dimensions 0.06 \times 0.12 \times 0.18 mm was used for data collection. Of 20410 measured reflections in the range 2.6–54° in 2θ (ω scans), 7512 were unique (*R*_{int} = 0.0791); a multiscan absorption correction based on this multiplicity was performed,²¹ with minimum/maximum transmission factors of 0.724/0.929. All non-hydrogen atoms were refined with anisotropic displacement parameters, except the carbon atoms of the cod ligands of the [Rh(μ -OH)(cod)]₂ complex. This dinuclear molecule sits on an inversion center located in the midpoint of the intermetallic vector; this symmetry constraint imposes the presence of a static disorder for the ligands (bridging hydroxides and terminal cyclooctadienes), with 2-folded dinuclear complexes of equal occupancy at both sides of the center of symmetry. Bond restraints in the C–C bond distances were necessary to make the refinement to converge; no hydrogens were included for this complex. The THF solvent was also partially disordered, with two oxygens in the model (complementary occupancy factors of 0.63(5) and 0.37(5)), and refined without hydrogens and with restraints in the C–O bond lengths. The positions of the remaining hydrogen atoms were geometrically calculated, except those bonded to nitrogen, oxygen, and the sp² carbons of the cod ligands in the [Rh₂(cod)₂(μ -NH(α -naphthyl))-(μ -OH)] complex, which were located in a difference Fourier map; all of them were refined riding on the corresponding atoms. Final agreement factors were obtained (Table 6) for 431 parameters and 63 restraints; GOF = 0.888. The largest peak and hole in the final difference map were 0.798 and -0.802 e Å⁻³.**

Crystal Data for [Rh(*o*-NO₂C₆H₄NH)(cod)] (8**). A purple needle of approximate dimensions 0.02 \times 0.04 \times 0.34 mm was used for data collection. Of 8167 reflections integrated in the range 2θ = 4.7–54° (ω scans), 2824 were unique (*R*_{int} = 0.1068); a multiscan absorption correction was performed,²¹ with minimum/maximum transmission factors of 0.536/0.925. All non-hydrogen atoms were refined with anisotropic displacement parameters;**

(19) Programs for Crystal Structure Analysis (release 97-2): G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen, Germany, 1998.

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

(21) *SADABS: Area-Detector Absorption Correction*; Siemens Industrial Automation, Inc.: Madison, WI, 1996.

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hydrogens were introduced in calculated positions and refined riding on the corresponding atoms. Final agreement factors were obtained (Table 6) for 175 parameters with no restraints; GOF = 0.866. The largest peak and hole in the final difference map were 0.973 and $-0.910 \text{ e } \text{\AA}^{-3}$.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of complexes **2**, **7'**, and **8** and the $^1\text{H}, ^1\text{H}$ -COSY spectrum of complex **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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