Key Factors Determining the Course of Methyl Iodide Oxidative Addition to Diamidonaphthalene-Bridged Diiridium(I) and Dirhodium(I) Complexes

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The course of methyl iodide oxidative addition to various nucleophilic complexes, $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**1**), $[IrRh(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**2**), and $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PR_3)_2]$ (R = *i*Pr, **3**; Ph, **4**; *p*-tolyl, **5**; Me, **6**), has been investigated. The CH_3I addition to complex **1** readily affords the diiridium(II) complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)I(CH_3)(CO)_2(PiPr_3)_2]$ (**7**), which undergoes slow rearrangement to give a thermodynamically stable stereoisomer, **8**. The reaction of the Ir−Rh complex **2** gives the ionic compound $[IrRh(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PiPr_3)_2]I$ (**10**). The dirhodium compounds, **3**−**5**, undergo one-center additions to yield acyl complexes of the formula $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)I(COCH_3)(CO)(PR_3)_2]$ (R = *i*Pr, **12**; Ph, **13**; *p*-tolyl, **14**). The structure of **12** has been determined by X-ray diffraction. Further reactions of these Rh(III)−Rh(I) acyl derivatives with CH_3I are productive only for the *p*-tolylphosphine derivative, which affords the bis-acyl complex $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3CO)_2I_2(P(p\text{-}tolyl)_3)_2]$ (**15**). The reaction of the PMe_3 derivative, **6**, allows the isolation of the bis-methyl complex $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}I)(CH_3)_2(CO)_2(PMe_3)_2]I$ (**16a**), which emanates from a double one-center addition. Upon reaction with methyl triflate, the starting materials, **1**, **2**, **3**, and **6**, give the isostructural cationic methyl complexes **9**, **11**, **17**, and **18**, respectively. The behavior of these cationic methyl compounds toward CH_3I, $CH_3OSO_2CF_3$, and tetrabutylamonium iodide is consistent with the role of these species as intermediates in the S_N2 addition of CH_3I. Compounds **18** and **17** react with an excess of methyl triflate to give $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}OSO_2CF_3)(CH_3)_2(CO)_2(PMe_3)_2][CF_3SO_3]$ (**19**) and $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(OSO_2CF_3)(COCH_3)(CH_3)(CO)(PiPr_3)_2][CF_3SO_3]$ (**20**), respectively. Upon treatment with acetonitrile, complexes **17** and **18** give the isostructural cationic acyl complexes $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(COCH_3)(NCCH_3)(CO)(PR_3)_2][CF_3SO_3]$ (R = *i*Pr, **21**; Me, **22**). A kinetic study of the reaction leading to **21** shows that formation of these complexes involves a slow insertion step followed by the fast coordination of the acetonitrile. The variety of reactions found in this system can be rationalized in terms of three alternative reaction pathways, which are determined by the effectiveness of the interactions between the two metal centers of the dinuclear complex and by the steric constraints due to the phosphine ligands.

Introduction

The oxidative addition of methyl iodide to low-valent dinuclear complexes of late transition metals can occur across the two metal atoms to give metal−metal bonded products, in a reaction frequently given as a characteristic example for dinuclear reactivity and cooperation between close metal centers. The first examples for such two-center additions were reported for gold(I) complexes,[1] and thereafter, the same behavior was found in rhodium(I), iridium(I), palladium(0), platinum(0), and mercury(II) dinuclear compounds.[2] However, despite the number of examples fitting such behavior, a significant number of exceptions also exists, including the reactions reported for rhodium and iridium dinuclear systems presenting "face-to-face" or "open-book" structures.[3]

Almost regularly, the iridium(I) complexes give two-center additions to afford Ir(II)−Ir(II) compounds.[4−7] The exceptions to this trend reported so far include one case of methyl iodide one-center addition leading to an Ir(III)−Ir(I) product,[8] a tautomeric equilibrium of oxidative addition products obtained from the addition of $PhCH_2Cl$,[9] and a single example for a double addition that affords an Ir(III)−Ir(III) species.[10] By contrast, only a few two-center additions have been reported for rhodium(I) compounds,[11,12] which most frequently undergo

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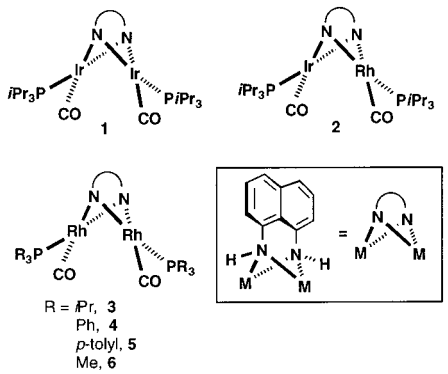
Scheme 1



double one-center reactions to yield Rh(III)−Rh(III) products.[10,13−16] Often, the Rh(III)−Rh(I) intermediates of these latter processes are labile species that can barely be detected;[10] however, in some intriguing cases, such mixed-valence compounds are the final products of the reaction, even in the presence of an excess of methyl iodide.[17] The presence of carbonyl ligands in the starting rhodium complex introduces more uncertainty about the resulting products of the addition, since insertion reactions may[15−17] or may not occur.[12,14] This latter aspect of the reaction may also be relevant to the mechanisms of hydroformylation reactions catalyzed by dinuclear rhodium compounds.[18]

The aforementioned panorama of reactivity illustrates that the behavior of each dinuclear system in this apparently simple reaction is, very often, singular and, in general, difficult to foretell. Alternatively, the above examples can be seen as snapshots taken from a complex reaction scheme consisting of several competitive pathways. Unfortunately, only a few systems can provide experimental access to this complexity, since, most frequently, the features of the ligands and the bridging system selectively determine a unique reaction pathway. Because of this situation, very little is known about the relative incidences of steric and electronic variables in the course of these oxidative additions.

This study focuses on the elementary steps involved in the addition of methyl iodide to dinuclear Rh(I) and Ir(I) complexes containing carbonyl ligands and the flexible 1,8-diamidonaphthalene bridging ligand.[19−22] The results show that the reactions follow an S_N2 mechanism, the nature of the products being dependent on the metal−metal interaction and the steric properties of the cationic methyl intermediates of these reactions.

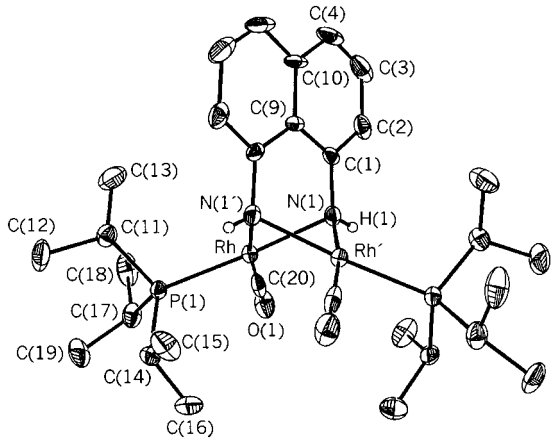


Figure 1. Molecular structure of complex **3**. Primed atoms are related to the unprimed ones by the C_2 symmetry transformation: $-x, y, 1/2-z$.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Rh···Rh′	2.8461(6)		
Rh−P(1)	2.2715(11)		
Rh−N(1)	2.134(3)	Rh−N(1′)	2.113(4)
Rh−C(20)	1.841(5)		
Rh−N(1)−Rh′	84.16(14)		
P(1)−Rh−C(20)	91.36(13)		
P(1)−Rh−N(1′)	95.90(10)	P(1)−Rh−N(1)	170.16(10)
N(1)−Rh−N(1′)	74.27(17)		
N(1)−Rh−C(20)	98.42(16)	N(1′)−Rh−C(20)	171.66(15)

Results

1. Synthesis and Characterization of the Starting Complexes. The complexes chosen as starting materials in this study are depicted in Scheme 1. The diiridium complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**1**) and the rhodium derivative $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PPh_3)_2]$ (**4**) have been previously reported to have symmetric C_2 structures.[20,23] The other rhodium derivatives, $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**3**), $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(P(p\text{-}tolyl)_3)_2]$ (**5**), and $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PMe_3)_2]$ (**6**), can be prepared in good yields following the same procedures employed in the synthesis of **1**. The spectroscopic data of **3**, **5**, and **6** also indicate C_2 symmetric structures, as has been confirmed in the case of complex **3** by X-ray diffraction (Figure 1). Selected bond distances and angles for this complex are presented in Table 1.

The hetero-bimetallic derivative $[IrRh(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**2**) has been prepared by treatment of a mixture of the mononuclear fragment $[Rh(1,8\text{-}(NH)_2naphth)(cod)](CF_3SO_3)$ and the dimer $[Ir(\mu\text{-}OMe)(cod)]_2$ with triethylamine, followed by reaction with carbon monoxide and the phosphine. The observation of the molecular ion of **2** in the FAB+ mass spectrum and the spectroscopic data support the proposed structure, in which a transoid disposition of the phosphine ligands is assumed by analogy with the homo-bimetallic derivatives.

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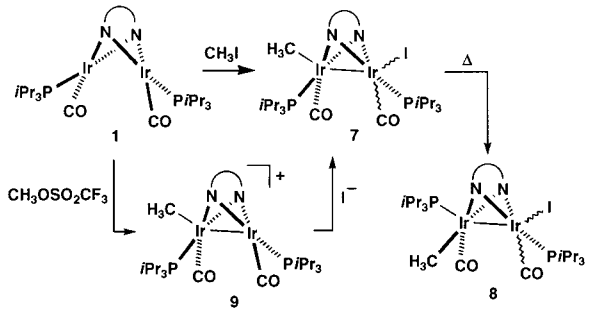
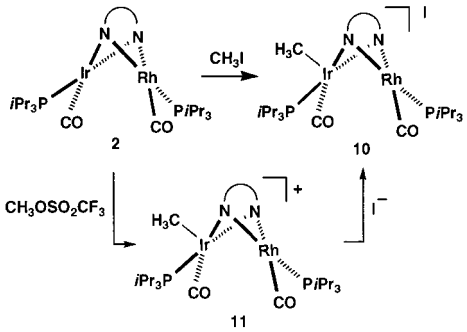
Scheme 2



Scheme 3



2. The Reaction of the Diiridium Complex 1 with Methyl Iodide. Compound **1** readily reacts with 1 equiv of CH_3I to afford the complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)I(CH_3)(CO)_2(PiPr_3)_2]$-(**7**). This species does not undergo further reaction with CH_3I, even at high temperature and in the presence of a large excess of reactant. The spectroscopic data of **7** support the structural proposal depicted in Scheme 2, which is similar to that previously reported for the PPh_3 analogue of **7**.[6] The assignment of oxidation state 2 to both iridium centers of **7** follows from the IR spectrum, which shows two ν(CO) modes at rather similar frequencies, 1979 and 1959 cm^{-1}, in the range expected for this oxidation state.[20]

In solution, complex **7** slowly isomerizes into a new compound, **8**, with the isomeric nature of both complexes being deduced from their similar mass spectra and elemental analyses. Comparison of the $^{13}C\{^1H\}$ NMR spectra of compounds **7** and **8** indicates that the isomerization reaction results in the rearrangement of the phosphine ligands. Thus, the signals due to the C_1 and C_8 carbons of the diamidonaphthalene bridge of **7** show the pattern expected for the phosphines in transoid positions: two doublets with J_{CP} coupling constants of about 2 Hz.[20,21] In turn, such carbons appear in **8** as a doublet and a singlet, supporting the structure shown in Scheme 2 in which a phosphine has moved to an axial position. In further agreement with this structure, the ^1H NOESY NMR spectrum of **8** shows the existence of NOE enhancement between the signal due to the methyl ligand and that of one N−H proton of the bridge, indicating the coordination of the methyl at one of the nonaxial positions of the complex.

Oxidative addition reactions such as that leading to **7** are assumed to follow S_N2 mechanisms.[5,10] Such a mechanism can be reproduced stepwise by the sequential addition to the starting complex of methyl triflate and an ionic iodide. The addition of methyl triflate to acetone solutions of **1** results in the formation of the complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PiPr_3)_2]$-$[CF_3SO_3]$ (**9**). The compound gives a 1:1 electrolyte in acetone and shows a sharp singlet in the $CDCl_3$ ^{19}F NMR spectrum at the chemical shift expected for a free triflate anion. The structure of **9** (Scheme 2), which can be deduced from the ^1H and $^{13}C\{^1H\}$ NMR spectra by using the same arguments detailed above for the previous complexes, is similar to that found for the complex $[Ir_2(\mu\text{-}Pz)_2(CH_3)(CO)_2(PiPr_3)_2][ClO_4]$ (Pz = pyrazolate).[5]

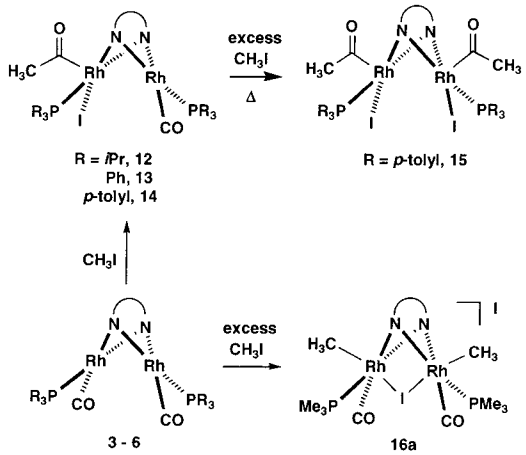
The structural and electronic features of cationic diiridium compounds analogous to **9**, which formally contains Ir(III)−Ir(I) centers, have been previously discussed in light of crystallographic information and theoretical calculations.[5,20] Such studies conclude that these compounds should be better described as Ir(III)−Ir(I) mixed-valence species containing a weak metal−metal bond which partially reduces the electronic differences between the metals. This model is consistent with the IR spectrum of **9**, which shows two ν(CO) modes at 2017 and 1977 cm^{-1}, indicative of rather different metal centers. The reactivity of **9** is also consistent with this description, since the complex does not undergo a second reaction with methyl triflate, even in the presence of an excess of reactant. In turn, upon treatment with tetrabutylamonium iodide, complex **9** is readily transformed into **7** (Scheme 2), as a result of the nucleophilic attack of iodide to the formally Ir(I) center. This reaction was monitored by ^{31}P NMR in acetone-d_6 at 233 K, and no reaction intermediates were observed.

3. The Reaction of the Iridium−Rhodium Complex 2 with Methyl Iodide. A yellow solid of composition $[IrRh(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PiPr_3)_2]I$ (**10**) has been isolated after treatment of the hetero-bimetallic complex **2** with 1 equiv of methyl iodide. The ^1H NMR spectrum of **10** in CD_2Cl_2 shows a slightly broadened doublet at δ 0.54, in which a J_{HP} coupling constant of 1.8 Hz can be estimated. Since no J_{HRh} coupling is observed, the signal can be attributed to a methyl ligand bonded to the Ir atom. The $^{31}P\{^1H\}$ NMR spectrum displays two signals corresponding to the two nonequivalent phosphine ligands: a doublet (J_{PRh} = 140.9 Hz) and a broad singlet. The broadening of this latter signal may correlate with the observation that the acetone solutions of **10** are conducting, although their molar conductivities (50 Ω^{-1} cm^2 mol^{-1}) are lower than those expected for a 1:1 electrolyte (100−140). These two observations together suggest that the solutions of **10** may contain cationic species in equilibrium with neutral ones. Our attempts to obtain more information about the dynamic process by low-temperature NMR measurements were unsuccessful, since decoalescence of the broad signals was not observed above 193 K.

The cationic species involved in the aforementioned equilibrium can be isolated, with triflate as counterion, by treatment of **2** with $CH_3OSO_2CF_3$. The spectroscopic data obtained for the complex $[IrRh(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PiPr_3)_2]$-$[CF_3SO_3]$ (**11**) confirm that the attack of the electrophile, CH_3^+, occurs at the iridium center. Products of CH_3^+ attack to the rhodium atom were not observed, even under an excess of methyl triflate. As expected, the treatment of **11** with tetrabutylamonium iodide readily affords complex **10**. Interestingly, the ^1H and $^{31}P\{^1H\}$ NMR spectra of **10** and **11** in acetone-d_6 are basically identical, although, as mentioned above, the former shows some broadened signals. In view of the data available, the most plausible description of **10** is the ionic species shown in Scheme 3, in which the iodide ligand may be involved in a weak bond with the iridium center or could form a relatively stable ion pair in solution.

4. Reactions of the Dirhodium Complexes with Methyl Iodide. Treatment of solutions of complexes **3**−**5** with 1 equiv of CH_3I leads to acyl derivatives of the formula $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)I(COCH_3)(CO)(PR_3)_2]$ (R = *i*Pr, **12**; Ph, **13**; *p*-tolyl, **14**) (Scheme 4). The structure of the triisopropylphosphine derivative, **12**, determined by X-ray diffraction, is shown in Figure 2, with selected bond distances and angles being

Scheme 4



collected in Table 2. The compound is the result of a one-center CH_3I addition. Rh(1) is formally a Rh(III) center that displays a regular square-pyramidal geometry, only being distorted by the small bite angle of the diamidonaphthalene ligand. As found in related dinuclear acyl compounds, the acyl ligand occupies an axial position, trans to the coordination vacancy.[24] Moreover, the Rh(2) is nearly square planar, as expected for a Rh(I). Although both metal atoms are coordinatively unsaturated, the intermetallic distance, 2.8465(4) Å, does not suggest the presence of a metal−metal bond, since it is the same distance found in the starting material **3**. The spectroscopic features of **12**, which are consistent with the solid-state structure, are similar to those of complexes **13** and **14**, suggesting analogous structures for the three derivatives.

The Rh(I) centers of compounds **12**−**14** do not undergo the oxidative addition of a second equivalent of methyl iodide at room temperature. Under more stringent reaction conditions (343 K and 10-fold excess of CH_3I), compounds **12** and **13** decompose, but the reaction of **14** allows the isolation of the product of a double addition, $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3CO)_2I_2(P(p\text{-}tolyl)_3)_2]$ (**15**) (Scheme 4), in modest yield. The elemental analysis and mass spectrum for **15** are consistent with the proposed stoichiometry, and its spectroscopic data are those expected for a bis-acyl complex of C_2 symmetry.

The reaction of the trimethylphosphine dirhodium complex **6** with CH_3I seems to be rather nonselective. The spectroscopic observation of equimolar mixtures of **6** and CH_3I in CD_2Cl_2 reveals the formation of several compounds at room temperature. Among these products, the species resulting from a double one-center addition, $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}I)(CH_3)_2(CO)_2(PMe_3)_2]I$ (**16a**), could be isolated due to its insolubility in chlorinated solvents. The complex is formed in relatively poor yields (below 40%) even in the presence of excess CH_3I. The elemental analysis of **16a** and its mass spectrum agree with the proposed stoichiometry, and its ^1H NMR spectrum in acetone-d_6 is consistent with a bis-methyl complex of C_2 symmetry.

Further characterization of the cationic complex **16** has been achieved by using the more soluble triflate analogue $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}I)(CH_3)_2(CO)_2(PMe_3)_2][CF_3SO_3]$ (**16b**), whose synthesis will be described below. The data collected for **16b**, including $^{13}C\{^1H\}$ NMR and NOESY spectra and molar conductivity, lead to the structural proposal depicted in Scheme 4, in which the two methyl groups occupy the axial positions of the complex and the two Rh(III) centers are bridged by an iodide ligand. Precedents for such double additions leading to similar structures have been reported.[13]

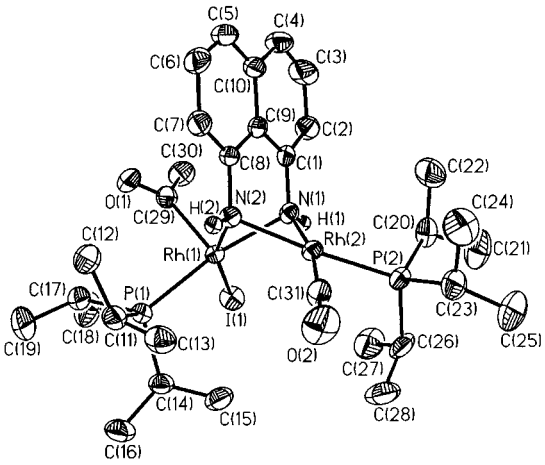


Figure 2. Molecular structure of the complex **12**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 12

Rh(1)···Rh(2)	2.8465(4)		
Rh(1)−I(1)	2.6823(4)		
Rh(1)−C(29)	1.974(4)	Rh(2)−C(31)	1.809(4)
Rh(1)−N(2)	2.080(3)	Rh(2)−N(2)	2.109(3)
Rh(1)−N(1)	2.130(3)	Rh(2)−N(1)	2.118(3)
Rh(1)−P(1)	2.3451(10)	Rh(2)−P(2)	2.2925(11)
P(1)−Rh(1)−I(1)	93.67(3)		
P(1)−Rh(1)−N(1)	167.69(9)	P(2)−Rh(2)−N(1)	98.91(9)
P(1)−Rh(1)−N(2)	101.02(10)	P(2)−Rh(2)−N(2)	172.21(10)
P(1)−Rh(1)−C(29)	92.03(12)	P(2)−Rh(2)−C(31)	89.57(13)
N(1)−Rh(1)−I(1)	89.03(9)		
N(1)−Rh(1)−N(2)	73.91(13)	N(1)−Rh(2)−N(2)	73.58(13)
N(1)−Rh(1)−C(29)	99.42(14)	N(1)−Rh(2)−C(31)	167.97(16)
N(2)−Rh(1)−I(1)	160.27(9)		
N(2)−Rh(1)−C(29)	93.62(14)	N(2)−Rh(2)−C(31)	98.16(16)
C(29)−Rh(1)−I(1)	98.99(12)		
Rh(1)−N(2)−Rh(2)	85.62(12)	Rh(2)−N(1)−Rh(1)	84.13(11)
Rh(1)−C(29)−C(30)	115.9(3)		
Rh(1)−C(29)−O(1)	122.4(3)		
C(30)−C(29)−O(1)	121.6(4)		

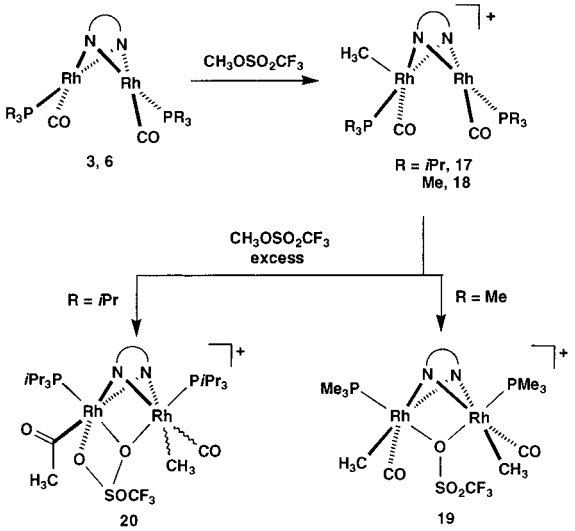
Despite the differences found for the CH_3I addition to the P*i*Pr$_3$ and PMe_3 analogues **3** and **6**, the reactions seem to proceed via the same initial step, since the treatment of these complexes with 1 equiv of $CH_3OSO_2CF_3$ affords isostructural complexes. The structures of derivatives $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PiPr_3)_2][CF_3SO_3]$ (**17**) and $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PMe_3)_2][CF_3SO_3]$ (**18**) (Scheme 5) could be established on the basis of the NMR spectra and NOE measurements, being similar to those previously described for the diiridium and iridium−rhodium compounds **9** and **11**.

5. Reactivity of the Cationic Methyl Complexes 17 and 18. In contrast with the behavior of their diiridium and iridium−rhodium analogues, the dirhodium derivatives, **17** and **18**, do react with a second equivalent of $CH_3OSO_2CF_3$ (Scheme 5). However, both the features of these reactions and the structures of the reaction products suggest that the addition of this second equivalent of methyl triflate is not as simple as just a new electrophilic attack.

The reaction of the PMe_3 derivative **18** with 1 equiv of $CH_3OSO_2CF_3$ in acetone-d_6 is slow, requiring 10 h at room temperature to form the complex $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}OSO_2CF_3)(CH_3)_2(CO)_2(PMe_3)_2][CF_3SO_3]$ (**19**). The ^{19}F NMR

(24) (a) Mayanza, A.; Bonnet, J.-J.; Galy, J.; Kalck, P.; Poilblanc, R. *J. Chem. Res., Synop.* **1980**, 146. (b) Pinillos, M. T.; Elduque, A.; Martín, E.; Navarro, N.; Oro, L. A.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1995**, *34*, 3105.

Scheme 5

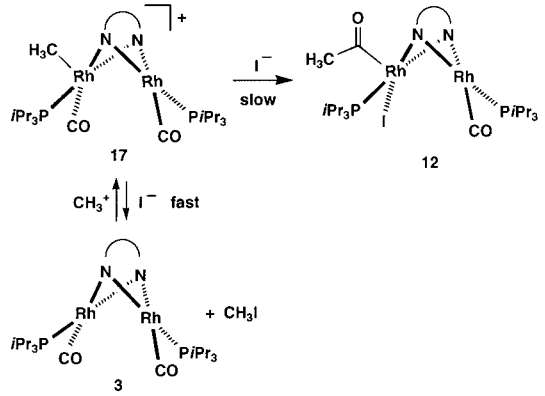


spectrum of **19**, in acetone-d_6 at room temperature, shows a broad signal at δ −78.06, which at 253 K gives rise to two singlets at δ −77.68 and −78.35. This suggests that one of the triflate groups is coordinated and undergoes fast exchange with free triflate at room temperature; in agreement with this observation, the molar conductivity of **19** in acetone indicates a 1:1 electrolyte. The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of the complex, which contains slightly broadened signals at room temperature, are indicative of a symmetric C_s structure. Moreover, the ^{13}C{^{1}H} NMR signals of the C1 and C8 carbons of the diamidonaphthalene bridge (both dd, showing couplings to both phosphorus atoms) and the ^{1}H NOESY spectrum strongly support the structural proposal depicted in Scheme 5, in which the phosphines occupy the two axial positions of the complex and the triflate bridges the metals in a μ-κO fashion. The bridging position of this ligand is the only one compatible with the C_s symmetry, and its monodentate character has been proposed by analogy with other structurally related dinuclear complexes determined by X-ray diffraction.[10]

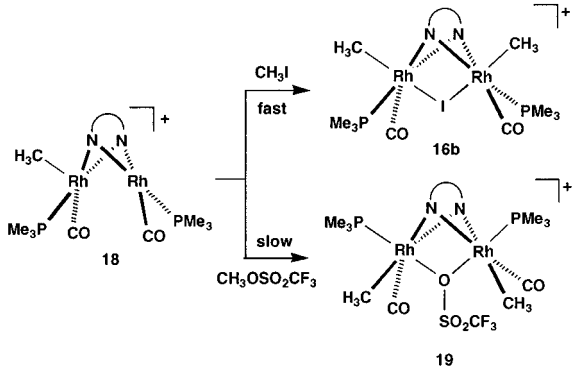
The addition of a second equivalent of methyl triflate to the P*i*Pr$_3$ derivative **17** is also a slow reaction, which affords the complex [Rh$_2$(μ-1,8-(NH)$_2$naphth)(COCH$_3$)(CH$_3$)(OSO$_2$CF$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$][CF$_3$SO$_3$] (**20**). This compound shows several features in common with the PMe$_3$ derivative **19**: a molar conductivity indicative of a 1:1 electrolyte, both phosphine ligands occupying axial positions, and two ^{19}F NMR signals (already at room temperature). However, complex **20** is asymmetric as a result of the presence of a terminal carbonyl and an acyl ligand, as can be seen in either the IR spectrum or the ^{1}H and ^{13}C{^{1}H} NMR spectra. These spectroscopic data lead to the structure depicted in Scheme 5, in which an unusual κO, μ-$\kappa O'$ coordination of the triflate is proposed. This proposal is mainly based on the consideration that any monodentate coordination of the triflate would leave at least one unsaturated metal center, located in close proximity of the free electron pairs of the noncoordinated oxygens. Further support for this coordination mode could be provided by the ^{13}C NMR signal corresponding to the coordinated triflate, which is displaced 3.5 ppm to higher field relative to that of the free triflate, and by the precedents for such complex coordination modes in sulfonate-polynuclear aggregates of alkaline and alkaline-earth elements.[25]

(25) 3D Search and Research using the Cambridge Structural Database. Allen, F. H.; Kennard, O. *Chem. Des. Auto. News* **1993**, *8* (1), 31.

Scheme 6



Scheme 7



The reactions of the cationic methyl compounds **17** and **18** with ionic iodides display noticeable differences. Treatment of acetone-d_6 solutions of the P*i*Pr$_3$ derivative **17** with tetrabutylamonium iodide readily generates an equilibrium of compounds **17**, **3**, and CH$_3$I (Scheme 6). Thus, none of the rhodium centers of **17** is initially attacked by the nucleophile, but the methyl ligand is. As expected, this equilibrium mixture, in which **17** is the minor component (less than 10%), slowly evolves to give the acyl complex **12**.

In contast, the reaction of the PMe$_3$ compound **18** with the ionic iodide is very fast, providing a mixture of unidentified complexes. When methyl iodide is used instead of tetrabutylamonium iodide, the reaction is still fast and affords the Rh(III)−Rh(III) complex **16b**, previously described (Scheme 7). Despite the formal similarity between this latter addition and that of methyl triflate, which leads to the Rh(III)−Rh(III) complex **19** (Scheme 7), the features of these two reactions are very different. Thus, CH$_3$I addition to **18** is fast and gives an iodide-bridged compound of C_2 symmetry, in which the methyl ligands are axial. In turn, the addition of CH$_3$OSO$_2$CF$_3$ to the same complex is very slow, providing a triflate-bridged compound of C_s symmetry in which the axial positions are occupied by the phosphines. The different behavior of **18** toward these two reactants suggests that the electrophilic attack of methyl to the formally Rh(I) center of **18** has to be preceded by the coordination of the anion at the bridging position. This coordination seems to be fast in the case of iodide, but the accommodation of the triflate would require a prior reorganization of the phosphines, which may account for the slowness of the reaction.

The reactions of **17** and **18** with neutral nucleophiles such as acetonitrile give, in both cases, acyl derivatives (Scheme 8). The spectroscopic data obtained for the complexes [Rh$_2$(μ-1,8-(NH)$_2$naphth)(COCH$_3$)(NCCH$_3$)(CO)(PiPr$_3$)$_2$][CF$_3$SO$_3$] (**21**) and

Scheme 8

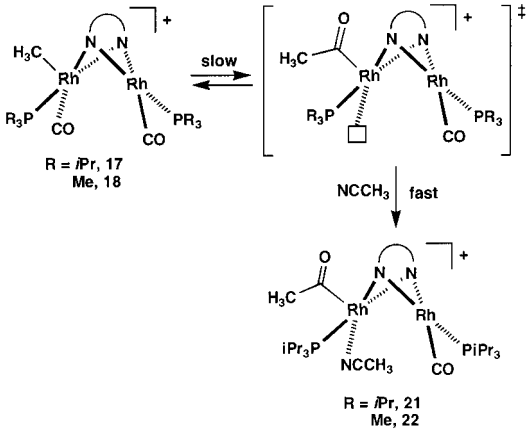


Table 3. Rate Constants for the Insertion Reaction in Complex 17[a] (Scheme 8)

T (K)	$[NCCH_3]$ (M)	k_{obs} (s^{-1})	$[CF_3SO_3^-]$
292	0.08	3.8×10^{-4}	0.06
303	0.08	8.6×10^{-4}	0.06
303	0.32	9.9×10^{-4}	0.06
303	3.18	8.9×10^{-4}	0.06
303	0.08	9.7×10^{-4}	0.12[b]
303	0.08	9.3×10^{-4}	BF_4^- [c]
313	0.08	1.9×10^{-3}	0.06
320	0.08	4.8×10^{-3}	0.06

[a] [**17**] = 0.06 M in $CDCl_3$. [b] Concentration of triflate was adjusted by addition of tetrabutylamonium triflate. [c] The BF_4^- analogue of **17** was used.

$[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(COCH_3)(NCCH_3)(CO)(PMe_3)_2][CF_3SO_3]$ (**22**) are consistent with the proposed structures, in which the axial position of the acyl ligands is assumed by analogy with the neutral acyl complexes already described.

The kinetics of the transformation of **17** into **21** were measured by ^{31}P NMR in $CDCl_3$ solutions, with pseudo-first-order rate constants (k_{obs}) for this reaction being obtained at different temperatures and various acetonitrile and triflate concentrations (Table 3). The process is zero order with respect to the acetonitrile concentration, in agreement with a two-step process: a slow insertion reaction, followed by the fast coordination of the nucleophile (Scheme 8). The activation parameters for this reaction can be reasonably estimated from the temperature dependence of k_{obs}, giving the values $\Delta H^{\ddagger} = 14 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27 \pm 4$ eu, which are in the range found for similar migratory insertions in mononuclear complexes.[26] Despite the negative entropy increment, the coordinating triflate anion does not participate in the insertion transition state, since rates are unaffected by the use of different triflate concentrations or the BF_4^- analogue of **17**.[27]

Discussion

The compounds resulting from the stoichiometric additions of CH_3I to the starting complexes **1**−**5** can be obtained through a series of sequential reactions with $CH_3OSO_2CF_3$ and I^-. This would be in agreement with an S_N2 mechanism, generally considered as the main pathway for the oxidative addition of methyl iodide to either mononuclear or dinuclear compounds.[5,10,28,29]

As nucleophiles, all the starting complexes used in this study behave similarly, being attacked by the electrophile CH_3^+ at the position where the steric constraints around the metal are minimized. In agreement with the features expected for this initial step of the oxidative addition, the Ir−Rh derivative **2** undergoes the attack of CH_3^+ at the (more nucleophilic) Ir center. All the cationic compounds resulting from these nucleophilic attacks have the same structure, which is that expected for the kinetic product. However, despite their similar structures, the compounds show significant electronic differences, which are reflected to some extent by spectroscopic data such as the ν(CO) frequencies, but become more obvious when their reactivities are analyzed.

The fast reaction of the diiridium cation $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PiPr_3)_2]^+$ (**9**) with iodide to give the diiridium(II) complex **7** reflects the efficacy of the Ir(III)−Ir(I) bond proposed for **9**. The reaction shows that electron delocalization away from the formally Ir(I) center, via the metal−metal bond, is enough to turn it into an electrophilic center. This electronic withdrawal seems to happen also in the cationic dirhodium analogue, $[Rh_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CH_3)(CO)_2(PiPr_3)_2]^+$ (**17**), although it leads to a less extreme situation. Thus, the formally Rh(I) center of **17** does not undergo electrophilic reaction with iodide, while its nucleophilic reaction with $CH_3OSO_2CF_3$ is very slow and requires the previous binding of the triflate at a bridging position of the dinuclear complex. Under these "neutral" electronic features, which can be extrapolated to the other dirhodium methyl cations and the iridium−rhodium derivative **11**, the fate of the reactions with iodide seems to be determined by steric factors.

Complex **18** undergoes fast attack of the iodide at the Rh(III) center, since the low steric requirements of the PMe_3 ligands allow the anion to reach the "pocket" of the dimetallic framework. The coordination of iodide at the position trans to the methyl ligand, which is in fact a bridging position, seems to enhance the nucleophilicity of the second rhodium center, which undergoes fast attack of a second methyl to give the cationic moiety **16**. Thus, under these conditions, the intermediates resulting from a single center addition are elusive and the reactions end in two-center addition products. This result coincides with the reactivity observed in other "open-book" dirhodium systems.[10,13]

Bulky phosphine ligands, such as PPh_3, $P(p\text{-tolyl})_3$, or $PiPr_3$, hinder the attack of iodide to the Rh(III) center. Then, this attack does not take place until the migratory insertion step provides an accessible coordination vacancy, giving rise to the formation of the neutral acyl derivatives **12**−**14**. In the case of the iridium−rhodium compound **11**, the insertion reaction at the iridium center does not seem to be favorable,[30] and, therefore, the product of CH_3I addition is essentially ionic.

A moderate electron withdrawal from the formally Rh(I) center seems to take place for the neutral acyl compounds **12**−**14**, since deactivation of this metal atom toward a second addition is apparent in these complexes. Nevertheless, such second additions are possible at temperatures close to those of decomposition of the complexes. In this respect, the correct balance between the thermal stability of the compounds and

(26) Maitlis, P. M.; Haynes, A.; Sunley, G. J., Howard, M. J. *J. Chem. Soc., Dalton Trans.* **1996**, 2187.
(27) This tetrafluoroborate complex has been prepared by abstraction of the iodide ligand from **12** using $AgBF_4$, a reaction that also indicates that the insertion step involved in the formation of the dirhodium acyl derivatives is reversible.
(28) Pudephatt, R. J.; Scott, J. D. *Organometallics* **1985**, *4*, 1221.
(29) Griffin, T. R.; Cook, D. B.; Haynes, A.; Pearson, J. M.; Monti, D.; Morris, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 3029.
(30) Ellis, P. R.; Pearson, J. M.; Haynes, A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *Organometallics* **1994**, *13*, 3215.

the basicity of the ligands seems to be important. In fact, the small difference in basicity between P(*p*-tolyl)$_3$ and PPh_3 determines whether the product of second addition can or cannot be obtained.

The reactivity studies presented indicate that the metal centers of these diamidonaphthalene-bridged compounds are not independent entities, since once a metal center has reacted, the reactivity of the other metal is substantially modified. This fact is apparent from the behavior of the mixed-valence M(III)−M(I) species, which are key intermediates in the transformations studied. In addition to their chemical behavior, some spectroscopic features of these M(III)−M(I) compounds can be regarded as an indication of the mutual influence between the metals. Thus, the IR ν(CO) frequencies, the ^{31}P NMR J_{PRh} coupling constants, and the J_{CRh} couplings observed for the carbonyl ligand signals of the $^{13}C\{^1H\}$ NMR spectra give values that are intermediate between those expected for independent M(III) and M(I) metal centers. These features have been explained in terms of a weak metal−metal bond connecting the M(III)−M(I) centers in the case of very related diiridium compounds,[5] an explanation that may be extrapolated to the dirhodium derivatives. However, such extrapolation seems to be a difficult exercise in view of the structural parameters obtained for the Rh(III)−Rh(I) complex, **12**. Indeed, the reactivity of **12** indicates that its Rh(I) center is less nucleophilic than those of the starting complex **3**, an observation that correlates with the magnitudes of ν(CO) (1960 cm^{-1} in **12** vs 1924, 1939 cm^{-1} in **3**) and J_{PRh} (151.6 Hz in **12** vs 156.9 Hz in **3**). However, since the intermetallic distances found in **3** and **12** are equal, the proposal of any kind of metal−metal interaction in the latter seems inadvisable, unless such interaction was established indirectly through the bridging ligand. This latter pathway has been shown to be feasible in edge-sharing dinuclear compounds.[31]

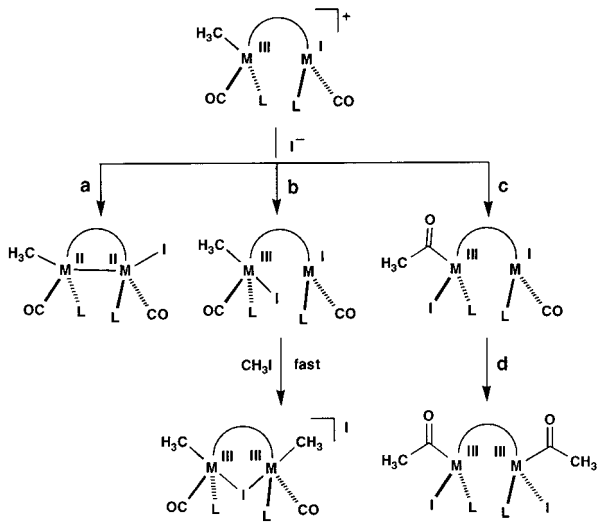
Conclusions

The nucleophilic M(I) diamidonaphthalene-bridged dinuclear complexes employed in these studies provide access to a variety of products by means of the oxidative addition of methyl iodide. This variety includes M(II)−M(II) methyl compounds, M(III)−M(III) dimethyl and diacyl derivatives, and M(III)−M(I) methyl and acyl complexes. In all cases, the reactions proceed via the initial formation of cationic M(III)−M(I) methyl intermediates, which can evolve following the three alternative pathways of Scheme 9.

Path **a** is viable only when the release of electron density from M(I) is large enough to turn this metal center into an electrophile. Path **b** requires ligands small enough to allow the iodide to enter the "pocket" of the dinuclear moiety. This path leads to double one-center additions, since once the iodide has bonded to the complex, the second attack of CH_3^+ seems to be very favorable. In contrast to **a** and **b**, which are both fast processes, path **c** has been found to be slow, although it is the only possible pathway when the requirements for **a** and **b** are not fulfilled. A new addition through path **d** has been found to be feasible, but at least in the systems used in these studies, it requires reaction conditions close to those leading to decomposition of the complexes. When none of these three pathways are feasible, the final product of the addition is the cationic methyl complex.

The Scheme 9 provides a comprehensive framework that fits most of the literature results on this reaction. In addition, they provide further evidence for the important role played by the cooperative effects between metal centers in this kind of dinuclear species, since the predominant factor determining the course of the reaction is the effectiveness of the intermetallic influence.

Scheme 9



Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. C, H, N, and S analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000, or a Bruker ARX, 300 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P and ^{19}F NMR chemical shifts were measured relative to H_3PO_4 (85%) and $CFCl_3$, respectively. Coupling constants, *J*, are given in hertz. Generally, spectral assignments were achieved by ^{1}H COSY, NOESY, and ^{13}C DEPT experiments. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with a Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Conductivities were measured in ca. 3 × 10^{-4} M solutions using a Philips PW 9501/01 conductimeter.

Synthesis. All reactions were carried out with exclusion of air by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use.[32] The complexes [Ir$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(PiPr$_3$)$_2$] (**1**),[20] [Ir(μ-OMe)(cod)]$_2$[33] and [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_4$][23] were prepared by known procedures. The mononuclear compound [Rh(1,8-(NH)$_2$naphth)(cod)](CF$_3$SO$_3$) was prepared following the procedure described in ref 34 for its perchlorate analogue. All the compounds whose preparations are described below are air sensitive in solution. The low-valent compounds **1**−**6** and the cationic species **9**−**11**, **16**−**22** are air and moisture sensitive also in the solid state.

Preparation of [IrRh(μ-1,8-(NH)$_2$naphth)(CO)$_2$(P*i*Pr$_3$)$_2$] (2). A thf solution (5 mL) of [Rh(1,8-(NH)$_2$naphth)(cod)](CF$_3$SO$_3$) (100 mg, 0.193 mmol) and [Ir(μ-OMe)(cod)]$_2$ (64 mg, 0.096 mmol) was treated with NEt$_3$ (26.8 μL, 0.193 mmol) and strirred for 30 min. The resulting solution was evaporated to dryness, treated with diethyl ether (5 mL), and filtered through Celite. Then, carbon monoxide was bubbled through the solution for 2 min, and triisopropylphosphine (36.9 μL, 0.193 mmol) was added. After 30 min of reaction, the orange solid

(31) Aullón, G.; Alemany. P.; Alvarez, S. *J. Organomet. Chem.* **1994**, *478*, 75.

(32) Shriver, D. F. *The Manipulation of Air-sensitive Compounds*; McGraw-Hill: New York, 1969.

(33) Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

(34) Oro, L. A.; Fernández, M. J.; Modrego, J.; López, J. M. *J. Organomet. Chem.* **1985**, *287*, 409.

formed was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 131 mg (82%); IR (cm^{-1}) 3358 (m, ν(NH)), 1915, 1936 (s, ν(CO)); ^1H NMR ($CDCl_3$, 293 K) δ 1.23 (dd, $J_{HP} = 15.6$, $J_{HH} = 8.1$, 9H, PCHCH_3), 1.25 (dd, $J_{HP} = 13.5$, $J_{HH} = 7.5$, 9H, PCHCH_3), 1.37 (dd, $J_{HP} = 13.5$, $J_{HH} = 7.2$, 18H, PCHCH_3), 2.25, 2.36 (both m, 3H, PCHCH$_3$), 4.19, 4.29 (both br, 1H, NH), 6.78 (d, $J_{HH} = 7.2$, 2H, CH), 7.07, 7.08 (both dd, $J_{HH} = 8.1$, 7.2, 1H, CH), 7.29, 7.30 (both d, $J_{HH} = 8.1$, 1H, CH); $^{31}P\{^1H\}$ ($CDCl_3$, 293 K) δ 36.62 (s), 63.57 (d, $J_{PRh} = 161.4$); MS (FAB+, *m*/*z* (%)) 828 (100) [M^+]. Anal. Calcd for $C_{30}H_{50}N_2IrO_2P_2Rh$: C, 43.53; H, 6.09; N, 3.38. Found: C, 43.33; H, 5.72; N, 3.27.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(P*i*Pr$_3$)$_2$] (3). A solution of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_4$] (0.5 g, 1.05 mmol) in a mixture of diethyl ether/acetone (5:1) (40 mL) was treated with P*i*Pr$_3$ (403.9 μL, 2.11 mmol). After 30 min, the resulting orange solid was separated by decantation, washed with hexane, and dried in vacuo: yield 575 mg (76%); IR (cm^{-1}) 3358 (m, ν(NH)), 1924, 1939 (s, ν(CO)); ^1H NMR ($CDCl_3$, 293 K) δ 1.33, 1.20 (both dd, $J_{HP} = 13.6$, $J_{HH} = 6.9$, 18 H, P(CHCH_3), 2.22 (m, 6H, PCHCH$_3$), 3.75 (br, 2H, NH), 6.67 (d, $J_{HH} = 8.1$, 2H, CH), 7.03 (dd, $J_{HH} = 8.1$, 7.2, 2H, CH), 7.18 (d, $J_{HH} = 7.2$, 2H, CH); $^{31}P\{^1H\}$ ($CDCl_3$, 293 K) δ 63.85 (d, $J_{PRh} = 156.9$); $^{13}C\{^1H\}$ ($CDCl_3$, 293 K) δ 19.80, 19.92 (both s, PCHCH$_3$), 25.44 (d, $J_{CP} = 22.6$, PCHCH$_3$), 110.33 (d, $J_{CP} = 2.8$, CH), 119.04 (s, CH), 119.23 (s, C), 126.26 (s, CH), 134.87 (s, C), 149.97 (d, $J_{CP} = 2.6$, C), 193.64 (dd, $J_{CRh} = 73.7$, $J_{CP} = 18.9$, CO); MS (FAB+, *m*/*z* (%)) 738 (100) [M^+]. Anal. Calcd for $C_{30}H_{50}N_2O_2P_2Rh_2$: C, 48.79; H, 6.82; N, 3.79. Found: C, 48.37; H, 6.65; N, 3.74.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(PPh$_3$)$_2$] (4). The compound was prepared as described for **3**, by using PPh$_3$ (553.4 mg, 2.11 mmol): yield 642 mg (65%); IR (cm^{-1}) 3335 (m, ν(NH)), 1948, 1906 (s, ν(CO)); ^1H NMR ($CDCl_3$, 293 K) 3.25 (br, 2H, NH), 6.12 (d, $J_{HH} = 7.5$, 2H, CH), 7.01 (dd, $J_{HH} = 7.8$, 7.5, 2H, CH), 7.29 (d, $J_{HH} = 7.8$, 2H, CH), 7.35−7.73 (m, 30H, CH); $^{31}P\{^1H\}$ (CD_2Cl_2, 293 K) δ 46.02 (d, $J_{PRh} = 161.3$); MS (FAB+, *m*/*z* (%)) 942 (15) [M^+]. Anal. Calcd for $C_{48}H_{38}N_2O_2P_2Rh_2$: C, 61.16; H, 4.06; N, 2.97. Found: C, 61.05; H, 4.41; N, 2.91.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(P(*p*-tolyl)$_3$)$_2$] (5). The compound was prepared as described for **3**, by using *p*-tolylphosphine (907.2 mg, 2.11 mmol): yield 700 mg (65%); IR (cm^{-1}) 3341 (m, ν(NH)), 1948, 1969 (s, ν(CO)); ^1H NMR (acetone-d_6, 293 K) δ 2.39 (s, 18H, CH$_3$), 3.31 (br, 2H, NH), 6.16 (d, $J_{HH} = 7.2$, 2H, CH), 6.99 (dd, $J_{HH} = 7.8$, 7.2, 2H, CH), 7.06 (d, $J_{HH} = 7.8$, 2H, CH), 7.29 (d, $J_{HH} = 7.8$, 12H, CH), 7.59 (dd, $J_{HP} = 10.5$, $J_{HH} = 7.8$, 12H, CH); $^{31}P\{^1H\}$ (acetone-d_6, 293 K) δ 43.82 (d, $J_{PRh} = 160.5$); MS (FAB+, *m*/*z* (%)) 1026 (100) [M^+]. Anal. Calcd for $C_{54}H_{50}N_2O_2P_2Rh_2$: C, 63.17; H, 4.91; N, 2.73. Found: C, 63.62; H, 5.29; N, 2.91

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(PMe$_3$)$_2$] (6). The compound was prepared as described for **3**, by using PMe$_3$ (225.2 μL, 2.11 mmol): yield 514 mg (86%); IR (cm^{-1}) 3362 (m, ν(NH)), 1927, 1952 (s, ν(CO)); ^1H NMR (CD_2Cl_2, 293 K) δ 1.45 (dd, $J_{HP} = 9.3$, $J_{HRh} = 1.4$, 18H, PCH$_3$), 3.88 (br, 2H, NH), 6.82 (d, $J_{HH} = 7.2$, 2H, CH), 7.11 (dd, $J_{HH} = 7.8$, 7.2, 2H, CH), 7.26 (d, $J_{HH} = 7.8$, 2H, CH); $^{31}P\{^1H\}$ (CD_2Cl_2, 293 K) δ −1.38 (d, $J_{PRh} = 150.7$); $^{13}C\{^1H\}$ (CD_2Cl_2, 293 K) δ 16.75 (d, $J_{CP} = 29.9$, PCH$_3$), 110.65 (d, $J_{CP} = 3.2$, CH), 119.53 (s, C), 119.88, 126.98 (both s, CH), 135.46 (s, C), 149.87 (d, $J_{CP} = 3.2$, C), 193.06 (dd, $J_{CRh} = 73.2$, $J_{CP} = 21.1$, CO); MS (FAB+, *m*/*z* (%)) 570 (100) [M^+]. Anal. Calcd for $C_{18}H_{26}N_2O_2P_2Rh_2$: C, 37.91; H, 4.59; N, 4.91. Found: C, 37.97; H, 4.94; N, 4.78.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)I(CH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$] (7). A solution of **1** (245 mg, 0.27 mmol) in CH_2Cl_2 (5 mL) was treated with methyl iodide (17 μL, 0.27 mmol). After 30 min, the resulting solution was concentrated to ca. 0.5 mL and treated with diethyl ether to give a yellow solid. The solid was separated by decantation, washed several times with diethyl ether, and dried in vacuo: yield 237 mg (83%); IR (cm^{-1}) 3375, 3342 (m, ν(NH)), 1979, 1959 (s, ν(CO)); ^1H NMR ($CDCl_3$, 293 K) δ 0.62 (d, $J_{HP} = 1.8$, 3H, Ir−CH$_3$), 1.02 (dd, $J_{HP} = 14.1$, $J_{HH} = 6.9$, 18H, PCHCH_3), 1.19 (dd, $J_{HP} = 12.9$, $J_{HH} = 7.2$, 9H, PCHCH_3), 1.37 (dd, $J_{HP} = 14.1$, $J_{HH} = 6.9$, 9H, P(CHCH_3), 2.05, 2.51 (both m, 3H, PCHCH$_3$), 5.03, 5.09 (both br, 1H, NH), 6.72 (d, $J_{HH} = 7.1$, 2H, CH), 7.02, 7.08 (both t, $J_{HH} = 8.1$, 1H, CH), 7.55, (d, $J_{HH} = 8.1$, 2H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 16.10 (s), 23.39 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −28.09 (d, $J_{CP} = 2.9$, Ir−CH$_3$), 19.06 (d, $J_{CP} = 1.8$, PCHCH$_3$), 19.62 (s, PCHCH$_3$), 19.72 (d, $J_{CP} = 1.8$, PCHCH$_3$), 20.59 (s, PCHCH$_3$), 24.57 (d, $J_{CP} = 28.6$, PCHCH$_3$), 26.14 (d, $J_{CP} = 29.0$, PCHCH$_3$), 112.57 (d, $J_{CP} = 4.1$, CH), 112.97 (d, $J_{CP} = 3.2$, CH), 121.44 (s, CH), 123.49 (s, C), 126.25, 126.35 (both s, CH), 134.93 (s, C) 147.09, 147.32 (both d, $J_{CP} = 2.2$, C), 179.10 (d, $J_{CP} = 9.6$, CO), 179.50 (d, $J_{CP} = 11.5$, CO); MS (FAB+, *m*/*z* (%)) 1059 (15) [M^+], 932 (100) [M^+ − I]. Anal. Calcd for $C_{31}H_{53}N_2IIr_2O_2P_2$: C, 35.16; H, 5.04; N, 2.64. Found: C, 34.91; H, 5.07; N, 2.74.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)I(CH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$] (8). A solution of **7** (200 mg, 0.19 mmol) in thf (5 mL) was refluxed for 8 h. The resulting solution was concentrated to ca. 0.5 mL and treated with diethyl ether to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 176 mg (88%); IR (cm^{-1}): 3396, 3321 (m, ν(NH)), 1973, 1952 (s, ν(CO)); ^1H NMR ($CDCl_3$, 293 K) δ 0.67 (dd, $J_{HP} = 12.9$, $J_{HH} = 7.2$, 9H, PCHCH_3), 1.10 (dd, $J_{HP} = 14.7$, $J_{HH} = 6.9$, 9H, PCHCH_3), 1.11 (d, $J_{HP} = 2.4$, 3H, Ir−CH$_3$), 1.40 (dd, $J_{HP} = 13.8$, $J_{HH} = 6.9$, 9H, PCHCH_3), 1.42 (dd, $J_{HP} = 13.5$, $J_{HH} = 6.9$, 9H, P(CHCH_3), 1.69, 2.86 (both m, 3H, PCHCH$_3$), 4.73, 4.98 (both br, 1H, NH), 6.84 (d, $J_{HH} = 7.5$, 1H, CH), 6.97, 7.04 (both dd, $J_{HH} = 7.5$, 7.8, 1H, CH), 7.12 (d, $J_{HH} = 7.5$, 2H, CH), 7.37, 7.43 (both d, $J_{HH} = 7.8$, 1H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 22.28 (s), −2.35 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −25.07 (d, $J_{CP} = 3.8$, Ir−CH$_3$), 18.45 (d, $J_{CP} = 3.1$, PCHCH$_3$), 19.90, 20.09, 20.25 (all s, PCHCH$_3$), 24.18 (d, $J_{CP} = 22.0$, PCHCH$_3$), 28.19 (d, $J_{CP} = 28.9$, PCHCH$_3$), 110.70 (s, CH), 111.45 (d, $J_{CP} = 3.4$, CH), 119.87, 121.01 (both s, CH), 123.07 (s, C), 126.30, 126.33 (both s, CH), 135.40 (s, C), 148.37 (d, $J_{CP} = 1.8$, C), 151.26 (s, C), 177.74 (d, $J_{CP} = 11.7$, CO), 178.36 (d, $J_{CP} = 13.3$, CO); MS (FAB+, *m*/*z* (%)) 1059 (7) [M^+], 932 (100) [M^+ − I]. Anal. Calcd for $C_{31}H_{53}N_2IIr_2O_2P_2$: C, 35.16; H, 5.04; N, 2.64. Found: C, 34.69; H, 5.01; N, 2.85.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(CH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$][CF$_3$SO$_3$] (9). A suspension of **1** (245 mg, 0.27 mmol) in acetone (5 mL) was treated with methyl triflate (30.9 μL, 0.27 mmol) and stirred for 30 min at room temperature. The resulting red solution was filtered through Celite and concentrated to ca. 0.5 mL. Addition of diethyl ether produced the precipitation of a red solid, which was separated by decantation, washed with ether, and dried in vacuo: yield 219 mg (75%); IR (cm^{-1}) 3314 (m, ν(NH)), 2017, 1977 (s, ν(CO)); ^1H NMR (acetone-d_6, 293 K) δ 1.13 (d, $J_{HP} = 2.0$, 3H, Ir−CH$_3$), 1.21 (dd, $J_{HP} = 14.0$, $J_{HH} = 7.1$, 9H, PCHCH_3), 1.43 (dd, $J_{HP} = 15.2$, $J_{HH} = 7.2$, 9H, PCHCH_3), 1.44 (dd, $J_{HP} = 14.5$, $J_{HH} = 7.4$, 9H, PCHCH_3), 1.51 (dd, $J_{HP} = 14.5$, $J_{HH} = 7.2$, 9H, PCHCH_3), 2.86, 3.01 (both m, 3H, PCHCH$_3$), 6.96, 7.21 (both br, 1H, NH), 7.34, 7.39 (both d, $J_{HH} = 7.9$, 1H, CH), 7.68, 7.72 (both d, $J_{HH} = 7.4$, 1H, CH), 7.80 (dd, $J_{HH} = 7.4$, 7.9, 2H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 41.79 (s), 24.75 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ − 19.57 (dd, $J_{CP} = 2.7$, 1.5, Ir−CH$_3$), 20.25, 19.92, 19.53 (all s, PCHCH$_3$), 25.86 (d, $J_{CP} = 29.8$, PCHCH$_3$), 26.51 (d, $J_{CP} = 30.7$, PCHCH$_3$), 114.18 (d, $J_{CP} = 2.3$, CH), 114.60 (d, $J_{CP} = 3.7$, CH), 123.33 (s, CH), 123.53 (s, C), 128.47, 128.84 (both s, CH), 136.22 (s, C), 144.82 (d, $J_{CP} = 2.8$, C), 144.86 (d, $J_{CP} = 3.7$, C), 172.58 (d, $J_{CP} = 10.0$, CO), 178.98 (d, $J_{CP} = 11.5$, CO); ^{19}F NMR ($CDCl_3$, 293 K) δ −79.17 (s); Λ_M (5×10^{-4} M, acetone) = 113 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 932 (10) [M^+]. Anal. Calcd for $C_{32}H_{53}N_2SF_3Ir_2O_5P_2$: C, 35.55; H, 4.94; N, 2.59. Found: C, 35.60; H, 5.22; N, 2.62.

Preparation of [IrRh(μ-1,8-(NH)$_2$naphth)(CH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$]I (10). The compound was prepared following the procedure detailed for **7**, by using complex **2** (250 mg, 0.3 mmol) and methyliodide (19 μL, 0.3 mmol): yield 224 mg (78%); IR (cm^{-1}) 3366, 3327 (m, ν(N−H)), 1983, 1958 (s, ν(CO)); ^1H NMR (CD_2Cl_2, 293 K) δ 0.54 (brd, $J_{HP} = 1.8$, 3H, Ir−CH$_3$), 1.35 (dd, $J_{HP} = 13.8$, $J_{HH} = 7.2$, 18H, PCHCH_3), 1.39 (dd, $J_{HP} = 12.6$, $J_{HH} = 6.9$, 18H, PCHCH_3), 2.54, 2.57 (both m, 3H, PCHCH$_3$), 4.94, 5.41 (both br, 1H, NH), 7.18 (m, $J_{HH} = 7.1$, 4H, CH), 7.57, (d, $J_{HH} = 8.1$, 2H, CH); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K) δ 58.47 (d, $J_{PRh} = 140.9$), 13.59 (br); Λ_M (5×10^{-4} M, acetone) = 50 Ω^{-1} cm^2 mol^{-1}; MS (FAB+, *m*/*z* (%)) 841(100) [M^+ − I]. Anal. Calcd for $C_{31}H_{53}N_2IIrO_2P_2Rh$: C, 38.31; H, 5.49; N, 2.89. Found: C, 38.39; H, 5.51; N, 3.15.

Preparation of [IrRh(μ-1,8-(NH)$_2$naphth)(CH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$][CF$_3$SO$_3$] (11). The compound was prepared following the procedure described for **9**, by using complex **2** (224 mg, 0.27 mmol): yield 225 mg (84%); IR (cm^{-1}) 3294 (m, ν(NH)), 2021, 1996 (s, ν(CO)); ^{1}H NMR (acetone-d_6, 293 K) δ 1.13 (d, J_{HP} = 1.8, Ir−CH$_3$), 1.19 (dd, J_{HP} = 14.4, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.41 (dd, J_{HP} = 13.5, J_{HH} = 6.6, 9H, PCHC*H*$_3$), 1.44 (dd, J_{HP} = 14.7, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 1.53 (dd, J_{HP} = 13.8, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 2.67, 3.03 (both m, 3H, PC*H*CH$_3$), 6.74, 7.28 (both br, 1H, NH), 7.29, 7.36 (both dd, J_{HH} = 7.5, 8.7, 1H, CH), 7.61, 7.67 (both d, J_{HH} = 7.5, 1H, CH), 7.74, 7.78 (d, J_{HH} = 8.7, 1H, CH); ^{31}P{^{1}H} NMR (acetone-d_6, 293 K) δ 18.58 (s), 60.85 (d, J_{PRh} = 150.7); ^{13}C{^{1}H} NMR (acetone-d_6, 293 K) δ −8.61 (d, J_{CP} = 4.1, Ir−CH$_3$), 19.89, 20.06, 20.31, 20.33 (all s, PCH*C*H$_3$), 25.14 (d, J_{CP} = 28.6, P*C*HCH$_3$), 26.32 (d, J_{CP} = 23.5, P*C*HCH$_3$), 113.94, 114.36 (both d, J_{CP} = 3.0, CH), 121.64 (s, C), 122.55 (q, J_{CF} = 321.0, CF$_3$SO$_3$), 123.00, 123.35, 128.31, 128.85 (all s, CH), 136.45 (s, C), 144.45 (d, J_{CP} = 3.7, C), 144.78 (d, J_{CP} = 2.2, C), 172.90 (d, J_{CP} = 9.7, CO), 192.39 (dd, J_{CRh} = 74.2, J_{CP} = 16.6, CO); ^{19}F NMR (CDCl$_3$, 293 K) δ − 79.17 (s); Λ$_M$ (5 × 10^{-4} M, nitromethane) 120 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 841 (100) [M$^+$]. Anal. Calcd for C$_{32}$H$_{53}$N$_2$SF$_3$IrO$_5$P$_2$Rh: C, 38.75; H, 5.39; N, 2.82; S, 3.23. Found: C, 38.84; H, 5.48; N, 2.80; S, 3.30.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)I(COCH$_3$)(CO)(P*i*Pr$_3$)$_2$] (12). The compound was prepared following the procedure detailed for **7**, by using complex **3** (200 mg, 0.27 mmol): yield 190 mg (80%); IR (cm^{-1}) 3375, 3296 (m, ν(NH)), 1960, 1686 (s, ν(CO)); ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ 1.11 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.33 (dd, J_{HP} = 13.5, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.44 (dd, J_{HP} = 13.5, J_{HH} = 7.5, 9H, PCHC*H*$_3$), 1.51 (dd, J_{HP} = 13.3, J_{HH} = 7.3, 9H, PCHC*H*$_3$), 2.21 (m, 3H, PC*H*CH$_3$), 2.29 (s, 3H, COCH$_3$), 2.73 (m, 3H, PC*H*CH$_3$), 4.52, 5.07 (both br, 1H, NH), 6.98 (d, J_{HH} = 7.6, 1H, CH), 7.06 (dd, J_{HH} = 7.6, 8.2, 1H, CH), 7.13 (d, J_{HH} = 8.2, 1H, CH), 7.15 (dd, J_{HH} = 7.6, 8.2, 1H, CH), 7.41 (d, J_{HH} = 7.6, 1H, CH), 7.49 (d, J_{HH} = 8.2, 1H, CH); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) δ 44.63 (d, J_{PRh} = 140.1), 62.21 (d, J_{PRh} = 151.6); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) δ 19.96, 20.12, 20.32, 21.29 (all s, PCH*C*H$_3$), 25.18 (d, J_{CP} = 23.1, P*C*HCH$_3$), 25.87 (d, J_{CP} = 20.7, P*C*HCH$_3$), 43.42 (s, CO*C*H$_3$), 112.58 (d, J_{CP} = 4.6, CH), 113.15 (d, J_{CP} = 2.2, CH), 120.12 (s, C), 120.93, 121.76, 126.79 (all, s, CH), 135.60 (s, C), 148.37, 149.42, (both d, J_{CP} = 3.2, C), 191.98 (dd, J_{CRh} = 74.4, J_{CP} = 17.7, CO), 220.07 (dd, J_{CRh} = 29.2, J_{CP} = 6.7, *C*OCH$_3$); MS (FAB+, *m*/*z* (%)) 880 (35) [M$^+$]. Anal. Calcd for C$_{31}$H$_{53}$N$_2$IO$_2$P$_2$Rh$_2$: C, 42.29; H, 6.07; N, 3.18. Found: C, 41.94; H, 5.64; N, 3.29.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)I(COCH$_3$)(CO)(PPh$_3$)$_2$] (13). The compound was prepared following the procedure detailed for **7**, by using complex **4** (254 mg, 0.27 mmol). The reaction time in this case was 20 h: yield 246 mg (84%); IR (cm^{-1}) 3305, 3325 (m, ν(NH)), 1973, 1688 (s, ν(CO)); ^{1}H NMR (CDCl$_3$, 293 K) δ 1.97 (s, 3H, COCH$_3$), 3.17, 4.13 (both br, 1H, NH), 5.91 (d, J_{HH} = 7.5, 1H, CH), 6.13 (d, J_{HH} = 7.2, 1H, CH), 6.84, 6.92 (both dd, J_{HH} = 7.5, 7.2, 1H, CH), 7.25−7.83 (m, 32H, CH); ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K) δ 41.38 (d, J_{PRh} = 145.4), 45.54 (d, J_{PRh} = 156.9). Anal. Calcd for C$_{49}$H$_{41}$N$_2$IO$_2$P$_2$Rh$_2$: C, 54.26; H, 3.81; N, 2.58. Found: C, 54.18; H, 3.98; N, 2.52.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)I(COCH$_3$)(CO)(P(*p*-tolyl)$_3$)$_2$] (14). The compound was prepared following the procedure described for **7**, by using complex **5** (277 mg, 0.27 mmol). The reaction time in this case was 8 h: yield 255 mg (81%); IR (cm^{-1}) 3322, 3302 (m, ν(NH)), 1979, 1683 (s, ν(CO)); ^{1}H NMR (CDCl$_3$, 293 K) δ 2.08 (s, 3H, COCH$_3$), 2.37, 2.38 (both s, 9H, CH$_3$), 3.31, 4.24 (both br, 1H, NH), 6.06, 6.25 (both d, J_{HH} = 7.5, 1H, CH), 6.95, 7.03 (both dd, J_{HH} = 7.5, 8.1, 1H, CH), 7.13 (brd, J_{HH} = 8.1, 6H, CH), 7.17 (d, J_{HH} = 8.1, 6H, CH), 7.35 (d, J_{HH} = 8.1, 1H, CH), 7.42 (d, J_{HH} = 8.1, 1H, CH), 7.43 (dd, J_{HP} = 11.0, J_{HH} = 8.1, 6H, CH), 7.77 (brdd, $J_{HP} \approx J_{HH}$ = 8.1, 6H, CH); ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K) δ 39.93 (d, J_{PRh} = 145.4), 43.81 (d, J_{PRh} = 155.1); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) δ 21.37, 21.32 (s, CH$_3$), 40.80 (s, CO*C*H$_3$), 112.51 (d, J_{CP} = 4.6, CH), 113.05 (d, J_{CP} = 2.8, CH), 119.78 (s, C), 120.34, 121.72, 126.20, 126.24 (all s, CH), 129.11 (d, J_{CP} = 10.1, CH), 129.50 (d, J_{CP} = 10.6, CH), 129.75 (s, C), 134.28 (d, J_{CP} = 12.4, CH), 134.87 (d, J_{CP} = 9.2, CH), 140.41 (d, J_{CP} = 2.3, C), 140.47 (d, J_{CP} = 2.8, C), 146.79, 147.92, (both d, J_{CP} = 3.7, C), 190.79 (dd, J_{CRh} = 72.3, J_{CP} = 16.5, CO), 219.31 (dd, J_{CRh} = 27.7, J_{CP} = 7.4, *C*OCH$_3$); MS (FAB+, *m*/*z* (%)) 1168 (18) [M$^+$]. Anal. Calcd for C$_{55}$H$_{53}$N$_2$IO$_2$P$_2$Rh$_2$: C, 56.52; H, 4.57; N, 2.40. Found: C, 56.52; H, 4.85; N, 2.11.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CH$_3$CO)$_2$I$_2$(P(*p*-tolyl)$_3$)$_2$] (15). A suspension of **5** (200 mg, 0.19 mmol) in acetone (5 mL) was treated with methyl iodide in excess (119 μL, 1.9 mL). The Schlenk tube was closed, heated at 343 K, and stirred for 20 h. The orange solid formed was separated by decantation, washed with diethyl ether, and dried in vacuo. Recrystallization of the solid from dicloromethane/diethyl ether gave orange crystals: yield 148 mg (58%); IR (cm^{-1}) 3289 (m, ν(NH)), 1709 (s, ν(CO)); ^{1}H NMR (CDCl$_3$, 293 K) δ 2.07 (s, 6H, COCH$_3$), 2.37 (br, 18H, CH$_3$), 4.43 (br, 2H, NH), 6.66 (d, J_{HH} = 7.5, 2H, CH), 7.03 (dd, J_{HH} = 8.1, 7.5, 2H, CH), 7.15 (br, 12H, CH), 7.48 (d, J_{HH} = 8.1, 2H, CH), 7.58 (brdd, $J_{HP} \approx J_{HH}$ = 9.0, 12H, CH); ^{31}P{^{1}H} (CDCl$_3$, 293 K) δ 36.34 (d, J_{PRh} = 143.7); ^{13}C{^{1}H} (CDCl$_3$, 293 K) δ 21.39 (s, CH$_3$), 42.29 (s, CO*C*H$_3$), 114.52 (d, J_{CP} = 4.6, CH), 119.58 (s, C), 125.95, 122.58 (both s, CH), 129.33 (br, CH), 129.76 (s, C), 134.95 (br, CH), 140.35 (br, C), 149.72 (d, J_{CP} = 4.1, C), 213.25 (dd, J_{CRh} = 28.6, J_{CP} = 7.4, CO); MS (FAB+, *m*/*z* (%)) 1310 (10) [M$^+$]. Anal. Calcd for C$_{56}$H$_{56}$N$_2$O$_2$P$_2$I$_2$Rh$_2$: C, 51.32; H, 4.31; N, 2.14. Found: C, 50.84; H, 4.35; N, 2.08.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(μ-I)(CH$_3$)$_2$(CO)$_2$(PMe$_3$)$_2$][CF$_3$SO$_3$] (16b). A solution of **18** (100 mg, 0.13 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with methyl iodide (11 μL, 0.17 mmol) and stirred at room temperature for 2 h. The solution was concentrated to ca. 1 mL and treated with diethyl ether to give an orange solid, which was washed with ether and dried in vacuo: yield 96 mg (84%); IR (cm^{-1}) 3285 (m, ν(NH)), 2058 (s, ν(CO)); ^{1}H NMR (acetone-d_6, 293 K) δ 0.11 (dd, J_{HRh} = 3.6, J_{HP} = 2.4, 6H, Rh−CH$_3$), 1.77 (dd, J_{HP} = 11.7, J_{HRh} = 0.6, 18H, PCH$_3$), 5.87 (br, 2H, NH), 7.34 (dd, J_{HH} = 8.1, 7.2, 2H, CH), 7.54 (d, J_{HH} = 7.2, 2H, CH), 7.68 (d, J_{HH} = 8.1, 2H, CH); ^{31}P{^{1}H} (acetone-d_6, 293 K) δ 2.29 (d, J_{PRh} = 108.1); ^{13}C{^{1}H} (acetone-d_6, 293 K) δ 15.55 (d, J_{CP} = 35.9, PCH$_3$), 15.64 (dd, J_{CRh} = 18.4, J_{CP} = 2.8, Rh−CH$_3$), 117.94 (d, J_{CP} = 4.1, CH), 123.62 (s, C), 124.16, 126.77 (both s, CH), 135.95 (s, C), 147.06 (d, J_{CP} = 4.7, C), 187.19 (dd, J_{CRh} = 59.4, J_{CP} = 11.5, CO); ^{19}F NMR (CDCl$_3$, 293 K) δ −79.17 (s); Λ$_M$ (5 × 10^{-4} M, acetone) 109 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 727 (100) [M$^+$]. Anal. Calcd for C$_{21}$H$_{32}$N$_2$SF$_3$IO$_5$P$_2$Rh$_2$: C, 28.78; H, 3.68; N, 3.20; S, 3.66. Found: C, 29.02; H, 4.13; N, 3.45; S 4.09.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$][CF$_3$SO$_3$] (17). The compound was prepared following the procedure described for **9**, by using complex **3** (200 mg, 0.27 mmol): yield 219 mg (90%); IR (cm^{-1}) 3296 (m, ν(NH)), 2048, 1988 (s, ν(CO)); ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ 1.12 (dd, J_{HP} = 14.4, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.33 (dd, J_{HP} = J_{HRh} = 2.4, Rh−CH$_3$), 1.35 (dd, J_{HP} = 14.7, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.43 (dd, J_{HP} = 15.0, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.50 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 2.64, 2.42 (both m, 3H, PC*H*CH$_3$), 5.82, 5.86 (both br, 1H, NH), 7.24−7.36 (m, 3H, CH), 7.39 (d, J_{HH} = 7.2, 1H, CH), 7.59 (d, J_{HH} = 9.6, 1H, CH), 7.61 (d, J_{HH} = 8.7, 1H, CH); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) δ 62.03 (d, J_{PRh} = 151.7), 50.83 (d, J_{PRh} = 110.8); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) δ 16.60 (dd, J_{CRh} = 24.3, J_{CP} = 5.2, Rh−CH$_3$), 20.20, 19.82, 19.77 (all s, PCH*C*H$_3$), 25.19 (d, J_{CP} = 21.9, P*C*HCH$_3$), 25.95 (d, J_{CP} = 23.4, P*C*HCH$_3$), 115.14 (d, J_{CP} = 2.5, CH), 116.02 (d, J_{CP} = 4.8, CH), 119.18 (s, C), 127.37, 127.27, 123.76, 125.57 (all s, CH), 135.29 (s, C), 142.86 (d, J_{CP} = 3.5, C), 143.33 (d, J_{CP} = 3.8, C), 188.12 (dd, J_{CRh} = 60.8, J_{CP} = 13.4, CO), 190.18 (dd, J_{CRh} = 74.3, J_{CP} = 17.1, CO); ^{19}F NMR (CDCl$_3$, 293 K) δ −79.17 (s); Λ$_M$ (5 × 10^{-4} M, nitromethane) 69 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 753 (100) [M$^+$]. Anal. Calcd for C$_{32}$H$_{53}$N$_2$SF$_3$O$_5$P$_2$Rh$_2$: C, 42.58; H, 5.92; N, 3.10; S, 3.55. Found: C, 42.15; H, 5.59; N, 3.38; S, 3.55.

Preparation of [Rh$_2$(μ-1,8-(NH)$_2$naphth)(CH$_3$)(CO)$_2$(PMe$_3$)$_2$][CF$_3$SO$_3$] (18). The compound was prepared following the procedure described for **9**, by using complex **6** (154 mg, 0.27 mmol): yield 154 mg (78%); IR (cm^{-1}) 3294 (m, ν(NH)), 2054, 1990 (s, ν(CO)); ^{1}H NMR (acetone-d_6, 293 K) δ 1.01 (dd, J_{HRh} = 3.9, J_{HP} = 2.1, 3H, Rh−CH$_3$), 1.66 (dd, J_{HP} = 10.5, J_{HRh} = 1.5, 9H, PCH$_3$), 1.84 (d, J_{HP} = 11.1, J_{HRh} = 0.6, 9H, PCH$_3$), 6.79, 6.92 (both br, 1H, NH), 7.28, 7.31 (both dd, J_{HH} = 7.5, 8.1, 1H, CH), 7.42, 7.50 (both d, J_{HH} = 7.5, 1H,

CH), 7.59, 7.63 (both d, J_{HH} = 8.1, 1H, CH); $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K) δ 2.21 (d, J_{PRh} = 145.4), 9.06 (d, J_{PRh} = 110.8); $^{13}C\{^1H\}$ (acetone-d_6, 293 K) δ 8.02 (dd, J_{CRh} = 24.4, J_{CP} = 4.8, Rh−CH_3), 13.95 (d, J_{CP} = 33.6, PCH_3), 15.03 (d, J_{CP} = 32.2, PCH_3), 114.95 (d, J_{CP} = 5.0, CH), 115.29 (d, J_{CP} = 3.7, CH), 119.78 (s, C), 122.92 (s, CH), 122.38 (q, J_{CF} = 323.3, CF_3SO_3), 123.56, 127.68, 127.93 (all s, CH), 136.32 (s, C), 145.73 (d, J_{CP} = 4.1, C), 145.78 (d, J_{CP} = 4.1, C), 190.15 (dd, J_{CRh} = 62.6, J_{CP} = 13.8, CO), 191.48 (dd, J_{CRh} = 74.6, J_{CP} = 18.9, CO); ^{19}F NMR (acetone-d_6, 293 K) δ −78.32 (s); Λ_M (5 × 10^{-4} M, acetone) 101 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 585 (15) [M^+]. Anal. Calcd for $C_{20}H_{29}N_2SF_3O_5P_2Rh_2$: C, 32.71; H, 3.98; N, 3.81; S, 4.36. Found: C, 32.56; H, 4.18; N, 3.66; S, 4.66.

Preparation of [Rh_2(μ-1,8-$(NH)_2$naphth)(μ-OSO_2CF_3)$(CH_3)_2$-$(CO)_2(PMe_3)_2$][CF_3SO_3] (19). A solution of **18** (200 mg, 0.27 mmol) in acetone (5 mL) was treated with methyl triflate (35 μL, 0.31 mmol) and stirred for 18 h at room temperature. The resulting yellow solution was concentrated to ca. 0.5 mL, and diethyl ether was added to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 191 mg (78%); IR (cm^{-1}) 3248 (m, ν(NH)), 2098 (s, ν(CO)); ^1H NMR (acetone-d_6, 293 K) δ 0.96 (brdd, 6H, RhCH_3), 1.94 (dd, J_{HP} = 12.6, J_{HRh} = 0.8, 18H, PCH_3), 7.19, 7.23 (both br, 1H, NH), 7.57, 7.59 (both dd, J_{HH} = 8.1, 7.5, 1H, CH), 7.83, 7.92 (both d, J_{HH} = 7.5, 1H, CH), 8.03, 8.04 (both d, J_{HH} = 8.1, 1H, CH); $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K) δ 11.88 (d, J_{PRh} = 106.4); $^{13}C\{^1H\}$ NMR (acetone-d_6, 293 K) δ 3.38 (brd, J_{CRh} = 22.1, RhCH_3), 13.28 (d, J_{CP} = 36.9, PCH_3), 122.62 (s, CH), 124.09 (m, CH), 127.14, 127.39, 129.10, 129.39 (all s, CH), 133.13 (d, J_{CP} = 6.0, C), 133.81 (dd, J_{CP} = 6.0, 4.0, C), 136.70 (s, C), 183.44 (dd, J_{CRh} = 64.4, J_{CP} = 16.6, CO); ^{19}F NMR (acetone-d_6, 293 K) δ −78.06 (br); Λ_M (5 × 10^{-4} M, acetone) 114 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{22}H_{32}N_2S_2F_6O_8P_2Rh_2$: C, 29.42; H, 3.59; N, 3.12; S, 7.14. Found: C, 29.77; H, 3.67; N, 3.18; S, 6.98.

Preparation of [Rh_2(μ-1,8-$(NH)_2$naphth)(OSO_2CF_3)$(COCH_3)$-$(CH_3)(CO)(P$*i*$Pr_3)_2$][CF_3SO_3] (20). A solution of **3** (100 mg, 0.35 mmol) in CH_2Cl_2 (5 mL) was treated with methyl triflate (38.9 μL, 0.34 mmol) and stirred at room temperature for 72 h. The resulting solution was concentrated to ca. 0.5 mL and treated with diethyl ether to give a yellow solid. The solid was separated by decantation, washed with ether, and dried in vacuo: yield 116 mg (81%); IR (cm^{-1}) 3238 (m, ν(NH)), 2077, 1590 (s, ν(CO)); ^1H NMR ($CDCl_3$, 293 K) δ 0.29 (dd, J_{HP} = J_{HRh} = 2.4, 3H, RhCH_3), 0.81 (dd, J_{HP} = 14.1, J_{HH} = 7.5, 9H, PCHCH_3), 1.15 (dd, J_{HP} = 14.4, J_{HH} = 7.5, 9H, PCHCH_3), 1.35 (dd, J_{HP} = 14.7, J_{HH} = 8.1, 9H, PCHCH_3), 1.38 (dd, J_{HP} = 14.7, J_{HH} = 7.2, 9H, PCHCH_3), 2.09, 2.54 (both m, 3H, PCHCH_3), 3.09 (d, J_{HP} = 1.5, 3H, $COCH_3$), 5.53, 5.66 (both br, 1H, NH), 7.35, 7.42 (both dd, J_{HH} = 8.1, 7.5, 1H, CH), 7.50 (d, J_{HH} = 7.5, 1H, CH), 7.74, 7.78 (both d, J_{HH} = 8.1, 1H, CH), 7.93 (d, J_{HH} = 7.5, 1H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 46.61 (d, J_{PRh} = 107.4), 38.15 (d, J_{PRh} = 130.3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −1.33 (dd, J_{CRh} = 23.7, J_{CP} = 6.6, RhCH_3), 19.13, 19.38, 19.59, 19.73 (all s, PCHCH_3), 24.33 (d, J_{CP} = 19.8, PCHCH_3), 25.25 (d, J_{CP} = 21.7, PCHCH_3), 40.73 (s, COCH_3), 117.02 (d, J_{CP} = 4.1, CH), 118.17 (q, J_{CF} = 316.8, CF_3SO_3), 119.35 (d, J_{CP} = 4.5, CH), 120.94 (s, C), 125.04, 126.16, 127.24, 127.63 (all s, CH), 135.01 (s, C), 138.60 (d, J_{CP} = 6.0, C), 141.97 (t, J_{CP} = 3.2, C), 182.63 (dd, J_{CRh} = 64.5, J_{CP} = 13.6, CO), 250.14 (dd, J_{CRh} = 36.4, J_{CP} = 6.6, $COCH_3$); ^{19}F NMR ($CDCl_3$, 293 K) δ −78.81 (s), − 79.18 (s); Λ_M (5 × 10^{-4} M, acetone) 114 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 917 (40) [$M^+ - CF_3SO_3$]. Anal. Calcd for $C_{34}H_{56}N_2S_2F_6O_8P_2Rh_2$: C, 38.28; H, 5.29; N, 2.63; S, 6.01. Found: C, 38.19; H, 5.33; N, 2.55; S, 6.16.

Preparation of [Rh_2(μ-1,8-$(NH)_2$naphth)$(COCH_3)(NCCH_3)(CO)$-$(P$*i*$Pr_3)_2$][CF_3SO_3] (21). A solution of **17** (200 mg, 0.22 mmol) in CH_2Cl_2 (5 mL) was treated with acetonitrile (0.1 mL) and stirred at room temperature for 3 h. The resulting yellow solution was taken to dryness and the residue treated with pentane, giving an orange solid. The solid was separated by decantation, washed with pentane, and dried in vacuo: yield 171 mg (82%); IR (cm^{-1}) 3300 (m, ν(NH)), 1961, 1707 (s, ν(CO)); ^1H NMR ($CDCl_3$, 293 K) δ 1.09 (dd, J_{HP} = 13.5, J_{HH} = 6.9, 9H, PCHCH_3), 1.34 (dd, J_{HP} = 14.2, J_{HH} = 7.1, 9H, PCHCH_3), 1.42 (dd, J_{HP} = 14.2, J_{HH} = 6.9, 9H, PCHCH_3), 1.43 (dd, J_{HP} = 13.5, J_{HH} = 6.9, 9H, PCHCH_3), 2.24 (s, 3H, $COCH_3$), 2.39, 2.45 (both m, 3H, PCHCH_3), 2.63 (s, 3H, $NCCH_3$), 4.72, 5.54 (both br, 1H, NH), 7.00 (d, J_{HH} = 7.8, 1H, CH), 7.14, 7.21 (both t, J_{HH} = 7.8, 1H, CH), 7.43, 7.50, 7.68 (all d, J_{HH} = 7.8, 1H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 63.61 (d, J_{PRh} = 153.3), 41.47 (d, J_{PRh} = 134.0); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 4.54 (s, NCCH_3), 19.31, 19.56, 19.85, 19.91 (all s, PCHCH_3), 23.57 (d, J_{CP} = 19.9, PCHCH_3), 25.19 (d, J_{CP} = 23.3, PCHCH_3), 36.25 (s, COCH_3), 113.20 (d, J_{CP} = 3.5, CH), 115.18 (d, J_{CP} = 4.2, CH), 119.47 (s, C), 121.60 (s, CH), 121.71 (q, J_{CF} = 319.7, CF_3SO_3), 122.63, 125.89, 127.10 (all s, CH), 127.30 (d, J_{CRh} = 7.0, NCCH_3), 134.72 (s, C), 145.98 (d, J_{CP} = 3.5, C), 146.23 (d, J_{CP} = 2.8, C), 191.60 (dd, J_{CRh} = 74.3, J_{CP} = 17.7, CO), 215.7 (dd, J_{CRh} = 29.0, J_{CP} = 5.7, CO); ^{19}F NMR ($CDCl_3$, 293 K) δ −79.17 (s); Λ_M (5 × 10^{-4} M, acetone) 114 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 794 (29) [M^+]. Anal. Calcd for $C_{34}H_{56}N_3SF_3O_5P_2Rh_2$: C, 43.27; H, 5.98; N, 4.45; S, 3.40. Found: C, 43.16; H, 5.89; N, 4.16; S, 3.46.

Preparation of [Rh_2(μ-1,8-$(NH)_2$naphth)$(COCH_3)(NCCH_3)(CO)$-$(PMe_3)_2$][CF_3SO_3] (22). A suspension of **6** (200 mg, 0.35 mmol) in acetonitrile (5 mL) was treated with methyl triflate (40 μL, 0.35 mmol) and stirred at room temperature for 2 h. The resulting yellow solution was concentrated to ca. 0.5 mL and worked up as described for **20**. A yellow solid was obtained: yield 160 mg (59%); IR (cm^{-1}) 3307 (m, ν(NH)), 1971, 1696 (s, ν(CO)); ^1H NMR (acetonitrile-d_3, 293 K) δ 1.52 (dd, J_{HP} = 9.9, J_{HRh} = 1.2, 9H, PCH_3), 1.60 (dd, J_{HP} = 11.1, J_{HRh} = 0.9, 9H, PCH_3), 2.11 (s, 3H, $COCH_3$), 4.95, 5.30 (both br, 1H, NH), 7.22 (d, J_{HH} = 7.8, 1H, CH), 7.26 (d, J_{HH} = 8.1, 1H, CH), 7.32 (t, J_{HH} = 7.8, 1H, CH), 7.33 (dd, J_{HH} = 7.8, 8.1, 1H, CH), 7.50, 7.56 (both d, J_{HH} = 7.8, 1H, CH); $^{31}P\{^1H\}$ NMR (acetonitrile-d_3, 293 K) δ 11.07 (d, J_{PRh} = 137.4), 2.34 (d, J_{PRh} = 147.1); ^{19}F NMR (acetonitrile-d_3, 293 K) δ −79.84 (s); Λ_M (5 × 10^{-4} M, acetonitrile) 118 Ω^{-1} cm^2 mol^{-1} (1:1); MS (FAB+, *m*/*z* (%)) 585 (15) [$M^+ - CH_3CN$]. Anal. Calcd for $C_{22}H_{32}N_3SF_3O_5P_2Rh_2$: C, 34.09; H, 4.16; N, 5.42; S, 4.14. Found: C, 34.22; H, 4.20; N, 5.78; S, 4.18.

Kinetic Analysis. The kinetics of the reaction of **17** with acetonitrile to give **21** were measured in 0.06 M solutions of **17** in $CDCl_3$. The decrease in the intensity of the $^{31}P\{^1H\}$ NMR signals of **17** was measured at intervals in a Varian Gemini 2000 spectrometer. The rate

Table 4. Crystallographic Data and Refinement Details for 3 and 12

	3	**12**
cryst color and habit	orange, needles	red, prismatic block
cryst size, mm	0.08 × 0.08 × 0.20	0.32 × 0.31 × 0.18
chem formula	$C_{30}H_{50}N_2O_2P_2Rh_2$	$C_{31}H_{53}IN_2O_2P_2Rh_2$
fw	738.48	880.41
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)
a, Å	17.8409(18)	14.7147(9)
b, Å	11.9065(12)	11.8158(8)
c, Å	15.8100(16)	21.6449(16)
β, deg	101.049(8)	106.449(5)
V, Å^3	3296.1(6)	3609.3(4)
Z	4	4
ρ(calcd), g cm^{-3}	1.488	1.620
μ, mm^{-1}	1.126	1.887
θ range data collecn, deg	2.33−28.30	1.96−25.01
index ranges	$-23 \le h \le 5$, $-10 \le k \le 14$, $-21 \le l \le 20$	$-1 \le h \le 17$, $0 \le k \le 14$, $-25 \le l \le 25$
no. of collected reflns	5844	7153
no. of unique reflns	3100 (R_{int} = 0.0471)	6350 (R_{int} = 0.0156)
min., max. transm factors	0.806, 0.915	0.583, 0.728
no. of data/restraints/ params	3100/0/231	6350/0/573
$R(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.0385	0.0282
$R_w(F^2)$ (all data)[b]	0.0759	0.0668
S (all data)[c]	0.997	1.032

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for 2073 (**3**) and 5405 (**12**) observed reflections. [b] $R_w(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (**3**: a = 0.0269, b = 0.000; **12**: a = 0.0303, b = 5.359). [c] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

constants were obtained by fitting the data to an exponential decay function with the routine programs of the spectrometer. The activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were obtained from a linear least-squares fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). Errors were computed by published methods.[35] The error in temperature was assumed to be 1 K, and the error in k_{obs} was estimated as 10%.

Crystal Structure Determination of 3 and 12. Suitable crystals for X-ray diffraction were obtained by slow diffusion of diethyl ether into dichloromethane solutions of the complexes. A summary of crystal data and refinement parameters is reported in Table 4. Intensity data were collected at 153 K on a CCD Bruker AXS-SMART diffractometer for **3**; data for **12** were measured on a Siemens P4 machine at 200 K; both diffractometers were equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$). ω rotations with narrow frames (0.3°; $4.6 \leq 2\theta \leq 56.6°$) were used for **3**, while intensities were measured with $\omega/2\theta$ scans in the case of **12** ($4.0° \leq 2\theta \leq 50°$). Instrument and crystal stability were evaluated from the measurement of equivalent (**3**) or standard (**12**) reflections at different measuring times, and no decay was observed. Data were corrected for Lorentz and polarization effects, and a semiempirical correction for **3** or a numerical face-based absorption correction was applied (see Table 4).[36]

The structures were solved by standard direct and difference Fourier methods.[37] Anisotropic thermal parameters have been used for all non-hydrogen atoms in both structures. Hydrogen atoms, except those of the terminal Me groups in **3**, have been included from observed positions and refined as free isotropic atoms in both structures. The methyl groups in **3** were included from calculated positions and refined with riding positional and displacement parameters (AFIX 138).[38] Refinements were carried out by full-matrix least-squares on F^2 (SHELXL-97).[38] No significant residual peaks were observed in the final difference maps. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

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Supporting Information Available: Full listings of crystallographic data, complete atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for complexes **3** and **12** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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