

## Oxidative-Addition Reactions of Diiodine to Dinuclear Rhodium Pyrazolate Complexes

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The pyrazolato (Pz) rhodium(I) complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$  ( $\text{L} = \text{CNBu}^t$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{P}(p\text{-tolyl})_3$ ) result from the reaction of  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}_2]$  with the appropriate L ligand in a trans:cis ratio ranging from 60:40 ( $\text{L} = \text{CNBu}^t$ ) to 95:5 ( $\text{L} = \text{P}(p\text{-tolyl})_3$ ). The pure trans isomers add 1 molar equiv of diiodine to give the dirhodium(II) complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})\}_2]$  ( $\text{L} = \text{CNBu}^t$  (**6**),  $\text{P}(\text{OMe})_3$  (**7**),  $\text{PMe}_2\text{Ph}$  (**8**),  $\text{P}(\text{OPh})_3$  (**9**)). These complexes incorporate two iodide ligands trans to the rhodium–rhodium bond, as substantiated by the X-ray structure for **7**, while the complex  $[(\text{P}\{p\text{-tolyl}\}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-CO})\text{Rh}(\text{I})(\text{P}\{p\text{-tolyl}\}_3)]$  (**10**) contains a bridging ketonic CO ligand, due to the insertion of a terminal CO into the metal–metal bond. The metal–metal bond formation involves a 2e oxidation, since identical compounds (**6–9**) are obtained by oxidation with  $[\text{Fe}(\text{Cp})_2](\text{PF}_6)$  followed by addition of potassium iodide. Further reactions of the dirhodium(II) complexes **6–9** with diiodine leading to the metal–metal rupture are electrophilic additions, as exemplified by the reactions with the positive iodine complex  $[\text{I}(\text{Py})_2]^+$ . They start at the “endo site” (the metal–metal bond) if it is sterically accessible to the electrophile, to give directly the dirhodium(III) complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})\}_2(\mu\text{-I})]^+$  ( $\text{L} = \text{CNBu}^t$ , CO). Otherwise, as for the complexes with P-donor ligands, abstraction of a iodide ligand trans to the metal–metal bond (the “exo site”) occurs first, to give the dirhodium(II) cationic complexes  $[(\text{PR}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CO})(\text{PR}_3)]^+$  and triiodide. These react again with diiodine to give dirhodium(III) complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})]^+$  similar to those described above, but with triiodide or pentaiodide as counterion, as substantiated by the X-ray structure of  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PMe}_2\text{Ph})\}_2(\mu\text{-I})\text{I}_5]$  (**18**). The diiridium(II) complexes  $[\{\text{Ir}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2]$  ( $\text{PR}_3 = \text{P}(\text{OPh})_3$ ,  $\text{PMe}_2\text{Ph}$ ) also react with diiodine to give the cationic diiridium(III) complexes  $[\{\text{Ir}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})\text{I}_3]$  through a reaction pathway involving the “exo site”, while no reaction is observed for  $[\{\text{Ir}(\mu\text{-Pz})(\text{I})(\text{CO})_2\}_2]$ . Finally, replacement of a carbonyl ligand in  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})\}_2(\mu\text{-I})]^+$  ( $\text{L} = \text{CNBu}^t$ , CO) by iodide gives the compounds  $[(\text{CO})(\text{L})(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-I})\text{Rh}(\text{I})_2(\text{L})]$ .

## Introduction

The increasing interest generated by dinuclear complexes has focused on the search for reactivity patterns and unusual chemical transformations, unavailable for mononuclear complexes, through cooperative electronic and/or steric effects between the metal centers.<sup>1</sup> Thus, formation and breaking of metal–metal bonds,<sup>2</sup> additions across the metal–metal bond,<sup>3</sup> insertions of organic fragments into the coordinated ligands,<sup>4</sup> ligand mobility from a terminal to a bridging site,<sup>5</sup> and transference of ligands from one center to the other<sup>6</sup> can be

observed. The central axis to this exploration has been the use of active metals held together with flexible and firmly bounded bridging ligands. This allows the metal–metal interaction and prevents the fragmentation of the bimetallic core. In this line, we are investigating<sup>7</sup> the reactivity of dinuclear rhodium and

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iridium pyrazolato complexes that seem to possess the above commented requirements to show cooperative bimetallic reactivity.

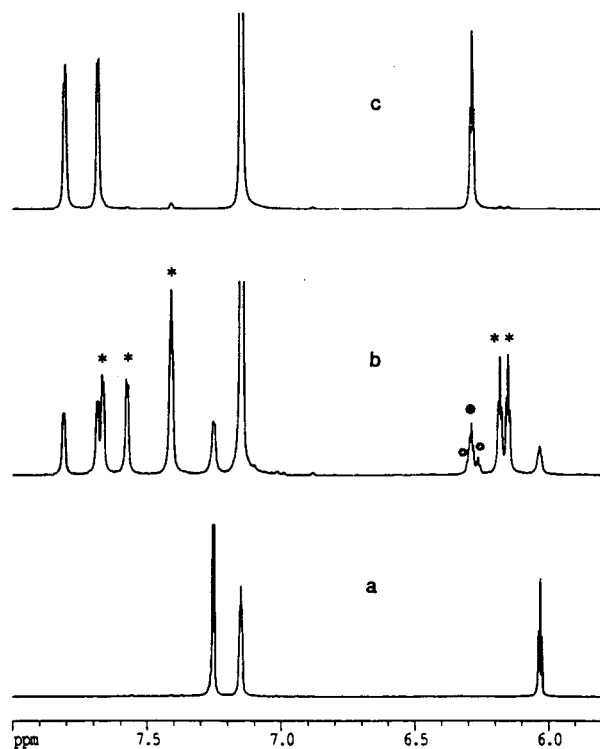
In particular, we have recently reported<sup>2a</sup> the oxidative-addition of diiodine to the highly nucleophilic complexes  $[\{M(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$  ( $M = \text{Rh}, \text{Ir}$ ) leading to the metal bonded complexes  $[\{M(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$ . This binuclear oxidative addition reaction is typical for related dinuclear iridium complexes such as  $[\{\text{Ir}(\mu\text{-L})(\text{CO})(\text{L}')\}_2]$  ( $\text{L} = \text{SBu}^t$ ,<sup>8</sup> pyrazolate,<sup>9</sup> 7-azaindolate,<sup>10</sup> 1,8-diamidonaphthalene,<sup>11</sup>  $\text{L}' =$  monodentate phosphine or CO) and  $[\text{Ir}_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(\text{CO})_2(\text{L}')_2]$ .<sup>2b</sup> On regarding their dirhodium counterparts, less studied in oxidative-addition reactions, similar results are obtained from the reactions of  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}_2]$ <sup>12</sup> or  $[\{\text{Rh}(\mu\text{-L})(\text{CO})(\text{PPh}_3)\}_2]$ <sup>13</sup> ( $\text{L} = 1,8$ -diamidonaphthalene) with diiodine, but dirhodium(III) complexes or mixed-valence  $\text{Rh}^{\text{I}}\text{-Rh}^{\text{III}}$  result from  $[\{\text{Rh}(\mu\text{-R}_2\text{Pz})(\text{CO})(\text{PPh}_3)\}_2]$ <sup>14</sup> or  $[\{\text{Rh}(\mu\text{-Cp-PPh}_2)(\text{CO})\}_2]$ ,<sup>15</sup> respectively.

Despite the various reports on the reactions, very little is known about the possible mechanisms that favor the formation and breaking of metal–metal bonds. Oxidative-addition reactions to yield dinuclear dirhodium(II) and diiridium(II) complexes are a good example of cooperation between the two metals, while mononuclear rhodium(II) and iridium(II) compounds are very rare.<sup>16</sup>

Herein we describe some reactions of diiodine with a family of dinuclear rhodium and iridium pyrazolato complexes looking for a deeper insight on the mechanism of reactions leading to the rupture of metal–metal bond, the reactive sites in these complexes, and the influence of steric and electronic effects. The reported studies confirm the influence between the neighboring metal centers in their reactivity.

## Results and Discussion

**$[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$  Complexes.** The new dinuclear rhodium pyrazolato complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$  ( $\text{L} = \text{CNBu}^t$  (**1**),  $\text{P}(\text{OMe})_3$  (**2**),  $\text{PMe}_2\text{Ph}$  (**3**)) result from the reaction of the yellow air-sensitive compound  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}_2]$  with the appropriate L ligand, as previously described<sup>17</sup> for  $\text{L} = \text{P}(\text{OPh})_3$  (**4**) and  $\text{P}(p\text{-tolyl})_3$  (**5**). The pure *trans*- $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$  isomers crystallize from anhydrous diethyl ether solutions while mixtures of (*trans*+*cis*)- $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$  are isolated if hexane is used to complete the crystallization. Both isomers are easily distinguished by <sup>1</sup>H NMR spectroscopy, since the *cis* isomers ( $C_s$  symmetry) show four resonances for the pyrazolate ligands while the *trans* isomers ( $C_2$  symmetry) show only three.



**Figure 1.** <sup>1</sup>H NMR spectra in the pyrazolate region of: (a)  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}_2]$ ; (b) upon addition of 1 molar equiv of  $\text{CNBu}^t$ , showing the intermediate  $[(\text{CO})_2\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CO})(\text{CNBu}^t)]$  (\*), *cis*-**1** (○) and *trans*-**1** (●); (c) isolated *trans*-**1** in  $\text{C}_6\text{D}_6$ .

By monitoring the reactions of  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}_2]$  with L, a mixture of the starting material, the (*trans*+*cis*)- $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$  isomers, and the intermediate  $[(\text{CO})_2\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CO})(\text{L})]$  is observed when 1 molar equiv of L is added. This is more noticeable for  $\text{L} = \text{CNBu}^t$  (Figure 1). These mixtures evolve to the final (*trans*+*cis*)- $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$  complexes upon addition of the second molar equivalent of L. A high *trans*:*cis* ratio ranging from 85:15 ( $\text{L} = \text{P}(\text{OMe})_3$ ) to 95:5 ( $\text{L} = \text{P}(p\text{-tolyl})_3$ ) is observed for  $\text{L} = \text{P}$ -donor ligands, while that observed for  $\text{L} = \text{CNBu}^t$  is 60:40. These results suggest a direct relationship between the bulkiness of the L ligand and the stereoselectivity of the reaction.

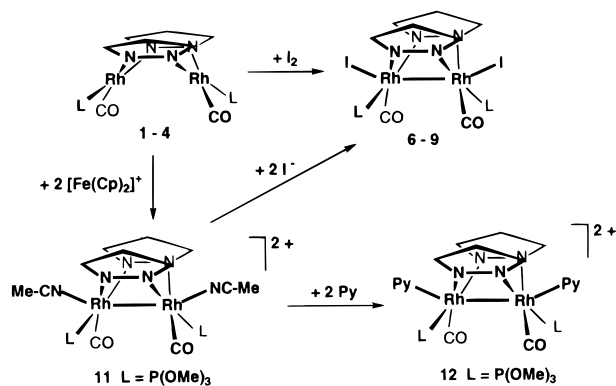
No *trans*:*cis* isomerizations were observed in the working conditions, and pure *trans* stereoisomers were used as starting materials in the present study. Thus, we will omit the term “*trans*” in the following discussion.

### Reactions Leading to Metal–Metal Bond Formation and Oxidative-Isomerization.

The addition of 1 molar equiv of diiodine to diethyl ether or pentane suspensions of the complexes **1–4** gives the compounds  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})\}_2]$  ( $\text{L} = \text{CNBu}^t$  (**6**),  $\text{P}(\text{OMe})_3$  (**7**),  $\text{PMe}_2\text{Ph}$  (**8**),  $\text{P}(\text{OPh})_3$  (**9**)) as dark-red crystalline solids. The elemental analyses agree with the incorporation of two iodine atoms in **6–9** and the observation of the molecular ions in the mass spectra confirms their dinuclear nature. A formal oxidation of both rhodium atoms is indicated by the decrease for the  $^1J_{\text{P-Rh}}$  and  $^1J_{\text{C-Rh}}$  values along with the shift of  $\nu(\text{CO})$  to higher frequencies relative to those observed for their  $\text{Rh}(\text{I})$  precursors. In addition, a single isomer having  $C_2$  symmetry results from the above reactions, since only three resonances for the pyrazolate protons appear in their <sup>1</sup>H NMR spectra. Therefore, complexes **6–9** are dinuclear and diamagnetic, possess a single metal–metal bond, and incorporate two iodide ligands *trans* to the rhodium–rhodium bond (Scheme 1). As the formation of these metal–metal bonds must be

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Scheme 1



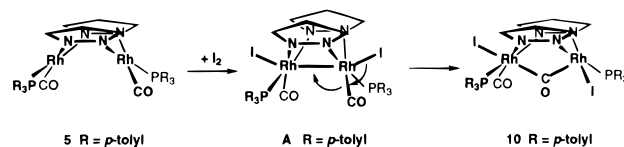
accomplished by an increase of the folding of the molecules, information concerning to the space available inside the pocket of these complexes was obtained by the study of  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{P}\{\text{OMe}\}_3)_2\}_2]$  (**7**) by X-ray methods (vide infra).

On the other hand, the addition of 1 molar equiv of diiodine to **5** gives a red crystalline compound analyzing for  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{P}\{p\text{-tolyl}\}_3)_2\}_2]$  (**10**) but showing quite different spectroscopic data than complexes **6–9**. Thus, complex **10** contains terminal and ketonic CO ligands, showing  $\nu(\text{CO})$  absorptions at 2095 and 1757  $\text{cm}^{-1}$  in the IR spectrum, respectively. In addition, complex **10** lacks elements of symmetry, and accordingly, two inequivalent phosphine ligands with  $^1J_{\text{P-Rh}}$  values of 131 and 111 Hz are observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. These data agree with a dinuclear complex in which two pyrazolate and one ketonic carbonyl group bridge the two rhodium atoms each one having one  $\text{P}(p\text{-tolyl})_3$  ligand. However, no clear information about the stereochemistry of the rhodium atoms could be obtained from the spectroscopic data, and the complete characterization of **10** as the complex  $[(\text{P}\{p\text{-tolyl}\}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-CO})\text{Rh}(\text{I})(\text{P}\{p\text{-tolyl}\}_3)]$  was achieved by a X-ray diffraction study (vide infra).

The reactions of the complexes **1–4** with diiodine leading to **6–9** are similar to that found for the related complexes  $[\{\text{M}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ), for which a two-electron oxidation has been proposed.<sup>2a</sup> The two electrons are abstracted from the HOMO of the dinuclear complex, which is an antibonding orbital.<sup>18</sup> Moreover, these reactions can be carried out either directly with diiodine or in two separate steps. Thus, the oxidation of the complexes **2–4** with 2 molar equiv of  $[\text{Fe}(\text{Cp})_2](\text{PF}_6)$  in acetonitrile followed by addition of potassium iodide gives also compounds **7–9** cleanly ( $^1\text{H}$  NMR evidence). Furthermore,  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{P}\{\text{OMe}\}_3)(\text{CH}_3\text{CN})\}_2](\text{PF}_6)_2$  (**11**) results from the oxidation of **2** with 2 molar equiv of  $[\text{Fe}(\text{Cp})_2](\text{PF}_6)$  in acetonitrile. Complex **11** was isolated as a yellow oil and characterized by spectroscopic studies and conductivity measurements (see Experimental Section). Replacement of the labile acetonitrile ligands in **11** by pyridine gives  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{P}\{\text{OMe}\}_3)(\text{Py})\}_2](\text{PF}_6)_2$  (**12**) immediately, while addition of iodide to **11** leads to the neutral complex **7**, as expected (Scheme 1).

The reaction of **5** with diiodine, which gives an anomalous result, should start in an analogous way as for **6–9**. Indeed, the hypothetical complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{P}\{p\text{-tolyl}\}_3)_2\}_2]$  (**A**, Scheme 2), showing a broad  $\nu(\text{CO})$  band at 2046  $\text{cm}^{-1}$ , is detected at the beginning of the reaction. However, this compound evolves to  $[(\text{P}\{p\text{-tolyl}\}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-CO})$

Scheme 2



$\text{Rh}(\text{I})(\text{P}\{p\text{-tolyl}\}_3)]$  (**10**) in 5 min, which decomposes finally into a mixture of compounds. This decomposition is avoided by carrying out the reaction in diethyl ether, where complex **10** is insoluble and crystallizes out as formed. Assuming the initial formation of the metal–metal bonded complex **A**, compound **10** results from an oxidative isomerization in which one terminal CO group migrates into the pocket of the complex and inserts into the rhodium–rhodium bond becoming a ketonic carbonyl. This isomerization reaction occurs with an increase of the intermetallic distance and consequently, with a decrease of the folding of the molecule. Most probably, the steric crowding in the proposed intermediate **A** is the driving force for this reaction, since the complexes **6–9**, which possess ancillary ligands less bulky than  $\text{P}(p\text{-tolyl})_3$ , do not undergo this isomerization. Furthermore, the formation of the previously reported ketonic carbonyl complexes  $[\{\text{Rh}(\mu\text{-3,5-R}_2\text{Pz})(\text{I})(\text{L})\}_2(\mu\text{-CO})]$  from the reactions of  $[\{\text{Rh}(\mu\text{-3,5-R}_2\text{Pz})(\text{CO})(\text{L})\}_2]$  with diiodine<sup>14</sup> could be understood in terms of a loss of a terminal CO ligand through an intermediate similar to **10**, due to additional steric effects of the substituents on the pyrazolate ring. In this context, we have previously observed reversible transformations involving dirhodium(III) ketonic carbonyls and metal–metal bonded dirhodium(II) species in A-frame pyrazolate-bridged dirhodium complex containing  $\text{CNBu}^t$  as ancillary ligand.<sup>5c</sup>

**Crystal and Molecular Structure of  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{P}\{\text{OMe}\}_3)_2\}_2]$  (**7**) and  $[(\text{P}\{p\text{-tolyl}\}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-CO})\text{Rh}(\text{I})(\text{P}\{p\text{-tolyl}\}_3)]$  (**10**).**<sup>1/2}(\text{CH}\_3\text{CH}\_2)\_2\text{O}. The crystal structures of **7** and **10** consist of dinuclear neutral complexes and, in **10**, diethyl ether solvent molecules, packed at normal van der Waals distances. Both molecules exhibit a common “ $\text{Rh}(\mu\text{-Pz})_2\text{Rh}$ ” framework, constituted by two rhodium atoms bridged through two *exo*-bidentate pyrazolate ligands; the two  $\text{Rh}_2\text{N}_4$  metallacycles formed adopt the usual boat conformation with different puckering magnitudes (see below).<sup>7a,c,19</sup></sup>

Two crystallographically independent molecules were detected in **7**, showing only statistically significant differences for bond parameters involving the heaviest atoms (Rh and I), which were refined with greater precision. The differences in bond angles are even more appreciable, but all these variances could be considered chemically irrelevant (see Table 1). Both metal centers in **7** (Figure 2) exhibit identical distorted *pseudo*-octahedral environments with a trimethyl phosphite, a carbonyl ligand and a iodide atom coordinated to each metal, and the presence of a clear intermetallic Rh–Rh bond, 2.6595(14) and 2.6781(12) Å. These Rh–Rh separations are comparable to those observed in other closely related doubly bridged pyrazolate  $\text{Rh}^{\text{II}}\text{–Rh}^{\text{II}}$  complexes where a Rh–Rh single bond has been proposed, such as  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})\}_2(\mu\text{-dppm})]$  (2.612(3)),<sup>12</sup>  $[\{\text{Rh}(\mu\text{-Pz})(\eta^5\text{-C}_5\text{H}_5)\}_2]$  (2.657(3) Å),<sup>20</sup> and the two dinuclear moieties of the cationic tetranuclear complex  $[\{\text{Rh}_2(\mu\text{-Pz})_2(\text{I})(\text{CNBu}^t)_4\}_2(\mu\text{-I})^+]$  (2.6320 and 2.6057(10) Å).<sup>2a</sup> Together with these data, the formation of the Rh–Rh bond is additionally supported by the shortening of the intermetallic distance

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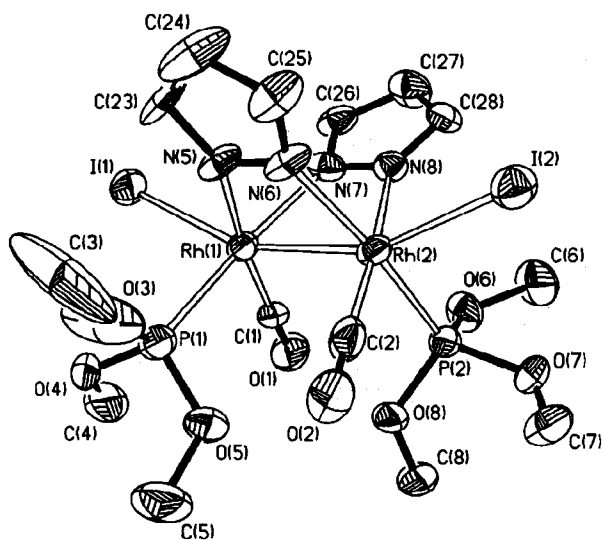
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**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for **7**<sup>a</sup>

Rh(1)–Rh(2)	2.6595(14)	2.6781(12)	Rh(2)–I(2)	2.7465(14)	2.7291(13)
Rh(1)–I(1)	2.7410(13)	2.7519(12)	Rh(2)–P(2)	2.245(3)	2.240(3)
Rh(1)–P(1)	2.254(3)	2.251(2)	Rh(2)–N(6)	2.087(8)	2.084(8)
Rh(1)–N(5)	2.062(8)	2.052(7)	Rh(2)–N(8)	2.058(7)	2.050(7)
Rh(1)–N(7)	2.095(8)	2.080(7)	Rh(2)–C(2)	1.869(11)	1.853(10)
Rh(1)–C(1)	1.862(12)	1.876(10)	C(2)–O(2)	1.131(12)	1.153(11)
C(1)–O(1)	1.143(12)	1.126(11)			
Rh(2)–Rh(1)–I(1)	158.78(4)	156.32(4)	Rh(1)–Rh(2)–I(2)	158.31(4)	157.77(4)
Rh(2)–Rh(1)–P(1)	101.79(11)	104.55(7)	Rh(1)–Rh(2)–P(2)	98.68(9)	99.64(7)
Rh(2)–Rh(1)–N(5)	72.2(3)	71.8(2)	Rh(1)–Rh(2)–N(6)	71.3(3)	71.2(2)
Rh(2)–Rh(1)–N(7)	70.7(3)	70.6(2)	Rh(1)–Rh(2)–N(8)	71.9(2)	72.0(2)
Rh(2)–Rh(1)–C(1)	101.7(3)	99.1(3)	Rh(1)–Rh(2)–C(2)	102.1(4)	103.0(3)
I(1)–Rh(1)–P(1)	93.36(10)	92.60(7)	I(2)–Rh(2)–P(2)	97.29(8)	95.65(7)
I(1)–Rh(1)–N(5)	93.9(3)	91.9(2)	I(2)–Rh(2)–N(6)	92.2(3)	92.6(2)
I(1)–Rh(1)–N(7)	92.7(3)	91.8(2)	I(2)–Rh(2)–N(8)	93.4(2)	92.0(2)
I(1)–Rh(1)–C(1)	92.6(3)	96.7(3)	I(2)–Rh(2)–C(2)	92.7(4)	93.2(3)
P(1)–Rh(1)–N(5)	92.3(2)	91.5(2)	P(2)–Rh(2)–N(6)	170.0(3)	170.6(2)
P(1)–Rh(1)–N(7)	172.4(3)	175.0(2)	P(2)–Rh(2)–N(8)	90.6(2)	90.3(2)
P(1)–Rh(1)–C(1)	91.3(3)	91.1(3)	P(2)–Rh(2)–C(2)	89.0(4)	89.3(3)
N(5)–Rh(1)–N(7)	85.4(3)	86.1(3)	N(6)–Rh(2)–N(8)	85.7(3)	84.9(3)
N(5)–Rh(1)–C(1)	173.4(4)	170.8(4)	N(6)–Rh(2)–C(2)	93.7(4)	94.8(4)
N(7)–Rh(1)–C(1)	90.3(4)	90.6(3)	N(8)–Rh(2)–C(2)	173.9(4)	174.7(4)
Rh(1)–C(1)–O(1)	177.3(10)	178.0(8)	Rh(2)–C(2)–O(2)	179.0(12)	176.6(9)

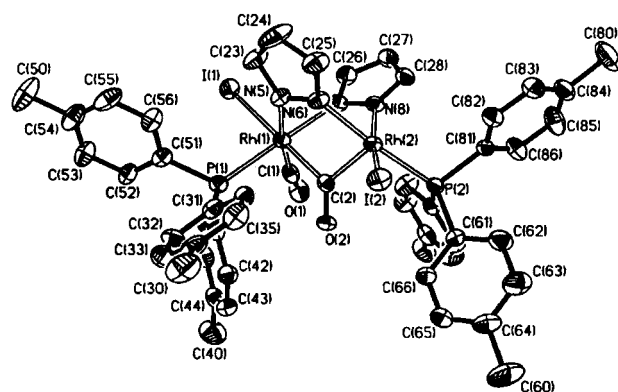
<sup>a</sup> The two values stated for each parameter correspond to the two crystallographically independent molecules.

**Figure 2.** View of the structure of the complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{P}\{\text{OMe}\}_3)_2\}]$  (**7**).

observed in **7** if compared with its parent compound analogue  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{P}\{\text{OPh}\}_3)_2\}]$  (3.568 Å), which implies a noticeable decrease in the Rh–Rh separation (0.9 Å approximately) upon the oxidative-addition reaction.<sup>17</sup>

The configuration of the ligands around the metals in **7** retains the trans arrangement of the phosphite ligands of the parent compound **2**. This fact, in conjunction with the boat conformation of the  $\text{Rh}_2\text{N}_4$  metallacycle, results in a structure possessing a noncrystallographic  $C_2$  molecular symmetry. Each of the two added iodide atoms is bonded to a different metal center with an eclipsed (I–Rh–Rh–I, 4.6(2)°) and nearly trans disposition (mean Rh–Rh–I, 157.80(2)°) relative to the Rh–Rh bond, confirming the nature of a formal two-fragment two-center oxidative addition reaction. The whole molecule closely resembles an iridium equivalent,  $[\{\text{Ir}(\mu\text{-}3,5\text{-Me}_2\text{Pz})(\text{I})(\text{CO})(\text{P}\{\text{OPh}\}_3)_2\}]$  which also presents a metal–metal bond (2.688 Å), a transoid arrangement of phosphites (triphenyl phosphite, in this case), and a nearly linear disposition of the I–Ir–Ir–I chain.<sup>14</sup>

Bridging pyrazolate ligands show expected bond distances for metal–nitrogen contacts of this type (range 2.050(7)–2.095-

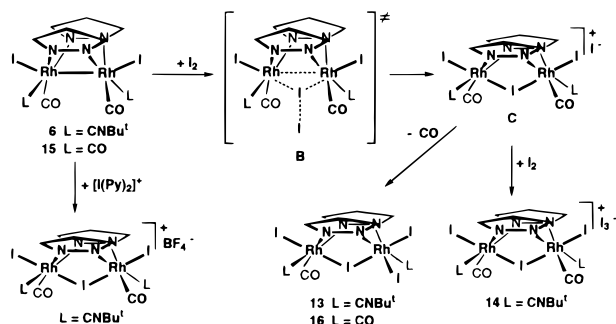
**Figure 3.** View of the structure of the complex  $[(\text{P}\{p\text{-tolyl}\}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-CO})\text{Rh}(\text{I})(\text{P}\{p\text{-tolyl}\}_3)]$  (**10**).

(8) Å),<sup>2a,7a,c,12</sup> but reflect the different trans influence of the ligands situated on the opposite side of the metal coordination sphere: 2.087(4) Å trans to phosphite, and 2.056(4) Å trans to the stronger  $\pi$ -acceptor carbonyl groups. The Rh–I bond lengths, ranging from 2.7291(13) to 2.7519(12) Å, are similar to those reported for the terminal iodide ligands in the related Rh(II) complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})_2(\mu\text{-dppm})\}]$  (2.736(3) and 2.710(3) Å),<sup>12</sup>  $[\{\text{Rh}_2(\mu\text{-Pz})_2(\text{I})(\text{CNBu}^t)_4\}_2(\mu\text{-I})^+]$  (2.7279 and 2.7545(10) Å),<sup>2a</sup> or  $[\{\text{Rh}(\mu\text{-dppm})(\text{I})(\text{CNBu}^t)\}_2(\mu\text{-Pz})^+]$  (2.738(3) and 2.766(6) Å),<sup>5c</sup> where the iodine atoms are nearly trans disposed to the Rh–Rh bond but are slightly longer than the mean values determined for Rh(III) complexes, 2.71(7) Å.<sup>21</sup>

Although having the same stoichiometry of **7**, complex **10** exhibits several remarkable structural changes (Figure 3). Based on the same dinuclear  $\text{Rh}_2\text{N}_4$  boatlike moiety, this molecule presents an additional bridging carbonyl group and a comparatively elongated Rh–Rh separation, 3.2603(8) Å, consistent with the absence of a metal–metal bond. Also notable, in **10**, are the different metal environments observed. While Rh(1) is located within a distorted octahedral environment, Rh(2) is in a distorted square pyramidal coordination with the bridging carbonyl in the apical position. The configuration around Rh-

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## Scheme 3



(1) maintains, as described for **7**, a terminal carbonyl and the phosphorus donor ligand trans-situated to the pyrazolate nitrogens, and consequently, the iodide is trans to the bridging carbonyl group ( $\text{I}(\text{1})\text{—Rh}(\text{1})\text{—C}(\text{2})$ ,  $174.49(15)^\circ$ ).

The bridging carbonyl shows a slight asymmetry in the  $\text{Rh—C}(\text{2})$  bond distances,  $2.072(6)$  and  $1.982(6)$  Å, with the shorter one to the pentacoordinated  $\text{Rh}(\text{2})$  atom. Similar asymmetric bridging CO groups have also been observed in the related complexes  $[(\text{PhMe}_2\text{P})(\text{Cl})_2\text{Rh}(\mu\text{-SCy})_2(\mu\text{-CO})\text{Rh}(\text{CO})(\text{PMe}_2\text{-Ph})_2]$ ,  $2.07(2)$  and  $1.97(2)$ ,<sup>22</sup> and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-Pz})_2(\mu\text{-CO})\text{Rh}(\text{dppp})]^+$ ,  $2.060(7)$  and  $2.032(8)$  Å,<sup>23</sup> where the carbonyl groups are bridging two different (hexa and pentacoordinated) rhodium atoms and occupy the apical position of the square-pyramidal metal coordination sphere (no trans ligand). The angles around the  $\text{C}(\text{2})$  atom are in agreement with a planar  $\text{sp}^2$  environment. The  $\text{Rh—C}(\text{2})\text{—Rh}$  bond angle,  $107.0(3)^\circ$ , together with the rather long  $\text{Rh—Rh}$  separation and the low  $\nu(\text{CO})$  absorption frequency observed ( $1757 \text{ cm}^{-1}$ ), supports a ketonic nature for the bridging CO ligand.

If we compare the structure of **7** with that of **10**, or with that of the related parent compound  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{P}\{\text{Oph}\}_3)_2\}]_2$ ,<sup>17</sup> the most noticeable feature, from a structural point of view, is the extraordinary flexibility of the boatlike  $\text{Rh}_2\text{N}_4$  framework. In the three structures this metallacycle adopts a strongly puckered, almost perfect, boat conformation ( $f = 0.8(3)$ ,  $q = 90.3(3)^\circ$  for **7**;  $f = 1.0(2)$ ,  $q = 88.8(2)^\circ$  for **10**) with high puckering amplitudes,  $1.582(5)$  (**7**) and  $1.386(3)$  Å (**10**).<sup>24</sup> These conformational changes are correlated<sup>7c</sup> to the dihedral angle  $\alpha$  formed by the rhodium coordination planes  $\text{N}(5)\text{N}(7)\text{Rh}(\text{1})\text{C}(\text{1})\text{P}(\text{1})$  and the analogue at  $\text{Rh}(\text{2})$ ,  $40.2(1)$  in **7** and  $87.61(6)^\circ$  in **10**, and consequently to the  $\text{Rh—Rh}$  separation. No clear relationship is observed for these structures between  $\alpha$  (and the  $\text{Rh—Rh}$  separation) and the dihedral angle between pyrazolate ligands,  $88.5(2)^\circ$  in **7** and  $98.1(1)^\circ$  in **10**.

**Addition Reactions of Diiodine to  $[\{\text{M}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})_2\}]_2$  Leading to Metal—Metal Bond Breaking.** (i)  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})_2\}]_2$  ( $\text{L} = \text{CNBu}^t, \text{CO}$ ). The result of reaction of **6** with diiodine is very sensitive to the experimental conditions. Thus, the slow diffusion of solutions of **6** and diiodine in diethyl ether gives the dark-red complex  $[(\text{CO})(\text{CNBu}^t)(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-I})\text{Rh}(\text{I})_2(\text{CNBu}^t)]$  (**13**) in good yields (Scheme 3). Complex **13** is an unsymmetrical dinuclear neutral complex that contains a single terminal carbonyl group. However, the addition of solid diiodine to a stirred suspension of **6** (1:1 molar ratio) in diethyl ether gives the dark-purple complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$  (**14**) in yields below 50%. As the mother liquor

still contains starting material, the reaction requires an additional molar equivalent of diiodine to be completed (Scheme 3). Complex **14** is ionic, contains two terminal carbonyl ligands, and possesses  $\text{C}_2$  symmetry. Accordingly, it behaves as a 1:1 electrolyte in acetone and shows the cation  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{CNBu}^t)_2(\mu\text{-I})\}]^+$  in the mass spectrum as the peak of highest  $m/e$  value.

We have previously reported<sup>2a</sup> that the oxidative-addition of diiodine to the related compound  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}]_2$  gives cleanly the ionic complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$ . In light of this, the formation of **13** and **14** from **6** is easily explained assuming the initial electrophilic attack of diiodine<sup>2a</sup> to the metal—metal bonded species **6** and **15** (**B**, Scheme 3) followed by the formation of the ionic intermediate  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$  (**C**, Scheme 3) analogous to the isolated  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$ . Once formed **C**, the reaction takes two distinct pathways depending on the relative concentration of diiodine in the reaction mixture. For very dilute solutions of diiodine, as occurs in the first experiment, the ionic iodide replaces a carbonyl ligand in **C** leading to **13**. Alternatively, the ionic iodide associates with unreacted diiodine in concentrated solutions to give the  $\text{I}_3^-$  anion, in such way that  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$  (**14**) precipitates. Two additional observations support our proposal. In a parallel experiment, addition of diiodine to  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$  gives cleanly the purple complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$ , the counterpart of **14**. In addition, complex **14** remains as such in acetone solutions, showing that the triiodide is unable to replace the carbonyl ligand in the cation  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{CNBu}^t)_2(\mu\text{-I})\}]^+$ , while complex **14** reacts immediately with  $\text{KI}$  leading cleanly to the neutral complex **13** in the same solvent. The distinct ability of iodide and triiodide for the replacement of a CO group allows the isolation of the cationic complex **14**. Moreover, comparison of the replacement of ancillary ligands in **14** and  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2(\mu\text{-I})\}]_3$  by iodide indicates that  $\text{CNBu}^t$  is more tightly bonded to rhodium than is the carbonyl group.

From this, we turned our attention to the previously reported tetracarbonyl complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})_2\}]_2$  (**15**).<sup>12</sup> Complex **15** reacts with diiodine (1:1 molar ratio, pentane) in a few minutes to yield a black solid of formula  $[(\text{CO})_2(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-I})\text{Rh}(\text{I})_2(\text{CO})]$  (**16**). The structure of **16** should be similar to that of **13** as supported by the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR and IR spectra, that show unequivocally the presence of three terminal carbonyl groups and the lack of symmetry of the complex. The formation of complex **16**, initially formulated as  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})_2(\text{CO})_2\}]_2$ , could be explained according to Scheme 3 assuming the replacement of one carbonyl group by the iodide counterion in the intermediate  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})_2\}]_2(\mu\text{-I})\text{I}$ , similar to **C**.

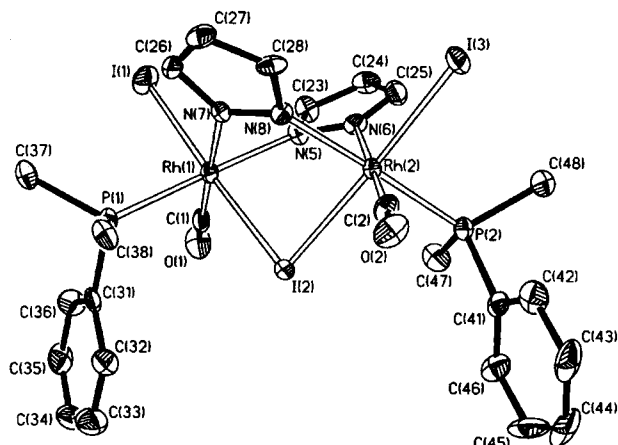
(ii)  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)_2\}]_2$  ( $\text{PR}_3 = \text{P}(\text{Oph})_3, \text{P}(\text{OMe})_3, \text{PMe}_2\text{Ph}$ ). The metal—metal bonded compounds **7—9** react with diiodine to give cationic complexes of the type  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)_2(\mu\text{-I})\}]^+$ . The spectroscopic data for these new dirhodium(III) cations agree with the presence of a  $\text{C}_2$  axis in the complexes, which are stable toward the replacement of a CO ligand by the counterion.

Noticeably, complex **9** needs 2 molar equiv of diiodine and complexes **7—8** need an additional third molar equivalent of diiodine to drive the reactions to completion. Accordingly, the analytical data of the products agree with the formulations  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{P}\{\text{Oph}\}_3)_2(\mu\text{-I})\}]_3$  (**19**) and  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)_2(\mu\text{-I})\}]_5$  ( $\text{PR}_3 = \text{P}(\text{OMe})_3$  (**17**),  $\text{PMe}_2\text{Ph}$  (**18**)). Thus, complex **19** must contain triiodide as counterion, while **17** and **18** should contain pentafluoride as counteranion as documented by a X-ray diffraction study on **18**.

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**Figure 4.** View of the structure of the complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PMe}_2\text{Ph})\}_2(\mu\text{-I})]\text{I}_5$  (**18**).

**Crystal Structure of  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PMe}_2\text{Ph})\}_2(\mu\text{-I})]\text{I}_5$  (**18**).** The dinuclear complex **18** consists of dimetallic rhodium cations and pentaiodide counteranions. The structure of the cation is presented in Figure 4, together with the atom numbering scheme used. Ignoring the change in the phosphorus donor ligand, the dinuclear cation in **18** could be derived from the structure of **7** with a simple addition of a bridging third iodide and a subsequent elongation of the intermetallic separation to a Rh–Rh distance of 3.6374(8) Å. This distance is clearly indicative of no metal–metal interaction.

The coordination around each rhodium is essentially octahedral, involving three terminal, namely iodide, carbon monoxide, and dimethylphenylphosphine, and three bridging ligands (two pyrazolates and an iodide). As observed in **7** and in **10**, the carbonyl and the phosphine ligands are trans disposed at each rhodium center to the nitrogen atoms of the bridging pyrazolates, with the terminal iodides occupying trans positions relative to the bridging iodo ligand. Across the metal–metal vector the terminal iodides may be considered *eclipsed* with respect to each other ( $\text{I}(1)\text{---Rh}(1)\cdots\text{Rh}(2)\text{---I}(2)$  10.54(5)°, while the phosphines—and consequently the carbonyls—occupy relative pseudo-trans positions (torsional angles of 117.0(1) and –115.2(4)°, respectively).

The terminal Rh–I bond lengths (2.6582 and 2.6453(8) Å), as well as the bridging ones (2.6621 and 2.6758(8) Å), are significantly shorter than those observed in **7**, or in other Rh(II) complexes with the iodides trans disposed to the metal–metal bond. They are identical to those reported for  $[(\text{C}_5\text{Me}_5)\text{Ir}(\mu\text{-Pz})(\mu\text{-I})_2\text{RhI}(\text{CO})(\text{COOMe})]$ , 2.654(1) and 2.646(1) Å,<sup>25</sup> where two iodides—one terminal and one bridging—are situated trans to each other but are slightly shorter than the average values reported for terminal or bridging iodide ligands in rhodium(III) complexes (2.71(7) and 2.73(1) Å, respectively).<sup>21</sup> The Rh–N bond distances, normal for this type of rhodium(III) complexes,<sup>2a,7a,c,12</sup> also reflect the different ligands situated opposite: phosphine or carbonyl (Table 3).

The iodine atoms that constitute the counteranion in the crystal structure are catenated forming a typical V-shaped pentaiodide anion,  $\text{I}_5^-$ . As is usual for this type of polyiodide anion,<sup>26</sup> two nearly linear  $\text{I}_3$  moieties (176.29 and 177.52(3)°,

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **10**

Rh(1)···Rh(2)	3.26103(8)		
Rh(1)–I(1)	2.7671(6)	Rh(2)–I(2)	2.6230(6)
Rh(1)–P(1)	2.3554(16)	Rh(2)–P(2)	2.2951(16)
Rh(1)–N(5)	2.051(5)	Rh(2)–N(6)	2.068(5)
Rh(1)–N(7)	2.079(5)	Rh(2)–N(8)	2.038(4)
Rh(1)–C(1)	1.892(7)		
Rh(1)–C(2)	2.072(6)	Rh(2)–C(2)	1.982(6)
C(1)–O(1)	1.119(7)	C(2)–O(2)	1.168(6)
I(1)–Rh(1)–P(1)	90.80(4)	I(2)–Rh(2)–P(2)	92.21(4)
I(1)–Rh(1)–N(5)	95.64(13)	I(2)–Rh(2)–N(6)	89.55(13)
I(1)–Rh(1)–N(7)	90.60(13)	I(2)–Rh(2)–N(8)	164.91(13)
I(1)–Rh(1)–C(1)	85.61(18)	I(2)–Rh(2)–C(2)	104.24(15)
I(1)–Rh(1)–C(2)	174.49(15)	P(2)–Rh(2)–N(6)	174.88(14)
P(1)–Rh(1)–N(5)	95.65(14)	P(2)–Rh(2)–N(8)	92.15(14)
P(1)–Rh(1)–N(7)	178.55(13)	P(2)–Rh(2)–C(2)	95.65(17)
P(1)–Rh(1)–C(1)	92.20(18)	N(6)–Rh(2)–N(8)	84.96(19)
P(1)–Rh(1)–C(2)	91.03(15)	N(6)–Rh(2)–C(2)	88.6(2)
N(5)–Rh(1)–N(7)	83.9(2)	N(8)–Rh(2)–C(2)	89.7(2)
N(5)–Rh(1)–C(1)	172.0(2)		
N(5)–Rh(1)–C(2)	89.3(2)	Rh(1)–C(1)–O(1)	173.9(5)
N(7)–Rh(1)–C(1)	88.3(2)	Rh(1)–C(2)–Rh(2)	107.0(3)
N(7)–Rh(1)–C(2)	87.6(2)	Rh(1)–C(2)–O(2)	127.5(4)
C(1)–Rh(1)–C(2)	89.1(2)	Rh(2)–C(2)–O(2)	125.4(4)

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **18**

Rh(1)···Rh(2)	3.6374(8)		
Rh(1)–I(1)	2.6582(8)	Rh(2)–I(3)	2.6453(8)
Rh(1)–I(2)	2.6621(8)	Rh(2)–I(2)	2.6758(8)
Rh(1)–P(1)	2.342(2)	Rh(2)–P(2)	2.347(2)
Rh(1)–N(5)	2.120(7)	Rh(2)–N(6)	2.064(6)
Rh(1)–N(7)	2.058(7)	Rh(2)–N(8)	2.099(7)
Rh(1)–C(1)	1.907(9)	Rh(2)–C(2)	1.900(8)
C(1)–O(1)	1.099(11)	C(2)–O(2)	1.115(10)
I(4)–I(5)	2.9739(9)	I(5)–I(6)	2.8334(9)
I(4)–I(8)	3.2154(11)	I(7)–I(8)	2.7542(11)
I(1)–Rh(1)–I(2)	176.48(3)	I(3)–Rh(2)–I(2)	175.21(3)
I(1)–Rh(1)–P(1)	93.22(6)	I(3)–Rh(2)–P(1)	92.59(6)
I(1)–Rh(1)–N(5)	89.64(18)	I(3)–Rh(2)–N(6)	91.48(19)
I(1)–Rh(1)–N(7)	91.61(19)	I(3)–Rh(2)–N(8)	90.16(18)
I(1)–Rh(1)–C(1)	87.2(3)	I(3)–Rh(2)–C(2)	86.2(3)
I(2)–Rh(1)–P(1)	90.07(6)	I(2)–Rh(2)–P(2)	91.41(6)
I(2)–Rh(1)–N(5)	87.01(18)	I(2)–Rh(2)–N(6)	91.19(19)
I(2)–Rh(1)–N(7)	89.35(19)	I(2)–Rh(2)–N(8)	85.97(18)
I(2)–Rh(1)–C(1)	91.8(3)	I(2)–Rh(2)–C(2)	90.8(3)
P(1)–Rh(1)–N(5)	176.35(19)	P(2)–Rh(2)–N(6)	89.5(2)
P(1)–Rh(1)–N(7)	89.6(2)	P(2)–Rh(2)–N(8)	176.11(18)
P(1)–Rh(1)–C(1)	92.1(3)	P(2)–Rh(2)–C(2)	94.7(3)
N(5)–Rh(1)–N(7)	88.1(3)	N(6)–Rh(2)–N(8)	87.7(3)
N(5)–Rh(1)–C(1)	90.2(3)	N(6)–Rh(2)–C(2)	175.3(3)
N(7)–Rh(1)–C(1)	178.0(3)	N(8)–Rh(2)–C(2)	88.2(3)
Rh(1)–C(1)–O(1)	175.9(9)	I(5)–I(4)–I(8)	115.18(2)
Rh(2)–C(2)–O(2)	175.0(7)	I(4)–I(5)–I(6)	176.29(3)
Rh(1)–I(2)–Rh(2)	85.91(2)	I(4)–I(8)–I(7)	177.52(3)

see Table 3) share a common vertex (I(5)–I(4)–I(8), 115.18(2)°), showing a distribution of I–I bond distances according with a short–long–long–short pattern along the V-shaped polyiodide chain (2.7542–3.2154–2.9739–2.8334 Å in **18**).

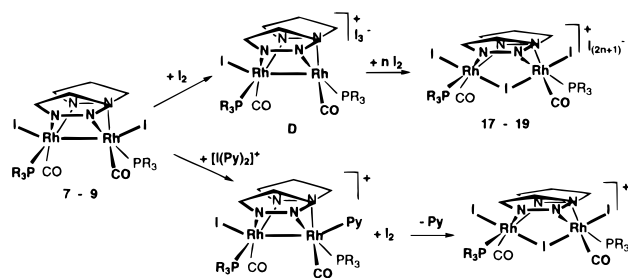
**An Approach to the Mechanism of the Rupture of the Metal–Metal Bond in Complexes 6–9 and 15.** At first glance, the pyrazolato dirhodium(II) complexes **6–9** and **15**, containing two iodide ligands trans to the single rhodium–rhodium bond, appear very similar. Moreover, these type of compounds  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})\}_2]$  should display, in principle, two sites suitable for electrophilic attack, the metal–metal bond (“endo site”) and the “exo site” occupied by iodide ligands. However they possess as a subtle structural difference the bulkiness of the ancillary ligands L, which modulates the accessibility of the electrophile to the “endo site”. This should be of key importance to discriminate the reaction mechanisms involving the “endo site” or the “exo site”. For complexes having sterically

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Scheme 4



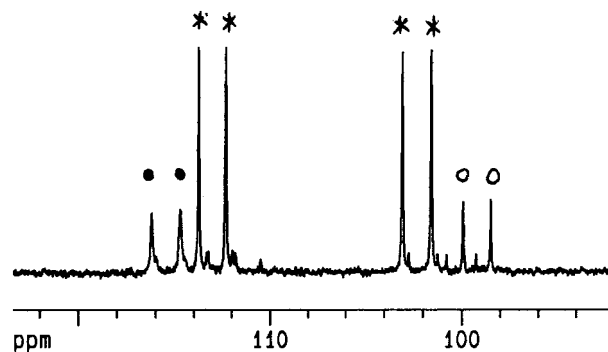
undemanding ancillary ligands such as **6** ( $L = \text{CNBu}^t$ ) and **15** ( $L = \text{CO}$ ), the access allowing the entry of the diiodine molecule (Scheme 3) in close proximity to the metal–metal bond is large enough. Thus, their reactions with diiodine should be initiated at the “endo site” through a possible transition state such as **B**, similar to that proposed previously for the reaction of the dirhodium (II) complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$  with diiodine.<sup>2a</sup> This transition state would give the ionic complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(L)\}_2(\mu\text{-I})\text{I}]$  (**C**) from which the products **13**, **14**, and **16** will be formed as discussed above (Scheme 3). Curiously, the reaction of equimolar amounts of **6** and  $[\text{I}(\text{Py})_2]\text{BF}_4$  gives directly the cationic complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{CNBu}^t)\}_2(\mu\text{-I})\text{BF}_4]$  ( $^1\text{H}$  NMR evidence), expected from an attack of the electrophilic iodine to the “endo site” in **6** (Scheme 3).

However, on the basis of steric arguments, a transition state such as **B** should be improbable for complexes **7–9** ( $L = \text{P-donor ligand}$ ). Thus, a close examination of the structure of complex **7**, which contains the P-donor ligand with the smallest cone angle, shows that the access of iodine to the metal–metal bond is restricted by the ancillary ligands. Therefore, the addition of diiodine to complexes **7–9** should proceed through a different pathway although the products are similar cationic complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(L)\}_2(\mu\text{-I})]^+$ , but containing triiodide or penta-iodide as counterions (Scheme 4). Thus, the reactions with  $[\text{I}(\text{Py})_2]\text{BF}_4$  were carried out to test the reactive sites in these complexes.

The dirhodium(II) cationic species  $[(\text{PR}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Py})(\text{CO})(\text{PR}_3)]\text{BF}_4$  ( $\text{PR}_3 = \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3, \text{PMe}_2\text{Ph}$ ), resulting from the reactions of **7–9** with the electrophile  $[\text{I}(\text{Py})_2]\text{BF}_4$ , indicate that the process should be initiated at the “exo site”, and that cationic species  $[(\text{CO})(\text{PR}_3)(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{PR}_3)(\text{CO})]^+$  (**D**) could be involved in the reactions with diiodine (Scheme 4). Moreover, the related cationic complexes  $[(\text{PR}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Py})(\text{CO})(\text{PR}_3)]^+$  also result from the treatment of **7–9** with 1 molar equiv of  $\text{Ag}(\text{BF}_4)$  in the presence of equimolar amounts of pyridine. Both reactions imply the removal of the iodide ligand from the “exo site”.

Figure 5 shows the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum corresponding to the reaction mixture between **7** and  $[\text{I}(\text{Py})_2]\text{BF}_4$  in which the major component is  $[(\text{P}\{\text{OMe}\}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Py})(\text{CO})(\text{P}\{\text{OMe}\}_3)]^+$ , along with small amounts of **7** and **12**. It should be noticed that the phosphorus chemical shifts and the  $J_{\text{P-Rh}}$  values for  $[(\text{PR}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Py})(\text{CO})(\text{PR}_3)]^+$  agree with dirhodium(II) complexes. The pyridine ligand is located trans to the rhodium–rhodium bond, since NMR difference NOE spectra show positive NOE effects between the  $\text{H}^3$  protons of the pyrazolate ligands and the  $\text{H}^{2,6}$  protons of the Py ligand due to their relative proximity in the molecule.

The second step in the reactions of  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2]$  with diiodine should be the addition of the second molecule of diiodine to the cationic intermediates  $[(\text{PR}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CO})(\text{PR}_3)]\text{I}_3$  (**D**) to give  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})]^+$ . In support of this view, the cationic complexes  $[(\text{PR}_3)(\text{CO})(\text{I})$



**Figure 5.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of  $[\text{I}(\text{Py})_2]\text{BF}_4$  and  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{P}\{\text{OMe}\}_3)\}_2]$  (**7**), showing the starting material (●), the major product  $[(\text{P}\{\text{OMe}\}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Py})(\text{CO})(\text{P}\{\text{OMe}\}_3)]^+$  (\*) and  $[\{\text{Rh}(\mu\text{-Pz})(\text{Py})(\text{CO})(\text{P}\{\text{OMe}\}_3)\}_2]^{2+}$  (**12**) (○).

$\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CO})(\text{PR}_3)]\text{BF}_4$  (prepared in situ) react with diiodine in chloroform to give the expected products  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})]\text{BF}_4$  ( $^1\text{H}$  NMR evidence). Moreover, the reactions of  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2]$  with the positive iodine complex  $[\text{I}(\text{Py})_2]\text{BF}_4$  finally give  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})]\text{BF}_4$  ( $\text{PR}_3 = \text{P}(\text{OPh})_3, \text{PMe}_2\text{Ph}$ ) because diiodine is formed along with the observed intermediates  $[(\text{PR}_3)(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Py})(\text{CO})(\text{PR}_3)]^+$ , which react further. Therefore, as diiodine is able to add to the cationic intermediate complexes **D** while triiodide cannot, the reactions with diiodine following Scheme 4 require at least 2 molar equiv of diiodine; one to add to **D** and more diiodine to form triiodide or penta-iodide. By contrast, for those cases in which the diiodine is added at the “endo site” following Scheme 3, complexes **6**, **15**, and  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$ , only 1 mol of diiodine is required to break the metal–metal bond.

**(iii) Dinuclear Iridium Pyrazolate Complexes.** We have also explored the response of some related diiridium(II) pyrazolate complexes toward the addition of diiodine. The compound  $[\{\text{Ir}(\mu\text{-Pz})(\text{I})(\text{CO})_2\}_2]$  (**20**) and its analogous<sup>27</sup>  $[\{\text{Ir}(\mu\text{-Me}_2\text{Pz})(\text{I})(\text{CO})_2\}_2]$  do not react with diiodine over several days, even if an excess of diiodine is added. This lack of reactivity seems to suggest that the metal–metal bond in these iridium complexes is stronger and more resistant toward the electrophilic attack of diiodine than the analogous rhodium compound, as shown in Scheme 3. In contrast, the new complexes  $[\{\text{Ir}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2]$  ( $\text{PR}_3 = \text{P}(\text{OPh})_3$  (**21**),  $\text{PMe}_2\text{Ph}$  (**22**)) react with diiodine, as for their rhodium counterparts, to give the cationic diiridium(III) complexes  $[\{\text{Ir}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})\text{I}_n]$  ( $n = 7, \text{PR}_3 = \text{P}(\text{OPh})_3$  (**23**);  $n = 3, \text{PR}_3 = \text{PMe}_2\text{Ph}$  (**24**)). Complexes **23** and **24** are 1:1 electrolytes, and the cations contain a bridging iodide ligand with structures similar to the rhodium complexes  $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})\text{I}_3]$ . As for the related rhodium compounds (Scheme 4) the iridium complexes **21** and **22** also react with  $[\text{I}(\text{Py})_2]\text{BF}_4$  at the “exo site” to give initially the cationic complexes of formula  $[(\text{PR}_3)(\text{CO})(\text{I})\text{Ir}(\mu\text{-Pz})_2\text{Ir}(\text{Py})(\text{CO})(\text{PR}_3)]\text{BF}_4$  (NMR tube experiments). As diiodine is formed in the reaction medium, a further reaction with the diiridium(II) cations follows, allowing the evolution to the products  $[\{\text{Ir}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{PR}_3)\}_2(\mu\text{-I})]\text{BF}_4$ .

Significant differences on the reactivity of  $[\{\text{M}(\mu\text{-Pz})(\text{CO})_2\}_2]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) complexes toward  $\text{MeI}$  have been observed. Thus, the rhodium(I) complex does not react with  $\text{MeI}$ , most probably because the rhodium centers are not basic enough to promote

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the oxidative-addition reaction, which is more favored for the iridium(I) compound to give<sup>28</sup> the diiridium (II) complex  $[\{\text{Ir}(\mu\text{-Pz})(\text{CO})_2(\text{Me})(\text{I})\}]$ . Moreover,  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{P}\{\text{Oph}\}_3)_2\}]$  does react with MeI to give the dirhodium(III) complex  $[\{\text{Rh}(\mu\text{-Pz})(\text{Me})(\text{CO})(\text{P}\{\text{Oph}\}_3)_2(\mu\text{-I})\}]\text{I}$  (**25**). In other words, the driving force for the oxidative-addition of MeI seems to be the nucleophilicity of the metal (higher for iridium than for rhodium and modulated by the electronic environment for the latter), while the formation of the dirhodium(II) or diiridium(II) complexes  $[\{\text{M}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})_2\}]$  from the reactions with diiodine should be due to a simple oxidation process.

### Concluding Remarks

This work describes reactions of pyrazolate rhodium and iridium complexes with diiodine leading initially to the formation and further rupture of metal–metal bonds. The studies performed revealed bimetallic processes resulting from the cooperative oxidation of both metal centers. The process of formation of the metal–metal bond, favoring the formation of dimetal(II) complexes, is a consequence of the abstraction of electrons from the HOMO orbital and is, in general, more favorable for iridium. The subsequent rupture of these metal–metal bonds, by the addition of a second molecule of diiodine, should imply an electrophilic attack of diiodine at the metal–metal bond if the access to the “endo site” is large enough, but when sterically demanding ligands disfavor the entry of diiodine to the “endo site”, the reaction is initiated at the “exo site” through ionic complexes  $[\text{R}_3\text{P}(\text{CO})(\text{I})\text{M}(\mu\text{-Pz})_2\text{M}(\text{CO})(\text{PR}_3)]^+$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) as key intermediates.

### Experimental Section

**Starting Materials and Methods.** All reactions were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled under argon before use by standard methods. For additional general information, including a list of spectrophotometers and equipment used for the physical characterization of the complexes, see ref 2a.

*trans*- $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})_2\}]$  ( $\text{L} = \text{CNBu}^+$  (**1**),  $\text{P}(\text{OMe})_3$  (**2**),  $\text{PMe}_2\text{Ph}$  (**3**)) was prepared by addition of the appropriate ligand L (0.884 mmol) to a solution of  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}]$  (200 mg, 0.442 mmol) in anhydrous diethyl ether (10 mL). After the CO evolution, the suspensions were concentrated to 5 mL and the resulting yellow microcrystals were filtered, washed with cold pentane and vacuum-dried. Complex **1**: yield, 58%. Anal. Calcd for  $\text{C}_{18}\text{H}_{24}\text{N}_6\text{O}_2\text{Rh}_2$ : C, 38.45; H, 4.30; N, 14.95. Found: C, 39.14; H, 4.66; N, 14.48. IR (diethyl ether,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1994 (s),  $\nu(\text{CN})$  2160 (s).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , rt):  $\delta$  7.81 (d, 1.9 Hz, 2H,  $\text{H}^3\text{Pz}$ ), 7.68 (d, 1.9 Hz, 2H,  $\text{H}^5\text{Pz}$ ), 6.29 (t, 1.9 Hz, 2H,  $\text{H}^4\text{Pz}$ ), 0.68 (s, 18H, CNBu<sup>+</sup>).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , rt):  $\delta$  190.1 (d,  $J_{\text{C-Rh}} = 68$  Hz, CO), 142.0 ( $\text{C}^3\text{Pz}$ ), 140.6 ( $\text{C}^5\text{Pz}$ ), 104.9 ( $\text{C}^4\text{Pz}$ ), 56.7 ( $\text{C}(\text{CH}_3)_3$ ), 29.5 ( $\text{C}(\text{CH}_3)_3$ ). MS ( $\text{FAB}^+$ ): 562 (100,  $\text{M}^+$ ). Complex **2**: yield, 85%. Anal. Calcd for  $\text{C}_{14}\text{H}_{24}\text{N}_4\text{O}_8\text{P}_2\text{Rh}_2$ : C, 26.10; H, 3.76; N, 8.70. Found: C, 26.26; H, 3.72; N, 8.64. IR (diethyl ether,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2002 (s).  $^1\text{H}\{^31\text{P}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  7.54 (d, 1.8 Hz, 2H,  $\text{H}^3\text{Pz}$ ), 7.39 (d, 1.8 Hz, 2H,  $\text{H}^5\text{Pz}$ ), 6.19 (t, 1.8 Hz, 2H,  $\text{H}^4\text{Pz}$ ), 3.67 (s, 18H,  $\text{P}(\text{OMe})_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  189.1 (dd,  $J_{\text{C-Rh}} = 69$  Hz,  $J_{\text{C-P}} = 23$  Hz, CO), 140.5 ( $\text{C}^3\text{Pz}$ ), 140.0 ( $\text{C}^5\text{Pz}$ ), 104.8 ( $\text{C}^4\text{Pz}$ ), 52.0 ( $\text{P}(\text{OMe})_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  142.4 (d,  $J_{\text{P-Rh}} = 241$  Hz). MS ( $\text{FAB}^+$ ): 644 (70,  $\text{M}^+$ ), 588 (100,  $\text{M}^+ - 2\text{CO}$ ). Complex **3**: yield, 64%. Anal. Calcd for  $\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_2\text{P}_2\text{Rh}_2$ : C, 42.88; H, 4.20; N, 8.33. Found: C, 43.15; H, 3.55; N, 8.14. IR (diethyl ether,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1971 (s).  $^1\text{H}\{^31\text{P}\}$  NMR ( $\text{C}_6\text{D}_6$ , rt):  $\delta$  7.81 (m, 6H,  $\text{H}^{m\text{-P}}\text{PMe}_2\text{Ph}$ ), 7.80 (d, 2.2 Hz, 2H,  $\text{H}^3\text{Pz}$ ), 7.09 (d, 7.9 Hz, 4H,  $\text{H}^p\text{PMe}_2\text{Ph}$ ), 7.02 (d, 2.2 Hz, 2H,  $\text{H}^5\text{Pz}$ ), 6.02 (t, 2.2 Hz, 2H,  $\text{H}^4\text{Pz}$ ), 1.30 (d,  $J_{\text{H-Rh}} = 1.6$  Hz, 6H) and 1.23 (d,  $J_{\text{H-Rh}} = 1.1$  Hz, 6H) ( $\text{PMe}_2\text{Ph}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , rt):  $\delta$  193.1 (dd,  $J_{\text{C-Rh}} = 70$  Hz,  $J_{\text{C-P}} = 20$  Hz, CO), 140.2 ( $\text{C}^3\text{Pz}$ ), 138.9 ( $\text{C}^5\text{Pz}$ ),

136.7 (d,  $J_{\text{C-P}} = 45$  Hz,  $\text{C}^i\text{PMe}_2\text{Ph}$ ), 132.0 (d,  $J_{\text{C-P}} = 12$  Hz,  $\text{C}^o\text{PMe}_2\text{Ph}$ ), 130.1 ( $\text{C}^p\text{PMe}_2\text{Ph}$ ), 128.6 (d,  $J_{\text{C-P}} = 10$  Hz,  $\text{C}^m\text{PMe}_2\text{Ph}$ ), 104.6 ( $\text{C}^4\text{Pz}$ ), 18.1 (dd,  $J_{\text{C-P}} = 33$  Hz,  $J_{\text{C-Rh}} = 2$  Hz) and 14.6 (dd,  $J_{\text{C-P}} = 31$  Hz,  $J_{\text{C-Rh}} = 1$  Hz) ( $\text{PMe}_2\text{Ph}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , rt):  $\delta$  14.8 (d,  $J_{\text{P-Rh}} = 146$  Hz). MS ( $\text{FAB}^+$ ): 672 (72,  $\text{M}^+$ ), 616 (100,  $\text{M}^+ - 2\text{CO}$ ).

$[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CO})(\text{L})_2\}]$  ( $\text{L} = \text{CNBu}^+$  (**6**),  $\text{P}(\text{OMe})_3$  (**7**),  $\text{PMe}_2\text{Ph}$  (**8**),  $\text{P}(\text{Oph})_3$  (**9**)). Addition of a solution of diiodine (0.30 mmol) in diethyl ether (10 mL) to yellow suspensions of  $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{L})\}]$  (**1–4**) (0.30 mmol) in diethyl ether (10 mL) immediately produces dark red suspensions. These were stirred for 30 min and concentrated to ca. 2 mL. Slow addition of pentane (15 mL) rendered the complexes **6–9** as dark red microcrystals, which were filtered, washed with cold pentane, and dried under vacuum. Complex **6**: yield, 85%. Anal. Calcd for  $\text{C}_{18}\text{H}_{24}\text{I}_2\text{N}_6\text{O}_2\text{Rh}_2$ : C, 26.49; H, 2.96; N, 10.30. Found: C, 26.57; H, 2.85; N, 10.17. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2073 (s),  $\nu(\text{CN})$  2216 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  7.62 (d, 2.1 Hz, 2H,  $\text{H}^3\text{Pz}$ ), 7.58 (d, 2.1 Hz, 2H,  $\text{H}^5\text{Pz}$ ), 6.05 (t, 2.1 Hz, 2H,  $\text{H}^4\text{Pz}$ ), 1.41 (s, 18H, CNBu<sup>+</sup>).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  186.5 (d,  $J_{\text{C-Rh}} = 57$  Hz, CO), 140.6 (d,  $J_{\text{C-Rh}} = 4$  Hz,  $\text{C}^3\text{Pz}$ ), 139.6 (d,  $J_{\text{C-Rh}} = 4$  Hz,  $\text{C}^5\text{Pz}$ ), 106.1 ( $\text{C}^4\text{Pz}$ ), 59.7 ( $\text{C}(\text{CH}_3)_3$ ), 29.9 ( $\text{C}(\text{CH}_3)_3$ ). MS ( $\text{FAB}^+$ ): 689 (100,  $\text{M}^+ - \text{I}$ ). Complex **7**: yield, 75%. Anal. Calcd for  $\text{C}_{14}\text{H}_{24}\text{I}_2\text{N}_4\text{O}_8\text{P}_2\text{Rh}_2$ : C, 18.72; H, 2.69; N, 6.24. Found: C, 18.73; H, 2.16; N, 6.24. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2066 (s).  $^1\text{H}\{^31\text{P}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  7.67 (m, 4H,  $\text{H}^3\text{Pz}$ ), 5.97 (t, 2.1 Hz, 2H,  $\text{H}^4\text{Pz}$ ), 3.66 (s, 18H,  $\text{P}(\text{OMe})_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  187.5 (dd,  $J_{\text{C-Rh}} = 59$  Hz,  $J_{\text{C-P}} = 19$  Hz, CO), 140.6 (d,  $J_{\text{C-P}} = 6$  Hz,  $\text{C}^3\text{Pz}$ ), 140.4 (d,  $J_{\text{C-P}} = 11$  Hz,  $\text{C}^5\text{Pz}$ ), 105.2 (dt,  $J_{\text{C-P}} = 6$  Hz,  $J_{\text{C-Rh}} = 2$  Hz,  $\text{C}^4\text{Pz}$ ), 54.5 (d,  $J_{\text{C-P}} = 8$  Hz,  $\text{P}(\text{OMe})_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  117.3 (d,  $J_{\text{P-Rh}} = 181$  Hz). MS ( $\text{FAB}^+$ ): 898 (4,  $\text{M}^+$ ), 714 (100,  $\text{M}^+ - \text{I} - \text{CO}$ ). Complex **8**: yield, 88%. Anal. Calcd for  $\text{C}_{24}\text{H}_{28}\text{I}_2\text{N}_4\text{O}_2\text{P}_2\text{Rh}_2$ : C, 31.13; H, 3.05; N, 6.05. Found: C, 30.24; H, 2.87; N, 6.17. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2046 (s).  $^1\text{H}\{^31\text{P}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  7.73 (d, 2.0 Hz, 2H,  $\text{H}^3\text{Pz}$ ), 7.58 (d, 2.0 Hz, 2H,  $\text{H}^5\text{Pz}$ ), 7.39 (m, 6H,  $\text{H}^{m\text{-P}}\text{PMe}_2\text{Ph}$ ), 7.20 (d, 7.9 Hz, 4H,  $\text{H}^p\text{PMe}_2\text{Ph}$ ), 6.02 (t, 2.0 Hz, 2H,  $\text{H}^4\text{Pz}$ ), 1.96 (s, 6H) and 1.63 (s, 6H) ( $\text{PMe}_2\text{Ph}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  189.7 (dd,  $J_{\text{C-Rh}} = 59$  Hz,  $J_{\text{C-P}} = 15$  Hz, CO), 141.8 (d,  $J_{\text{C-P}} = 7$  Hz,  $\text{C}^3\text{Pz}$ ), 139.8 (d,  $J_{\text{C-P}} = 4$  Hz,  $\text{C}^5\text{Pz}$ ), 135.3 (d,  $J_{\text{C-P}} = 50$  Hz,  $\text{C}^i\text{PMe}_2\text{Ph}$ ), 130.8 (d,  $J_{\text{C-P}} = 3$  Hz,  $\text{C}^o\text{PMe}_2\text{Ph}$ ), 129.7 (d,  $J_{\text{C-P}} = 9$  Hz,  $\text{C}^m\text{PMe}_2\text{Ph}$ ), 129.0 (d,  $J_{\text{C-P}} = 10$  Hz,  $\text{C}^p\text{PMe}_2\text{Ph}$ ), 106.1 (dt,  $J_{\text{C-P}} = 4$  Hz,  $J_{\text{C-Rh}} = 1$  Hz,  $\text{C}^4\text{Pz}$ ), 21.0 (d,  $J_{\text{C-P}} = 37$  Hz) and 16.6 (d,  $J_{\text{C-P}} = 37$  Hz) ( $\text{PMe}_2\text{Ph}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  5.0 (d,  $J_{\text{P-Rh}} = 109$  Hz). MS ( $\text{FAB}^+$ ): 926 (15,  $\text{M}^+$ ), 799 (100,  $\text{M}^+ - \text{I}$ ). Complex **9**: yield, 68%. Anal. Calcd for  $\text{C}_{44}\text{H}_{36}\text{I}_2\text{N}_4\text{O}_8\text{P}_2\text{Rh}_2$ : C, 41.60; H, 2.85; N, 4.41. Found: C, 41.74; H, 2.80; N, 4.38. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2073 (s).  $^1\text{H}\{^31\text{P}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  7.69 (d, 2.0 Hz, 2H,  $\text{H}^3\text{Pz}$ ), 7.31 (d, 2.0 Hz, 2H,  $\text{H}^5\text{Pz}$ ), 7.08 (m, 18H,  $\text{H}^{m\text{-P}}\text{P}(\text{Oph})_3$ ), 6.85 (d, 8.0 Hz, 12H,  $\text{H}^p\text{P}(\text{Oph})_3$ ), 5.81 (t, 2.0 Hz, 2H,  $\text{H}^4\text{Pz}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  186.7 (dd,  $J_{\text{C-Rh}} = 58$  Hz,  $J_{\text{C-P}} = 18$  Hz, CO), 151.1 (d,  $J_{\text{C-P}} = 14$  Hz,  $\text{C}^i\text{P}(\text{Oph})_3$ ), 141.1 (d,  $J_{\text{C-P}} = 6$  Hz,  $\text{C}^3\text{Pz}$ ), 141.0 (d,  $J_{\text{C-P}} = 11$  Hz,  $\text{C}^5\text{Pz}$ ), 129.7 ( $\text{C}^m\text{P}(\text{Oph})_3$ ), 125.5 ( $\text{C}^p\text{P}(\text{Oph})_3$ ), 129.0 (d,  $J_{\text{C-P}} = 4$  Hz,  $\text{C}^o\text{P}(\text{Oph})_3$ ), 106.0 (d,  $J_{\text{C-P}} = 6$  Hz,  $\text{C}^4\text{Pz}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , rt):  $\delta$  101.8 (d,  $J_{\text{P-Rh}} = 198$  Hz). MS ( $\text{FAB}^+$ ): 1270 (2,  $\text{M}^+$ ), 1142 (40,  $\text{M}^+ - \text{I}$ ).

$[\{\text{P}\{p\text{-tolyl}\}_3\}(\text{CO})(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-CO})\text{Rh}(\text{I})\{\text{P}\{p\text{-tolyl}\}_3\}]$  (**10**). Addition of a solution of diiodine (12.6 mg, 0.05 mmol) to a suspension of complex **5** (50 mg, 0.05 mmol) in diethyl ether gives instantaneously a red solution along with small amounts of a brown solid, which was filtered through kieselguhr. The filtrate was left in a freezer at  $-30$  °C for 2 days to render red monocystals, which were filtered, washed with cold pentane, and vacuum-dried. Yield: 30%. Anal. Calcd for  $\text{C}_{50}\text{H}_{48}\text{I}_2\text{N}_4\text{O}_2\text{P}_2\text{Rh}_2$ : C, 47.72; H, 3.84; N, 4.45. Found: C, 47.60, H, 4.13; N, 4.21. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2095 (s), 1757 (s).  $^1\text{H}\{^31\text{P}\}$  NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  8.54 (d, 2.2 Hz, 1H,  $\text{H}^3\text{Pz}$ ), 8.09 (d, 2.2 Hz, 1H,  $\text{H}^5\text{Pz}$ ), 7.31 (d, 2.2 Hz, 1H,  $\text{H}^4\text{Pz}$ ), 7.38 ( $\delta_A$ , 6H,  $\text{P}^a\{p\text{-tolyl}\}_3$ ), 7.18 ( $\delta_B$ ,  $J_{A-B} = 8.2$  Hz, 6H,  $\text{P}^a\{p\text{-tolyl}\}_3$ ), 7.48 ( $\delta_A$ , 2H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ), 7.28 ( $\delta_B$ ,  $J_{A-B} = 8.1$  Hz, 2H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ), 7.25 ( $\delta_A$ , 2H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ), 7.07 ( $\delta_B$ ,  $J_{A-B} = 8.0$  Hz, 2H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ), 6.90 ( $\delta_A$ , 2H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ), 6.17 ( $\delta_B$ ,  $J_{A-B} = 8.1$  Hz, 2H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ), 6.06 (t, 2.2 Hz, 1H,  $\text{H}^4\text{Pz}$ ), 5.90 (d, 2.2 Hz, 1H,  $\text{H}^5\text{Pz}$ ), 5.85 (t, 2.2 Hz, 1H,  $\text{H}^4\text{Pz}$ ), 2.42 (s, 3H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ), 2.33 (s, 12H,  $\text{P}^b\{p\text{-tolyl}\}_3 + \text{P}^a\{p\text{-tolyl}\}_3$ ), 2.21 (s, 3H,  $\text{P}^b\{p\text{-tolyl}\}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 218 K):  $\delta$  30.4 (d,  $J_{\text{P-Rh}} = 131$  Hz), 17.5 (d,  $J_{\text{P-Rh}} = 111$  Hz).

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**[{Rh( $\mu$ -Pz)(CO)(P(OMe)<sub>3</sub>)(CH<sub>3</sub>CN)}<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**11**). Solid [FeCp<sub>2</sub>]-PF<sub>6</sub> (51.8 mg, 0.154 mmol) was added to a yellow solution of [{Rh( $\mu$ -Pz)(CO)(P(OMe)<sub>3</sub>)<sub>2</sub>]} (**2**) (50.0 mg, 0.077 mmol) in acetonitrile. The resulting orange solution was evaporated to dryness and the residue washed with 4 × 10 mL of diethyl ether to remove [FeCp<sub>2</sub>]. The resulting yellow oil was dried under vacuum. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2104 (s). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  7.80 (m, 4H, H<sup>3,5</sup>Pz), 6.28 (m, 2H, H<sup>4</sup>Pz), 3.92 (d, <sup>3</sup>J<sub>H-P</sub> = 11 Hz, 18H, P(OMe)<sub>3</sub>), 2.84 (s, 6H, CH<sub>3</sub>-CN). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  103.6 (d, *J*<sub>P-Rh</sub> = 169 Hz), -143.0 (h, *J*<sub>P-F</sub> = 726 Hz). MS (FAB<sup>+</sup>): 644 (50, M<sup>+</sup> - 2CH<sub>3</sub>CN), 588 (100, M<sup>+</sup> - 2CH<sub>3</sub>CN - 2CO).  $\Lambda_M$  (5 × 10<sup>-4</sup> M in acetone) = 205 S mol<sup>-1</sup> cm<sup>-1</sup>.**

**[{Rh( $\mu$ -Pz)(CO)(P(OMe)<sub>3</sub>)(Py)}<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**12**). The yellow oil obtained as described above was dissolved in dichloromethane and pyridine (Py) (12.55  $\mu$ L, 0.154 mmol) was added dropwise. The initial yellow solution turned orange almost immediately and then was evaporated to dryness and washed with diethyl ether (2 × 5 mL) and pentane (2 × 5 mL) to render an orange oil. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2095 (s). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  8.95 (d, 6.6 Hz, 4H, H<sup>6</sup>Py), 8.41 (t, 6.6 Hz, 2H, H<sup>7</sup>Py), 7.96 (t, 6.6 Hz, 4H, H<sup>8</sup>Py), 7.77 (m, 2H, H<sup>3</sup>Pz), 7.46 (m, 2H, H<sup>5</sup>Pz), 6.42 (m, 2H, H<sup>4</sup>Pz), 3.86 (d, <sup>3</sup>J<sub>H-P</sub> = 11 Hz, 18H, P(OMe)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  184.2 (dd, *J*<sub>C-Rh</sub> = 61 Hz, <sup>2</sup>J<sub>C-P</sub> = 25 Hz, CO), 154.3, 139.0, 127.7 (Py), 141.2 (C<sup>3</sup>Pz), 138.3 (C<sup>5</sup>Pz), 109.1 (C<sup>4</sup>Pz), 56.0 (d, <sup>2</sup>J<sub>C-P</sub> = 10 Hz, P(OMe)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  100.8 (d, *J*<sub>P-Rh</sub> = 175 Hz), -143.0 (h, *J*<sub>P-F</sub> = 726 Hz). MS (FAB<sup>+</sup>): 644 (70, M<sup>+</sup> - 2Py), 588 (100, M<sup>+</sup> - 2Py - 2CO).  $\Lambda_M$  (5 × 10<sup>-4</sup> M in acetone) = 205 S mol<sup>-1</sup> cm<sup>-1</sup>.**

**[{CO(CNBu<sup>t</sup>)(I)Rh( $\mu$ -Pz)<sub>2</sub>( $\mu$ -I)Rh(I)<sub>2</sub>(CNBu<sup>t</sup>)}<sub>2</sub>](**13**). **Method A.** Solid diiodine (18.6 mg, 0.073 mmol) was added to a solution of [{Rh( $\mu$ -Pz)(I)(CO)(CNBu<sup>t</sup>)<sub>2</sub>]} (**6**) (60 mg, 0.073 mmol) in diethyl ether (20 mL). The resulting dark suspension was stirred for 12 h to give a dark red solid, which was filtered, washed with pentane (2 × 5 mL), and vacuum-dried. Yield: 70%. This crude contains about 5% of complex **14**.**

**Method B.** An excess of solid KI was added to a solution of [{Rh( $\mu$ -Pz)(I)(CO)(CNBu<sup>t</sup>)<sub>2</sub>( $\mu$ -I)]<sub>2</sub> (**14**) (50 mg, 0.038 mmol) in acetone (5 mL). The initial purple solution turned dark red almost immediately. After stirring for 20 min, the solution was evaporated to dryness and the residue extracted with dichloromethane and filtered over kieselguhr (to remove the KI excess and the KI<sub>3</sub> formed). The resulting solution was evaporated to ca. 1 mL, and pentane was added (10 mL) to produce the complete crystallization of **13**. Yield: 90%. Anal. Calcd for C<sub>17</sub>H<sub>24</sub>I<sub>4</sub>N<sub>6</sub>O<sub>2</sub>Rh<sub>2</sub>: C, 19.60; H, 2.32; N, 8.06. Found: C, 19.49; H, 1.77; N, 7.51. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2123,  $\nu$ (CN) 2240 (s) and 2214 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, rt):  $\delta$  8.55 (d, 2.4 Hz, 1H), 8.09 (d, 2.4 Hz, 1H) and 8.05 (m, 2H) (H<sup>3,5,5'</sup>Pz), 6.16 (t, 2.4 Hz, 1H) and 6.14 (t, 2.4 Hz, 1H) (H<sup>4,4'</sup>Pz), 1.66 (s, 9H) and 1.60 (s, 9H) (CNBu<sup>t</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  176.2 (d, *J*<sub>C-Rh</sub> = 47 Hz, CO), 149.0, 147.1, 146.5 and 144.7 (C<sup>3,3',5,5'</sup>Pz), 107.5 and 107.3 (C<sup>4,4'</sup>Pz), 61.3 and 59.3 (C(CH<sub>3</sub>)<sub>3</sub>), 30.4 and 30.1 (C(CH<sub>3</sub>)<sub>3</sub>). MS (FAB<sup>+</sup>): 1013 (12, M<sup>+</sup> - CO). MW calcd for C<sub>17</sub>H<sub>24</sub>I<sub>4</sub>N<sub>6</sub>O<sub>2</sub>Rh<sub>2</sub>: 1041. Found: 992.

**[{Rh( $\mu$ -Pz)(I)(CO)(L)}<sub>2</sub>]( $\mu$ -I)]<sub>2</sub> (**L** = CNBu<sup>t</sup> (**14**), P(OPh)<sub>3</sub> (**19**)). To a solution of [{Rh( $\mu$ -Pz)(I)(CO)(L)}<sub>2</sub>] (**L** = CNBu<sup>t</sup> (**6**), P(OPh)<sub>3</sub> (**9**)) (0.100 mmol) in diethyl ether (20 mL) was added a solution of diiodine (50.6 mg, 0.200 mmol) dropwise. After stirring for 2 h, the dark suspensions were concentrated to ca. 2 mL and pentane (15 mL) was added. The resulting dark purple microcrystalline solids were filtered, washed with pentane (2 × 5 mL), and vacuum-dried. Complex **14**: yield, 85%. Anal. Calcd for C<sub>18</sub>H<sub>24</sub>I<sub>4</sub>N<sub>6</sub>O<sub>2</sub>Rh<sub>2</sub>: C, 16.33; H, 1.83; N, 6.35. Found: C, 16.49; H, 1.21; N, 6.20. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2133 (s),  $\nu$ (CN) 2245 (s). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  8.37 (d, 2.4 Hz, 2H, H<sup>3</sup>Pz), 8.34 (d, 2.4 Hz, 2H, H<sup>5</sup>Pz), 6.41 (t, 2.4 Hz, 2H, H<sup>4</sup>Pz), 1.65 (s, 18H, CNBu<sup>t</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  174.6 (d, *J*<sub>C-Rh</sub> = 49 Hz, CO), 147.7 (C<sup>3</sup>Pz), 147.1 (C<sup>5</sup>Pz), 109.0 (C<sup>4</sup>Pz), 62.2 (C(CH<sub>3</sub>)<sub>3</sub>), 30.0 (C(CH<sub>3</sub>)<sub>3</sub>). MS (FAB<sup>+</sup>): 943 (100, M<sup>+</sup>), 812 (40, M<sup>+</sup> - I).  $\Lambda_M$  (5 × 10<sup>-4</sup> M in acetone) = 94 S mol<sup>-1</sup> cm<sup>-1</sup>. Complex **19**: yield, 66%. Anal. Calcd for C<sub>44</sub>H<sub>36</sub>I<sub>4</sub>N<sub>6</sub>O<sub>8</sub>P<sub>2</sub>Rh<sub>2</sub>: C, 29.72; H, 2.04; N, 3.15. Found: C, 29.66; H, 1.66; N, 3.15. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2126 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (CDCl<sub>3</sub>, rt):  $\delta$  8.51 (d, 1.9 Hz, 2H, H<sup>3</sup>Pz), 8.37 (d, 1.9 Hz, 2H, H<sup>5</sup>Pz), 7.26 (t, 7.7 Hz, 12H, H<sup>m</sup>P(OPh)<sub>3</sub>), 7.19 (t, 7.7 Hz, 6H, H<sup>p</sup>P(OPh)<sub>3</sub>), 6.97 (d, 7.7 Hz, 12H, H<sup>p</sup>P(OPh)<sub>3</sub>), 6.26 (t,**

1.9 Hz, 2H, H<sup>4</sup>Pz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  174.8 (dd, *J*<sub>C-Rh</sub> = 49 Hz, <sup>2</sup>J<sub>C-P</sub> = 17 Hz, CO), 150.6 (d, <sup>2</sup>J<sub>C-P</sub> = 14 Hz, C<sup>1</sup>P(OPh)<sub>3</sub>), 148.9 (d, <sup>3</sup>J<sub>C-P</sub> = 4 Hz, C<sup>3</sup>Pz), 147.7 (d, <sup>3</sup>J<sub>C-P</sub> = 6 Hz, C<sup>5</sup>Pz), 130.7 (C<sup>m</sup>P(OPh)<sub>3</sub>), 126.7 (C<sup>p</sup>P(OPh)<sub>3</sub>), 120.2 (d, <sup>3</sup>J<sub>C-P</sub> = 4 Hz, C<sup>p</sup>P(OPh)<sub>3</sub>), 108.5 (d, <sup>4</sup>J<sub>C-P</sub> = 4 Hz, C<sup>4</sup>Pz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  81.0 (d, *J*<sub>P-Rh</sub> = 151 Hz). MS (FAB<sup>+</sup>): 1397 (100, M<sup>+</sup>).  $\Lambda_M$  (5 × 10<sup>-4</sup> M in acetone) = 87 S mol<sup>-1</sup> cm<sup>-1</sup>.

**[{CO<sub>2</sub>(I)Rh( $\mu$ -Pz)<sub>2</sub>( $\mu$ -I)Rh(I)<sub>2</sub>(CO)}<sub>2</sub>](**16**). The slow diffusion of a solution of diiodine (25.2 mg, 0.099 mmol) in pentane (15 mL) into a solution of [{Rh( $\mu$ -Pz)(I)(CO)<sub>2</sub>]} (**15**) (70 mg, 0.099 mmol) in dichloromethane (5 mL) lead to fine black needles in 2 days. The crystals were filtered, washed with cold pentane (3 × 5 mL), and vacuum-dried. Yield: 70%. Anal. Calcd for C<sub>9</sub>H<sub>6</sub>I<sub>4</sub>N<sub>4</sub>O<sub>3</sub>Rh<sub>2</sub>: C, 11.60; H, 0.65; N, 6.01. Found: C, 12.15; H, 0.76; N, 5.94. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2158 (s), 2135 (s), 2098 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, rt):  $\delta$  8.68 (d, 2.4 Hz, 1H), 8.19 (m, 2H) and 8.15 (d, 2.4 Hz, 1H) (H<sup>3,3',5,5'</sup>Pz), 6.27 (t, 2.4 Hz, 1H) and 6.25 (t, 2.4 Hz, 1H) (H<sup>4,4'</sup>Pz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  178.4 (d, *J*<sub>C-Rh</sub> = 50 Hz), 171.7 (d, *J*<sub>C-Rh</sub> = 47 Hz) and 171.3 (d, *J*<sub>C-Rh</sub> = 47 Hz) (CO), 150.6, 148.5, 147.3 and 146.6 (C<sup>3,3',5,5'</sup>Pz), 108.9 and 108.8 (C<sup>4,4'</sup>Pz). MS (FAB<sup>+</sup>): 932 (55, M<sup>+</sup>), 904 (100, M<sup>+</sup> - CO). MW calcd for C<sub>9</sub>H<sub>6</sub>I<sub>4</sub>N<sub>4</sub>O<sub>3</sub>Rh<sub>2</sub>: 932. Found: 1065.**

**[{Rh( $\mu$ -Pz)(I)(CO)(PR<sub>3</sub>)<sub>2</sub>( $\mu$ -I)]<sub>2</sub> (PR<sub>3</sub> = P(OMe)<sub>3</sub> (**7**), PMe<sub>2</sub>Ph (**8**))** (**18**) was prepared as described for **14** starting from [{Rh( $\mu$ -Pz)(I)(CO)(PR<sub>3</sub>)<sub>2</sub>]} (PR<sub>3</sub> = P(OMe)<sub>3</sub> (**7**), PMe<sub>2</sub>Ph (**8**)) (0.100 mmol) and I<sub>2</sub> (76 mg, 0.300 mmol). Complex **17**: yield, 65%. Anal. Calcd for C<sub>14</sub>H<sub>24</sub>I<sub>4</sub>N<sub>4</sub>O<sub>8</sub>P<sub>2</sub>Rh<sub>2</sub>: C, 10.13; H, 1.45; N, 3.37. Found: C, 10.76; H, 1.23; N, 3.39. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2122 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  8.41 (d, 2.1 Hz, 2H, H<sup>3</sup>Pz), 8.32 (d, 2.1 Hz, 2H, H<sup>5</sup>Pz), 6.32 (t, 2.1 Hz, 2H, H<sup>4</sup>Pz), 3.97 (s, 18H, P(OMe)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, rt):  $\delta$  94.0 (d, *J*<sub>P-Rh</sub> = 138 Hz). MS (FAB<sup>+</sup>): 1025 (76, M<sup>+</sup>), 715 (100, M<sup>+</sup> - 2I - 2CO).  $\Lambda_M$  (5 × 10<sup>-4</sup> M in acetone) = 123 S mol<sup>-1</sup> cm<sup>-1</sup>. Complex **18**: yield, 68%. Anal. Calcd for C<sub>24</sub>H<sub>28</sub>I<sub>4</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Rh<sub>2</sub>: C, 17.08; H, 1.67; N, 3.32. Found: C, 17.50; H, 1.30; N, 3.28. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2110 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (CDCl<sub>3</sub>, rt):  $\delta$  8.26 (d, 2.2 Hz, 2H, H<sup>3</sup>Pz), 7.97 (d, 2.2 Hz, 2H, H<sup>5</sup>Pz), 7.55 (m, 10H, PMe<sub>2</sub>Ph), 6.16 (t, 2.2 Hz, 2H, H<sup>4</sup>Pz), 2.52 (s, 6H) and 2.15 (s, 6H) (PMe<sub>2</sub>Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  177.7 (dd, *J*<sub>C-Rh</sub> = 50 Hz, <sup>2</sup>J<sub>C-P</sub> = 12 Hz, CO), 148.6 (C<sup>3</sup>Pz), 145.8 (C<sup>5</sup>Pz), 132.9 (d, *J*<sub>C-P</sub> = 57 Hz, C<sup>m</sup>PMe<sub>2</sub>Ph), 132.7 (d, *J*<sub>C-P</sub> = 3 Hz, C<sup>p</sup>PMe<sub>2</sub>Ph), 129.9 (d, <sup>2</sup>J<sub>C-P</sub> = 11 Hz, C<sup>m</sup>PMe<sub>2</sub>Ph), 129.7 (d, <sup>3</sup>J<sub>C-P</sub> = 9 Hz, C<sup>m</sup>PMe<sub>2</sub>Ph), 108.3 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz, C<sup>4</sup>Pz), 21.3 (d, *J*<sub>C-P</sub> = 40 Hz) and 19.6 (d, *J*<sub>C-P</sub> = 40 Hz, PMe<sub>2</sub>Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  3.2 (d, *J*<sub>P-Rh</sub> = 82 Hz). MS (FAB<sup>+</sup>): 1053 (100, M<sup>+</sup>).  $\Lambda_M$  (5 × 10<sup>-4</sup> M in acetone) = 111 S mol<sup>-1</sup> cm<sup>-1</sup>.

**[{Ir( $\mu$ -Pz)(I)(CO)<sub>2</sub>]}<sub>2</sub> (**20**). Addition of a solution of diiodine (32 mg, 0.127 mmol) in diethyl ether (10 mL) to a yellow solution of [{Ir( $\mu$ -Pz)(CO)<sub>2</sub>]} (80 mg, 0.127 mmol) in diethyl ether (10 mL) immediately produces an orange solution. Concentration to ca. 2 mL and addition of pentane (15 mL) rendered the complex as red-orange microcrystals which were filtered, washed with cold pentane, and dried under vacuum. Yield: 55%. Anal. Calcd for C<sub>10</sub>H<sub>6</sub>I<sub>2</sub>Ir<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: C, 13.58; H, 0.68; N, 6.33. Found: C, 14.02; H, 0.33; N, 6.25. IR (diethyl ether, cm<sup>-1</sup>):  $\nu$ (CO) 2125 (s), 2098 (m), 2075 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, rt):  $\delta$  7.43 (d, 2.2 Hz, 4H, H<sup>3,5</sup>Pz), 6.10 (t, 2.2 Hz, 2H, H<sup>4</sup>Pz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  161.8 (CO), 141.4 (C<sup>3,5</sup>Pz), 107.1 (C<sup>4</sup>Pz). MS (FAB<sup>+</sup>): 884 (10, M<sup>+</sup>), 757 (100, M<sup>+</sup> - I).**

**[{Ir( $\mu$ -Pz)(I)(CO)(PR<sub>3</sub>)<sub>2</sub>]}<sub>2</sub> (PR<sub>3</sub> = P(OPh)<sub>3</sub> (**21**), PMe<sub>2</sub>Ph (**22**))** was prepared as described for **8** starting from [{Ir( $\mu$ -Pz)(CO)(PR<sub>3</sub>)<sub>2</sub>]} (PR<sub>3</sub> = P(OPh)<sub>3</sub>, PMe<sub>2</sub>Ph) (0.200 mmol) and I<sub>2</sub> (50.8 mg, 0.200 mmol). Complex **21**: yield, 69%. Anal. Calcd for C<sub>44</sub>H<sub>36</sub>I<sub>2</sub>N<sub>4</sub>O<sub>8</sub>P<sub>2</sub>Ir<sub>2</sub>: C, 36.50; H, 2.50; N, 3.86. Found: C, 36.78; H, 2.38; N, 4.14. IR (diethyl ether, cm<sup>-1</sup>):  $\nu$ (CO) 2056 (s), 2048 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (CDCl<sub>3</sub>, rt):  $\delta$  7.72 (d, 2.1 Hz, 2H, H<sup>3</sup>Pz), 7.33 (d, 2.1 Hz, 2H, H<sup>5</sup>Pz), 7.08 (m, 18H, H<sup>m</sup>P(OPh)<sub>3</sub>), 6.88 (d, 8.5 Hz, 12H, H<sup>p</sup>P(OPh)<sub>3</sub>), 5.67 (t, 1.1 Hz, 2H, H<sup>4</sup>Pz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  168.2 (d, <sup>2</sup>J<sub>C-P</sub> = 16 Hz, CO), 151.2 (d, <sup>2</sup>J<sub>C-P</sub> = 13 Hz, C<sup>1</sup>P(OPh)<sub>3</sub>), 140.5 (C<sup>3</sup>Pz), 140.1 (d, <sup>3</sup>J<sub>C-P</sub> = 9 Hz, C<sup>5</sup>Pz), 129.6 (C<sup>m</sup>P(OPh)<sub>3</sub>), 125.3 (C<sup>p</sup>P(OPh)<sub>3</sub>), 120.6 (d, <sup>3</sup>J<sub>C-P</sub> = 4 Hz, C<sup>p</sup>P(OPh)<sub>3</sub>), 105.6 (C<sup>4</sup>Pz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  53.2. MS (FAB<sup>+</sup>): 1449 (5, M<sup>+</sup>), 1322 (100, M<sup>+</sup> - I). Complex **22**: yield, 65%. Anal. Calcd for C<sub>24</sub>H<sub>28</sub>I<sub>2</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ir<sub>2</sub>: C, 26.09; H, 2.55; N, 5.07. Found: C, 26.41; H, 2.13; N, 5.03. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2010

**Table 4.** Crystal Data and Data Collection and Refinement for Complexes **7**, **10**·C<sub>4</sub>H<sub>10</sub>O, and **18**

	<b>7</b>	<b>10</b>	<b>18</b>
empirical formula	C <sub>14</sub> H <sub>24</sub> I <sub>2</sub> N <sub>4</sub> O <sub>8</sub> P <sub>2</sub> Rh <sub>2</sub>	C <sub>50</sub> H <sub>48</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> P <sub>2</sub> Rh <sub>2</sub>	C <sub>24</sub> H <sub>28</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> P <sub>2</sub> Rh <sub>2</sub> · <sup>1/2</sup> C <sub>4</sub> H <sub>10</sub> O
fw	897.93	1295.54	1687.46
cryst size, mm	0.40 × 0.20 × 0.06	0.16 × 0.10 × 0.06	0.28 × 0.11 × 0.04
space group	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
<i>a</i> , Å	10.550(2)	11.3869(9)	11.8522(5)
<i>b</i> , Å	15.763(3)	16.2642(13)	13.4689(6)
<i>c</i> , Å	16.353(3)	16.5072(14)	25.3911(11)
$\alpha$ , deg	83.94(3)	95.340(2)	90.0
$\beta$ , deg	79.975(15)	96.410(2)	90.0
$\gamma$ , deg	83.97(3)	110.191(2)	90.0
<i>V</i> , Å <sup>3</sup>	2652.5(9)	2822.8(4)	4053.3(3)
<i>Z</i>	4	2	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	2.249	1.524	2.765
$\mu$ , mm <sup>-1</sup>	3.736	1.775	7.014
no. of measd reflns	9365 (2.5 ≤ $\theta$ ≤ 25.0°)	19 571 (1.3 ≤ $\theta$ ≤ 28.5°)	25 135 (1.6 ≤ $\theta$ ≤ 28.3°)
no. of unique reflns	9336 ( <i>R</i> <sub>int</sub> = 0.1006)	12 242 ( <i>R</i> <sub>int</sub> = 0.0353)	9258 ( <i>R</i> <sub>int</sub> = 0.0333)
min, max transm fact	0.140, 0.212	0.685, 0.831	0.458, 0.670
<i>R</i> ( <i>F</i> ) ( <i>F</i> <sup>2</sup> ≥ 2 $\sigma$ ( <i>F</i> <sup>2</sup> )) <sup>a</sup>	0.0494	0.0504	0.0359
w <i>R</i> ( <i>F</i> <sup>2</sup> ) (all data) <sup>b</sup>	0.1180	0.1289	0.0896

<sup>a</sup> *R*(*F*) =  $\sum ||F_o| - |F_c|| / \sum |F_o|$  for 6594 (**7**), 8412 (**10**), and 8336 (**18**) observed reflections. <sup>b</sup> w*R*(*F*<sup>2</sup>) =  $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ ;  $w^{-1} = [(\sigma^2(F_o^2) + (aP)^2 + bP)]$ , where  $P = [\max(F_o^2, 0) + 2F_c^2] / 3$  (**7**, *a* = 0.0589, *b* = 1.9609; **10**, *a* = 0.0595, *b* = 0; **18**, *a* = 0.0487, *b* = 9.2941).

(s), 2008 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (CDCl<sub>3</sub>, rt):  $\delta$  7.74 (d, 2.1 Hz, 2H, H<sup>3</sup>Pz), 7.48 (d, 2.1 Hz, 2H, H<sup>5</sup>Pz), 7.34 (m, 10H, PMe<sub>2</sub>Ph), 5.85 (t, 2.1 Hz, 2H, H<sup>4</sup>Pz), 1.94 (s, 6H) and 1.77 (s, 6H) (PMe<sub>2</sub>Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  172.3 (dd, <sup>2</sup>*J*<sub>C-P</sub> = 11 Hz, <sup>3</sup>*J*<sub>C-P</sub> = 2 Hz, CO), 141.0 (d, <sup>3</sup>*J*<sub>C-P</sub> = 5 Hz, C<sup>3</sup>Pz), 139.3 (d, <sup>3</sup>*J*<sub>C-P</sub> = 3 Hz, C<sup>5</sup>Pz), 134.0 (d, *J*<sub>C-P</sub> = 59 Hz, C<sup>1</sup>PMe<sub>2</sub>Ph), 130.6 (d, <sup>4</sup>*J*<sub>C-P</sub> = 2 Hz, C<sup>2</sup>PMe<sub>2</sub>Ph), 129.7 (d, <sup>3</sup>*J*<sub>C-P</sub> = 9 Hz, C<sup>m</sup>PMe<sub>2</sub>Ph), 128.6 (d, <sup>2</sup>*J*<sub>C-P</sub> = 11 Hz, C<sup>o</sup>PMe<sub>2</sub>Ph), 105.7 (d, <sup>4</sup>*J*<sub>C-P</sub> = 3 Hz, C<sup>4</sup>Pz), 19.1 (d, *J*<sub>C-P</sub> = 43 Hz) and 16.5 (d, *J*<sub>C-P</sub> = 43 Hz) (PMe<sub>2</sub>Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  -37.4. MS (FAB<sup>+</sup>): 1105 (10, M<sup>+</sup>), 977 (100, M<sup>+</sup> - I).

[{Ir( $\mu$ -Pz)(I)(CO)(PR<sub>3</sub>)<sub>2</sub>( $\mu$ -I)]<sub>n</sub> (*n* = **7**, PR<sub>3</sub> = P(OPh)<sub>3</sub> (**23**); *n* = **3**, PR<sub>3</sub> = PMe<sub>2</sub>Ph (**24**)) was prepared as described above for **19** starting from [{Ir( $\mu$ -Pz)(I)(CO)(PR<sub>3</sub>)<sub>2</sub>}] (PR<sub>3</sub> = P(OPh)<sub>3</sub> (**21**), PMe<sub>2</sub>-Ph (**22**)) (0.100 mmol), and I<sub>2</sub> (50.8 mg, 0.200 mmol). Complex **23**: yield, 20%. Anal. Calcd for C<sub>44</sub>H<sub>36</sub>I<sub>10</sub>N<sub>4</sub>O<sub>8</sub>P<sub>2</sub>Ir<sub>2</sub>: C, 21.42; H, 1.46; N, 2.27. Found: C, 21.11; H, 0.98; N, 2.27. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2104 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (CDCl<sub>3</sub>, rt):  $\delta$  8.57 (d, 2.3 Hz, 2H, H<sup>3</sup>Pz), 8.44 (d, 2.3 Hz, 2H, H<sup>5</sup>Pz), 7.23 (m, 18H, H<sup>m,p</sup>P(OPh)<sub>3</sub>), 6.98 (d, 7.9 Hz, 12H, H<sup>o</sup>P(OPh)<sub>3</sub>), 6.23 (t, 2.3 Hz, 2H, H<sup>4</sup>Pz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  27.7. MS (FAB<sup>+</sup>): 1576 (100, M<sup>+</sup>). Complex **24**: yield, 61%. Anal. Calcd for C<sub>24</sub>H<sub>28</sub>I<sub>6</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ir<sub>2</sub>: C, 17.88; H, 1.75; N, 3.47. Found: C, 17.77; H, 1.38; N, 3.25. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2087 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (CDCl<sub>3</sub>, rt):  $\delta$  8.32 (d, 2.5 Hz, 2H, H<sup>3</sup>Pz), 7.91 (m, 2H, H<sup>5</sup>Pz), 7.54 (m, 10H, PMe<sub>2</sub>Ph), 6.88 (br, 2H, H<sup>4</sup>Pz), 2.50 (s, 6H) and 2.29 (s, 6H) (PMe<sub>2</sub>Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  -45.9. MS (FAB<sup>+</sup>): 1231 (100, M<sup>+</sup>).

[{Rh( $\mu$ -Pz)(Me)(CO)(P(OPh)<sub>3</sub>)<sub>2</sub>( $\mu$ -I)]<sub>2</sub>·2H<sub>2</sub>O (**25**). A pale orange solution of [{Rh( $\mu$ -Pz)(CO)(P(OPh)<sub>3</sub>)<sub>2</sub>}] (60 mg, 0.059 mmol) in MeI (2 mL) was carefully layered with pentane (15 mL) and left in the dark for 2 days to give white crystals. The liquid phase was decanted, and the solid was washed with pentane and vacuum-dried. Yield: 66%. Anal. Calcd for C<sub>46</sub>H<sub>46</sub>I<sub>2</sub>N<sub>4</sub>O<sub>10</sub>P<sub>2</sub>Rh<sub>2</sub>: C, 41.31; H, 3.47; N, 4.19. Found: C, 41.58; H, 3.32; N, 4.10. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2102 (s). <sup>1</sup>H{<sup>31</sup>P} NMR (CDCl<sub>3</sub>, rt):  $\delta$  7.73 (d, 2.1 Hz, 2H, H<sup>3</sup>Pz), 7.53 (d, 2.1 Hz, 2H, H<sup>5</sup>Pz), 7.26 (m, 18H, H<sup>m,p</sup>P(OPh)<sub>3</sub>), 6.88 (d, 8.5 Hz, 12H, H<sup>o</sup>P(OPh)<sub>3</sub>), 6.36 (t, 2.1 Hz, 2H, H<sup>4</sup>Pz), 2.23 (d, <sup>2</sup>*J*<sub>H-Rh</sub> = 1.6 Hz, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  181.2 (dd, *J*<sub>C-Rh</sub> = 56 Hz, <sup>2</sup>*J*<sub>C-P</sub> = 18 Hz, CO), 150.4 (d, <sup>2</sup>*J*<sub>C-P</sub> = 12 Hz, C<sup>1</sup>P(OPh)<sub>3</sub>), 141.6 (C<sup>3,5</sup>Pz), 130.3 (C<sup>m</sup>P(OPh)<sub>3</sub>), 126.7 (C<sup>o</sup>P(OPh)<sub>3</sub>), 120.4 (d, <sup>3</sup>*J*<sub>C-P</sub> = 4 Hz, C<sup>o</sup>P(OPh)<sub>3</sub>), 108.2 (C<sup>4</sup>Pz), 15.2 (dd, *J*<sub>C-Rh</sub> = 20 Hz, <sup>2</sup>*J*<sub>C-P</sub> = 6 Hz, Me). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, rt):  $\delta$  93.8 (d, *J*<sub>P-Rh</sub> = 181 Hz). MS (FAB<sup>+</sup>): 1173 (100, M<sup>+</sup>).  $\Lambda_M$  (5 × 10<sup>-4</sup> M in acetone) = 90 S mol<sup>-1</sup> cm<sup>-1</sup>.

**Crystal Structure Determination of Complexes **7**, **10**·0.5C<sub>4</sub>H<sub>10</sub>O, and **18**.** A summary of crystal data, data collection, and refinement parameters for the three structural analyses is reported in Table 4. An orange (**7** and **10**) or a red crystal (**18**) was glued to a glass fiber and mounted on a Bruker AXS-Stöe (**7**) or Bruker AXS-SMART diffrac-

tometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å) and low-temperature equipment. Cell constants were obtained from the least-squares fit on the setting angles of 25 reflections (18 ≤  $2\theta$  ≤ 48°) for **7**, 11 823 (3.8 ≤  $2\theta$  ≤ 56.4°) for **10**, and 18 743 (3.4 ≤  $2\theta$  ≤ 56.5°) for **18**. A set of independent reflections with  $2\theta$  up to 50° was measured at 160 K for **7** using the  $\omega/\theta$  scan technique. Data for **10** and **18** were also collected at 160 K through the use of CCD recording of  $\omega$  rotation frames (0.3° each). All data were corrected for Lorentz and polarization effects. Reflections were also corrected for absorption by semiempirical methods.<sup>29,30</sup> In the case of **7** five standard reflections were monitored every hour throughout data collection as a check on crystal and instrument stability; a 1.5% decay was observed. For **10** and **18**, intensity decay was evaluated from the measurement of equivalent reflections at different measuring times.

All the structures were solved by direct methods and subsequent difference Fourier techniques (SHELXTL)<sup>29</sup> and refined by full-matrix least-squares on *F*<sup>2</sup> (SHELXL-97).<sup>31</sup> For **7**, two crystallographically independent molecules were observed. All non-hydrogen atoms (excepting those of solvent molecule in **10**) were refined in the last cycles with anisotropic displacement parameters. All hydrogen atoms were placed at their calculated positions and refined riding on carbon atoms with isotropic displacement parameters. The function minimized was  $\sum [w(F_o^2 - F_c^2)^2]$ . The calculated weighting scheme was  $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = ((F_o^2) + 2F_c^2)/3$ . All the refinements converged to reasonable *R* factors (Table 4). In **18** the absolute structure has been checked by the estimation of the Flack parameter *x* in the final cycles of refinement, 0.04(3).<sup>32</sup> All the residual electron density peaks over 1.0 e<sup>-</sup>/Å<sup>3</sup> in **10** (1.49–1.01 e<sup>-</sup>/Å<sup>3</sup>) and **18** (3.65–1.77 e<sup>-</sup>/Å<sup>3</sup>, three peaks) were situated in close proximity to solvent atoms (**10**) or to the iodine atoms of the pentaiodide anion (**18**). Scattering factors were used as implemented in the refinement program.<sup>31</sup>

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for complexes **7**, **10**, and **18**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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