# Synthesis of Bi- and Trinuclear Bis(alkynyl) Complexes [PtM (M = Rh, Ir), PtRh<sub>2</sub>] Starting from [cis-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CR)<sub>2</sub>]<sup>2-</sup>

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The course of the reactions of  $Q_2[cis-Pt(C_6F_5)_2(C \equiv CR)_2]$  (Q = PPh<sub>3</sub>Me, R = Ph **1a**; Q = NBu<sub>4</sub>,  $R = {}^{t}Bu$  **1b**, SiMe<sub>3</sub> **1c**) with  $[M(\mu-Cl)(COD)]_2$  (M = Rh, Ir) is strongly influenced by the metal and the substituents, as well as the stoichiometry. Thus, whereas treatment of **1a** with either 0.5 or 1 equiv of  $[Rh(\mu-Cl)(COD)]_2$  gives the chelating-type binuclear highly polar compound (PPh<sub>3</sub>Me)[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>( $\mu$ -1 $\kappa$ C<sup> $\alpha$ </sup>: $\eta$ <sup>2</sup>-C=CPh)<sub>2</sub>Rh(COD)], **2a**, analogous reactions using **1b** as the precursor afford only the trinuclear complex (NBu<sub>4</sub>)[{*cis*-Pt( $\overline{C}_6F_5$ )<sub>2</sub>( $\mu$ -1 $\kappa$ C<sup>u</sup>:  $\eta^2$ -C=C<sup>t</sup>Bu)<sub>2</sub>}{Rh<sub>2</sub>( $\mu$ -Cl)(COD)<sub>2</sub>}], **4b**. On the other hand, related bi- and trinuclear SiMe<sub>3</sub> derivatives (NBu<sub>4</sub>)[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>( $\mu$ -1 $\kappa$ C<sup> $\alpha$ </sup>: $\eta$ <sup>2</sup>-C=CSiMe<sub>3</sub>)<sub>2</sub>Rh(COD)], **2c**, and (NBu<sub>4</sub>)[{*cis*-Pt- $(C_6F_5)_2(\mu-1\kappa C^{\alpha}:\eta^2-C\equiv CSiMe_3)_2$  {  $Rh_2(\mu-Cl)(COD)_2$  ], **4c**, are easily obtained by treating **1c** with the binuclear rhodium substrate in the adequate molar ratio [1:0.5 for **2c**; 1:1 for **4c**]. Complex **2b** and, alternatively, **2a**, **c** derivatives can be produced by reacting **1** with the cationic solvento species  $[Rh(COD)(Et_2O)_x]^+$  (prepared in situ). The molecular structures of **2a** and 4b have been confirmed by X-ray diffraction. By contrast, whereas the reactions of 1a,b with  $[Ir(\mu-Cl)(COD)]_2$  lead to the formation of undefined products, the heterobinuclear  $\sigma_{,\pi}$ double-alkynyl-bridged complex (NBu<sub>4</sub>)[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>( $\mu$ -1 $\kappa$ C<sup>u</sup>: $\eta$ <sup>2</sup>-C $\equiv$ CSiMe<sub>3</sub>)( $\mu$ - $\eta$ <sup>2</sup>:2 $\kappa$ C<sup>u</sup>-C $\equiv$ CSiMe<sub>3</sub>)Ir(COD)], **3c**, (X-ray) is isolated from reaction of **1c** with the dimer iridium complex regardless of the molar ratio used (1:0.5 or 1:1).

# Introduction

The chemistry of metal alkynyl complexes is an intensely researched area, particularly due to the versatile reactivity of the unsaturated fragment and its wide variety of modes of interaction with transition metals.<sup>1–3</sup> In this area, homo and hetero double-alkynyl-bridged complexes<sup>4–7</sup> have gained particular significance as frozen structures at various points on the reaction paths for either C–C bond coupling alkynide processes<sup>6a.8</sup> or C–C bond cleavage on butadiynes<sup>6b–f,7a.9</sup> mediated by metal centers (Scheme 1).<sup>10,11</sup>

Binuclear  $M(\mu-C\equiv CR)_2M'$  compounds have been prepared through the activation and cleavage of the central C-C single bond of  $R-C\equiv C-C\equiv C-R$  with " $Cp_2M$ " (M= Ti, Zr) fragments, <sup>6b-f,7a,9</sup> but the most widely used route is based on the addition of a second metal fragment " $L_{\alpha}M'$ " to a  $M-\sigma$ -bis(alkynyl) compound. Usually, in the resulting complexes, the  $L_n M(C \equiv CR)_2$ compound used as the starting material acts as a chelating ligand toward the second metal center, forming planar (tweezer-like) or hinged (V-shaped)  $M_2C_4$ central cores (**B**, Scheme 1).<sup>2c,4,7</sup> However, monoalkynyl transfer processes yielding type **C** symmetrical or

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unsymmetrical  $\sigma/\pi$  bridging systems (Scheme 1) have also been reported.<sup>6g-i,k,q,12</sup> We have recently reported a new family of  $bis(\mu$ -C=CR) binuclear [(PEt<sub>3</sub>)Cp\*M( $\mu$ - $C \equiv CR)_2 M'(C_6F_5)_2 d^6(Rh, Ir) - d^8(Pt, Pd) \text{ complexes.}^{11,13}$ The Ir-Pt complexes (chelating type, V-shape) were prepared by an unprecedented double intramolecular alkynyl migration from Pt to Ir, whereas the analogous Rh derivatives  $(\sigma/\pi)$  were formed through a unique

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alkynyl migration, either from Pt to Rh or from Rh to Pt. A double alkynyl migration has also been recently suggested by Choukroun et al.<sup>14</sup> to explain the formation of the coupled product  $[Cp_2V(\mu-\eta^2:\eta^4-butadiyne)MCp'_2]$  $(Cp' = Cp, M = Ti, Zr; Cp' = C_5H_4SiMe_3, M = Zr)$  (E, Scheme 1) starting from  $[Cp_2M(C \equiv CPh)_2]$  and vanadocene and could also be related to the oxidatively induced coupling of C=CR moieties to free butadiynes (eq 1), only observed with very electrophilic  $ML_n$  fragments<sup>15</sup> (Ni(II) or Pd(II) vs Ni(0) or Pd(0); AuCl<sub>3</sub>py vs AuR or AgPF<sub>6</sub>).

$$L_m M'(C \equiv CR)_2 + ML_n \rightarrow L_m M'L_n + M(0) + RC \equiv C - C \equiv CR$$
(1)

The driving force of these alkynyl transfer processes is still an open question.  $^{6g-i,k,12,16}$  With this in mind, we have studied the reactivity of alkynyl platinum complexes toward low-valence substrates of Rh or Ir(I), and the synthesis and characterization of several new biand trinuclear bis(alkynyl)-bridged [PtM, M = Rh, Ir; PtRh<sub>2</sub>] complexes are reported.

## **Results and Discussion**

Preparation of Complexes. We have recently shown that treatment of the allyl chloride-bridged dimer [Pd- $(\mu$ -Cl) $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> with the anionic platinum complexes  $Q_2[cis-Pt(C_6F_5)_2(C\equiv CR)_2]$  1 (Q = PPh<sub>3</sub>Me, R = Ph; Q = NBu<sub>4</sub>,  $R = {}^{t}Bu$ , SiMe<sub>3</sub>) provides an excellent route to the heterobinuclear double-alkynyl V-shaped anionic derivatives  $[{cis-Pt(C_6F_5)_2(\mu-C=CR)_2}{Pd(\eta^3-C_3H_5}]^{-17}$ (B, Scheme 1). In these reactions the chloride ligands are easily displaced as NBu<sub>4</sub>Cl or PPh<sub>3</sub>MeCl. These results led us to investigate the reactivity of 1 toward the chloride-bridged dimers  $[M(\mu-Cl)(COD)]_2$  (M = Rh, Ir) as a reasonable route to the desired alkynyl bridging Pt-M (M = Rh, Ir) compounds. These reactions display a surprising dependence on the nature of M, the alkynyl organic substituent R, and the proportions of the reagents as summarized in Scheme 2. The expected

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#### Scheme 2



heterobinuclear platinum-rhodium complexes Q[cis-Pt- $(C_6F_5)_2(\mu$ -C $\equiv$ CR $)_2$ Rh(COD)] (Q = PPh\_3Me, R = Ph **2a**;  $Q = NBu_4$ ,  $R = SiMe_3 2c$ ) can be isolated, as orange solids, in good (81%, 2a) or moderate (42%, 2c) yield by the reaction of  $[Rh(\mu-Cl)(COD)]_2$  with 2 equiv of **1a** and 1c, respectively (Rh/Pt, 1:1 ratio). As expected, both complexes can also be obtained directly by the reaction of **1a** and **1c** with the solvento species  $[Rh(COD)S_2]$ -(ClO<sub>4</sub>) in diethyl ether. The analogous *tert*-butylalkynyl derivative **2b** can only be synthesized (64% yield) starting from  $[Rh(COD)S_2]^+$  (S = diethyl ether) and the corresponding *tert*-butylalkynyl platinum precursor **1b**. Attempts to synthesize **2b** by the reaction of [Rh(*u*-Cl)- $(COD)_2$  with 2 molar equiv of **1b** lead to the trinuclear anionic complex (NBu<sub>4</sub>)[{cis-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>( $\mu$ -C=C<sup>t</sup>Bu)<sub>2</sub>}{Rh<sub>2</sub>- $(\mu$ -Cl)(COD)<sub>2</sub>], **4b**, instead. This is isolated in low yield (56% based on Rh) as a microcrystalline orange solid. If the reaction is carried out in a 1:1 molar ratio, complex 4b is generated in higher yield (67%). The reaction of  $[Rh(\mu-Cl)(COD)]_2$  with 1 equiv of **1c** also results in the displacement of one of the chloride ligands

to afford the analogous trinuclear 4c. In these 4b,c complexes, as has been shown by an X-ray diffraction study on **4b**, the bis(alkynyl)platinate precursor acts as a bidentate bridging ligand replacing one chloride group in the rhodium chloride-bridged dimer. Attempts to obtain the phenyl derivative 4a using the appropiate platinum-rhodium molar ratio were unsuccessful, and instead, after workup, an orange solid which is identified (IR and NMR spectroscopy) as a mixture of the dimer **2a** and unreacted  $[Rh(\mu-Cl)(COD)]_2$  (2.5:1) is obtained. No other product can be detected by NMR techniques. The formulation given in Scheme 2 for complexes 2 and 4 is based on spectroscopic data (IR, <sup>1</sup>H, <sup>19</sup>F, <sup>13</sup>C NMR) and confirmed by X-ray diffraction studies of complexes 2a and 4b, respectively. All complexes have been additionally characterized by elemental analyses, mass spectrometry (FAB), and conductivity measurements (see Experimental Section).

As it is shown in the formulas that appear in Scheme 2, no alkynylation processes have been observed in the formation of complexes 2 and 4. The platinum centers retain the  $\sigma$ -coordination to the alkynyl fragments while the rhodium centers are stabilized through  $\eta^2$ -alkyne interactions, indicating that, as expected for a thirdrow metal, the platinum center shows a greater preference for the  $\sigma$ -electron density than the Rh center does.

In contrast to the behavior observed in relation to the rhodium species, we were able to obtain only a mixedmetal binuclear species stabilized by a double alkynylbridging system by the reaction of **1c** and the dimeric iridium complex  $[Ir(\mu-Cl)(COD)_2]$ . As shown in Scheme 2, the Ir-Pt complex (NBu<sub>4</sub>)[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>( $\mu$ -C=CSiMe<sub>3</sub>)<sub>2</sub>-Ir(COD)], **3c**, is readily obtained as a deep yellow microcrystalline solid by reacting **1c** with the chloridedimer iridium complex in acetone, regardless of the Pt/ Ir ratio used (1:0.5 31% yield; 1:1 65% yield). Complex **3c** is also generated in very good yield, as is observed by NMR spectroscopy (<sup>19</sup>F), by mixing equimolar amounts of **1c** and the solvento  $[Ir(COD)S_2](ClO_4)$  species in acetone. However, due to the presence of NBu<sub>4</sub>ClO<sub>4</sub> in the reaction mixture, 3c can be isolated as a pure compound only in extremely low yield (15%). All attempts to prepare any other alkynyl-bridged Pt(II)-Ir-(I) dimer (or trimer) using **1a** and **1b** as the reagents for the Ir derivatives have been unsuccessful. The reaction mixtures of **1a**,**b** with either  $[Ir(\mu-Cl)(COD)]_2$ or  $[Ir(COD)S_2]^+$  evolve giving a complex mixture of products from which we were not able to isolate any pure compound. Interestingly, NMR examination of the initial reaction mixture of **1a** and  $[Ir(\mu-Cl)(COD)]_2$  (1: 0.5 or 1:1 molar ratio) reveals the presence of the doubly alkynyl bridged diplatinum complex  $(PPh_3Me)_2[Pt(\mu-C=$ CPh)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>,<sup>6i</sup> suggesting that, in this case, after initial alkynyl transfer from Pt to Ir, the resulting fragments probably disproportionate, producing the diplatinum and presumably the dimer  $[Ir(\mu-C=CPh)(COD)]_2$ . By usual workup (see Experimental Section) an orange solid was obtained and identified (NMR) as a mixture of products, with the known dimer  $(PPh_3Me)_2[Pt(\mu-C=$  $(C_6F_5)_2]_2$  as the major component.

For complex **3c**, the formulation given with a type **C**  $\sigma/\pi$  double-alkynyl bridging system (Scheme 1) coincides with its spectroscopic data (IR, NMR) and has been confirmed by a single-crystal X-ray diffraction study.

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**Figure 1.** Molecular structure of the anion complex **2a**, showing the atom-numbering scheme.

This well-studied bridging system has been found to stabilize both early  $(d^1-d^1),^{6a-c,e-g,k-o,q}\,middle(d^6-d^6),^{6p}$ and late  $(d^8-d^8)^{6h-j}$  transition metal homobinuclear molecules, but the number of heterodimetallic systems is rather scarce.<sup>6b,d,11,12</sup> As far as we know, the only related metal complexes (Pt, Rh, or Ir) previously reported are the dimers [(COD)M(C=CSiMe<sub>3</sub>)]<sub>2</sub> [M = Ir (X-ray), Rh],<sup>6j</sup> and we have also shown that anionic  ${[Pt(C \equiv CR)(C_6F_5)_2]_2}^{2-6i}$  and neutral  $[Pt(C \equiv CR)(C_6F_5)-$ (PPh<sub>3</sub>)]<sub>2</sub><sup>6h</sup> binuclear complexes display a similar structural disposition. Complex 3c represents the first heterobimetallic d<sup>8</sup>-d<sup>8</sup> compound characterized by an X-ray diffraction study that also possesses a  $\sigma/\pi$  doubly alkynyl bridging system. The formation of 3c implies the migration of one  $\sigma$ -C=CSiMe<sub>3</sub> group from Pt to Ir. However, the migration of the second alkynyl ligand, previously observed in the reaction between [cis-Pt- $(C_6F_5)_2(C \equiv CR)_2]^{2-}$  and  $[Cp^*Ir(PEt_3)(acetone)_2]^{2+}$ ,<sup>11</sup> is not observed with the "Ir(COD)+" fragment.

Structural Investigations. The structures of complexes 2a, 3c, and 4b have been established by an X-ray crystal study. The drawing of complex anion [cis-Pt- $(C_6F_5)_2(\mu$ -C=CPh)<sub>2</sub>Rh(COD)]<sup>-</sup>, **2a**, is presented in Figure 1, and selected bond distances and angles are given in Table 1. The type of structure with a chelating doubly alkynyl bridging system (B, Scheme 1) is not new, but, to the best of our knowledge, this is the first example involving these metal centers [Pt(II) and Rh(I)]. We have recently described the Pt(II)-Rh(III) binuclear zwitterionic neutral complex [(PEt<sub>3</sub>)Cp\*Rh<sup>+</sup>(µ-C=CSiMe<sub>3</sub>)<sub>2</sub>Pt<sup>-</sup>- $(C_6F_5)_2$ , but it contains a  $\sigma/\pi$  bis(alkynyl) system (**C**, Scheme 1).<sup>11</sup> In **2a** both alkynyl groups are  $\sigma$ -bonded to the platinum atom [Pt(1)-C(13) 2.02(2) Å, Pt(1)-C(21) 2.04(3) Å] and  $\eta^2$ -bonded to the rhodium center, resulting in a very polar anion (formally zwitterionic). It has to be mentioned that the final arrangement around the rhodium atom is actually new. Athough there is a large number of examples of  $\eta^2$ -acetylene-rhodium bonds,<sup>18</sup> the easy activation of the alkynes coordinated to rhodium centers to give metallacyclopentadiene<sup>19</sup> and

cyclobutadiene<sup>18a,20</sup> complexes has precluded the isolation of derivatives with a rhodium atom  $\eta^2$ -bonded to two alkyne ligands. We have recently reported two similar complexes,<sup>21</sup> but this structure represents the first crystallographically characterized example of this structural situation.

The platinum and rhodium atoms exhibit conventional square-planar environments, and each organometallic core shows the expected structural features.<sup>4,11,13,16a,17a,21,22</sup> The rhodium atom is located out of the 3-metalla-1,4-divne plane (V-shape). We have previously observed this structural feature when using square-planar d<sup>8</sup> metal moieties as chelating fragments.<sup>6i,7e,11,13,16a,17,21</sup> The dihedral angle formed by the best least-squares planes around the Pt and Rh atoms [96.86(1)°] is notably smaller than those found for other related complexes [121.54(6)-148.3(4)°],<sup>6i,7e,13,16a</sup> allowing the metal centers to be in a closer position. Finally, the  $\pi$ -interactions between the acetylene fragments and the Rh atom are rather unsymmetrical [Rh– $C_{\alpha}$  2.29(2) Å, 2.29(3) Å; Rh–C<sub> $\beta$ </sub> 2.53(3) Å, 2.49(2) Å]. This type of asymmetry (Rh $-C_{\alpha}$  < Rh $-C_{\beta}$  bond distances), although not as marked, has been previously found in the pentanuclear species  $[{Pt(C \equiv C^{t}Bu)_{4}} {Rh_{2}(\mu - X)(COD)_{2}}] (X =$ OH, Cl), [PtRh<sub>4</sub>X<sub>2</sub>], previously reported<sup>21</sup> and in related complexes containing  $\eta^2$ -Rh-acetylide interactions.<sup>23</sup>

The structure of the dimetallic anion of **3c** is shown in Figure 2 together with the atom-numbering scheme. Selected bond distances and angles are displayed in Table 1. As can be seen, the anion is formed by two organometallic "(COD)Ir" and "Pt(C<sub>6</sub>F<sub>5</sub>)" moieties [Ir···Pt = 3.639(1) Å] with the metal centers connected by two alkynyl groups. Each alkynyl ligand is  $\sigma$ -bonded to one metal atom (Pt/Ir) and leans over the other metal center (Ir/Pt). All structural data are in good agreement with the structures of the previously reported homobimetallic species { $[Pt(C \equiv CPh)(C_6F_5)_2]_2$ }<sup>2-</sup>,  $[Pt_2]^{2-}$ , <sup>6i</sup> and  $[Ir-(C \equiv CSiMe_3)(COD)]_2$ ,  $[Ir_2]$ , <sup>6j</sup> which display a similar geometric arrangement of the alkynyl ligands. In particular, the central organometallic framework IrPtC<sub>4</sub> adopts a puckered conformation, the dihedral angle between the planes Pt(1)Ir(1)C(18)C(19) and Pt(1)Ir-(1)C(1)C(2) being  $21.5(3)^{\circ}$ . It is worth noting that the influence of the metal centers in the bonding parameters of the  $Ir(\mu$ -alkynide)<sub>2</sub>Pt unit is quite insignificant. Thus, both the M–C  $\sigma$ -bonds [1.987(8), 2.005(8) Å] and the equivalent complexed  $\eta^2$ -bond lengths [2.339(8), 2.233-

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Table 1. Selected Bond Lengths (A) and Angles	(deg) for Complexes Za, 3C, and 4	łD.
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		Comple	ex 2a		
Pt(1)-C(13) Pt(1)-C(1) Rh(1)-C(34)	2.02(2) 2.13(3) 2.13(3)	$\begin{array}{c} Pt(1)-C(21) \\ Rh(1)-C(33) \\ Rh(1)-C(29) \end{array}$	2.04(3) 2.12(3) 2.14(3)	Pt(1)-C(7) Rh(1)-C(30) Rh(1)-C(21)	2.08(3) 2.12(3) 2.29(3)
Rh(1)-C(13) C(13)-C(14) C(33)-C(34)	2.29(2) 1.24(4) 1.43(4)	Rh(1)-C(22) C(21)-C(22) Pt(1)-Rh(1)	2.49(2) 1.18(4) 2.889(3)	Rh(1)-C(14) C(29)-C(30)	2.53(3) 1.44(5)
$\begin{array}{c} C(13)-Pt(1)-C(21)\\ C(21)-Pt(1)-C(1)\\ C(13,14)-Rh(1)-C(21,22)\\ C(29,30)-Rh(1)-C(33,34)\\ C(14)-C(13)-Pt(1)\\ C(22)-C(21)-Pt(1) \end{array}$		80.6(10) 93.2(10) 85.69(2) 86.98(2) 164(2) 168(3)	$\begin{array}{cccc} C(13)-Pt(1)-C(7) & 94.6 \\ C(7)-Pt(1)-C(1) & 91.9 \\ C(21,22)-Rh(1)-C(29,30) & 97.2 \\ C(33,34)-Rh(1)-C(13,14) & 91.0 \\ C(13)-C(14)-C(15) & 173(3) \\ C(21)-C(22)-C(23) & 167(3) \end{array}$		94.6(11) 91.9(11) 97.26(2) 91.08(2) 173(3) 167(3)
		Comple	ex <b>3c</b>		
$\begin{array}{c} Pt(1)-C(1) \\ Pt(1)-C(18) \\ Ir(1)-C(2) \\ Ir(1)-C(26) \\ C(1)-C(2) \end{array}$	1.987(8) 2.339(8) 2.186(9) 2.123(10) 1.273(12)	$\begin{array}{c} Pt(1)-C(6)\\ Pt(1)-C(19)\\ Ir(1)-C(18)\\ Ir(1)-C(27)\\ C(18)-C(19) \end{array}$	2.016(9) 2.233(9) 2.005(8) 2.117(9) 1.244(12)	$\begin{array}{c} Pt(1)-C(12) \\ Ir(1)-C(1) \\ Ir(1)-C(23) \\ Ir(1)-C(30) \\ Pt(1)\cdots Ir(1) \end{array}$	$\begin{array}{c} 2.054(8) \\ 2.308(8) \\ 2.199(9) \\ 2.199(10) \\ 3.639(1) \end{array}$
$\begin{array}{c} C(1)-Pt(1)-C(\\ C(12)-Pt(1)-C(\\ C(12)-Ir(1)-C\\ C(18)-Ir(1)-C\\ Pt(1)-C(1)-C(\\ Ir(1)-C(18)-C\\ \end{array}$	6) C(18,19) C(23,30) (26,27) 2) (19)	90.4(3) 103.4(2) 105.3(1) 88.2(2) 174.6(7) 173.3(7)	$\begin{array}{c} C(6) - Pt(1) - C(\\ C(1) - Pt(1) - C(\\ C(1,2) - Ir(1) - C(\\ C(26,27) - Ir(1) \\ Si(1) - C(2) - C(\\ Si(2) - C(19) - C(2) \\ \end{array}$	(12) (18,19) C(18) -C(23,30) 1) C(18)	$87.1(3) \\79.1(2) \\80.2(2) \\86.3(1) \\136.9(7) \\145.0(8)$
		Comple	ex <b>4b</b>		
$\begin{array}{c} Pt(1)-C(13)\\ Pt(1)-C(7)\\ Rh(1)-C(25)\\ Rh(1)-Cl(1)\\ Rh(2)-C(34)\\ Rh(2)-C(19)\\ C(13)-C(14)\\ C(29)-C(30)\\ Pt(1)\cdots Rh(1) \end{array}$	$\begin{array}{c} 1.995(14)\\ 2.076(13)\\ 2.14(2)\\ 2.421(4)\\ 2.12(2)\\ 2.266(12)\\ 1.21(2)\\ 1.44(2)\\ 3.238(1) \end{array}$	$\begin{array}{c} Pt(1)-C(19) \\ Rh(1)-C(26) \\ Rh(1)-C(29) \\ Rh(1)-C(14) \\ Rh(2)-C(38) \\ Rh(2)-Cl(1) \\ C(19)-C(20) \\ C(33)-C(34) \\ Pt(1)\cdots Rh(2) \end{array}$	$\begin{array}{c} 2.01(2) \\ 2.11(2) \\ 2.15(2) \\ 2.500(14) \\ 2.15(2) \\ 2.420(4) \\ 1.21(2) \\ 1.45(3) \\ 3.206(1) \end{array}$	Pt(1)-C(1) Rh(1)-C(30) Rh(1)-C(13) Rh(2)-C(33) Rh(2)-C(37) Rh(2)-C(20) C(25)-C(26) C(37)-C(38) Rh(1)Rh(2)	$\begin{array}{c} 2.072(13)\\ 2.14(2)\\ 2.238(13)\\ 2.11(2)\\ 2.16(2)\\ 2.547(14)\\ 1.43(3)\\ 1.44(3)\\ 3.670(1) \end{array}$
$\begin{array}{c} C(13)-Pt(1)-C(\\ C(19)-Pt(1)-C(\\ Cl(1)-Rh(1)-C(\\ Cl(1)-Rh(1)-C(\\ C(13,14)-Rh(1)\\ Rh(2)-Cl(1)-Rl\\ C(13)-C(14)-C\\ C(19)-C(20)-C \end{array}$		98.1(5) 85.2(5) 88.3(2) 88.1(2) 95.0(1) 98.60(14) 169(2) 169(2)	$\begin{array}{c} C(13)-Pt(1)\\ C(1)-Pt(1)-C\\ Cl(1)-Rh(2)-\\ Cl(1)-Rh(2)-\\ C(19,20)-Rh(\\ C(14)-C(13)-\\ C(20)-C(19)-\\ \end{array}$	C(1) C(19,20) C(33,34) 1)-C(37,38) Pt(1) Pt(1)	$\begin{array}{c} 85.9(5)\\ 91.0(5)\\ 87.4(2)\\ 89.7(2)\\ 96.8(1)\\ 172.2(12)\\ 171.2(12)\end{array}$
Q C(21)		Chart 1			
C(28) C(28) C(27) C(25) C(27) C(19) C(27) C(19) C(22) C(17) C(16) F(9) C(16) F(8) C(15) C(15) C(14) C(14) C(14) C(14) C(14) C(14) C(14) C(14) C(15) C(14) C(15) C		SiMe <sub>3</sub>			
		C(17) C(15) C(14) C(13) F(7)	$[Pt] \begin{bmatrix} C & \\ [Ir] \\ C & \\ [Ir] = Ir(COD) \end{bmatrix}$		
C(23)	C(1) Pe(1) C(11)	З <sub>F(6)</sub>	Me <sub>3</sub> Si <sup>-C</sup>		
Sitt	2) C(6) C(7)	D <sub>F(4)</sub> (10)	structural situati	ion of the alkynyl liga	nds. In accord

**Figure 2.** View of the molecular structure of the anion complex **3c**, showing the atom-numbering scheme.

ပ် <sup>E(3)</sup>

(9) Å for Pt(1) and 2.308(8), 2.186(9) Å for Ir(1)] are comparable within experimental error. The  $\eta^2$ -metal acetylenic linkages are asymmetric, the  $M-C_\beta$  bonds ca. 0.1 Å (0.10 for Pt and 0.122 for Ir) being shorter than the corresponding  $M-C_\alpha$  distances. This asymmetry has been previously found in related complexes,<sup>6</sup> and it would now seem to be characteristic of this particular

, C(3)

Ö<sub>C(4)</sub>

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structural situation of the alkynyl ligands. In accordance with this structural fact, the  $M-C_{\alpha}\equiv C_{\beta}$  fragments remain almost linear [174.6(7)°, 173.3(7)°] and the  $C_{\alpha}\equiv C_{\beta}$ -Si units deviate significantly from linearity [136.9-(7)°, 145.0(8)°], suggesting, as has been previously pointed out,<sup>6d.g.h</sup> a considerable vinylidene contribution to the bonding mode of the bridging alkynyl ligands (Chart 1). The opposite asymmetry ( $M-C_{\alpha} < M-C_{\beta}$ ) or more symmetrical  $\eta^2$ -metal acetylenic bonding interactions have usually been observed in complexes with chelating-type structural arrangements (M in-plane, tweezer-like and outside-plane, V-shaped),<sup>2c,4,7</sup> although we have also found some exceptions.<sup>4,7d</sup>

The Ir-(olefin) distances fall within the range of 2.117(9)-2.199(10) Å, with the two metal-carbon dis-



Figure 3. Molecular structure of the anion complex 4b, showing the atom-numbering scheme.

tances trans to the C=C triple bond shorter than those trans to the sp  $C_{\alpha}$  carbon donor, thus revealing not only the asymmetric arrangement of the  $\mu$ -C= CSiMe<sub>3</sub> ligands but also the stronger trans influence of the  $\sigma$ -donor  $C_{\alpha}$  carbon atom. Similar observations have previously been made on the basis of <sup>195</sup>Pt-<sup>31</sup>P coupling constants.<sup>6h</sup>

For complex 4b the unit cell contains 1.5 independent anions. The half anion sits on a crystallographic symmetry element. Both anions are essentially similar; therefore, the discussion will be limited to only one. The molecular structure of the trinuclear anion of 4b is presented in Figure 3. This type of structure features a different behavior of the anionic substrates [cis-Pt- $(C_6F_5)_2(C \equiv CR)_2]^{2-}$ . In this case, the bis(alkynyl) fragment acts as a bridging divne ligand  $(\eta^2:\eta^2)$  to two nearly identical "Rh(COD)" units. The structure is similar to the pentanuclear species [PtRh<sub>4</sub>X<sub>2</sub>],<sup>21</sup> in which the tetraalkynylplatinate(II) anion acts as a tetradentate bridging ligand between two related cationic dirhodium " $Rh_2(\mu - X)(COD)_2$ " units. The anion contains two pseudosquare-planar Rh(I) units sharing a common bridged chlorine atom [Rh(1,2)-Cl(1) 2.421(4), 2.420(4) Å; Rh-(1)-Cl-Rh(2) 98.60(14)°]. The two chelating diolefin ligands (COD) are not identical, but all the rhodiumcarbon separations are very similar [2.11(2)-2.16(2) Å], in agreement with the values indicated in the literature.<sup>21,24,25</sup> Both rhodium centers complete their coordination, being  $\eta^2$ -bonded to a 3-platinadiyne bridging building block "*cis*-( $C_6F_5$ )<sub>2</sub>Pt( $C \equiv C^tBu$ )<sub>2</sub>". In this fragment the coordination around Pt(1), including bond lengths and angles, is similar to those found in other heteropolynuclear bis(alkynyl)platinum compounds.<sup>4,7d,17,21</sup> As for **2a**, the most remarkable feature is that the  $\eta^2$ -interactions to the Rh atom show asymmetry opposite that found in **3c**: the Rh– $C_{\alpha}$  distances [2.238(13), 2.266(12) Å] are considerably shorter than the corresponding Rh–C $_{\beta}$  [2.500(14), 2.547(14) Å]. The parameters of the acetylenic fragments [C=C 1.21(2) Å;  $Pt-C_{\alpha} \equiv C_{\beta} 172.2(12)^{\circ}, 171.2(12)^{\circ}; C_{\alpha} \equiv C_{\beta} - C(^{t}Bu) 169$ 

(2)°] are similar to those found in **[PtRh<sub>4</sub>X<sub>2</sub>]**<sup>21</sup> and in **2a**. The  $\pi$ -complexed Rh atoms are located in a pseudotrans arrangement with respect to the platinum coordination plane, resulting in rather long Pt-Rh(1,2) [3.238(1) and 3.206(1) Å] and Rh(1)-Rh(2) [3.670(1) Å] separations, which exclude any significant metal-metal bonding interaction.

Spectroscopic Studies (IR, NMR). In accordance with previous observations,<sup>11</sup> the  $\nu$ (C=C) for the binuclear platinum rhodium compounds 2 (1940-2044 cm<sup>-1</sup>) and, particularly, the  $\Delta \nu$ (C=C) shift in relation to the precursors  $1 \ (\sim 60 \ \mathrm{cm}^{-1})$  are in keeping with a chelating-type arrangement. In contrast, the formation of complex 3c is accompanied by a considerably larger shift of the  $\nu$ (C=C) to lower frequencies (1868, 1823) cm<sup>-1</sup>,  $\Delta \nu$ (C=C)<sub>average</sub> 173 cm<sup>-1</sup>), clearly reflecting stronger  $\eta^2$ -M-alkyne interactions with this type of arrangement of both alkynyl ligands.

Complex **3c**, like many other examples that have this  $\sigma/\pi$  structural formulation, <sup>6a-i,q,11,12,16a</sup> is dynamic and undergoes an intramolecular exchange of both alkynyl groups within the dimetallic framework that is rapid on the NMR time scale at room temperature. Thus, at 16 °C it shows only one proton and carbon olefinic resonances due to the COD ligands, only one type of  $C_6F_5$  ligand (AA'MXX' system), and only one set of C= CSiMe<sub>3</sub> signals (<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR), evidencing an apparent overall  $C_{2\nu}$  symmetry. Lowering the temperature produces a broadening of CH= and SiMe<sub>3</sub> resonances in the proton spectra and of the o-F signals (broadening of *p*-F and *m*-F is also observed) in the <sup>19</sup>F NMR spectra, which eventually split in each case into two separate signals (1:1 ratio) at low temperature (-50)°C). Using the coalescence temperatures for the olefinic protons (253 K), SiMe<sub>3</sub> (230 K), and o-F (253 K), a similar Gibbs activation barrier<sup>26</sup> is obtained ( $\Delta G^{\#}$ 10.84, 11.86, and 11.13 kcal·mol<sup>-1</sup>, respectively), suggesting that all these signals are involved in the same dynamic process. However, the low-temperature NMR patterns indicate that only the intramolecular  $C \equiv$ CSiMe<sub>3</sub> migration between the metal centers is frozen at low temperature  $(-50 \degree C)$ . For a rigid puckered dimer one should expect to observe four proton and carbon olefinic resonances for the chelating COD ligand and four different fluorine signals (endo and exo of each C<sub>6</sub>F<sub>5</sub> group) in the *o*-F region. Therefore, the reduced number of observable HC= (<sup>1</sup>H  $\delta$  4.89, 3.55; <sup>13</sup>C  $\delta$  62.3, 58.1) and *o*-F signals (-114.21,  ${}^{3}J_{Pt-o-F} = 373$  Hz, 2 *o*-F trans to  $\sigma$ -C=C; -116.26,  ${}^{3}J_{Pt-o-F} = 520$  Hz, 2 *o*-F trans to  $\eta^2$ -C=C) clearly indicates that a very fast inversion of the central dimetallacycle is taking place, even at 223 K, to account for the apparent time-averaged plane of symmetry.

Fluxional behavior for binuclear chelating platinum rhodium compounds 2a-2c is also evident. At ambient temperature their proton and fluorine NMR spectra correspond to species for which the central  $Pt(C \equiv C)_2 Rh$ framework is, on the NMR time scale, an average plane (see Experimental Section for data). The observed apparent overall  $C_{2v}$  symmetry is consistently explained<sup>6i,7d,11,17</sup> by means of a fast exchange of the "Rh-

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<sup>(26)</sup> Günther, H. NMR Spectroscopy; Wiley: New York, 1980; p 241.

(COD)" unit below and above the 3-platina-1,4-diyne fragments " $(C_6F_5)_2$ Pt $(C \equiv CR)_2$ ", as is shown in eq 2.



As has been previously suggested,<sup>6i</sup> the formal inversion of the central PtC<sub>4</sub>Rh core could occur through intermediate species (or transition state) with one or both C=CR symmetrically bridging the two metal centers. According to this proposal, the process should be more favorable for the phenylethynyl derivative 2a, as the positive charge developed at the  $\beta$ -position should be stabilized by conjugation with the  $\pi$ -electron density of the phenyl group. This is further supported by the fact that for complex 2a both the <sup>19</sup>F and proton NMR spectra did not change significantly over the observed temperature range (16 to -50 °C in CDCl<sub>3</sub> or 16 to -90 °C in acetone- $d_6$ ), indicating that the dynamic process has a very low energetic barrier. In contrast, for complexes **2b** and **2c** upon cooling at low temperature (below -50 °C in acetone- $d_6$ ) usual line broadening takes place and the signals due to olefinic protons for complex 2c and to o-F for both complexes finally split into two different resonances at -80 °C ( $\delta$ -114.11, -114.63 o-F;  $\Delta G_{198}^{\#} \approx 9.15 \text{ kcal·mol}^{-1}$ ; **2b**.  $\delta$ 4.79, 4.60 olefinic protons;  $\Delta G_{213}^{\#} \approx 10.27 \text{ kcal} \cdot \text{mol}^{-1}$ and  $\delta - 114.21$ , -114.73 o-F;  $\Delta G_{200}^{\#} = 9.25 \text{ kcal} \cdot \text{mol}^{-1}$ ; 2c).

Interestingly, dissolution of crystals of the trinuclear complexes 4b and 4c occurs with partial dissociation according to eq 3, to yield an equilibrium mixture of compounds 4b,c with the related 2b,c and the corresponding rhodium dimer [Rh(µ-Cl)(COD)]<sub>2</sub>, [Rh<sub>2</sub>]. Similar final ratios  $4/2/[Rh_2]$  are observed by monitoring equimolar mixtures of **1b**, **c** and the rhodium chloride dimer [Rh<sub>2</sub>], suggesting that 4b and 4c formed in situ rapidly equilibrate with the thermodynamically more stable dimers **2b** and **2c**, respectively. In each case, the final ratio of the three complexes  $4/2/[Rh_2]$ , which is obtained by the integration of the olefinic signals of 1,5-COD in the three species, strongly depends on the solvent (see Experimental Section). However, in the range observed (-80 to 50 °C), the temperature has very little influence on the extent of the dissociation in both species. We note that this equilibration process requires only small changes in the central bridging framework.

$$\begin{split} [\{cis-\operatorname{Pt}(\operatorname{C}_{6}\operatorname{F}_{5})_{2}(\mu-\operatorname{C}\equiv\operatorname{CR})_{2}\}\{\operatorname{Rh}_{2}(\mu-\operatorname{Cl})(\operatorname{COD})_{2}\}]^{-} \rightarrow \\ & \mathbf{4b,c} \\ [cis-\operatorname{Pt}(\operatorname{C}_{6}\operatorname{F}_{5})_{2}(\mu-\operatorname{C}\equiv\operatorname{CR})_{2}\operatorname{Rh}(\operatorname{COD})\}]^{-} + \\ & \mathbf{2b,c} \\ & 1/2[\operatorname{Rh}(\mu-\operatorname{Cl})(\operatorname{COD})]_{2} (3) \end{split}$$

Spectroscopic data for 4b and 4c are easily extracted from these mixtures. Only a single olefinic resonance was seen at 16 °C for both complexes in the <sup>1</sup>H NMR spectra, and the <sup>19</sup>F NMR spectra at the same temperature exhibit a typical AA'MXX' system, consistent with the existence of mirror planes on the three metal centers and, in the case of the rhodium atoms, with an additional time-averaged plane which equilibrates both halves (trans to Cl and trans to acetylenic unit) of the COD ligands. This latter equilibration could be related to the equilibrium shown in eq 3, which presumably requires the involvement of three-coordinated rhodium species resulting from cleavage of either rhodiumchloride and/or rhodium $-\eta^2$ -alkyne linkages. However, the <sup>1</sup>H phase-sensitive NOESY spectra at room temperature of **4b** in CDCl<sub>3</sub> and **4c** in acetone- $d_6$  do not show cross negative peaks correlating the olefinic signals of 4 with those in 2 and  $[Rh_2]$ , thus suggesting that the intermolecular exchange between these species is very slow on the NMR time scale. In fact, coalescence of the three olefinic signals is not reached up to the maximum temperature registered ( $\sim$ 50 °C). For **4c**, the ortho-fluorine signal ( $\delta$  –114.69, acetone- $d_6$ ) broadens as the temperature is lowered, coalesces at ca. -73 °C, and finally splits into two very broad humps at -80 °C  $(\delta - 112.7, -117.0)$ . However, in the <sup>1</sup>H NMR spectrum the broad singlet olefinic signal at  $\delta$  4.55 attributed to **4c** does not change within the observed range (-80 to 50 °C), indicating that it is still dynamic on the NMR time scale. For 4b the o-F resonance broadens by lowering the temperature, but does not split. The coalescence was very near to the lower accessible temperature limit (ca. -80 °C). In contrast, its proton spectrum displays a marked dependence on the temperature. Thus, the broad olefinic signal of **4b** ( $\delta$  4.62) coalesces at ca.  $-30 \degree C (\Delta G_{243}^{\#} = 11.1 \text{ kcal} \cdot \text{mol}^{-1})$  and splits at -50 °C into two broad proton resonances ( $\delta$ 4.91 and 4.20). These signals belong to protons of different C=C bonds (trans to Cl  $\delta$  4.20 and trans to acetylenic  $\delta$  4.91) since a correlation <sup>1</sup>H-COSY spectrum at -50 °C confirms that they are not coupled. At the same temperature, its <sup>13</sup>C NMR also displays, in addition to alkynyl carbon signals ( $C_{\alpha}/C_{\beta}$  81.1/105.2), only two olefinic ( $\delta$  75.9, 74.9) and two aliphatic carbon resonances ( $\delta$  30.0, 29.9). This suggests the existence of a fast intramolecular process, presumably a rapid ring inversion of the central six-membered Pt(acetylenic)-Rh<sub>2</sub>Cl, which equilibrates the endo and exo CH= units in the diolefin. This process cannot be frozen even at -80 °C. Below -50 °C, the olefinic proton signals broaden again, but only the high-frequency signal (trans to acetylenic fragment) disappears into the baseline at -80 °C.

# **Experimental Section**

General methods and instrumentation have been described previously.<sup>21</sup> All coupling constants are given in hertz. <sup>1</sup>H- COSY and <sup>1</sup>H phase-sensitive NOESY spectra were recorded following literature methods.<sup>27</sup>  $Q_2[cis-Pt(C_6F_5)_2(C \equiv CR)_2]$  (Q = PPh<sub>3</sub>Me, R = Ph;<sup>28</sup> Q = NBu<sub>4</sub>, R = <sup>t</sup>Bu,<sup>28</sup>SiMe<sub>3</sub><sup>17a</sup>), [Rh( $\mu$ -Cl)-(COD)]<sub>2</sub>,<sup>29</sup> [Ir( $\mu$ -Cl)(COD)]<sub>2</sub>.<sup>30</sup> and AgClO<sub>4</sub><sup>31</sup> were prepared by published methods.

**Preparation of Q**[{*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>( $\mu$ -1*k C*<sup>a</sup>: $\eta$ <sup>2</sup>-C=CR)<sub>2</sub>}Rh-(COD)] (Q = PPh<sub>3</sub>Me, R = Ph 2a; Q = NBu<sub>4</sub>, R = 'Bu 2b, SiMe<sub>3</sub> 2c). A yellow solution of [Rh( $\mu$ -Cl)(COD)]<sub>2</sub> (0.0476 g, 0.096 mmol) in Et<sub>2</sub>O (40 mL) was treated with AgClO<sub>4</sub> (0.040 g, 0.190 mmol), and the mixture was stirred for 1 h at room temperature and then filtered through Kieselgurh. To the resulting yellow solution, which probably contains [Rh(COD)-(Et<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>), was added (PPh<sub>3</sub>Me)<sub>2</sub>[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CPh)<sub>2</sub>] (0.240 g, 0.190 mmol), and a white suspension (PPh<sub>3</sub>MeClO<sub>4</sub>) in a deep orange solution immediately formed. After stirring for 30 min, the suspension was filtered through Kieselgurh and the filtrate evaporated to dryness. Treatment of the resulting oily residue with 5 mL of cold hexane afforded **2a** (orange, 70% yield).

Complexes **2b** and **2c** (orange solids) were obtained similarly starting from  $(NBu_4)_2[cis\cdotPt(C_6F_5)_2(C\equiv CR)_2]$  (R = <sup>t</sup>Bu, 0.250 g, 0.21 mmol **2b**; R = SiMe\_3, 0.300 g, 0.25 mmol **2c**) and [Rh-(COD)(Et<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>) (**2b** 0.23 mmol, 64% yield; **2c** 0.27 mmol, 88% yield).

Data for 2a. Anal. Calcd for  $C_{55}F_{10}H_{40}PPtRh$ : C, 54.15; H, 3.30. Found: C, 53.96; H, 3.17. Λ<sub>M</sub>: 84.5 Ω<sup>-1</sup>·cm<sup>2</sup>·mol<sup>-1</sup>. MS FAB(-): m/z = 942 [M] 100; 835 [M - COD + 1] 15; 774 [M  $C_6F_5 - 1$ ] 9; 733 [Pt( $C_6F_5$ )<sub>2</sub>( $C_2Ph$ )<sub>2</sub> + 2] 15; 630 [Pt( $C_6F_5$ )<sub>2</sub>( $C_2$ -Ph)] 27; 529 [Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] 32; 510 [Pt(C<sub>6</sub>F<sub>5</sub>)(C<sub>6</sub>F<sub>4</sub>)] 57; 362 [Pt-(C<sub>6</sub>F<sub>5</sub>)] 43. IR (cm<sup>-1</sup>): ν(C≡C) 2024(m br); ν(C<sub>6</sub>F<sub>5</sub>)<sub>x-sensitive</sub> 798 (s), 790 (s). <sup>1</sup>H NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, 7.84, 7.54, 7.29 (m, Ph, PPh<sub>3</sub>Me, C<sub>2</sub>Ph, 25H); 4.43 (s, CH=, COD, 4H); 3.22 (d,  ${}^{2}J_{P-H} = 14.0$ , PPh<sub>3</sub>(CH<sub>3</sub>)); 2.47 (s br, CH<sub>2</sub><, COD, 4H); 1.84 (d,  $J_{H-H} = 7.3$ , CH<sub>2</sub><, COD, 4H). A similar but slightly broader pattern was observed at -75 °C: 7.97, 7.85, 7.57, 7.34 (m, Ph, PPh<sub>3</sub>Me, C<sub>2</sub>Ph, 25 H); 4.34 (v br, CH=, COD, 4H); 3.32 (d,  ${}^{2}J_{P-H} = 14.4$ , PPh<sub>3</sub>(CH<sub>3</sub>)); 2.43 (v br, CH<sub>2</sub><, COD, 4H); 1.82 (d,  $J_{\rm H-H} = 7.7$ , CH<sub>2</sub><, COD, 4H). <sup>19</sup>F NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, -114.76 (d,  ${}^{3}J_{Pt-o-F} = 395.1$ , 4 *o*-F); -167.31 (m, 4 *m*-F, 2 p-F). A similar pattern was observed at -75 °C: -114.65 (s,  ${}^{3}J_{Pt-o-F} = 402.9, 4 \text{ o-F}$ ); -165.87 (m, 4 m-F, 2 p-F).  ${}^{13}C$  NMR (CDCl<sub>3</sub>,  $\delta$ ): at -50 °C, 147.3 (dd,  ${}^{1}J_{C-F} = 227$ ,  ${}^{2}J_{C-F} = 25$ ), 135.7 (dm) (C<sub>6</sub>F<sub>5</sub>); 134.8 (s, *p*-C, PPh<sub>3</sub>Me); 132.4 (d,  ${}^{3}J_{P-C} =$ 10.7, *m*-C, PPh<sub>3</sub>Me); 132.1 (s, Ph,C<sub>2</sub>Ph); 129.9 (d,  ${}^{2}J_{P-C} = 12.9$ , o-C, PPh<sub>3</sub>Me); 127.8, 127.0, 126.4 (s, Ph, C<sub>2</sub>Ph); 118.0 (d, <sup>1</sup>J<sub>P-C</sub> = 89, *i*-C, PPh<sub>3</sub>Me); 109.6 (s br,  ${}^{1}J_{Pt-C}$  = 856 Hz,  $C_{\alpha}$ ,  $C_{\alpha} \equiv C_{\beta}$ -Ph); 99.4 (s,  ${}^{2}J_{Pt-C} = 254$  Hz,  $C_{\beta}$ ,  $C_{\alpha} \equiv C_{\beta}Ph$ ); 81.0 (s br, CH=, COD); 30.8 (s br,  $CH_2$ <, COD); 9.4 (d,  ${}^{1}J_{P-C} = 57$ ,  $PPh_3(CH_3)$ ).

**Data for 2b.** Anal. Calcd for  $C_{48}F_{10}H_{66}NPtRh$ : C, 50.35; H, 5.81; N, 1.22. Found: C, 50.19; H, 6.40; N, 1.39.  $\Lambda_{M}$ : 76.6  $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ . MS FAB(-): m/z = 902 [M] 100; 794 [M - COD] 13; 692 [Pt( $C_6F_5$ )\_2( $C_2^{t}Bu$ )<sub>2</sub> + 1] 22; 611 [Pt( $C_6F_5$ )\_2( $C_2^{t}Bu$ ) + 1] 20; 530 [Pt( $C_6F_5$ )<sub>2</sub> + 1] 20; 511 [Pt( $C_6F_5$ )\_2( $C_2^{t}Bu$ ) + 1] 20; 530 [Pt( $C_6F_5$ )<sub>2</sub> + 1] 20; 511 [Pt( $C_6F_5$ )( $C_6F_4$ ) + 1] 47; 362 [Pt( $C_6F_5$ )] 35%. IR (cm<sup>-1</sup>):  $\nu$ (C=C) 2044 (m), 2017 (m);  $\nu$ ( $C_6F_5$ )<sub>x-sensitive</sub> 783 (vs), 776 (vs). <sup>1</sup>H NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, 4.76 (s br, CH=, COD, 4H); 3.46 (m, N-CH<sub>2</sub>-, NBu<sub>4</sub>, 8H); 2.52 (br, CH<sub>2</sub><, COD, 4H); 1.84 (m, CH<sub>2</sub>< (COD) and  $-CH_2$ - (NBu<sub>4</sub>), 12H); 1.43 (m,  $-CH_2$ -, NBu<sub>4</sub>, 8H); 1.24 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H); 0.98 (t,  $-CH_3$ , NBu<sub>4</sub>, 12H). At -80 °C a similar pattern is observed with the exception of the signal due to the olefinic protons of the COD, which practically coalesces: 4.66 (v br, CH=, COD, 4H); 3.41 (s br, N-CH<sub>2</sub>-, NBu<sub>4</sub>, 8H); 2.46

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(m br, CH<sub>2</sub><, COD, 4H); 1.74 (m, CH<sub>2</sub>< (COD) and -CH<sub>2</sub>-(NBu<sub>4</sub>), 12H); 1.32 (m, -CH<sub>2</sub>-, NBu<sub>4</sub>, 8H); 1.18 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H); 0.89 (s br,  $-CH_3$ , NBu<sub>4</sub>, 12H). <sup>19</sup>F NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, -114.44 (dm,  ${}^{3}J_{Pt-o-F} = 400.9$ , 4 *o*-F); -167.82 (m, 4 m-F); -168.40 (t, 2 p-F). The signal due to the o-F of the  $C_6F_5$  groups coalesces at ca. -75 °C ( $\Delta G_{198}^{\#} \approx 9.15$  kcal· mol<sup>-1</sup>), splitting into two broad signals at -80 °C: -114.11 (2 o-F), -114.63 (2 o-F) (v br, platinum satellites are observed but are not well resolved); -166.29 (m, 4 m-F, 2 p-F). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): at -50 °C, 147.5 (dd,  ${}^{1}J_{C-F} = 220$ ,  ${}^{2}J_{C-F} = 24$ ), 135.7 (dm,  ${}^1J_{C-F} \approx$  250), 134.8 (dm,  ${}^1J_{C-F} \approx$  244) (C<sub>6</sub>F<sub>5</sub>); 109.1 (s,  ${}^{2}J_{\text{Pt-C}} \approx 240$ ,  $C_{\beta}$ ,  $C_{\alpha} \equiv C_{\beta}{}^{t}\text{Bu}$ ); 95.0 (s br,  ${}^{1}J_{\text{Pt-C}} \approx 825$  Hz,  $C_{\alpha}$ ,  $C_{\alpha} \equiv C_{\beta}^{t}Bu$ ); 75.7, 73.8 (br, CH=, COD); 58.1 (s, N-CH<sub>2</sub>- $(CH_2)_2 - CH_3$ ; 32.5 (s,  $C(CH_3)_3$ ); 31.0 (br,  $CH_2 <$ , COD); 30.5 (s, CMe<sub>3</sub>); 23.2, 19.3 (s, N-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 13.5 (s, N-(CH<sub>2</sub>)<sub>3</sub>- $CH_3$ ).

Data for 2c. Anal. Calcd for C<sub>46</sub>F<sub>10</sub>H<sub>66</sub>NPtRhSi<sub>2</sub>: C, 46.93; H, 5.65; N, 1.19. Found: C, 46.72; H, 6.01; N, 1.43. Λ<sub>M</sub>: 115.2  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ . MS FAB(-): m/z = 934 [M] 100; 836 [M - C<sub>2</sub>- $SiMe_3 - 1$ ] 4; 626 [Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>2</sub>SiMe<sub>3</sub>)] 16; 362 [Pt(C<sub>6</sub>F<sub>5</sub>)] 12. IR (cm<sup>-1</sup>):  $\nu$ (C=C) 1965 (vs), 1940 (vs);  $\nu$ (C<sub>6</sub>F<sub>5</sub>)<sub>x-sensitive</sub> 786 (vs), 777 (vs). <sup>1</sup>H NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, 4.78 (s br, CH=, COD, 4H); 3.46 (m, N–CH<sub>2</sub>–, NBu<sub>4</sub>, 8H); 2.56 (br, CH<sub>2</sub><, COD, 4H); 1.85 (m, CH<sub>2</sub>< (COD) and -CH<sub>2</sub>- (NBu<sub>4</sub>), 12H); 1.44 (m, -CH2-, NBu4, 8H); 0.98 (t, -CH3, NBu4, 12H); 0.18 (s, SiMe3, 18H). The signal due to the olefinic protons of the COD coalesces at ca. -60 °C ( $\Delta G_{213}^{\#} \approx 10.27 \text{ kcal·mol}^{-1}$ ), splitting into two broad singlets at lower temperature [e.g., at -80 °C, 4.79 (2H), 4.60 (2H) (s br, CH=, COD); 3.41 (m br, N-CH<sub>2</sub>-, NBu<sub>4</sub>, 8H); 2.50 (4H), 1.96 (4H) (m br, CH<sub>2</sub><, COD); 1.74 (8H), 1.31 (8H) (m br, -CH<sub>2</sub>-, NBu<sub>4</sub>); 0.89 (m, -CH<sub>3</sub>, NBu<sub>4</sub>, 12H); 0.13 (s, SiMe<sub>3</sub>, 18H)]. <sup>19</sup>F NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, -114.51 (dm,  ${}^{3}J_{Pt-o-F} = 386$ , 4 *o*-F); -167.42 (m, 4 *m*-F, 2 *p*-F)]. The signal due to the *o*-F of the C<sub>6</sub>F<sub>5</sub> groups coalesces at ca. -73 °C ( $\Delta G_{200}^{\#} \approx 9.25$  kcal·mol<sup>-1</sup>) and, finally, splits in two broad singlets at -80 °C: -114.21 (s br,  ${}^{3}J_{\text{Pt}-o-\text{F}} = \approx 340, 2$ *o*-F),  $-11\overline{4}.73$  (s br,  ${}^{3}J_{\text{Pt}-o-F} = 380.6$ , 2 *o*-F); -165.55 (t, 2 *p*-F), -165.90 (m, 4 m-F). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): at 16 °C, 148.0 (dd,  ${}^{1}J_{C-F} = 224$ ,  ${}^{2}J_{C-F} = 25$ ), 135.8 (dm) (C<sub>6</sub>F<sub>5</sub>); a badly resolved signal at 134.4, which overlaps with one of the multiplets due to the carbon of  $C_6F_5$  groups, is probably due to  $C_{\alpha}$ : 101.7 (d,  ${}^{1}J_{\text{Rh-C}} = 5.4$ ,  ${}^{2}J_{\text{Pt-C}} \approx 240$ , C<sub> $\beta$ </sub>, C<sub> $\alpha$ </sub> $\equiv$ C<sub> $\beta$ </sub>SiMe<sub>3</sub>); 79.0 (d,  ${}^{1}J_{\text{Rh-C}} =$ 12.6, CH=, COD); 58.8 (s,  $N-CH_2-(CH_2)_2-CH_3$ ); 31.2 (s, CH<sub>2</sub><, COD); 23.8, 19.3 (s, N-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 13.5 (s, N-(CH<sub>2</sub>)<sub>3</sub>-*C*H<sub>3</sub>); 1.9 (s, <sup>1</sup>*J*<sub>C-Si</sub> = 55.5, SiMe<sub>3</sub>). At -50 °C, 147.4 (dm,  ${}^{1}J_{C-F} = 226$ ), 135.4 (dm) (C<sub>6</sub>F<sub>5</sub>); 101.3 (s br,  ${}^{2}J_{Pt-C} \approx 235$ ,  $C_{\beta}$ ,  $C_{\alpha} \equiv C_{\beta}SiMe_3$ ); 78.0 (v br, CH=, COD); 58.1 (s, N-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 31.0 (v br, CH<sub>2</sub><, COD); 23.3, 19.3 (s, N-CH<sub>2</sub>- $(CH_2)_2 - CH_3$ ; 13.5 (s, N-(CH<sub>2</sub>)<sub>3</sub>- $CH_3$ ); 1.6 (s,  ${}^1J_{C-Si} = 55.3$ , SiMe<sub>3</sub>).

**Reactions of**  $Q_2[cis-Pt(C_6F_5)_2(C=CR)_2]$  ( $Q = PPh_3Me$ , R = Ph;  $Q = NBu_4$ ,  $R = {}^tBu$ , SiMe<sub>3</sub>) with  $[M(\mu-Cl)(COD)]_2$  (M = Rh, Ir). All the reactions were carried out treating suspensions of  $[M(\mu-Cl)(COD)]_2$  (M = Rh, Ir) in 20 mL of acetone at -20 °C with  $Q_2[cis-Pt(C_6F_5)_2(C=CR)_2]$  ( $Q = PPh_3$ -Me, R = Ph;  $Q = NBu_4$ ,  $R = {}^tBu$ , SiMe<sub>3</sub>), varying only the reaction time. The resulting solutions were evaporated to dryness, and the residues thus obtained were treated with ca. 5 mL of cold EtOH.

**Reactions of (PPh<sub>3</sub>Me)<sub>2</sub>[cis**-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡CPh)<sub>2</sub>] with [Rh( $\mu$ -Cl)(COD)]<sub>2</sub>. Starting from 0.0766 g (0.155 mmol) of [Rh( $\mu$ -Cl)(COD)]<sub>2</sub> and 0.200 g (0.155 mmol) of (PPh<sub>3</sub>Me)<sub>2</sub>[cis-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡CPh)<sub>2</sub>] (molar ratio Rh/Pt 2:1), and after 15 min of stirring, an orange solid identified (<sup>1</sup>H NMR) as a mixture of **2a** and [Rh( $\mu$ -Cl)(COD)]<sub>2</sub> (molar ratio 2.5:1) was obtained. Monitoring of the reaction by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopies reveals that no other product is formed.

An orange solid identified as **2a** was also obtained when the reaction was performed with 0.0287 g (0.058 mmol) of [Rh-( $\mu$ -Cl)(COD)]<sub>2</sub> and 0.150 g (0.117 mmol) of (PPh<sub>3</sub>Me)<sub>2</sub>[*cis*-Pt-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CPh)<sub>2</sub>] (molar ratio Rh/Pt 1:1, 15 min, 81% yield).

<sup>(27)</sup> Braun, S.; Kalinonowski, H.-O.; Berger, S. 100 and More Basic NMR Experiments; VCH: Weinheim, Germany, 1996.

<sup>(28)</sup> Espinet, P.; Forniés, J.; Martínez, F.; Sotés, M.; Lalinde, F.; Moreno, M. T.; Ruiz, A.; Welch, A. J. *J. Organomet. Chem.* **1991**, *403*, 253.

**Reactions of (NBu<sub>4</sub>)<sub>2</sub>[***cis***·Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡C<sup>t</sup>Bu)<sub>2</sub>] with [Rh-(\mu-Cl)(COD)]<sub>2</sub>. Starting from 0.063 g (0.128 mmol) of [Rh(\mu-Cl)(COD)]<sub>2</sub> and 0.151 g (0.128 mmol) of (NBu<sub>4</sub>)<sub>2</sub>[***cis***-Pt-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡C<sup>t</sup>Bu)<sub>2</sub>] (molar ratio Rh/Pt 2:1), and after 40 min of stirring, an orange solid identified as (NBu<sub>4</sub>)[{***cis***·Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(\mu-1\kappa C^{u}:\eta^2-C≡C<sup>t</sup>Bu)<sub>2</sub>}{Rh<sub>2</sub>(\mu-Cl)(COD)<sub>2</sub>}], <b>4b**, was obtained. Yield: 67%.

Complex **4b** was also obtained using the same reaction time and an equimolar Rh/Pt ratio: 0.063 mg (0.128 mmol) of [Rh-( $\mu$ -Cl)(COD)]<sub>2</sub> and 0.300 mg (0.256 mmol) of (NBu<sub>4</sub>)<sub>2</sub>[*cis*-Pt-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=C<sup>t</sup>Bu)<sub>2</sub>]. Yield: 56% (based on Rh).

Data for 4b. Anal. Calcd for C<sub>56</sub>ClF<sub>10</sub>H<sub>78</sub>NPtRh<sub>2</sub>: C, 48.34; H, 5.64; N, 1.01. Found: C, 48.16; H, 5.11; N, 1.02. Λ<sub>M</sub>: 89.8  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ . MS FAB(-): m/z = 1148 [M - 1] 16; 902 [2b]100; 794 [**2b** – COD] 15; 692 [Pt( $C_6F_5$ )<sub>2</sub>( $C_2$ <sup>t</sup>Bu)<sub>2</sub> + 1] 15; 611  $[Pt(C_6F_5)_2(C_2^tBu) + 1]$  28; 565  $[Rh_2(COD)_3Cl]$  31; 510  $[Pt(C_6F_5) (C_6F_4)$ ] 90; 362  $[Pt(C_6F_5)]$  41. IR  $(cm^{-1})$ :  $\nu(C=C)$  2033 (s);  $\nu(C_6F_5)_{x-sensitive}$  788 (s), 780 (s). This complex dissociates in solution to give an equilibrium mixture of 2b, 4b, and [RhCl-(COD)]<sub>2</sub>. In CDCl<sub>3</sub>,  $\hat{K} \approx 5.1 \times 10^{-2} \text{ mol}^{1/2} \cdot \text{L}^{-1/2}$  at 16 °C (e.g., for a  $[\textbf{4}]_{initial}$  = 1.47  $\times$  10  $^{-2}$  M, dissociation ca. 43%, molar ratio **4b**/**2b**/[Rh( $\mu$ -Cl)(COD)] 2.7:2:1). In acetone- $d_6$  complex **4b** dissociates to a lesser extent ( $K \approx 9.2 \times 10^{-3} \text{ mol}^{1/2} \cdot \text{L}^{-1/2}$  at 16 °C, e.g., for a  $[\mathbf{4b}]_{\text{initial}} = 1.35 \times 10^{-2}$  M, dissociation ca. 20%, molar ratio 4b/2b/[Rh(u-Cl)(COD)] 8:2:1). <sup>1</sup>H NMR (acetoned<sub>6</sub>, δ): at 16 °C, 4.62 (s br, CH=, COD); 3.46 (m, N-CH<sub>2</sub>-, NBu<sub>4</sub>); 2.48 (m br, CH<sub>2</sub><, COD); 1.84 (m, -CH<sub>2</sub>-, NBu<sub>4</sub>); 1.69 (d,  $J_{H-H} = 7.9$ , CH<sub>2</sub><, COD); 1.44 (m, -CH<sub>2</sub>- (NBu<sub>4</sub>) and s, C(CH<sub>3</sub>)<sub>3</sub>); 0.98 (t, -CH<sub>3</sub>, NBu<sub>4</sub>). A similar pattern was observed at 40 °C. By lowering the temperature, the olefinic signal broadens, coalesces at ca.  $-30 \degree C (\Delta G_{243}^{\#} = 11.1 \text{ kcal·mol}^{-1}),$ and splits at -50 °C: 4.91 (br, CH=, COD); 4.20 (br, CH= protons of the COD ligand of 4b overlapped with olefinic protons of [RhCl(COD)]<sub>2</sub> present due to the dissociation process); 3.42 (m, N-CH<sub>2</sub>-, NBu<sub>4</sub>); 2.42 (m br, CH<sub>2</sub><, COD); 1.77 (m, -CH<sub>2</sub>-, NBu<sub>4</sub>), 1.66 (m br, CH<sub>2</sub><, COD) (both of the signals are overlapped); 1.39 (m, -CH<sub>2</sub>- (NBu<sub>4</sub>) and s, C(CH<sub>3</sub>)<sub>3</sub>); 0.93 (t, -CH<sub>3</sub>, NBu<sub>4</sub>). At lower temperatures both olefinic signals ( $\delta$  4.91, 4.20) broaden again, and at ca. -80 °C the lower-field signal coalesces. <sup>19</sup>F NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, -114.39 (dm,  ${}^{3}J_{Pt-o-F} = 384$ , 4 *o*-F); -168.31 (m, 4 m-F); -168.98 (t, 2 p-F). At -80 °C, -114.30 (hump, 4 o-F); -167.05 (m, 4 m-F); -167.48 (t, 2 p-F). In all the spectra (<sup>1</sup>H and <sup>19</sup>F NMR) signals due to **2b** and [RhCl(COD)]<sub>2</sub> are also observed. <sup>13</sup>C NMR (acetone- $d_6$ ,  $\delta$ ): at -50 °C, 147.0 (dm, <sup>1</sup> $J_{C-F}$ = 226), 134.4 (dm,  ${}^{1}J_{C-F} \approx 230$ ) (C<sub>6</sub>F<sub>5</sub>); 105.2 (s,  ${}^{2}J_{Pt-C} \approx 270$ ,  $C_{\beta}$ ,  $C_{\alpha} \equiv C_{\beta}^{t}Bu$ ); 81.1 (m,  $C_{\alpha}$ ,  $C_{\alpha} \equiv C_{\beta}^{t}Bu$ ); 75.9, 74.9 (m br, CH= , COD); 57.2 (s, N-CH2-(CH2)2-CH3); 31.5 (s, C(CH3)3); 31.0 (s, CMe<sub>3</sub>); 30.3, 29.9 (br, CH<sub>2</sub><, COD); 22.6, 18.8 (s, N-CH<sub>2</sub>-(*C*H<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 12.6 (s, N-(CH<sub>2</sub>)<sub>3</sub>-*C*H<sub>3</sub>). A small singlet at 31.7  $[C(CH_3)_3, 2b]$  is also observed.

**Reactions of (NBu<sub>4</sub>)**<sub>2</sub>[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CSiMe<sub>3</sub>)<sub>2</sub>] with [Rh( $\mu$ -Cl)(COD)]<sub>2</sub>. Starting from 0.075 g (0.152 mmol) of [Rh-( $\mu$ -Cl)(COD)]<sub>2</sub> and 0.183 g (0.152 mmol) of (NBu<sub>4</sub>)<sub>2</sub>[*cis*-Pt-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CSiMe<sub>3</sub>)<sub>2</sub>] (molar ratio Rh/Pt 2:1), and after 10 min of stirring, an orange solid identified as (NBu<sub>4</sub>)[{*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-( $\mu$ -1 $\kappa$ C<sup> $\alpha$ </sup>: $\eta$ <sup>2</sup>-C=CSiMe<sub>3</sub>)<sub>2</sub>]{Rh<sub>2</sub>( $\mu$ -Cl)(COD)<sub>2</sub>]], **4c**, was obtained. Yield: 71%.

By using the same reaction time and a 1:1 Rh/Pt ratio  $(0.0225 \text{ g}, 0.046 \text{ mmol}, [Rh(\mu-Cl)(COD)]_2 \text{ and } 0.110 \text{ g}, 0.091 \text{ mmol}, (NBu_4)_2[cis-Pt(C_6F_5)_2(C=CSiMe_3)_2]) an orange solid which is identified as complex$ **2c**was obtained. Yield: 42%.

**Data for 4c.** Anal. Calcd for  $C_{54}$ ClF<sub>10</sub>H<sub>78</sub>NPtRhSi<sub>2</sub>: C, 45.56; H, 5.52; N, 0.98. Found: C, 45.31; H, 5.28; N, 0.89.  $\Lambda_{M}$ : 78.1  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ . MS FAB(-): m/z = 1181 [M] 13; 934 [**2c**] 100; 724 [Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> + 1] 12; 528 [Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> - 1] 24; 361 [Pt(C<sub>6</sub>F<sub>5</sub>) - 1] 30. IR (cm<sup>-1</sup>):  $\nu$ (C=C) 1966 (vs), 1952 (vs);  $\nu$ (C<sub>6</sub>F<sub>5</sub>)<sub>x-sensitive</sub> 789 (vs), 778 (vs). This complex dissociates in solution to give an equilibrium mixture of **2c**, **4c**, and [RhCl-(COD)]<sub>2</sub>. In CDCl<sub>3</sub>,  $K = 4.51 \times 10^{-1}$  mol<sup>1/2</sup>·L<sup>-1/2</sup> at 16 °C, e.g., for a [**4c**]<sub>initial</sub> = 2.46 × 10<sup>-2</sup> M, dissociation ca. 82%, molar

ratio **4c/2c**/[Rh( $\mu$ -Cl)(COD)] 1:4.5:2.25; in acetone- $d_6$ , K = 3.5 $\times$  10^{-2} mol^{1/2} L^{-1/2} at 16 °C, e.g., for a  $[4c]_{\rm initial}$  = 2.6  $\times$  10^{-2} M, dissociation ca. 38%, molar ratio 4c/2c/[Rh(µ-Cl)(COD)] 3.3: 2:1. <sup>1</sup>H NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, 4.55 (s br, CH=, COD); 3.46 (m, N–CH<sub>2</sub>–, NBu<sub>4</sub>); 2.54 (m br, CH<sub>2</sub><, COD); 1.83 (m, -CH<sub>2</sub>-, NBu<sub>4</sub>); 1.74 (m, CH<sub>2</sub><, COD); 1.44 (m, -CH<sub>2</sub>-, NBu<sub>4</sub>); 0.98 (t, -CH<sub>3</sub>, NBu<sub>4</sub>), 0.25 (s, SiMe<sub>3</sub>). At -80 °C the same pattern is observed: 4.45 (s br, CH=, COD); 3.42 (m, N-CH<sub>2</sub>-, NBu<sub>4</sub>); 2.46 (m br, CH<sub>2</sub><, COD); 1.75 (m br, -CH<sub>2</sub>-, NBu<sub>4</sub>); 1.32 (m br, CH<sub>2</sub>< (COD) and -CH<sub>2</sub>- (NBu<sub>4</sub>)); 0.89 (t, -CH<sub>3</sub>, NBu<sub>4</sub>), 0.20 (s, SiMe<sub>3</sub>). <sup>19</sup>F NMR (acetone- $d_6$ ,  $\delta$ ): at 16 °C, -114.69 (dm,  ${}^{3}J_{Pt-o-F} = 384$ , 4 o-F); -168.04 (m, 4 m-F, 2 p-F). The signal due to the *o*-F coalesces at ca. -73 °C. At -80 °C, -112.7 (v br, 2 o-F), -117.0 (v br, 2 o-F); -166.54 (m, 4 m-F, 2 p-F). In all the spectra (<sup>1</sup>H and <sup>19</sup>F NMR) signals due to **2c** and [RhCl(COD)]<sub>2</sub> are also observed. Due to the extent of the dissociation, the assignment of the <sup>13</sup>C NMR spectra in acetone- $d_6$  is rather uncertain: at 16 °C, 148.9 (dm,  ${}^1J_{\rm C-F} \approx$ 211), 136.4 (dm) (C<sub>6</sub>F<sub>5</sub>); 128.1 (m), 97.8 (m) (C<sub> $\alpha$ </sub> or C<sub> $\beta$ </sub>, C<sub> $\alpha$ </sub>=C<sub> $\beta$ </sub>-SiMe<sub>3</sub>, 2c or 4c); 79.5 (m), 78.7 (h) (CH=, COD, 2c or 4c); 59.3  $(t, {}^{1}J_{C^{-14}N} = 2.8, N - CH_2 - (CH_2)_2 - CH_3); 31.5 (s, CH_2 <, COD);$ 24.3 (s, N-(CH<sub>2</sub>)<sub>2</sub>-*C*H<sub>2</sub>-CH<sub>3</sub>); 20.3 (t,  ${}^{2}J_{C-{}^{14}N} = 1.3$ , N-CH<sub>2</sub>-CH2-CH2-CH3); 13.8 (s, N-(CH2)3-CH3); 1.8 (s, SiMe3). Two singlets at 31.9 (CH<sub>2</sub><, COD, 2c) and 2.0 (SiMe<sub>3</sub>, 2c) are also observed.

**Reactions of (NBu<sub>4</sub>)**<sub>2</sub>[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CSiMe<sub>3</sub>)<sub>2</sub>] with [Ir( $\mu$ -Cl)(COD)]<sub>2</sub>. The reactions between [Ir( $\mu$ -Cl)(COD)]<sub>2</sub> and (NBu<sub>4</sub>)<sub>2</sub>[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CSiMe<sub>3</sub>)<sub>2</sub>] in a 2:1 Ir/Pt ratio (0.100 g, 0.149 mmol, [Ir( $\mu$ -Cl)(COD)]<sub>2</sub> and 0.180 g, 0.149 mmol, (NBu<sub>4</sub>)<sub>2</sub>[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CSiMe<sub>3</sub>)<sub>2</sub>]; 10 min) or 1:1 Ir/Pt ratio (0.056 g, 0.084 mmol, [Ir( $\mu$ -Cl)(COD)]<sub>2</sub> and 0.200 g, 0.164 mmol, (NBu<sub>4</sub>)<sub>2</sub>[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C=CSiMe<sub>3</sub>)<sub>2</sub>]; 2 h) afforded a yellow solid, which was identified as (NBu<sub>4</sub>)[*cis*-Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>( $\mu$ -1 $\kappa$ C<sup>u</sup>: $\eta$ <sup>2</sup>-C=CSiMe<sub>3</sub>)( $\mu$ -2 $\kappa$ C<sup>u</sup>: $\eta$ <sup>2</sup>-C=CSiMe<sub>3</sub>)Ir(COD)], 3c. Yields (based on Pt): 65 and 30.5%, respectively.

Complex **3c** can also be obtained in a very low yield (15%) by treatment of an equimolar amount of **1c** (0.170 g, 0.140 mmol) with a solution of [Ir(COD)(acetone)](ClO<sub>4</sub>), prepared from 0.0497 mg (0.074 mmol) of [Ir( $\mu$ -Cl)(COD)]<sub>2</sub> and 0.0307 mg (0.148 mmol) of AgClO<sub>4</sub> and 1 h of stirring, in 20 mL of acetone. The resulting yellow solution, which was shown to contain **3c** by <sup>19</sup>F NMR, was evaporated to dryness and the residue treated with 20 mL of Et<sub>2</sub>O to give a white suspension (NBu<sub>4</sub>ClO<sub>4</sub>) in a yellow solution. Filtration of the mixture, evaporation to dryness, and treatment of the resulting oily residue with cold hexane (~10 mL) afforded 0.027 g of a yellow solid, which was identified as complex **3a**.

Data for 3c. Anal. Calcd for C<sub>46</sub>F<sub>10</sub>H<sub>66</sub>IrNPtSi<sub>2</sub>: C, 43.63; H, 5.25; N, 1.10. Found: C, 43.40; H, 4.87; N, 1.07. Λ<sub>M</sub>: 71.1  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ . MS FAB(-): m/z = 1024 [M] 100; 926 [M - $C_2SiMe_3] \; 35; \; 627 \; [Pt(C_6F_5)_2(C_2SiMe_3) \, + \, 1] \; 78; \; 529 \; [Pt(C_6F_5)_2]$ 48; 509  $[Pt(C_6F_5)(C_6F_4) - 1]$  69; 362  $[Pt(C_6F_5)]$  67. IR  $(cm^{-1})$ :  $\nu$ (C=C) 1868 (vs), 1823 (vs);  $\nu$ (C<sub>6</sub>F<sub>5</sub>)<sub>x-sensitive</sub> 796 (vs), 781 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): at 16 °C, 4.27 (s br, CH=, COD, 4H); 3.15 (m br, N-CH<sub>2</sub>-, NBu<sub>4</sub>, 8H); 2.16 (m, CH<sub>2</sub><, COD, 4H); 1.89 (m,  $CH_2$ <, COD, 4H); 1.60 (8H), 1.40 (8H) (m,  $-CH_2$ -NBu<sub>4</sub>); 0.96 (t, -CH<sub>3</sub>, NBu<sub>4</sub>, 12H); -0.12 (s, SiMe<sub>3</sub>, 18H). At -50 °C, 4.89 (2H), 3.55 (2H) (s br, CH=, COD); 3.15 (br, N-CH<sub>2</sub>-, NBu<sub>4</sub>, 8H); 2.14 (4H), 1.87 (4H) (s br, CH<sub>2</sub><, COD); 1.58 (8H), 1.33 (8H) (s br, -CH2-, NBu4); 0.91 (s br, -CH3, NBu<sub>4</sub>, 12H); -0.16 (9H), -0.20 (9H) (s, SiMe<sub>3</sub>, the singlets overlapped partially). The signal due to the SiMe<sub>3</sub> protons coalesces between -40 and -50 °C ( $\Delta G_{230}^{\#} = 11.86 \text{ kcal} \cdot \text{mol}^{-1}$ ) and the signal due to the olefinic protons of the COD coalesces at  $-20 \ ^{\circ}C \ (\Delta G_{253}^{\#} = 10.84 \ \text{kcal} \cdot \text{mol}^{-1})$ . <sup>19</sup>F NMR (CDCl<sub>3</sub>,  $\delta$ ): at 16 °C, -114.95 (d,  ${}^{3}J_{Pt-o-F} = 444.5$ , 4 o-F); -166.29 (t, 2 *p*-F); -166.76 (m, 4 *m*-F). At -50 °C: -114.21 (d,  ${}^{3}J_{Pt-o-F} =$ 373, 2 *o*-F trans to  $\sigma$ -C=C); -116.26 (d,  ${}^{3}J_{Pt-o-F} = 520$ , 2 *o*-F trans to  $\eta^2$ -C=C); -165.23 (m br, 2 *p*-F); -166.30 (m, 4 *m*-F). The signal due to the o-F coalesces at ca. -20 °C and the corresponding one to the *p*-F at ca. -40 °C ( $\Delta G_{253}^{\#} = 11.13$ 

Table 2. Crystallographic Data and Structure Refinement Parameters for Complexes 2a, 3c, and 4b

	2a	<b>3c</b>	<b>4b</b>			
empirical formula	$C_{55}H_{40}F_{10}PPtRh$	C46H66NF10Si2PtIr	C <sub>87.5</sub> H <sub>150.5</sub> N <sub>1.5</sub> Cl <sub>3</sub> F <sub>15</sub> Rh <sub>3</sub> Pt <sub>1.5</sub>			
fw	1219.84	1266.48	2216.31			
a (Å)	21.921(4)	14.667(7)	36.629(7)			
b (Å)	10.765(2)	18.946(6)	22.882(5)			
<i>c</i> (Å)	19.765(4)	17.603(6)	28.661(6)			
α (deg)	90	90	90			
$\beta$ (deg)	90	96.23(6)	127.21(3)			
$\gamma$ (deg)	90	90	90			
volume (Å <sup>3</sup> ), Z	4664.14(2)	4862.79	19132(7)			
wavelength (Å)	0.71073	0.71073	0.71073			
temperature (K)	200	210	200			
radiation	graphite monochomated	graphite monochromated	graphite monochromated			
	Μο Κα	Μο Κα	Μο Κα			
crystal system	orthorhombic	monoclinic	monoclinic			
space group	$Pna2_1$	$P2_1/n$	C2/c			
cryst dimens (mm)	0.3 imes 0.2 imes 0.3	0.4 imes 0.3 imes 0.2	0.70 imes 0.45 imes 0.36			
abs coeff $(mm^{-1})$	3.462	5.73	2.848			
transmission factors	0.975, 0.809	0.2927, 0.1418	1.000, 0.591			
abs corr	$\Psi$ scans	$\Psi$ scans	$\Psi$ scans			
diffractometer	Siemens P4	Siemens Stoe AED2	Siemens P4			
$2\theta$ range (deg)	4 - 50	4-47	4-48			
no. of reflns collected	4827	7750	15430			
no. of indep reflns	4495 ( $R_{\rm int} = 0.074$ )	7163 ( $R_{\rm int} = 0.028$ )	14788 ( $R_{\rm int} = 0.021$ )			
refinement method	full-matrix least-squares on $F^2$	full matrix leasts-squares on $F$	full-matrix least squares on $F^{z}$			
goodness-of-fit on F <sup>2</sup>	1.049	1.225	1.045			
final <i>R</i> indices $(I > 2\sigma(I))^b$	R1 = 0.0681,	R1 = 0.0383,	R1 = 0.0686,			
	wR2 = 0.1576	wR = 0.0477	wR2 = 0.1832			
R indices (all data)	R1 = 0.1050,	-	R1 = 0.1208,			
	wR2 = 0.1947	-	wR2 = 0.2210			
<sup>a</sup> Goodness-of-fit = $[\sum w(F_0^2 - F_c^2)^2/(n_{obs} - n_{naram})]^{1/2}$ . $w = [\sigma^2(F_0) + (g_1P)^2 + g_2P]^{-1}$ ; $P = [\max(F_0^2; 0) + 2F_c^2]/3$ . <sup>b</sup> R1 = $\sum ( F_0  -  F_c )/2$						

$$\sum |F_0|$$
: wR2 =  $\sum w(F_0^2 - F_c^2)^2 / \sum w(F_c^2)^2 ]^{1/2}$ 

kcal·mol<sup>-1</sup>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): at 16 °C, 147.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 223, <sup>2</sup>*J*<sub>C-F</sub> = 25), 135.9 (dm) (C<sub>6</sub>F<sub>5</sub>); 124.2, 112.85 (m, tentatively ascribed to C<sub>a</sub> and C<sub>β</sub>, C<sub>a</sub>≡C<sub>β</sub>SiMe<sub>3</sub>); 69.4 (v br, CH=, COD); 58.7 (s, N-*C*H<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 31.9 (s, CH<sub>2</sub><, COD); 23.8, 19.6 (s, N-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 13.4 (s, N-(CH<sub>2</sub>)<sub>3</sub>-*C*H<sub>3</sub>); 1.3 (s, SiMe<sub>3</sub>, <sup>1</sup>*J*<sub>Si-C</sub> = 54.6). At -50 °C, 147.1 (dm, <sup>1</sup>*J*<sub>C-F</sub> = 226), 135.5 (dm, <sup>1</sup>*J*<sub>C-F</sub> = 240) (C<sub>6</sub>F<sub>5</sub>); 122.9, 121.7, 117.5, 108.1 (m, tentatively ascribed to two C<sub>a</sub> and two C<sub>β</sub>, C<sub>a</sub>≡C<sub>β</sub>SiMe<sub>3</sub>); 62.3 (s br, CH=, COD); 58.1 (s br, CH= (COD) and N-*C*H<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 32.0, 31.5 (s br, CH<sub>2</sub><, COD, both of the signals are overlapped); 23.4, 19.4 (s, N-CH<sub>2</sub>-(*C*H<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>); 13.5 (s, N-(CH<sub>2</sub>)<sub>3</sub>-*C*H<sub>3</sub>); 1.2, 1.0 (s br, SiMe<sub>3</sub>).

X-ray Crystal Structure Determination of Complexes 2a, 3c, and 4b. Crystals of the three respective complexes were obtained at low temperature (-30 °C) by slow diffusion of hexane into chloroform solutions. Suitable crystals of 2a, 3c, or 4b were selected and fixed with epoxy on top of glass fibers and transferred to the cold stream of the low-temperature device of automated four-circle difractometers Siemens P4 (2a, 4b) or Siemens STOE AED2 (3c). For complex 2a, the enantiomorph was chosen on the basis of the Flack parameter x = -0.0163 with esd 0.0183 (expected values are 0 for correct and +1 for inverted absolute structure). Crystallographic data and structure refinement parameters are shown in Table 2. Cell constants were calculated from 100 well-centered reflections with  $2\theta$  angles ranging from  $16^{\circ}$  to  $30^{\circ}$  (**2a**, **4b**) or 24 reflections with  $2\theta$  angles from  $24^{\circ}$  to  $29^{\circ}$  (3c). Data were collected at 200 K (2a, 4b) or 210 K (3c) by the  $\omega/2\theta$  (2a),  $\omega/\theta$ (3c), or  $\omega$  (4b) methods. Three check reflections measured at regular intervals showed no significant loss of intensity at the end of data collection in each case. An empirical absorption correction based on  $\psi$  scans was applied. The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters except four C atoms in 2a. No hydrogen atoms were added to the models. In complex 2a the anisotropically refined C(1), C(6), C(13), and C(21) have large displacement parameters, and some disorder was observed. In complex 3c the C(33) and C(34) atoms that

belong to a NBu4 group were refined as disordered over two positions. In the asymmetric unit of **4b** there are 1.5 molecules of the complex, the other half-molecule being generated by symmetry since the Pt atom and the bridging Cl are located in special positions. The half-molecule of NBu<sub>4</sub> is disordered over two positions, having two common carbon atoms, C(78) and C(79). N(2) and C(99), which belong to different NBu<sub>4</sub> units, occupy the same site at half-occupancy. Regions of electron density located at nonbonding distances were modeled as interstitial solvents: a molecule of CHCl<sub>3</sub>, refined at halfoccupancy with anisotropic thermal parameters, and three carbon atoms of a molecule of cyclohexane (the other carbon atoms being generated by a symmetry center) refined with isotropic thermal parameters at full occupancy. That makes one-third of each solvent molecule per formula unit. There are some peaks of electron density higher than 1 e/A<sup>3</sup> in the final map in all three structures (maximum 2.02 for 2a, 1.16 for 3c, and 1.69 for 4b). In all cases, they are located very close to the heavy atoms or in the disordered solvent areas and have no chemical significance. All calculations were carried out using the programs SHELXTL-PLUS<sup>32</sup> and SHELXL-93.33

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**Supporting Information Available:** Tables giving positional and thermal parameters and bond distances and bond angles for **2a**, **3c**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(32)</sup> SHELXTL-PLUS, Software Package for the Determination of Crystal Structures, Release 4.0; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

<sup>(33)</sup> Sheldrick, G. M. SHELXL-93, a Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1993.