Inorg. Chem. **2004**, *43*, 2213–2219

Carbene Complexes of Rhodium and Iridium from Tripodal N-Heterocyclic Carbene Ligands: Synthesis and Catalytic Properties

Elena Mas-Marzá,[†] Macarena Poyatos,[†] Mercedes Sanaú,[‡] and Eduardo Peris*[,†]

Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, Avenida Sos Baynat s/n 12071 Castellón, Spain, and Departamento de Química Inorgánica, Universidad de Valencia, Avenida Dr. Moliner s/n 46100-Burjassot (Valencia), Spain

Received November 14, 2003

Two tripodal trisimidazolium ligand precursors have been tested in the synthesis of new N-heterocyclic carbene rhodium and iridium complexes. [Tris(3-methylbenzimidazolium-1-yl)]methane sulfate gave products with coordination of the decomposed precursor. [1,1,1-Tris(3-butylimidazolium-1-yl)methyl]ethane trichloride ($TIMEH_3^{Bu}$) coordinated to the metal in a chelate and bridged-chelate form, depending on the reaction conditions. The crystal structures of two of the products are described. The compounds resulting from the coordination with $TIME^{Bu}$ were tested in the catalytic hydrosilylation of terminal alkynes.

Introduction

N-Heterocyclic carbenes have emerged as promising materials for the design of new homogeneous catalysts.[1] The possibility of predetermining the structure and chemical properties of a metal complex has been the main driving force in the design of new ligand systems. Carbene ligand precursors are easy to prepare, and their chemical and topological versatility affords the preparation of a wide variety of complexes whose chemical properties can be easily modulated. However, coordination of the carbene precursors to transition metals can be difficult, but over the past years many methods of activating and coordinating such precursors have been developed (deprotonation with a weak/strong base,[2−9] transmetalation from a silver complex,[10−14] C−H oxidative addition to a low valent metal complex,[15−17] etc.).

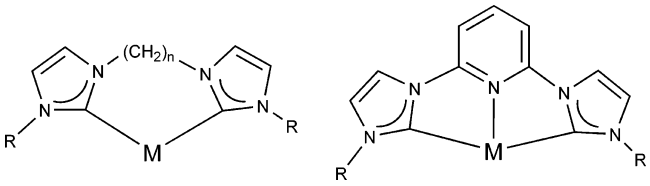
Bis- and polycarbene ligands have also attracted great attention recently. The chelate effect confers the complexes high thermal stability and, as a result, broadens their potential catalytic applications. Most of the polycarbenes reported so far are bidentate (C, C) biscarbene, or pincer (tridentate-mer, C, N, C) ligands (Scheme 1) which were initially coordinated to palladium and subsequently to other Pt-group metals such as Rh,[3,5,6,8,9,15,18] Ru,[2,7] and Ir.[10,15,19,20] The

* Author to whom correspondence should be addressed. Telephone: 34 964728243. Fax: 34 964728214. E-mail: eperis@qio.uji.es.
[†] Universitat Jaume I.
[‡] Universidad de Valencia.

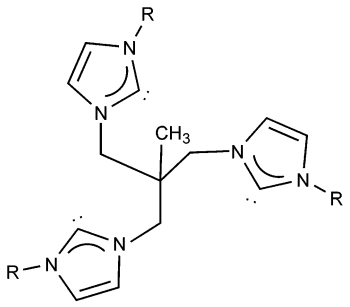
(1) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1291. Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. Crabtree, R. H. *Pure Appl. Chem.* **2003**, *75*, 435. Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913. Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.
(2) Poyatos, M.; Mata, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E. *Organometallics* **2003**, *22*, 1110.
(3) Poyatos, M.; Sanau, M.; Peris, E. *Inorg. Chem.* **2003**, *42*, 2572.
(4) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700.
(5) Poyatos, M.; Mas-Marza, E.; Mata, J. A.; Sanau, M.; Peris, E. *Eur. J. Inorg. Chem.* **2003**, 1215.
(6) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. *Chem. Commun.* **2002**, 32.
(7) Danopoulos, A. A.; Winston, S.; Motherwell, W. B. *Chem. Commun.* **2002**, 1376.
(8) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Chem.—Eur. J.* **1996**, *2*, 772.
(9) Kocher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261.
(10) Chianese, A. R.; Li, X. W.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.
(11) Hu, X. L.; Tang, Y. J.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, *22*, 612.
(12) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2002**, *327*, 116. Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499.
(13) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617*, 546.
(14) Garrison, J. C.; Simons, R. S.; Talley, J. M.; Wesdemiotis, C.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2001**, *20*, 1276. Simons, R. S.; Garrison, J. C.; Kofron, W. G.; Tessier, C. A.; Youngs, W. J. *Tetrahedron Lett.* **2002**, *43*, 3423. Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2003**, *22*, 1979.
(15) Danopoulos, A. A.; Winston, S.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2002**, 3090.
(16) Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274. McGuinness, D. S.; Cavell, K. J.; Yates, B. F.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 8317.
(17) Grundemann, S.; Albrecht, M.; Kovacevic, A.; Faller, J. W.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2163.

10.1021/ic035317p CCC: $27.50
Published on Web 02/24/2004

Scheme 1



Scheme 2

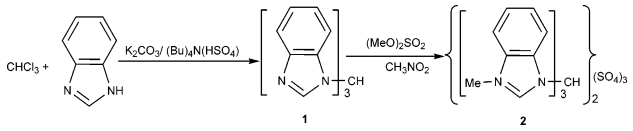


catalytic properties of these metal complexes were explored in a variety of reactions (hydrogen transfer,[2,5,19] alkene oxidation,[2] hydrosilylation,[5,10,17] C−C couplings,[4,13,21] hydroformylation,[18] etc.).

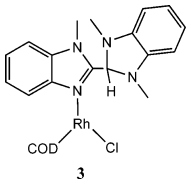
Despite the fact that the number of polyheterocyclic carbenes is continuously increasing, the design of such ligands with a tripodal topology is restricted to a few articles describing their coordination to Fe,[22] Ag,[11] and Tl.[23] Three-coordinated transition metal complexes with nonphosphine tripodal heterocyclic ligands are known to provide interesting chemical and catalytic applications, but most of the ligands reported so far are restricted to N-donor compounds, such as polypyrazolyl borates[24] and triamidoamine[25] ligands.

Meyer et al.[11,26] have recently reported the synthesis of a novel tripodal N-heterocyclic carbene ligand, and its coordination to Ag and Cu afforded a helicoidal 3-fold geometry. We thought that the use of this ligand could be extended to some other metals providing novel catalytic properties (Scheme 2).

Scheme 3



Scheme 4



On the basis of our previous experience, we now report the synthesis and reactivity of new Rh and Ir complexes with [1,1,1-tris(3-butylimidazol-2-ylidene)methyl]ethane ($TIME^{Bu}$). The synthesis of such compounds is performed under very mild conditions affording moderate yields. The crystal structures of two of the rhodium complexes are reported, and the catalytic activity for the homogeneous hydrosilylation of alkynes is also described.

Results and Discussion

In the first stage in the design of new triscarbene tripodal ligands, we synthesized [tris(3-methylbenzimidazolium-1-yl)]methane sulfate, **2**, from the reaction of (trisbenzimidazol-1-yl)methane, **1**,[27] and dimethyl sulfate (Scheme 3). We thought that the ligand precursor **2** met all the topological requirements for coordination in a tridentated tripodal form. The tris(imidazol-1-yl)methane cannot be prepared, for reasons described in the literature.[27]

Based on our experience in preparing Rh chelated N-heterocyclic carbene complexes, we tried to coordinate **2** to $[(COD)RhCl]_2$ [(COD) = 1,5-cyclooctadiene]. This was accomplished by activating the ligand precursor with a weak base such as NaOAc or NEt_3. In all the cases that we tried, the reaction gave mixtures of compounds that were difficult to separate and characterize. From the data that we obtained (NMR spectroscopy of some of the fractions, single crystal X-ray diffraction), we concluded that the ligand precursor is not stable under the reaction conditions used, probably due to a nucleophilic attack on the trisubstituted CH group, which favored the decomposition of the precursor into separated alkyl−benzimidazolyl fragments. The compounds resulting from this reaction were difficult to characterize due to their extremely low yields. Besides, the separation of the reaction products by conventional methods was difficult because we obtained mixtures for which we did not obtain good NMR spectra. However, we were able to unambiguously characterize one of the products (**3**, Scheme 4), whose structure was determined by means of single crystal X-ray crystallography. This compound is obviously produced as a consequence of the coupling of two methyl−benzimidazole fragments. The ^1H NMR spectrum of **3** showed a complicated system with broad signals probably due to a fluxional behavior that is out of the scope of the present work.

(18) Poyatos, M.; Uriz, P.; Mata, J. A.; Claver, C.; Fernandez, E.; Peris, E. *Organometallics* **2003**, *22*, 440.

(19) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596.

(20) Miller, B.; Altman, J.; Leschke, C.; Schunack, W.; Sunkel, K.; Knizek, J.; Noth, H.; Beck, W. *Z. Anorg. Allg. Chem.* **2000**, *626*, 978. Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473.

(21) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741. Schwarz, J.; Bohm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem.—Eur. J.* **2000**, *6*, 1773. Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162. Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93. Bohm, V. P. W.; Gstottmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *595*, 186. Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201.

(22) Kernbach, U.; Ramm, M.; Luger, P.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 310.

(23) Nakai, H.; Tang, Y. J.; Gantzel, P.; Meyer, K. *Chem. Commun.* **2003**, 24.

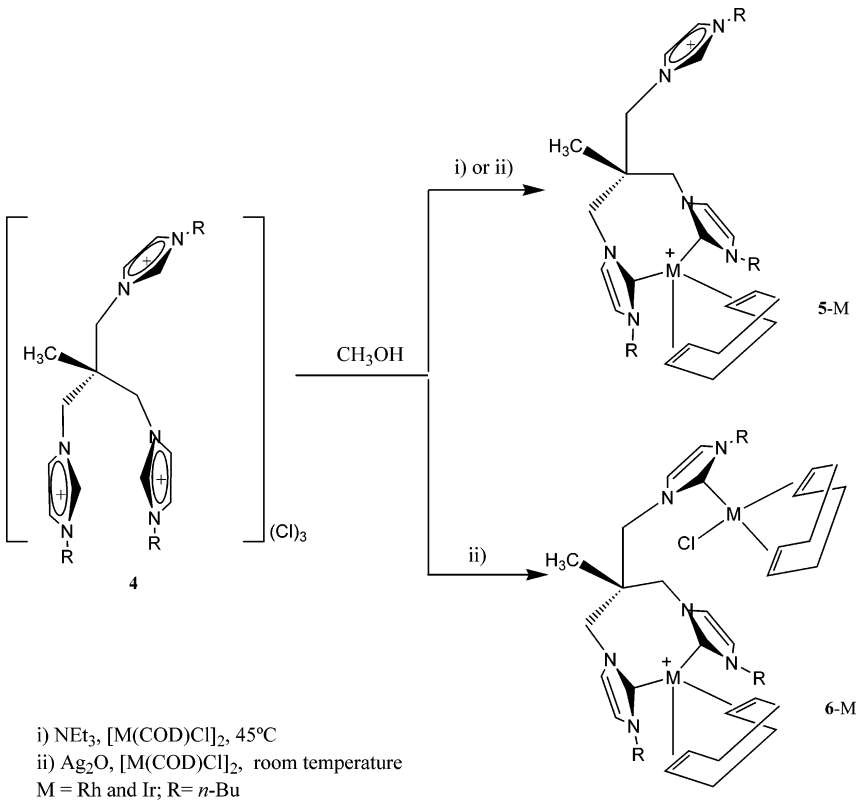
(24) Trofimenko, S. *Scorpionates: The coordination chemistry of polypyrazolylborate ligands*; Imperial College Press: London, 1999.

(25) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9. Gade, L. H. *Acc. Chem. Res.* **2002**, *35*, 575.

(26) Hu, X.; Castro-Rodriguez, I.; Meyer, K. *Organometallics* **2003**, *22*, 3016.

(27) Julia, S.; Delmazo, J. M.; Avila, L.; Elguero, J. *Org. Prep. Proced. Int.* **1984**, *16*, 299.

Scheme 5



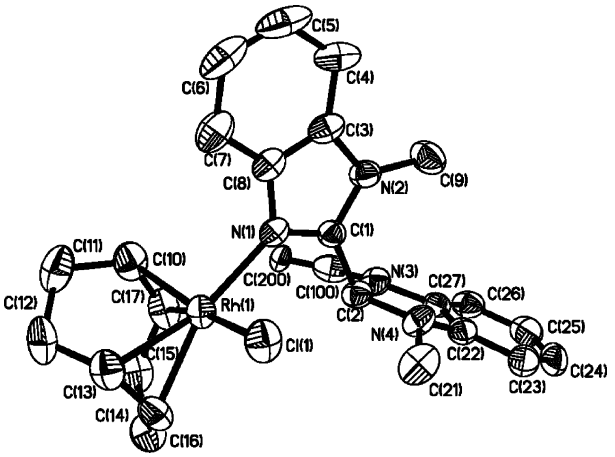


Figure 1. Molecular diagram of compound **3** (50% probability; hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−Cl(1) 2.379(2), Rh(1)−N(1) 2.116(6), C(1)−C(2) 1.515(9), C(1)−N(2) 1.365(9), C(1)−N(1) 1.311(8), C(2)−N(3) 1.480(9), C(2)−N(4) 1.458(9), C(1)−C(2)−N(4) 112.1(6), C(1)−C(2)−N(3) 113.2(6), N(1)−C(1)−C(2) 123.1(6), N(2)−C(1)−C(2) 124.3(6).

Figure 1 shows the molecular structure of **3**. The rhodium atom is surrounded by the ligands in a pseudo-square-planar disposition. The bisheterocyclic ligand is coordinated to the rhodium atom through one nitrogen atom (Rh(1)−N(1) 2.116(6) Å). The C(1)−C(2) distance lies in the range of the single C−C bonds (1.515(9) Å). The C−N distances in the coordinated benzimidazole ring are shorter than the C−N distances in the saturated heterocyclic ring (1.45 vs 1.34 Å, average), and C(2) lies out of the plane of its heterocycle. The angles about C(1) and C(2) confirm the different hybridization for these two atoms (C(1)−C(2)−N(4) 112.1; C(1)−C(2)−N(3) 113.2; N(1)−C(1)−C(2) 123.1; N(2)−C(1)−C(2) 124.3): sp^2 for C(1) and sp^3 for C(2). A chlorine atom and a COD ligand complete the coordination sphere about the rhodium atom. Even though the synthesis of **3** is difficult to explain, we believe that the presence of an sp^3 carbon (C(2), Figure 1) which originally existed as an sp^2 carbon may be due to a migratory insertion of a hydride from a reaction intermediate in the heterocyclic carbene. Danopoulos et al. have observed a similar reaction for the migratory insertion of a methyl group in a heterocyclic carbene of palladium.[28] Attempts to elucidate the reaction mechanism by detection of reaction intermediates preceding the formation of **3** were unsuccessful.

To obtain a more stable ligand capable of coordinating to the metal in a tripodal form, we prepared the precursor [1,1,1-tris(3-butylimidazolium-1-yl)methyl]ethane trichloride, **4**, ($TIMEH_3^{Bu}$ trichloride), from the reaction of 1,3-dichloro-2-(chloromethyl)-2-methylpropane and *N*-butylimidazole. Meyer and co-workers recently made the same precursor, which they coordinated to Ag[11] and Cu.[26] The compound has an advantage over **2** because the three imidazolium rings are coordinated to three different carbon atoms, which lowers the reactivity of the precursor toward nucleophilic attack.

The reaction of **4** with $[(COD)MCl]_2$ (M = Rh, Ir) yielded monometallic and dimetallic species depending on the reaction conditions, as shown in Scheme 5. The reaction products were obtained by two different methods: (i) deprotonation of the ligand precursor with a weak base (NEt_3) and then direct coordination to Rh or Ir, and (ii) transmetalation from a silver carbene intermediate[11] (not isolated) to

(28) Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756.

Rh or Ir. Both reactions were carried out in MeOH. The NEt_3 method is carried out in MeOH at 45 °C for 12 h, and the product is separated from the reaction mixture by column chromatography, yielding **5**-M (M = Rh and Ir) as the only isolable compounds. The silver−transmetalation method is carried out by treating the imidazolium salt **4** with Ag_2O at room temperature in MeOH, to form the corresponding silver−carbene compounds. Silver−carbene complexes of this type are known to have a variety of different structures in the solid state,[10,12,29] and a solution equilibrium between Ag(carbene)X and $Ag(carbene)_2^+$ species has been proposed.[29] We did not isolate the silver−carbene complexes in this reaction, but Hu et al. have reported the crystal structure of one of these compounds with [1,1,1-tris((3-methylimidazol-2-ylidene)methyl)ethane] ($TIME^{Me}$).[11] The reaction of the silver−carbene complexes with $[(COD)MCl]_2$ (M = Rh, Ir) at room temperature yields the desired metal−carbene compounds. This method gives mixtures of **5**-Rh and **6**-Rh, while for the iridium case only **6**-Ir was obtained. The products so obtained were characterized by NMR and mass spectroscopy, and gave satisfactory elemental analyses. Under the reaction conditions used, we did not manage to coordinate the ligand in the tripodal form to only one metal atom.

The ^{1}H NMR spectra of compounds **5**-Rh and **5**-Ir show that two of the imidazolyl fragments of the ligand precursor **4** have coordinated to the metal, as seen from the shift to lower frequencies of the coordinated rings (δ 7.28 and 7.22, **5**-Rh; 7.35 and 7.30, **5**-Ir) compared to the uncoordinated ring (δ 8.00 and 7.92, **5**-Rh; 7.99 and 7.97, **5**-Ir). The NC(*H*)N hydrogen atom of the unmetalated ring appears as a singlet at δ 9.28 (**5**-Rh) and 9.54 (**5**-Ir). Both ^{1}H and ^{13}C NMR spectra show that the ligand is coordinated in a 2-fold symmetry, as seen from the equivalent signals due to the coordinated imidazolium rings. The ^{13}C NMR spectra confirms the metalation of the ligand with signals due to the metalated carbon atoms at δ 181.80 (**5**-Rh) and 177.45 (**5**-Ir), which in the case of **5**-Rh appears as a doublet ($^1J_{C-Rh}$ = 52.9 Hz).

Compound **6**-Rh shows six sets of signals for the three imidazolylidene rings in the ^{1}H NMR spectrum (δ 7.78−6.63), four of them corresponding to the biscarbene−metal fragment (δ 7.21−6.63) and two to the monocarbene−metal fragment (δ 7.78−7.52). The same pattern is observed for **6**-Ir with six signals between δ 7.51 and 7.18. The metalation of the ligand is confirmed by the ^{13}C NMR spectra, which displays two signals with a 2:1 ratio at δ 181.9 ($^1J_{C-Rh}$ = 52.7 Hz) and 181.7 ($^1J_{C-Rh}$ = 51.9 Hz). **6**-Ir shows the two metalated signals (2:1 ratio) at δ 179.82 and 177.81. The dinuclear nature of the compounds was confirmed by mass spectrometry and elemental analysis.

Slow evaporation of a MeOH/CH_2Cl_2 solution of **5**-Rh yielded crystals suitable for single crystal X-ray diffraction. The molecular structure of **5**-Rh confirms the pseudo-square-planar coordination of the Rh atom (Figure 2). The carbene ligand is chelating, with a bite angle of 82.1(8)°, considerably

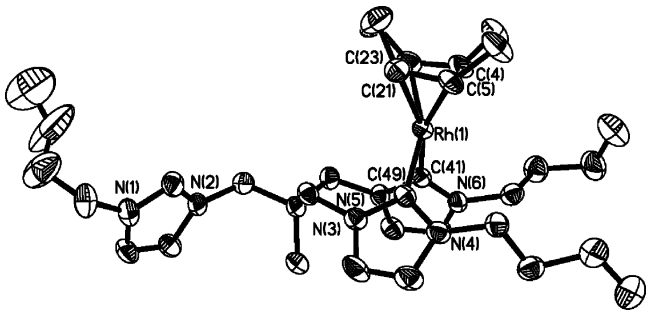


Figure 2. Molecular diagram of compound $[(COD)Rh(TIME^{Bu}H)](PF_6)_2$, **5**-Rh (30% probability, hydrogen atoms and PF_6 have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−C(49) 2.02(2), Rh(1)−C(41) 2.08(3), C(49)−Rh(1)−C(41) 82.1(8).

smaller than that shown for our previously reported biscarbene Rh complexes.[3,6] The Rh−C distances (2.02−2.08 Å) are in the range of other reported complexes, and typical for Rh−C σ bond with very little back-donation. The third butyl−imidazolium−ethylene leg is pointing out of the Rh coordination plane. The two coordinated imidazolylidene rings lie perpendicular to the molecular plane, with a relative angle of 75.73°. The coordination sphere of the Rh atom is completed by the COD ligand, with Rh−C distances in the normal range.

Catalytic Hydrosilylation. Hydrosilylation of multiple bonds represents a useful class of catalytic processes to functionalize organic molecules. Vinylsilanes, widely used as intermediates for organic synthesis, could be efficiently prepared by transition metal catalyzed addition of silanes to alkynes. Most of the recent efforts in the study of catalytic hydrosilylation concern the design of new and efficient catalysts, which enable the preparation of both (*Z*)- and (*E*)-alkenylsilanes independently.[30−32] For this reason, the number of works regarding mechanistic studies in order to rationalize the factors affecting the selectivity of this reaction has increased in the past few years.[30,32,33] In view of the compounds that we report in the present paper, we thought that catalytic hydrosilylation would be a good test of the catalytic potential of these new complexes. Our Rh(I) and Ir(I) complexes display all the structural and chemical requirements for this catalytic system and could shed some light on the reaction process.

To test the catalytic activity of our compounds in hydrosilylation of alkynes, we decided to use phenylacetylene and 1-hexyne as terminal alkynes and dimethylphenylsilane. This combination of reactants is normally used as standard in the determination of the activity of potential catalysts. All the reactions were carried out without any special attention to

(29) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

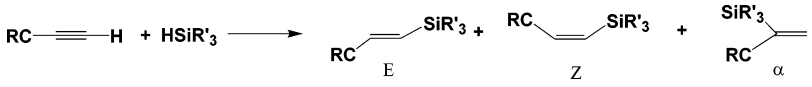
(30) Faller, J. W.; D'Alliessi, D. G. *Organometallics* **2002**, *21*, 1743.

(31) Isobe, M.; Nishizawa, R.; Nishikawa, T.; Yoza, K. *Tetrahedron Lett.* **1999**, *40*, 6927. Dash, A. K.; Gourevich, I.; Wang, J. Q.; Wang, J. X.; Kapon, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5084. Itami, K.; Mitsudo, K.; Nishino, A.; Yoshida, J. *J. Org. Chem.* **2002**, *67*, 2645.

(32) Cervantes, J.; Gonzalez-Alatorre, G.; Rohack, D.; Pannell, K. H. *Appl. Organomet. Chem.* **2000**, *14*, 146. Katayama, H.; Taniguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, *645*, 192.

(33) Maruyama, Y.; Yamamura, K.; Sagawa, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 1308. Jun, C. H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

Table 1. Hydrosilylation of Alkynes[a]



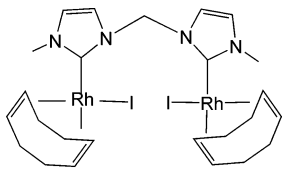
entry	RC≡CH	% catalyst	catalyst	*T* (°C)	time (h)	*E*/Z/α	yield (%)
1	PhC≡CH	0.1	**5**-Rh	60	12	25/56/19	55
2	PhC≡CH	0.1	**5**-Rh	60	72	38/47/15	99
3	^{n}BuC≡CH	0.1	**5**-Rh	60	12	41/40/19	35
4	^{n}BuC≡CH	0.1	**5**-Rh	60	72	18/75/7	65
5	PhC≡CH	0.1	**5**-Ir	60	72		0
6	^{n}BuC≡CH	0.1	**5**-Ir	60	72	29/55/16	7
7	PhC≡CH	0.1	**6**-Rh	60	24	16/67/17	96
8	PhC≡CH	0.1	**6**-Rh	60	72	36/47/17	>99
9	^{n}BuC≡CH	0.1	**6**-Rh	60	24	18/62/20	50
10	^{n}BuC≡CH	0.1	**6**-Rh	60	72	21/50/30	80
11	PhC≡CH	0.1	**6**-Ir	60	24	37/46/17	12
12	PhC≡CH	0.1	**6**-Ir	60	72	30/51/25	12
13	^{n}BuC≡CH	0.1	**6**-Ir	60	24	29/51/20	44
14	^{n}BuC≡CH	0.1	**6**-Ir	60	72	24/57/19	46
15	PhC≡CH	0.1	**7**-Rh	60	6	21/66/13	96
16	PhC≡CH	0.1	**7**-Rh	60	24	28/65/7	>99
17	^{n}BuC≡CH	0.1	**7**-Rh	60	24	21/67/12	80
18	^{n}BuC≡CH	0.1	**7**-Rh	60	72	21/62/17	>99
19	PhC≡CH	0.1	**7**-Rh	25	24	20/66/14	50
20	PhC≡CH	0.1	**7**-Rh	25	48	7/89/4	70
21	PhC≡CH	0.1	**7**-Rh	25	96	12/82/6	>99
22	^{n}BuC≡CH	0.1	**7**-Rh	25	24	5/93/2	13
23	^{n}BuC≡CH	0.1	**7**-Rh	25	48	26/61/13	40
24	^{n}BuC≡CH	0.1	**7**-Rh	25	96	21/70/9	60
25	PhC≡CH	1	**7**-Rh	25	24	15/80/5	>99
26	^{n}BuC≡CH	1	**7**-Rh	25	24	30/59/11	55
27	^{n}BuC≡CH	1	**7**-Rh	25	48	11/80/9	65
28	^{n}BuC≡CH	1	**7**-Rh	25	72	22/70/8	>99

[a] Conditions: 0.077 mmol of alkyne; 0.085 mmol of silane $HSiMe_2Ph$. Reactions carried out in $CDCl_3$. Yields determined by ^1H NMR.

keep inert conditions, since the catalysts used proved to be fairly stable under oxygen-containing atmospheres, even at high temperatures. The reactions were carried out at 60 °C in NMR tubes using $CDCl_3$ as solvent, with 0.1% mol catalyst loadings. All the catalysts used give a mixture of the *β-E*- and *β-Z*- and α-isomers, although the *β-Z* seems to be preferred in all cases. In most metal-catalyzed hydrosilylations, the regioselectivity is capriciously affected by factors such as types of alkynes and silanes, catalyst, solvent, or temperature. However, it has been reported that cationic Rh complexes catalyze the hydrosilylation of alkynes to give *β-E*-vinylsilanes as the major products, while neutral Rh complexes showed a higher preference to yield the *β-Z* ones.[30,34] For our cationic complexes, we observed the opposite tendency.

From the data shown in Table 1, we can see that the Rh catalysts are much more active than the analogous Ir ones. Dimetallic complexes **6**-Rh and **6**-Ir are far more active than the monometallic **5**-Rh and **5**-Ir species, probably due to the fact that the latter cationic compounds have shown some propensity toward oxidation to the corresponding M(III) species, this preventing the silane from oxidatively adding to the metal in the catalytic cycle. With this in mind, we thought that the "neutral" metal fragment in the dimetallic compounds **6**-M should be responsible for the main catalytic activity of such complexes. To confirm this point, we decided

Scheme 6



7-Rh

to test compound **7**-Rh (Scheme 6), a dimetallic neutral complex previously reported by us[3] and Herrmann,[9] which we thought possessed the electronic and geometric requirements to be compared to compounds **5**-Rh and **6**-Rh.

As seen in Table 1, the catalytic activity of **7**-Rh is much higher than that shown for the related compounds **5**-Rh and **6**-Rh. We believe that this observation is due to the fact that **7**-Rh can be more readily oxidized to Rh(III) species than **5**-Rh and **6**-Rh,[3] thus facilitating the catalytic cycle to proceed via oxidative addition of the silane. Isomer *β-Z* continues to be the preferred one for this catalyst, although the selectivity is still low. The catalytic activity of **7**-Rh is high even at room temperature (entries 19−28). Catalyst loadings of 1% gave quantitative conversions after 24 h for the hydrosilylation of phenylacetylene and after 72 h for 1-hexyne, while loadings of 0.1% needed longer reaction times.

Conclusions

We have used two trisimidazolium carbene ligand precursors to obtain new Rh and Ir complexes. [Tris(3-methylbenzimidazolium-1-yl)]methane sulfate is not stable under the

(34) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Chem. Soc., Chem. Commun.* **1994**, 1777. Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443. Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045.

reaction conditions used, and the only metal complex that we could isolate and characterize showed the coupling of two benzimidazolyl fragments. To obtain a more stable ligand that could coordinate to the metal in a tripodal form, we synthesized the precursor [1,1,1-tris(3-butylimidazolium-1-yl)methyl]ethane trichloride, **4** ($TIMEH_3^{Bu}$ trichloride), which we coordinated to Rh and Ir. The ligand failed to coordinate in a tridentated tripodal form, probably due to steric reasons. The two different coordinations of this ligand show that it binds to the metal in a bidentate form (compounds **5**-Rh and **5**-Ir), and in a bridged-tridentate form (bimetallic complexes **6**-Rh and **6**-Ir). The new compounds obtained were tested in the homogeneous catalytic hydrosilylation of terminal alkynes and compared with a related neutral complex, **7**-Rh, which was recently described in our group. The catalytic results show that all Rh complexes are far more active than the analogous Ir ones, but in any case all our new complexes show lower catalytic activity than **7**-Rh. We believe that this fact is due to the chemical inertness that **5** and **6** show toward oxidation to the M(III) species, compared to **7**-Rh, for which the Rh(III) counterpart is easily obtained and has been described.[3] Oxidative addition of the silane to the metal complex may be the rate-dependent step in the hydrosilylation of the alkynes.

Experimental Section

General Methods. The ligand precursor **1**[27] and compound **7**-Rh[3] were prepared according to literature methods. All subsequent syntheses were performed in air using reagent grade solvents, which were used as received. All other reagents are commercially available and were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 300 and 500 MHz spectrometers, using $CDCl_3$ and DMSO-d_6 as solvents.

Synthesis of [Tris(3-methylbenzimidazolium-1-yl)]methane Sulfate, 2. Dimethyl sulfate (1.56 mL, 16.5 mmol) was added to a solution of **1** (1.00 g, 2.7 mmol) in 10 mL of nitromethane. The mixture was stirred at room temperature for 24 h, until a white solid appeared. The solid was isolated by filtration and washed with nitromethane (2 × 3 mL) and then with ether (5 mL). Yield: 1.35 g (93%). ^{1}H NMR (DMSO-d_6, 500 MHz): 10.68 (s, 1H, CH), 10.14 (s, 3H, NC*H*N), 8.26 (d, $^2J_{H-H}$ = 8.0 Hz, 3H, benzimidazole-H), 7.93 (d, $^2J_{H-H}$ = 8.5 Hz, 3H, benzimidazole-H), 7.88 (t, 3H, benzimidazole-H), 7.79 (t, 3H, benzimidazole-H), 4.17 (s, 9H, CH_3). Anal. Calcd for $C_{50}H_{50}N_{12}S_3O_{12}$ (1007.20): C, 54.24; H, 4.55; N, 15.18. Found: C, 54.29; H, 4.60; N, 15.20.

Synthesis of [1,1,1-Tris(3-butylimidazol-1-yl)methyl]ethane Trichloride, $[TIMEH_3^{Bu}]Cl_3$, 4. A mixture of 1,3-dichloro-2-(chloromethyl)-2-methylpropane (0.60 mL, 4.3 mmol), *N*-butylimidazole (1.70 mL, 13.1 mmol), and tetrabutylammonium bromide (TBAB) (150 mg) was heated at 170 °C for 24 h in a sealed tube. The white solid so obtained was then washed with CH_2Cl_2 to remove the TBAB and dried in vacuo. Yield: 2.1 g (88%). ^{1}H NMR (DMSO-d_6, 300 MHz): 9.77 (s, 3H, NC*H*N), 7.96 (s, 3H, imidazole-*H*), 7.92 (s, 3H, imidazole-*H*), 4.48 (s, 6H, CH_2-N), 4.22 (t, 6H, NCH_2CH$_2$CH$_2$CH$_3$), 1.81 (q, 6H, NCH$_2$CH_2CH$_2$CH$_3$), 1.26 (m, 6H, NCH$_2$CH$_2$CH_2CH$_3$), 0.99 (s, 3H, CH_3-N), 0.89 (t, 9H, NCH$_2$CH$_2$CH$_2$CH_3). Anal. Calcd for $C_{26}H_{45}N_6Cl_3$ (548.03): C, 56.98; H, 8.28; N, 15.33. Found: C, 57.08; H, 8.25; N, 15.38.

Synthesis of 3. A mixture of $[(COD)RhCl]_2$ (163 mg, 0.33 mmol), **2** (350 mg, 0.33 mmol), and NEt_3 (0.5 mL, 3.5 mmol) was refluxed for 12 h in 10 mL of CH_3CN. The solvent was eliminated under vacuum. The crude solid was redissolved in CH_2Cl_2, and the solution was transferred to a chromatography column. Elution with CH_2Cl_2 separated a yellow band that contained $[(COD)RhCl]_2$. Further elution with gradient CH_2Cl_2/acetone (10/1) afforded the separation of an orange-yellow band that contained **3**. The product is precipitated with CH_2Cl_2/ether. Further elution with gradient CH_2Cl_2/acetone afforded the separation of three minor bands that we were unable to characterize. The ^{1}H NMR spectrum of **3** showed a complicated system with broad signals that we were not able to assign. The NMR spectra did not improve, even after recrystallizing **3** in a CH_2Cl_2/MeOH mixture, which afforded single crystals. Compound **3**, yield: 18 mg (5%). Anal. Calcd for $C_{25}H_{30}N_4ClRh$ (524.89): C, 57.21; H, 5.76; N, 10.67. Found: C, 57.25; H, 5.82; N, 10.58.

Synthesis of $[(COD)Rh(TIME^{Bu}H)](PF_6)_2$, 5-Rh. A mixture of $[(COD)RhCl]_2$ (100 mg, 0.20 mmol), **4** (222 mg, 0.41 mmol), and NEt_3 (0.5 mL, 3.5 mmol) was heated at 45 °C for 12 h in CH_3OH. The solvent was eliminated under vacuum. The crude solid was redissolved in CH_2Cl_2 and the solution was transferred to a chromatography column. Elution with CH_2Cl_2 separated a minor yellow band that contained $[(COD)RhCl]_2$. Further elution with gradient CH_2Cl_2/CH_3OH (10/1) and KPF_6 afforded the separation of a major yellow band that contained **5**-Rh. The product was precipitated with CH_2Cl_2/ether. Yield: 153 mg (40%). ^{1}H NMR (DMSO-d_6, 500 MHz) (COD and *n*-Bu signals omitted): 9.28 (s, 1H, NC*H*N), 8.00 (s, 1H, imid-H), 7.92 (s, 1H, imid-H), 7.28 (s, 2H, imid-H), 7.22 (s, 2H, imid-H), 4.78 (d, $^2J_{H-H}$ = 14.5 Hz, 2H, CH_2), 4.46 (s, 2H, CH_2), 4.15 (d, $^2J_{H-H}$ = 14.5 Hz, 2H, CH_2), 0.76 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (DMSO-d_6, 300 MHz) (COD and *n*-Bu signals omitted): 181.80 (d,$^1J_{C-Rh}$ = 52.9 Hz, C−Rh), 138.18 (s, imid), 125.54 (s, imid), 125.02 (s, imid), 123.35 (s, imid), 120.91 (s, imid), 57.25 (s, *C*-CH_3). Anal. Calcd for $C_{34}H_{55}F_{12}N_6P_2Rh$ (940.67): C, 43.41; H, 5.89; N, 8.93. Found: C, 43.49; H, 5.88; N, 8.95. Electrospray MS. Cone 30 V. *m*/*z* (fragment): 795 [M$^\bullet$ PF_6]$^+$.

Synthesis of $[(COD)Ir(TIME^{Bu}H)](PF_6)_2$, 5-Ir. A mixture of $[(COD)IrCl]_2$ (100 mg, 0.15 mmol), **4** (163 mg, 0.30 mmol), and NEt_3 (0.5 mL, 3.5 mmol) was heated at 45 °C for 12 h in CH_3OH. The solvent was eliminated under vacuum. The crude solid was redissolved in CH_2Cl_2 and the solution was transferred to a chromatography column. Elution with CH_2Cl_2/acetone separated a minor yellow band that was discarded. Further elution with gradient CH_2Cl_2/CH_3OH (10/1) and KPF_6, afforded the separation of a major orange band that contained **5**-Ir. The product was precipitated with CH_2Cl_2/ether. Yield: 169 mg (55%). ^{1}H NMR (DMSO-d_6, 300 MHz) (COD and *n*-Bu signals omitted): 9.54 (s, 1H, NC*H*N), 7.99 (s, 1H, imid-H), 7.97 (s, 1H, imid-H), 7.35 (s, 2H, imid-H), 7.30 (s, 2H, imid-H), 4.52 (b, 2H, CH_2), 4.30 (s, 2H, CH_2), 4.25 (b, 2H, CH_2), 0.73 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (DMSO-d_6, 300 MHz) (COD and *n*-Bu signals omitted): 177.45 (s, C−Ir), 138.25 (s, imid), 125.30 (s, imid), 124.86 (s, imid), 123.38 (s, imid), 120.67 (s, imid), 58.18 (s, *C*-CH_3). Anal. Calcd for $C_{34}H_{55}F_{12}N_6P_2Ir$ (1029.99): C, 39.65; H, 5.38; N, 8.16. Found: C, 40.07; H, 5.29; N, 8.25. Electrospray MS. Cone 30 V. *m*/*z* (fragment): 886 [M$^\bullet$ PF_6]$^+$, 740 [M − H] $^+$.

Synthesis of $[(COD)_2Rh_2(TIME^{Bu})Cl]Cl$, 6-Rh. Ag_2O (141 mg, 0.61 mmol) and **4** (222 mg, 0.41 mmol) were combined in CH_3OH (10 mL), stirred at room temperature for 90 min, and filtered through Celite. Then $[(COD)RhCl]_2$ (200 mg, 0.41 mmol) was added; the mixture was stirred at room temperature for 90 min and filtered through Celite. The solvent was eliminated under vacuum. The crude solid was redissolved in CH_2Cl_2 and the solution was

transferred to a chromatography column. Elution with CH_2Cl_2/acetone (10/1) separated a minor yellow band that was discarded. Elution with gradient CH_2Cl_2/CH_3OH (10/1) afforded the separation of a major yellow band that contained **6**-Rh. The product was precipitated with CH_2Cl_2/hexane. Further elution with gradient CH_2Cl_2/CH_3OH (10/1) and KPF_6 afforded the separation of a minor yellow band that contained **5**-Rh (yield: 12%). Yield of **6**-Rh: 227 mg (60%). ^{1}H NMR ($CDCl_3$, 300 MHz) (COD and *n*-Bu signals omitted): 7.78 (d, 1H, $^2J_{H-H}$ = 1.50 Hz, imid-H), 7.52 (d, 1H, $^2J_{H-H}$ = 1.53 Hz, imid-H), 7.21 (d, 1H, $^2J_{H-H}$ = 1.52 Hz, imid-H), 6.89 (d, 1H, $^2J_{H-H}$ = 1.50 Hz, imid-H), 6.70 (d, 1H, $^2J_{H-H}$ = 1.52 Hz, imid-H), 6.63 (d, 1H, $^2J_{H-H}$ = 1.53 Hz, imid-H), 5.43 (d, $^2J_{H-H}$ = 14.5 Hz, 2H, CH_2), 5.27 (s, 2H, CH_2), 5.12 (d, $^2J_{H-H}$ = 14.5 Hz, 2H, CH_2), 0.90 (s, 3H, CH_3). ^{13}C {^{1}H} NMR ($CDCl_3$, 300 MHz) (COD and *n*-Bu signals omitted): 181.9 (d, $^1J_{Rh-C}$ = 52.7 Hz, 2C, C−Rh), 181.7 (d, $^1J_{C-Rh}$ = 51.9 Hz, 1C, C−Rh), 126.50 (s, imid), 126.18 (s, imid), 125.40 (s, imid), 120.03 (s, imid), 118.72 (s, imid), 118.56 (s, imid), 58.32 (s, *C*-CH_3). Anal. Calcd for $C_{42}H_{66}Rh_2N_6Cl_2$ (931.73): C, 54.14; H, 7.14; N, 9.02. Found: C, 54.20; H, 7.10; N, 9.05. Electrospray MS. Cone 40 V. *m*/*z* (fragment): 895 $[M]^+$.

Synthesis of [(COD)$_2$Ir$_2$(TIME^{Bu})Cl]Cl, 6-Ir. Ag_2O (103 mg, 0.44 mmol) and **4** (163 mg, 0.30 mmol) were combined in CH_3OH (10 mL), stirred at room temperature for 90 min, and filtered through Celite. Then $[(COD)IrCl]_2$ (200 mg, 0.30 mmol) was added; the mixture was stirred at room temperature for 90 min and filtered through Celite. The solvent was eliminated under vacuum. The crude solid was redissolved in CH_2Cl_2 and the solution was transferred to a chromatography column. Elution with CH_2Cl_2/acetone (10/1) separated a minor yellow band that was discarded. Further elution with gradient CH_2Cl_2/CH_3OH (10/1) afforded the separation of a major orange band that contained **6**-Ir. The product was precipitated with CH_2Cl_2/hexane. Yield: 215 mg (65%). ^{1}H NMR (DMSO-d_6, 500 MHz) (COD and *n*-Bu signals omitted): 7.51 (s, 1H, imid-H), 7.50 (s, 1H, imid-H), 7.32 (s, 1H, imid-H), 7.30 (s, 1H, imid-H), 7.27 (s, 1H, imid-H), 7.18 (s, 1H, imid-H), 4.97 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, CH_2), 4.83 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, CH_2), 4.55 (m, 2H, CH_2), 0.81 (s, 3H, CH_3). ^{13}C {^{1}H} NMR ($CDCl_3$, 500 MHz) (COD and *n*-Bu signals omitted): 179.82 (s, 1C, C−Ir), 177.81 (s, 2C, C−Ir), 126.10 (s, imid), 125.84 (s, imid), 124.94 (s, imid), 119.89 (s, imid), 118.45 (s, imid), 118.30 (s, imid), 57.95 (s, *C*-CH_3). Anal. Calcd for $C_{42}H_{66}Ir_2N_6Cl_2$ (1110.40): C, 45.43; H, 5.99; N, 7.57. Found: C, 45.40; H, 6.03; N, 7.62. Electrospray MS. Cone 40 V. *m*/*z* (fragment): 1076 $[M]^+$.

Hydrosilylation of 1-Alkynes with Silanes. General Procedure. A typical procedure was performed as follows. In a 5 mm NMR tube, ^{n}BuC≡CH or PhC≡CH (0.077 mmol), silane ($HSiMe_2$-Ph, 0.085 mmol), and a catalytic amount of **5**-Rh, **5**-Ir, **6**-Rh, **6**-Rh, and **7**-Rh (1 mol %, 7.7×10^{-5} mmol; 0.1 mol %, 7.7×10^{-6} mmol) were dissolved in $CDCl_3$ (0.5 mL). The mixture was kept at 60 °C by immersion in a hot oil bath. The progress of the reaction was monitored by ^{1}H NMR, according to the data of the products obtained from the literature.[34]

X-ray Diffraction Studies. Single crystals of **3** and **5**-Rh were mounted on a glass fiber in a random orientation. Crystal data are summarized in Table 2. Data collection was performed at room temperature (298 K) on a Siemens Smart CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was collected based on three ω-scan runs (starting $\omega = -28°$) at values $\phi = 0°$, 90°, and 180° with the detector at $2\theta = 28°$. At each of these runs, frames (606, 435, and 230) were collected at 0.3° intervals and 30 s per frame. Space group assignment was based on systematic absences, *E* statistics, and successful refinement of the structures. The structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package.[35] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 2. The diffraction frames were integrated using the SAINT[36] package.

Table 2. Crystallographic Data

	5-Rh	**3**
empirical formula	$C_{34}H_{55}F_{12}N_6P_2Rh$	$C_{25}H_{30}ClN_4Rh$
formula weight	940.69	524.89
wavelength (Å)	0.710 73	0.710 73
crystal system	monoclinic	monoclinic
space group	Cc	*P*2(1)/*c*
a (Å)	33.544(7)	8.041(2)
b (Å)	10.027(2)	18.474(5)
c (Å)	28.873(6)	15.849(4)
α (deg)	90.00	90.00
β (deg)	120.20(3)	100.248(6)
γ (deg)	90.00	90.00
V (Å)^3	839(3)	2316.8(11)
Z	8	4
density (calcd) (Mg/m^3)	1.483	1.505
abs coeff (mm^{-1})	0.569	0.872
reflns collected	29 035	18 589
goodness-of-fit on F^2	0.955	1.042
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0867	R1 = 0.0799
	wR2 = 0.3230	wR2 = 0.2606

Electrospray Mass Spectrometry. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument using CH_2Cl_2:CH_3CN (1:1) as the mobile phase solvent. Nitrogen was employed as drying and nebulizing gas. Isotope experimental patterns were compared with theoretical patterns obtained using the Masslynx 3.5 program. In all cases there was good agreement between the experimental and calculated isotopic mass distributions.

Acknowledgment. We gratefully acknowledge financial support from the DGESIC (MAT2002-04421-C02-01) and Bancaixa (P1.1B2001-03) for financial support. We also thank the Spanish MECD for a fellowship (E.M.). We also thank Cristian Vicent from the SCIC-UJI for his helpful comments in the interpretation of the ESI spectra.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035317P

(35) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker AXS, Inc.: Madison, WI, 1997.
(36) *SAINT*, version 5.0; Bruker Analytical X-ray Systems: Madison, WI, 1998.