

ORGANOMETALLICS

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Unidos en Excelencia: GEQO & Organometallics

30 Years of Excellence

XXX
REUNIÓN
GEQO
Castellón 2012



University of Zaragoza (1973)



Organometallics Founding Editor
Dietmar Seyferth (1953)



Organometallics Founding Editor
Dietmar Seyferth and Current
Editor John A. Gladysz (2010)



XXVI-GEQO (2008)



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ORGANOMETALLICS

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Vicente, José, 1997-1999
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Otero, Antonio, 2000-2002
Esteruelas, Miguel A., 2003-2005
Gimeno, José, 2005-2007
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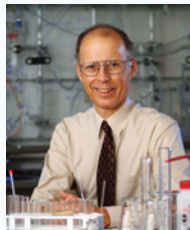
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FROM THE EDITOR:

Dear Friends and Colleagues in the Spanish Organometallic Community,



On behalf of all past and present Editors of *Organometallics*, it is a pleasure to extend a special thanks to our many authors in Spain for their support of the journal over the last thirty years. There has been no other country that has matched the dedication of the Spanish community, and we owe much of our success to you. We very much hope that our bonds to the next generation of organometallic chemists in Spain will be as strong and long lasting.

Organometallics has published 1,495 articles from Spain since the journal was founded in 1982 with Dietmar Seyferth as Editor-in-Chief. In 2011 alone, the first year of my Editorship, we published 80 articles from Spain.

In this context, there are many individuals to thank. First, we would like to recognize the many Spanish chemists who have served on our Advisory Board. Their names and terms are listed at left. Second, we are grateful not only to the corresponding authors, but the entire team of coauthors. Third, some of our most thorough and incisive reviewers hail from Spain; these are the “unsung heroes” of our publishing enterprise.

Obviously, *Organometallics* has an interest in the continued prosperity of organometallic chemistry in Spain. Constructive pressure is needed on granting agencies and funding sources in all countries. Towards this end, we hope to make the recently published “*Organometallics* Roundtable”¹ a regular biennial feature. Sadly, we do not have a travel budget for the panelists. However, we would welcome a delegate from the Spanish community when the next Roundtable is held at the fall 2013 ACS meeting (Indianapolis, 8-13 September).

In a similar vein, *Organometallics* now profiles individuals who have received awards for research in organometallic chemistry from societies and organizations world-wide. Please inform us immediately when a colleague from the Spanish community is recognized. This reflects just one facet of our desire to be as international a journal as possible. For example, 41 of our current 51 Board members (80%) come from outside of North America. Furthermore, we will hold our first advisory board meeting outside of North America later this year, in conjunction with the XXVth International Conference on Organometallic Chemistry in Lisbon (2-7 September).

In conclusion, we would like to congratulate the Spanish Organometallic Chemistry Group (GEQO) on the occasion of their 30th anniversary and 30th meeting, as measured from their initial June 1982 gathering—an event that closely corresponds to the founding date of this journal. The entire international community eagerly awaits more fantastic chemistry from your ranks, and we wish you the best success and prosperity for the next thirty years.

John A. Gladysz
Editor-in-Chief, *Organometallics*

¹ Gladysz, J. A.; Ball, Z. T.; Bertrand, G.; Blum, S. A.; Dong, V. M.; Dorta, R.; Hahn, F. E.; Humphrey, M. G.; Jones, W. D.; Klosin, J.; Manners, I.; Marks, T. J.; Mayer, J. M.; Rieger, B.; Ritter, J.; Sattelberger, A. P.; Schomaker, J. M.; Yam, V. W. W. *Organometallics* 2012, 31 (1), pp 1-18

Spanish Organometallic Pioneers: The First Papers Published in the Journal from Spanish Researchers

Synthesis and Reactivity of Anionic Mono- and Binuclear Pentachlorophenyl Complexes of Palladium(II) and Platinum(II)

Rafael Usón, Juan Forniés, Francisco Martínez, Milagros Tomás, Inmaculada Reoyo

Organometallics, 1983, 2 (10), pp 1386–1390

DOI: 10.1021/om50004a023

Publication Date: October 1983

Department of Inorganic Chemistry, University of Zaragoza, Zaragoza, Spain

Study of the reactivity of [Fe₂(CO)₆(μ-CO)(μ-CPhCPhH)]- toward the MeOC(O)C.tplbond.CC(O)OMe and CF₃C.tplbond.CCF₃ alkynes. Crystal structure of the products resulting from two different modes of combination of the alkynes with the bridging ligands [Fe₂(CO)₆(μ-C(C(O)OMe)C(C(O)OMe)C(O)CPhCPhH)]- and [Fe₂(CO)₆(μ-CPhCPhC(CF₃)C(CF₃H))]-

Josep Ros, Xavier Solans, Manuel Font-Altava, Rene Mathieu

Organometallics, 1984, 3 (7), pp 1014–1020

DOI: 10.1021/om00085a009

Publication Date: July 1984

Laboratoire de Chimie de Coordination du CNRS, 31400 Toulouse, France, and Departamento de Cristalografía y Mineralogía Universitat de Barcelona, Barcelona 7, Spain

Synthesis and reactivity of (chlorovinyl)nickel complexes: an unusual symmetrization reaction. X-ray crystal structure of [Ni(CCl:CCl₂)₂(PMe₂Ph)₂]

Jorge Carvajal, Guillermo Muller, Joaquim Sales, Xavier Solans, Carles Miravittles

Organometallics, 1984, 3 (7), pp 996–1002

DOI: 10.1021/om00085a006

Publication Date: July 1984

Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Barcelona 28, Spain
Xavier Solans, Departament de Cristallografia i Mineralogía, Facultat de Geologia, Universitat de Barcelona, Barcelona, 7, Spain
Carles Miravittles, Institut "Jaume Almera " de Geologia (C.S. IC), Barcelona 28, Spain

Alkyne insertion reactions in nickel acyl complexes. Occurrence of a 1,2-trimethylphosphine shift and the x-ray structures of [cyclic] Ni[C(Ph):C(H)(COCH₂SiMe₃)]Cl(PMe₃)₂ and [cyclic] Ni[C(Ph)(PMe₃)C(H)(COCH₂CMe₂Ph)]Cl(PMe₃)₆

Ernesto Carmona, Enrique Gutiérrez-Puebla, Angeles Monge, José M. Marín, Margarita Paneque, Manuel L. Poveda

Organometallics, 1984, 3 (9), pp 1438–1440

DOI: 10.1021/om00087a022

Publication Date: September 1984

Departamento de Química Inorgànica, Facultad de Química, Universidad de Sevilla, Sevilla, Spain
Instituto de Química Inorgànica Elhuyar, C.S.I.C., Serrano 113, Madrid
and Departamento de Química, Facultad de Química, Universidad Complutense, Madrid-3, Spain

Theoretical analysis of bonding in monomeric and polymeric C₅H₅M compounds

Enric Canadell, Odile Eisenstein, Jaime Rubio

Organometallics, 1984, 3 (5), pp 759–764

DOI: 10.1021/om00083a020

Publication Date: May 1984

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48 109
Jaime Rubio, Facultat de Química, Universitat de Barcelona, Tarragona, Spain

Short history of the GEQO-group

(Specialized Group in Organometallic Chemistry),

on the occasion of the 30th anniversary of *Organometallica* and the XXX-GEQO meeting, it is worth approaching with a historical perspective what was the social, economic and educational situation of Spain when the GEQO-group was created, and how the group has evolved since then.

A series of circumstances prompted the foundation of the GEQO-group. First, the Federation of European Chemical Societies (FECS, representing 180 European centers in the Chemistry area in 1980) had expressed their interest in incorporating the Spanish Royal Society of Chemistry (RSEQ) into the FECS. This demand was mainly based on the scientific production of the Spanish chemistry researchers, who in the 1970s had produced around 150 publications in international journals of high impact factor.

Based on these circumstances, on May 9th of 1980, a formal application of the GEQO was presented to the RSEQ. A special committee created to study the application supported the creation of the GEQO, which was subsequently born on June 19th of 1980. Prof Dr. Pascual Royo was designated as the temporary President of the Group. Figure 1 shows the first official letter sent by

Prof. Pascual Royo to the RSEQ General Secretary, explaining the reasons for the GEQO group to be created.

The first official GEQO meeting took place in Alcalá de Henares (Madrid) on June 12th of 1981. Figure 2, shows a manuscript where the list of participants is displayed.

Since that moment, different well-known organometallic chemistry researchers have presided the GEQO-group: Pascual Royo (1980-1988), Pascual Lahuerta (1988-93), Juan Forniés (1993-95), Pablo Espinet (1995-02), Javier Cabeza (2002-10) and Pedro Pérez since 2010.

The economic situation of Spain had a great impact in the development of the recently created GEQO-group. The number of students going to the universities had increased with respect to earlier times, but was still low compared to European standards. From 1975-80, the research activity was very low due the lack of facilities and budget. The availability of researcher positions was also very scarce, and it was always accompanied by low-income contracts compared to other professional orientations.

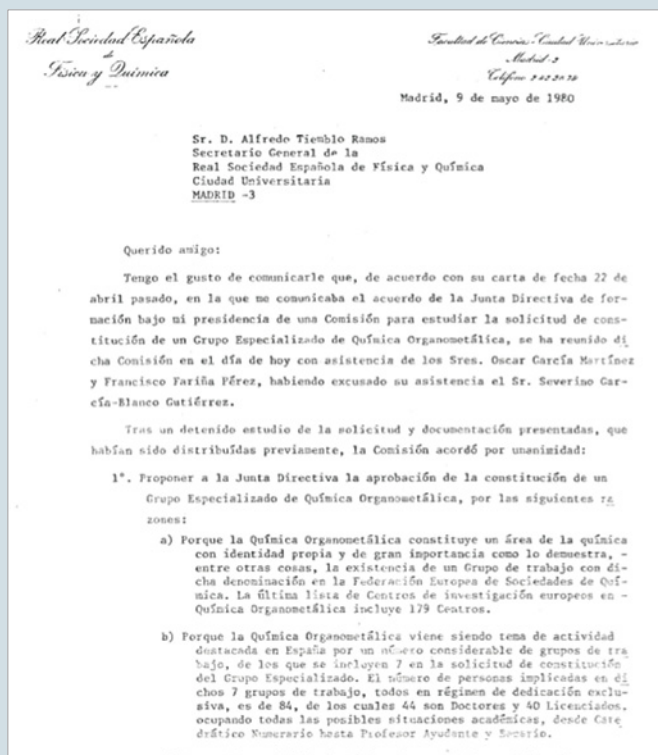


Figure 1. Letter of Prof. Pascual Royo to the Secretary of the RSEQ, applying for the constitution of the GEQO-group. This historical document constitutes the germ of the GEQO.

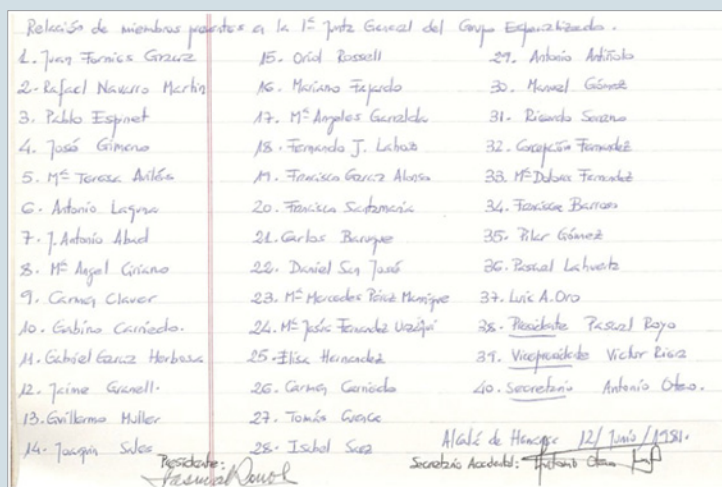


Figure 2. List of participants to the first official GEQO-meeting on the 12th of June of 1981 (Alcalá de Henares).

In the 1980s, this situation started to improve due to different factors:

1. The research centers increased their budgets by getting higher public grants, although these budgets were always well below European standards.
2. New teaching and research positions were available, thus allowing the creation of a first generation of highly qualified scientific researchers.
3. The boost of research-fellowship programs for younger students to travel and work in internationally recognized research centers promoted a broader collaboration between Spanish and foreign scientific institutions.



Figure 3. From left to right: José Gimeno, M. Angel Ciriano, Pablo Espinet, Juan Forniés and José Vicente in their laboratory at the University of Zaragoza (1973). This group of GEQO founders represents a first generation of Spanish Chemistry researchers who postdoctored abroad in internationally recognized research institutions.

Group meetings

As previously mentioned, the first official GEQO-meeting took place at the University of Alcalá de Henares in June of 1981. At this meeting, the GEQO regulations were approved. The following meetings were scheduled alternating with the biannual meetings of the RSEQ. In addition to these ordinary meetings, two additional scientific events are worth mentioning. The first one was the VII FEChem Conference on Organometallic Chemistry, held in Toledo, in August 30th through September 4th of 1987. The second one was a one-day scientific session organized on May 24th of 2011 at the Universidad Complutense of Madrid, in order to commemorate the 30th anniversary of the GEQO.

Due to the increasing number of members, the presence of Organometallic Chemistry at the RSEQ has gained importance. This growth from about 40 members in 1981 to more than 550 today, makes the GEQO-group the largest of the RSEQ. As a consequence, a very intense activity has been developed in the last decade, providing an increasing



Figure 4. XXVI-GEQO meeting in Santiago de Compostela, 2008.

influence of the Spanish contributions in scientific high impact journals.



Prof. Pascual Royo, the day he was awarded the RSEQ Medal in 1998.

It is worth mentioning that during the last decade (2002-2012), the number of Spanish contributions to *Organometallics* represents 9% of the total number of published articles in the journal.

Several of the GEQO members have been awarded national and international prizes, a fact that can be interpreted as an indirect acknowledgement to the whole GEQO group. In this regard, Luis Oro obtained the National Research award (2007). The RSEQ Medal was given to Rafael Usón (1994), Pascual Royo (1998), José Vicente (2001), Ernesto Carmona (2006), Luis Oro (2007), Pablo Espinet (2008) and Antonio Echavarren (2010). The RSEQ-Inorganic Chemistry award has been given to Miguel A. Esteruelas (2001), Santiago Álvarez (2003), José Gimeno (2004), Pedro J. Pérez (2007) and Margarita Paneque (2009). The RSEQ Organic Chemistry and Physical Chemistry awards were given to Antonio Echavarren (2004) and Feliu Maseras (2011), respectively. The internationally recognized Jaume I Award has been given to Luis Oro (1999) and Ernesto Carmona (2010).

Acknowledgments. This article has been written by Eduardo Peris, thanks to the information provided by Pascual Royo, Pablo Espinet, Pascual Lahuerta, Pedro Pérez and José Vicente.

Many of the GEQO members have struggled for the scientific development of the GEQO-organization, and participated in all aspects of its establishment. That devotion is just a sample of the effort shown by the Spanish organometallic chemistry researchers, who had to fight against the lack of facilities and supporting programs until the present date, in which our researchers occupy a privileged position in the international scene.

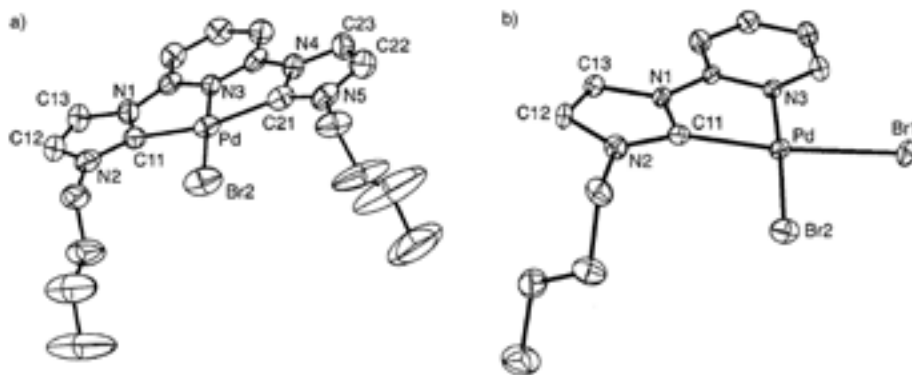
Palladium Complexes with Tridentate Pincer Bis-Carbene Ligands as Efficient Catalysts for C–C Coupling

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The synthesis and X-ray crystallographic characterization of a Pd complex (**3**) with a rigid C,N,C-tridentate pincer carbene ligand are described. At high temperatures (165 °C) it is an active and robust catalyst in the Heck reaction. Complex **3** gives some of the highest turnover numbers yet reported for coupling with aryl chlorides. Time dependence, reuse, and Heck reaction conditions are discussed for **3**. Data with F⁻ as base did not support Shaw's Heck mechanism. Suzuki and Sonogashira coupling reactions are also catalyzed by **3**. The palladium carbene complex **5**, containing an analogous C,N-bidentate ligand, is compared to **3** in terms of stability, catalytic activity, and reaction profile in the Heck reaction.



Organometallics, **2002**, 21 (4), pp 700–706

DOI: 10.1021/om010852n

Publication Date (Web): January 18, 2002

The Difficulty of Coordinating Mutually *trans* Phosphine and Aryl Ligands in Palladium Complexes and Its Relation to Important Coupling Processes. Syntheses and Crystal Structures of a Family of Palladium Phosphino, Triflato, Perchlorato, and Aquo-2-(arylazo)aryl Complexes

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Grupo de Química Organometálica,[†] Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Aptdo. 4021, E-30071 Murcia, Spain

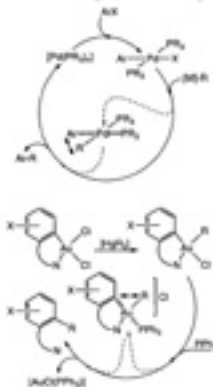
Peter G. Jones^{*§}

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

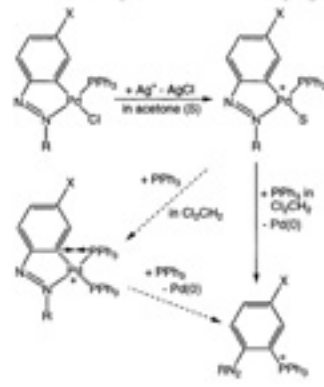
Received December 26, 1996[¶]

The reaction between $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NR}-2, \text{X}-5)\text{Cl}]_2$ and phosphines gives $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NTo}-2, \text{Me}-5)\text{Cl}(\text{L})]$ [$\text{To} = \text{C}_6\text{H}_4\text{Me}-4$, $\text{L} = \text{PEt}_3$ (**1a**), PPh_2Me (**1b**)] or *trans*- $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2\text{To}-2, \text{Me}-5)\text{ClL}_2]$ ($\text{L} = \text{PEt}_3$ (**2a**), PPh_2Me (**2b**), $\text{L}_2 = \text{bis}(\text{diphenylphosphino})\text{methane} = \text{dppm}$ (**2c**)) or *trans*- $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2\text{X}-2, \text{R}-5)\text{Cl}(\mu\text{-dppm})_2]$ ($\text{X} = \text{Me}$, $\text{R} = \text{To}$ (**3a**); $\text{X} = \text{H}$, $\text{R} = \text{Ph}$ (**3b**)), depending on the molar ratio of the reagents. $\text{Ti}(\text{OTf})$ ($\text{OTf} = \text{O}_3\text{SCF}_3$), AgClO_4 , or AgSbF_6 react with **1a,b**, **2a**, **2c**, or **3a** to give, variously, $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NTTo}-2, \text{Me}-5)(\text{Y})(\text{L})]$ ($\text{L} = \text{PEt}_3$, $\text{Y} = \text{TfO}$ (**4a**); $\text{L} = \text{PPh}_2\text{Me}$, $\text{Y} = \text{TfO}$ (**4b**), ClO_4 (**4b'**)), *trans*- $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2\text{To}-2, \text{Me}-5)(\text{OTf})(\text{PEt}_3)_2]$ (**5**), $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2\text{To}-2, \text{Me}-5)(\eta^1\text{-dppm})(\eta^2\text{-dppm})\text{TfO}$ (**6**), or $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NR}-2, \text{X}-5)(\eta^2\text{-dppm})\text{Y}$ ($\text{X} = \text{Me}$, $\text{R} = \text{To}$, $\text{Y} = \text{TfO}$ (**7a**)). Complexes $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NR}-2, \text{X}-5)(\eta^2\text{-dppm})\text{SbF}_6]$ ($\text{X} = \text{Me}$, $\text{R} = \text{To}$ (**7a'**); $\text{X} = \text{H}$, $\text{R} = \text{Ph}$ (**7b**)) can be prepared by reacting $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NR}-2, \text{X}-5)\text{Cl}]_2$ with AgSbF_6 and dppm . Complex **4b'** reacts with PPh_2Me to give $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2\text{To}-2, \text{Me}-5)(\text{PPh}_2\text{Me})_3]\text{ClO}_4$ (**8**). Attempts to obtain single crystals of **4a**, $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NR}-2, \text{X}-5)(\text{PPh}_3)(\text{Me}_2\text{CO})]\text{ClO}_4$, or **7b** lead to different products. From **4**, an insertion into the $\text{Pd}-\text{OTf}$ bond of one molecule of water gives $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NTTo}-2, \text{Me}-5)(\text{OH}_2\cdots\text{OTf})(\text{PEt}_3)]$ (**9**) while substitution of the acetone molecule by two water molecules occurs in the second case to give $[\text{Pd}(\text{C}_6\text{H}_3\text{N}=\text{NTTo}-2, \text{Me}-5)\{(\mu_3\text{-OH}_2)(\cdots\text{OClO}_3)(\cdots\text{OH}_2)\}(\text{PPh}_3)]$ (**10**). Finally, ready oxidation in the air of **7b** gives $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NPh}-2)(\eta^2\text{-dppmO})\text{SbF}_6]$ (**11**) [$\text{dppmO} = \text{bis}(\text{diphenylphosphino})\text{methane monoxide}$]. $[\text{Pt}(\text{PPh}_3)_3]$ reacts with $[\text{Hg}(\text{C}_6\text{H}_3\text{N}_2\text{To}-2, \text{Me}-5)\text{Cl}]$ to give *trans*- $[\text{Pt}(\text{C}_6\text{H}_3\text{N}_2\text{To}-2, \text{Me}-5)\text{Cl}(\text{PPh}_3)_2]$ (**12**), which in turn reacts with $\text{Ti}(\text{OTf})$ to give $[\text{Pt}(\text{C}_6\text{H}_3\text{N}=\text{NTTo}-2, \text{Me}-5)(\text{PPh}_3)_2]\text{TfO}$ (**13**). Crystal structures of **2c**· $\frac{1}{2}\text{CH}_2\text{Cl}_2$, **4b'**, **5**, **6**, **7a**, **9**, **10**, and **11**·**2MeOH** have been determined.

Scheme 1. Examples of C-C Coupling*



Scheme 2. Examples of C-P and C-N Couplings*



Organometallics, **1997**, *16* (10), pp 2127–2138

DOI: 10.1021/om961094h

Publication Date (Web): May 13, 1997

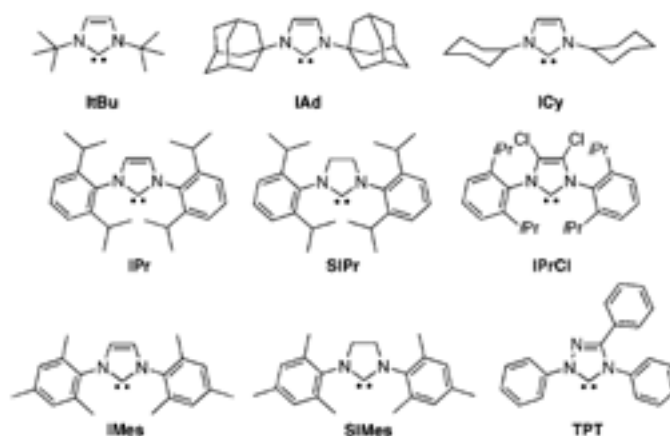
Determination of N-Heterocyclic Carbene (NHC) Steric and Electronic Parameters using the [(NHC)Ir(CO)₂Cl] System

Roy A. Kelly III,[†] Hervé Clavier,[‡] Simona Giudice,[§] Natalie M. Scott,[†] Edwin D. Stevens,[†] Jon Bordner,[‡] Ivan Samardjiev,[‡] Carl D. Hoff,[¶] Luigi Cavallo,[§] and Steven P. Nolan^{*,†‡}

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Received October 6, 2007

Complexes of iridium bearing NHC (NHC = N-heterocyclic carbene) ligands were synthesized and fully characterized. The series [(NHC)Ir(cod)Cl] were obtained by simple cleavage of [Ir(cod)Cl]₂. The [(NHC)Ir(cod)Cl] complexes were reacted with excess carbon monoxide, leading to [(NHC)Ir(CO)₂Cl]. The infrared carbonyl stretching frequencies of these were recorded to quantify the electronic parameter of NHC ligands. X-ray diffraction study results allow for determination of NHC steric parameters within this series. These data allow for comparison with other ligand families.



Organometallics, **2008**, 27 (2), pp 202–210

DOI: 10.1021/om701001g

Publication Date (Web): December 27, 2007

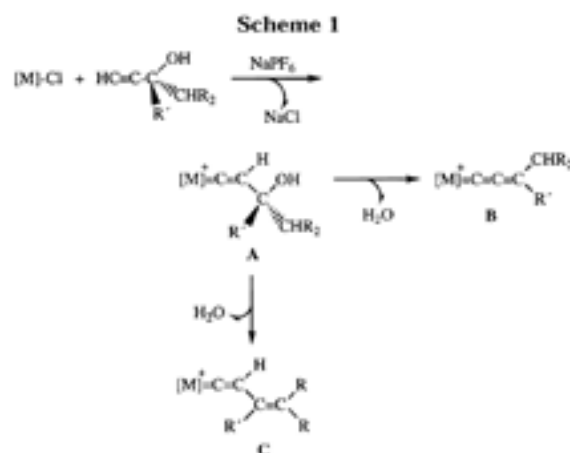
Activation of 2-Propyn-1-ol Derivatives by Indenylruthenium(II) and -osmium(II) Complexes: X-ray Crystal Structures of the Allenylidene Complexes $[M(=C=C=CPh_2)(\eta^5-C_9H_7)(PPh_3)_2][PF_6] \cdot CH_2Cl_2$ (M = Ru, Os) and EHMO Calculations

Victorio Cadierno,[†] M. Pilar Gamasa,[†] José Gimeno,^{*,†}
Mercedes González-Cueva,[†] Elena Lastra,[†] Javier Borge,[‡]
Santiago García-Granda,[‡] and Enrique Pérez-Carreño[‡]

Departamento de Química Orgánica e Inorgánica and Departamento de Química Física y Analítica, Instituto de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

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The allenylidene complexes $[M(=C=C=CR_2)(\eta^5-C_9H_7)L_2][PF_6]$ (M = Ru, L = PPh₃, L₂ = 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm), R₂ = 2 Ph (**1a–c**), C₁₂H₈ (2,2'-biphenyldiyl) (**2a–c**); M = Os, L = PPh₃, R₂ = 2Ph (**3**), C₁₂H₈ (**4**)) have been prepared by reaction of the complexes $[MCl(\eta^5-C_9H_7)L_2]$ with HC≡CC(OH)R₂ and NaPF₆ in refluxing methanol. The crystal structures of $[M(=C=C=CPh_2)(\eta^5-C_9H_7)(PPh_3)_2][PF_6] \cdot CH_2Cl_2$ (M = Ru (**1a**), Os (**3**)) were determined by X-ray diffraction methods. In the structures the M=C=C=C chains are nearly linear (M–C(1)–C(2) = 168.5(5)° (**1a**) and 169.3(4)° (**3**); C(1)–C(2)–C(3) = 168.2(7)° (**1a**) and 168.0(5)° (**3**) with M–C(1) distances of 1.878(5) Å (**1a**) and 1.895(4) Å (**3**). The indenyl ligand is η^5 -bonded to the metal with the benzo ring orientated "cis" with respect to the allenylidene group. Extended Hückel molecular orbital calculations have been used to rationalize the preferred "cis" orientation. The reaction of $[RuCl(\eta^5-C_9H_7)L_2]$ (L = PPh₃, L₂ = dppe, dppm) with HC≡CCMe(OH)Ph and NaPF₆ in refluxing methanol leads to the formation of the allenylidene complexes $[Ru\{=C=C=C(Me)Ph\}(\eta^5-C_9H_7)L_2][PF_6]$ (**6a–c**) along with the vinylvinylidene isomers $[Ru\{=C=C(H)C(Ph)=CH_2\}(\eta^5-C_9H_7)L_2][PF_6]$ (L = PPh₃ (**5a**), L₂ = dppe (**5b**), dppm (**5c**)). Only complex **6a** could be isolated by chromatography (SiO₂) from these mixtures along with complex **7a** obtained from the deprotonation of the vinylvinylidene complex **5a**. The treatment of these reaction mixtures with potassium carbonate yields the neutral σ -enynyl derivatives $[Ru\{C=CC(Ph)=CH_2\}(\eta^5-C_9H_7)L_2]$ (**7a–c**). The monosubstituted allenylidene complex $[Ru\{=C=C=C(H)Ph\}(\eta^5-C_9H_7)(PPh_3)_2][PF_6]$ (**9**) has been prepared by the reaction of $[RuCl(\eta^5-C_9H_7)(PPh_3)_2]$ with HC≡CCH(OH)Ph and NaPF₆ in methanol. Under similar reaction conditions $[RuCl(\eta^5-C_9H_7)L_2]$ reacts with HC≡CCH(OH)R and NaPF₆ to afford the alkenylmethoxycarbene derivatives $[Ru\{=C(OMe)C(H)=CH(R)\}(\eta^5-C_9H_7)L_2][PF_6]$ (L₂ = dppe, R = Ph (**11b**); L₂ = dppm, R = Ph (**11c**), H (**13**)). $[RuCl(\eta^5-C_9H_7)(PPh_3)_2]$ also reacts with HC≡CC(OH)H₂ to give the hydroxyvinylidene complex $[Ru\{=C=CH(CH_2OH)\}(\eta^5-C_9H_7)(PPh_3)_2][PF_6]$ (**12**), which is stable toward the dehydration process.



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Publication Date (Web): April 16, 1996

Five- and Six-Membered Exo-Cyclopalladated Compounds of *N*-Benzylideneamines. Synthesis and X-ray Crystal Structure of $[\text{PdBr}\{p\text{-MeOC}_6\text{H}_3(\text{CH}_2)_2\text{N}=\text{CH}(2,6\text{-Cl}_2\text{C}_6\text{H}_3)\}(\text{PPh}_3)]$ and $[\text{PdBr}\{\text{C}_6\text{H}_4\text{CH}_2\text{N}=\text{CH}(2,6\text{-Cl}_2\text{C}_6\text{H}_3)\}(\text{PEt}_3)_2]$

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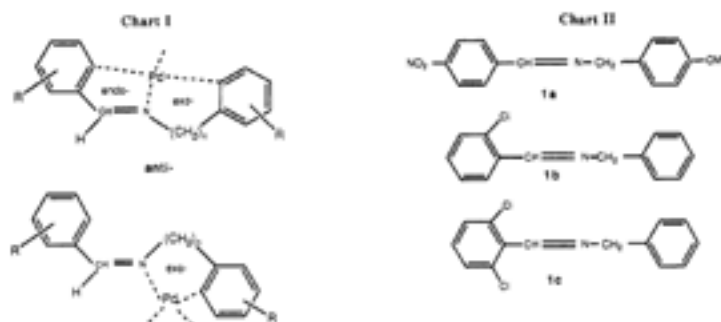
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The reaction of *N*-(2,6-dichlorobenzylidene)amines, $2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}=\text{N}(\text{CH}_2)_n\text{C}_6\text{H}_4\text{-}p\text{-R}$ ($n = 1, 2$; $\text{R} = \text{H, MeO}$), with $\text{Pd}(\text{AcO})_2$ in refluxing acetic acid has been studied. With *N*-benzylidenebenzylamines ($n = 1$) exo five-membered derivatives were obtained. From *N*-benzylidene(2-phenylethyl)amines ($n = 2$) endo five-membered cyclopalladated compounds were formed by oxidative addition of C-Cl bonds of the ligand to Pd(0) formed in situ. Under milder conditions (acetic acid at 80 °C) the exo six-membered compound $[\text{Pd}(\text{AcO})\{p\text{-MeOC}_6\text{H}_3(\text{CH}_2)_2\text{N}=\text{CH}(2,6\text{-Cl}_2\text{C}_6\text{H}_3)\}]_2$ was obtained. All exo derivatives contain the imine ligand in the syn form. By reaction with PR_3 ($\text{R} = \text{Et, Ph}$), monophosphine complexes $[\text{PdX}(\text{C}=\text{N})(\text{PR}_3)]$ and bisphosphine derivatives $[\text{PdX}(\text{C}=\text{N})(\text{PR}_3)_2]$, where the Pd-N bond has been broken, can be obtained. $[\text{PdBr}\{p\text{-MeOC}_6\text{H}_3(\text{CH}_2)_2\text{N}=\text{CH}(2,6\text{-Cl}_2\text{C}_6\text{H}_3)\}(\text{PPh}_3)]$ (**6f**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 20.321$ (4) Å, $b = 12.561$ (3) Å, $c = 12.608$ (3) Å, $\beta = 97.50$ (2)°, and $Z = 4$. The exo six-membered ring displays a boat conformation with Pd and C(7) atoms out of the plane defined by the remaining atoms. $[\text{PdBr}\{\text{C}_6\text{H}_4\text{CH}_2\text{N}=\text{CH}(2,6\text{-Cl}_2\text{C}_6\text{H}_3)\}(\text{PEt}_3)_2]$ (**9c**) has been characterized by X-ray crystallography; it crystallizes in the monoclinic space group $P2_1/a$ with $a = 45.352$ (6) Å, $b = 8.884$ (2) Å, $c = 7.556$ (2) Å, $\beta = 99.02$ (3)°, and $Z = 4$. The Pd atom has a roughly planar coordination, and the imine ligand is in the anti form.



Organometallics, 1990, 9 (5), pp 1405–1413

DOI: 10.1021/om00119a009

Publication Date: May 1990



From the ACS Legacy Archives

Ligand Effects in Gold- and Platinum-Catalyzed Cyclization of Enynes: Chiral Gold Complexes for Enantioselective Alkoxy cyclization

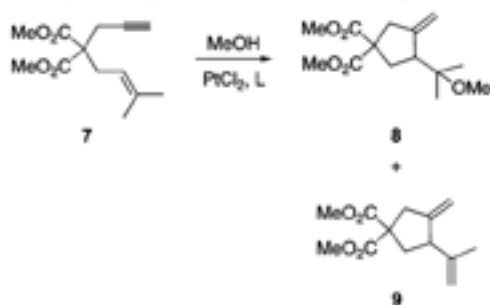
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Received October 27, 2004

Phosphine and bidentate N–N ligands inhibit the Alder-ene-type cycloisomerization of enynes catalyzed by Pt(II) and favor the alkoxy cyclization process. The enantioselective Pt(II)-catalyzed alkoxy cyclization has been studied in the presence of chiral mono- and bidentate phosphines, as well as chiral bidentate N–N ligands. Modest levels of enantioselection (up to 50% ee) have been obtained with Tol-BINAP as ligand. The alkoxy cyclizations with a catalyst formed from [Au(L)Cl]/AgX proceed more readily, and up to 94% ee's have been obtained using [(AuCl)₂(Tol-BINAP)] (**47**) as the precatalyst. The X-ray crystal structures of Au(I) complexes **47** and chloro-(*R*)-2-(*tert*-butylsulfenyl)-1-(diphenylphosphino)ferrocene gold(I) (**39**) show the AuCl fragments monocoordinated with the P centers of the chiral phosphine ligands.

Table 1. Influence of Phosphine Ligands in the PtCl₂-Catalyzed Reaction of Enyne **7^a**



Organometallics, **2005**, *24* (6), pp 1293–1300

DOI: 10.1021/om0491645

Publication Date (Web): February 12, 2005

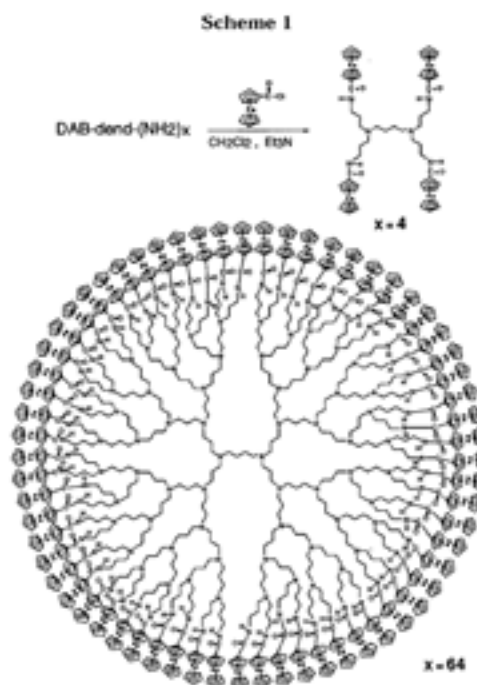
Ferrocenyl-Functionalized Poly(propylenimine) Dendrimers

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Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco 28049-Madrid, Spain, and Departamento de Ingeniería Química Industrial, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, 28006-Madrid, Spain

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Summary: New ferrocenyl dendritic macromolecules based on flexible poly(propylenimine) dendrimer cores, built up to the fifth generation, containing 4, 8, 16, 32, and 64 peripheral ferrocenyl moieties, have been prepared and characterized. Solution electrochemical studies showed that all the ferrocenyl redox centers attached to the dendritic surface are electrochemically independent and that, in CH_2Cl_2 and THF as solvents, the neutral dendrimers undergo oxidative precipitation onto the electrode surfaces.



Organometallics, **1996**, 15 (25), pp 5278–5280

DOI: 10.1021/om9605948

Publication Date (Web): December 10, 1996

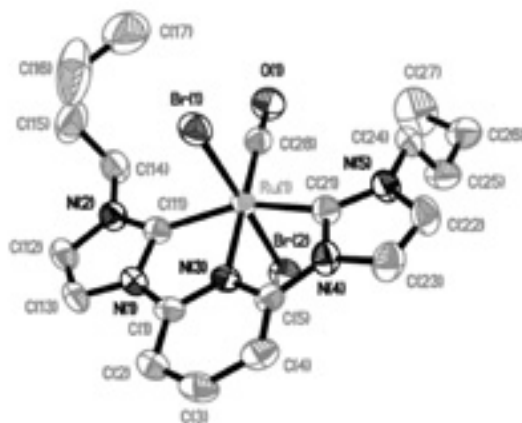
New Ruthenium(II) CNC-Pincer Bis(carbene) Complexes: Synthesis and Catalytic Activity

Macarena Poyatos,[†] José A. Mata,[†] Eva Falomir,[†] Robert H. Crabtree,[‡] and Eduardo Peris^{*†}

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Ru(CNC)(CO)Br₂ and [Ru(CNC)₂](PF₆)₂ complexes (CNC = 2,6-bis(butylimidazol-2-ylidene)pyridine) are accessible via a simple synthesis. The crystal structures of both complexes have been determined by means of X-ray diffractometry. The catalytic activity of the Ru(CNC)(CO)Br₂ precursor toward hydrogen transfer from alcohols to ketones and oxidation of olefins confirms the versatility of this new phosphine-free Ru catalyst.



Organometallics, **2003**, 22 (5), pp 1110–1114

DOI: 10.1021/om020817w

Publication Date (Web): January 25, 2003

Tripodal Polyphosphine Ligands in Homogeneous Catalysis. 1. Hydrogenation and Hydroformylation of Alkynes and Alkenes Assisted by Organorhodium Complexes with $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$

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Piero Frediani

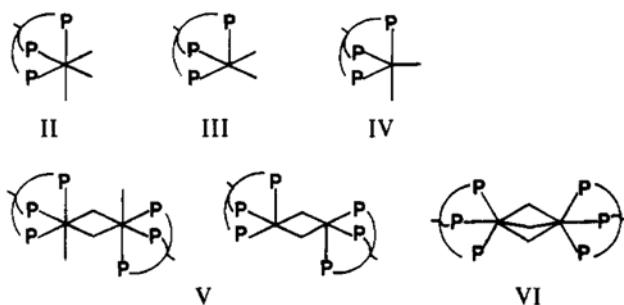
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Received April 3, 1989

The crystal structure of the complex $[(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)]$ (1) has been determined by X-ray methods (triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$). The rhodium atom is coordinated to an ethylene molecule, a chlorine atom, and the triphos ligand, which occupies three *fac* positions of an octahedron. The $\text{Rh}-\text{C}_2\text{H}_4$ coordination exhibits a C-C distance that is among the longest found in metal-ethylene structures (1.49 (4) Å). Compound 1 is the starting point to synthesize a number of ethylene complexes of rhodium containing hydride or σ -organyl coligands: $[(\text{triphos})\text{RhH}(\text{C}_2\text{H}_4)]$, $[(\text{triphos})\text{Rh}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)]$, $[(\text{triphos})\text{Rh}(\text{CH}_3)(\text{C}_2\text{H}_4)]$, $[(\text{triphos})\text{Rh}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_4)]$. All of the ethylene complexes but 1 react with CO, forming σ -acyl carbonyls of general formula $[(\text{triphos})\text{Rh}(\text{COR})(\text{CO})]$ via the σ -organyl carbonyls $[(\text{triphos})\text{Rh}(\text{R})(\text{CO})]$ (R = CH_3 , C_2H_5 , C_6H_5). Compound 1 reacts with CO, yielding the carbonyl $[(\text{triphos})\text{RhCl}(\text{CO})]$. The hydrogenolysis reactions of the σ -organyl ethylene complexes invariably give the trihydride $[(\text{triphos})\text{Rh}(\text{H})_3]$ and the corresponding hydrocarbon. In contrast, the σ -acyl carbonyls and the σ -organyl carbonyls react with H_2 to form the hydride carbonyl $[(\text{triphos})\text{RhH}(\text{CO})]$ and the corresponding hydrocarbon or aldehyde. Another excellent synthetic entry to organorhodium complexes of triphos is the η^2 -alkyne complex $[(\text{triphos})\text{Rh}(\eta^2\text{-DMAD})\text{BPh}_4]$ (DMAD = dimethyl acetylenedicarboxylate). This reacts with H_2 to give the tetrahydride $[(\text{triphos})\text{RhH}(\mu\text{-H})_2\text{HRh}(\text{triphos})](\text{BPh}_4)_2$ and dimethyl succinate. Reaction of the η^2 -alkyne complex with CO affords the dicarbonyl $[(\text{triphos})\text{Rh}(\text{CO})_2]\text{BPh}_4$ which is converted into the ethylene carbonyl $[(\text{triphos})\text{Rh}(\text{CO})(\text{C}_2\text{H}_4)]\text{BPh}_4$ by treatment with Me_3NO under a C_2H_4 atmosphere. The ethylene carbonyl is much better synthesized by protonation of $[(\text{triphos})\text{RhH}(\text{CO})]$ under C_2H_4 . In the absence of ethylene, the reaction gives $[(\text{triphos})\text{Rh}(\text{H})_2(\text{CO})]\text{BPh}_4$. The hydrogenolysis and carbonylation reactions have been carried out at room temperature and 1 atm of H_2 or CO. All of the compounds have been properly characterized by spectroscopic technique, including the computer simulation of the second-order ^1H and ^{31}P NMR spectra. The activities of all of the compounds as catalyst precursors for the homogeneous hydrogenation, isomerization, and hydroformylation reactions of alkenes and alkynes have been studied in detail. Particular attention has been focused on the substrates 1-hexene, *cis*-stilbene, diphenylacetylene, dimethyl maleate, and dimethyl acetylenedicarboxylate.



Organometallics, 2002, 9 (1), pp 226–240

DOI: 10.1021/om00115a035

Publication Date: January 1990



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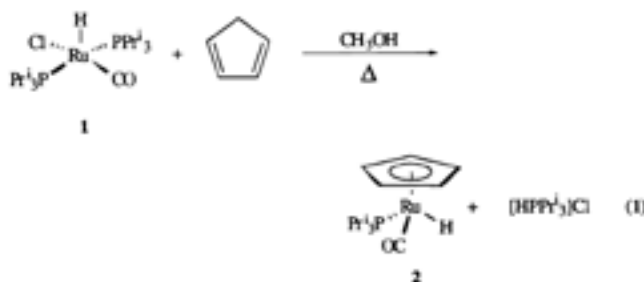
Five-Coordinate Complex $[\text{RuHCl}(\text{CO})(\text{PPr}^i_3)_2]$ as a Precursor for the Preparation of New Cyclopentadienylruthenium Compounds Containing Unsaturated η^1 -Carbon Ligands[†]

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Received February 20, 1996[®]

The five-coordinate complex $[\text{RuHCl}(\text{CO})(\text{PPr}^i_3)_2]$ (**1**) reacts with cyclopentadiene in methanol under reflux to give $[\text{RuH}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPr}^i_3)]$ (**2**) and $[\text{HPPr}^i_3]\text{Cl}$. The protonation of **2** in dichloromethane-*d*₂ leads to the dihydrogen complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-H}_2)(\text{CO})(\text{PPr}^i_3)]\text{-BF}_4$ (**3**) in equilibrium with traces of the dihydrido tautomer $[\text{RuH}_2(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPr}^i_3)]\text{-BF}_4$ (**4**). The reaction of **2** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in acetone affords the solvated complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\eta^1\text{-OC}(\text{CH}_3)_2\}(\text{PPr}^i_3)]\text{BF}_4$ (**5**), which reacts with CO, dimethyl acetylenedicarboxylate, and NaCl to give $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPr}^i_3)]\text{BF}_4$ (**6**), $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-C}_2(\text{CO}_2\text{CH}_3)_2\}(\text{CO})(\text{PPr}^i_3)]\text{-BF}_4$ (**7**), and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{CO})(\text{PPr}^i_3)]$ (**8**), respectively. Complex **5** also reacts with alkyn-1-ols. The reaction with 1,1-diphenyl-2-propyn-1-ol leads to the allenylidene complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{PPr}^i_3)]\text{BF}_4$ (**9**), which affords $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{OH})\text{CH}=\text{CPh}_2\}(\text{CO})(\text{PPr}^i_3)]\text{BF}_4$ (**10**) by reaction with water. **10** is converted into the acyl derivative $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{O})\text{CH}=\text{CPh}_2\}(\text{CO})(\text{PPr}^i_3)]$ (**11**), when a CH_2Cl_2 solution of **10** is passed through an Al_2O_3 column. The structure of **11** was determined by an X-ray investigation. The reaction of **5** with 2-propyn-1-ol leads to the α,β -unsaturated hydroxycarbene complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{OH})\text{CH}=\text{CH}_2\}(\text{CO})(\text{PPr}^i_3)]\text{BF}_4$ (**12**). Similarly to **10**, **12** is converted into $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{O})\text{CH}=\text{CH}_2\}(\text{CO})(\text{PPr}^i_3)]$ (**13**), when the solutions of **12** are passed through an Al_2O_3 column. Treatment of **5** with 1-ethynyl-1-cyclohexanol leads to a mixture of organometallic compounds including $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{OH})\text{CH}=\overline{\text{C}}(\text{CH}_2)_4\text{CH}_2\}(\text{CO})(\text{PPr}^i_3)]\text{BF}_4$ (**14**). Chromatography of the mixture affords $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{O})\text{CH}=\overline{\text{C}}(\text{CH}_2)_4\text{CH}_2\}(\text{CO})(\text{PPr}^i_3)]$ (**15**) and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\overline{\text{C}}=\text{CH}(\text{CH}_2)_3\text{CH}_2\}(\text{CO})(\text{PPr}^i_3)]$ (**16**). **9** reacts with alcohols and thiols to give $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{ER})\text{CH}=\text{CPh}_2\}(\text{CO})(\text{PPr}^i_3)]\text{BF}_4$ (ER = OMe (**17**), OEt (**18**), SPr^n (**21**)), which by treatment with NaOMe afford $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{ER})=\text{C}=\text{CPh}_2\}(\text{CO})(\text{PPr}^i_3)]$ (ER = OMe (**19**), OEt (**20**), SPr^n (**22**)). Similarly, the reaction of **9** with benzophenone imine leads to $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}=\text{CPh}_2)=\text{N}=\text{CPh}_2\}(\text{CO})(\text{PPr}^i_3)]\text{BF}_4$ (**23**), which by reaction with NaOMe gives $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{N}=\text{CPh}_2)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{PPr}^i_3)]$ (**24**). The structure of **23** was also determined by an X-ray investigation. The C=N bond lengths are 1.283(9) and 1.252(9) Å, while the C-N-C angle is 149.9(6)°.



Organometallics, 1996, 15 (15), pp 3423–3435

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Publication Date (Web): July 23, 1996

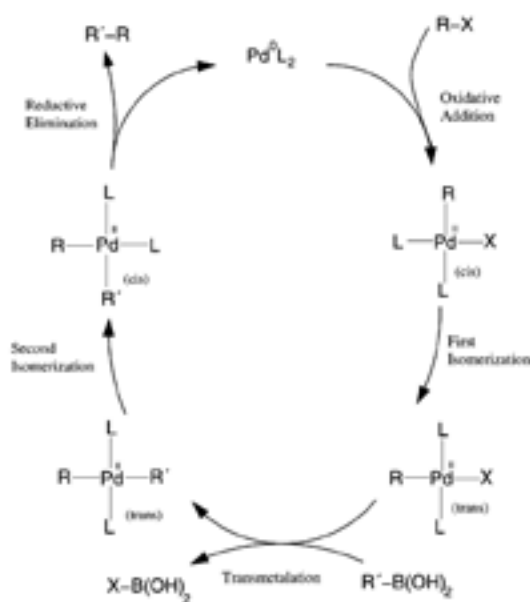
A DFT Study of the Full Catalytic Cycle of the Suzuki–Miyaura Cross-Coupling on a Model System

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Received May 2, 2006

A computational study with the Becke3LYP DFT functional is carried out on the cross-coupling reaction of vinyl bromide $\text{H}_2\text{C}=\text{CHBr}$ and vinylboronic acid $\text{H}_2\text{C}=\text{CHB}(\text{OH})_2$ catalyzed by palladium diphosphine $[\text{Pd}(\text{PH}_3)_2]$ in the presence of an excess of base OH^- . The full catalytic cycle is computed, starting from the separated reactants and the catalyst and finishing with the cross-coupled product and the regeneration of the catalyst. The different stages in the cycle (oxidative addition, isomerization, transmetalation, reductive elimination) are characterized through calculation of the corresponding intermediates and transition states. Different alternative mechanisms are considered, depending on the number of phosphine ligands at palladium, and on the *cis* or *trans* isomery around the metal center. The results indicate the existence of a number of competitive pathways of reasonably low energy.



Organometallics, **2006**, 25 (15), pp 3647–3658

DOI: 10.1021/om060380i

Publication Date (Web): June 15, 2006

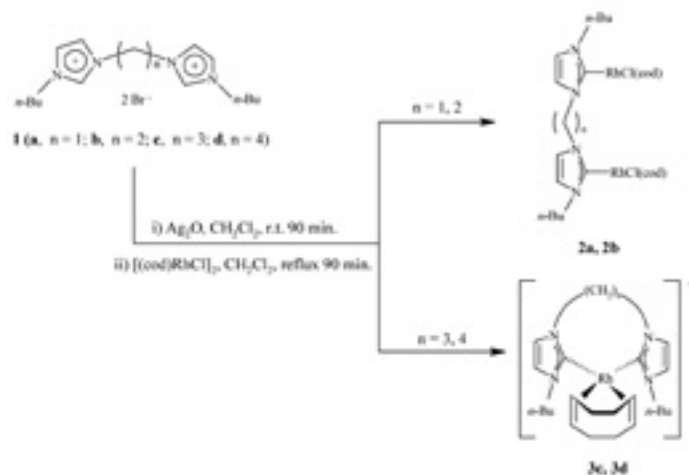
Reactivity Differences in the Syntheses of Chelating N-Heterocyclic Carbene Complexes of Rhodium Are Ascribed to Ligand Anisotropy

José A. Mata,[†] Anthony R. Chianese,[†] John R. Miecznikowski,[†] Macarena Poyatos,[‡] Eduardo Peris,[‡] Jack W. Faller,^{*,†} and Robert H. Crabtree^{*,†}

Chemistry Department, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, and Departamento Química Inorgànica i Orgànica, Universitat Jaume I, Av. de Vicent Sos Baynat s/n, E-12071 Castellón, Spain

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Chelating bis(imidazolium) salts having $(\text{CH}_2)_n$ chains of different lengths ($n = 1-4$) linking the diazole rings show very large reactivity differences on metalation with $[(\text{cod})\text{RhCl}]_2$. Long linkers favor a square-planar Rh(I) product, while short linkers favor octahedral Rh(III). We ascribe the origin of the effect to the restricted rotation of the highly sterically anisotropic diazole rings and the different preferred orientations of these rings as n changes. Defining the x and y axes as the Rh-carbene bond directions, we find that with short linkers the diazole rings tend to be oriented close to the xy plane. This tends to favor Rh(III) because these complexes, $[\text{Rh}(\text{bis-carbene})\text{I}_2(\text{OAc})]$, have the lowest steric hindrance in the xy plane. With long linkers, the diazole rings tend to be aligned face to face along the $\pm z$ axis. This tends to favor Rh(I) because these complexes, $[(\text{cod})\text{Rh}(\text{bis-carbene})]\text{PF}_6$, have the lowest steric hindrance along the $\pm z$ axis. Crystallographic studies are reported. Electrospray MS data provide evidence for strong metal-carbene binding.



Organometallics, **2004**, 23 (6), pp 1253–1263

DOI: 10.1021/om034240+

Publication Date (Web): February 13, 2004

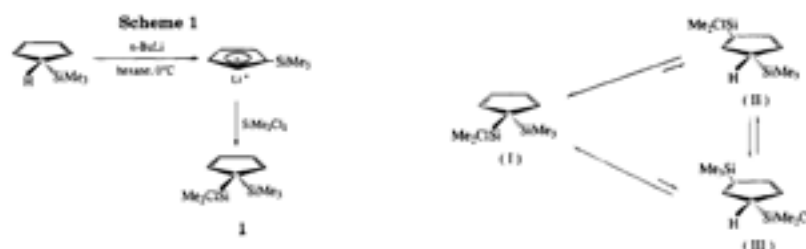
New Silyl-Substituted Cyclopentadienyl Titanium and Zirconium Complexes. X-ray Molecular Structures of $[\text{TiCl}_2\{\mu\text{-(OSiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\}]_2$ and $[\text{ZrCl}_2\{\mu\text{-}[(\eta^5\text{-C}_5\text{H}_4)\text{SiMe}_2\text{OSiMe}_2(\eta^5\text{-C}_5\text{H}_4)]\}]$

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Received July 28, 1994[®]

We report the synthesis of 1-(chlorodimethylsilyl)-1-(trimethylsilyl)cyclopentadiene, **1**. The reaction of a toluene solution of **1** with one equivalent of MCl_4 ($\text{M} = \text{Ti, Zr}$) leads to the mono(cyclopentadienyl) derivatives $[\text{MCl}_3(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})]$ [$\text{M} = \text{Ti}$ (**2**); $\text{M} = \text{Zr}$ (**3**)] in 76 and 87% yields, respectively. The same reaction with ZrCl_4 in a Zr/Cp molar ratio 1:2 in refluxing methylene dichloride yields the dicyclopentadienyl derivative $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})_2]$, **4**, whereas the related titanium compound cannot be synthesized by this method. These mono- and bis(cyclopentadienyl) complexes are very moisture sensitive and react with water to give different oxo complexes. Reaction of one equivalent of water with $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})]$ in toluene takes place with elimination of HCl , resulting in formation of the dinuclear titanium methylsiloxane derivative $[\text{TiCl}_2\{\mu\text{-(OSiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\}]_2$, **5**, in a quantitative yield, which by further addition of one equivalent of water gives the mononuclear compound $[\text{TiCl}_2\{\text{OSiMe}_2\text{OSiMe}_2(\eta^5\text{-C}_5\text{H}_4)\}]$, **6**, in very low yield. However the best procedure to obtain **6** (in 45% yield) is the direct reaction of $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})]$ with two equivalents of water. The analogous reaction of $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})_2]$ with one equivalent of water proceeds to give $[\text{ZrCl}_2\{\mu\text{-}[(\eta^5\text{-C}_5\text{H}_4)\text{SiMe}_2\text{OSiMe}_2(\eta^5\text{-C}_5\text{H}_4)]\}]$, **7**. Alkylation of $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})]$ with $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{THF})_2$ leads to the tribenzyl derivative $[\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_3(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})]$, **8**, and alkylation of $[\text{TiCl}_2\{\mu\text{-(OSiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\}]_2$ with MgClMe and $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{THF})_2$ allows the isolation of the oxoalkyl complexes $[\text{TiR}_2\{\mu\text{-(OSiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\}]_2$ [$\text{R} = \text{Me}$, **9**; $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$, **10**]. Reaction of $[\text{MCl}_3(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})]$ with $\text{LiN}(\text{SiMe}_3)_2$ gives the amido complex $[\text{TiCl}_2\{\text{N}(\text{SiMe}_3)_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\}]$, **11**, whereas a similar reaction with LiNH^tBu takes place with simultaneous elimination of HCl to give the cyclic amido pendant cyclopentadienyl complex $[\text{TiCl}_2\{\text{N}^t\text{BuSiMe}_2(\eta^5\text{-C}_5\text{H}_4)\}]$, **12**. The molecular structures of $[\text{TiCl}_2\{\mu\text{-(OSiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\}]_2$ and $[\text{ZrCl}_2\{\mu\text{-}[(\eta^5\text{-C}_5\text{H}_4)\text{SiMe}_2\text{OSiMe}_2(\eta^5\text{-C}_5\text{H}_4)]\}]$ have been determined by X-ray diffraction methods. Complex **5** is a dimer formed by two $[\text{Me}_2\text{-SiCpTiCl}_2]$ fragments bonded by two oxygen bridges, connecting the silicon and titanium atoms from different units. **5** crystallizes in monoclinic space group $P2_1/n$ with $a = 9.461(7)$, $b = 10.926(1)$, $c = 10.507(3)$ Å, $\beta = 95.20(2)^\circ$, and $V = 1081(1)$ Å³ for $Z = 2$. The molecular structure of **7** corresponds to a typical bent dicyclopentadienyl system. Complex **7** crystallizes in the space group $P2_1/c$ with $a = 13.479(4)$, $b = 8.654(1)$, $c = 15.343(5)$ Å, $\beta = 97.18(2)^\circ$, and $V = 1775(2)$ Å³ for $Z = 4$.



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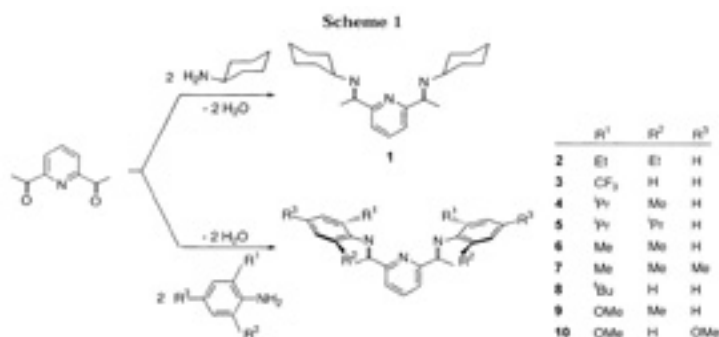
Preparation, Structure, and Ethylene Polymerization Behavior of Bis(imino)pyridyl Chromium(III) Complexes

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The synthesis, characterization, and ethylene polymerization behavior of a family of chromium(III) complexes of formula [2,6-bis(imino)pyridyl]CrCl₃ is reported. The X-ray diffraction studies of two of the new compounds show that the geometry around the chromium atom is octahedral, with the three chlorine ligands in a *mer* disposition. The distance between the metal and one of the trans-disposed chlorine atoms is significantly longer than the other two Cr–Cl distances. Treatment of the complexes [2,6-bis(imino)pyridyl]CrCl₃ with methylaluminumoxane (MAO) leads to very active ethylene polymerization catalysts that afford highly linear polyethylene. The substituents at the ortho position of the N-aryl groups of the 2,6-bis(imino)pyridyl ligands modulate both the catalytic activity and the molecular weights of the resulting polyethylene. The most active catalysts are those with two substituents at the ortho position of the N-aryl groups (activities up to 4×10^7 g (mol of Cr)⁻¹ bar⁻¹ h⁻¹ are achieved). Regarding the size of the substituents, the activity and the molecular weights follow an opposite trend. Systems with two small substituents lead to very active systems, but the molecular weight of the polyethylene is lower than when bulkier substituents are present.



Organometallics, **2003**, 22 (3), pp 395–406

DOI: 10.1021/om020561u

Publication Date (Web): January 1, 2003

Neutral Bis(perhalophenyl)dicarbonylpalladium(II) and -platinum(II) Complexes

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Received April 29, 1985

Summary: Normal pressure carbonylation of *cis*-[M(C₆X₅)₂(OC₄H₈)₂] (M = Pd, Pt; X = F, Cl; OC₄H₈ = tetrahydrofuran) leads to the isolation of *cis*-[M(C₆X₅)₂(CO)₂]. High $\nu(\text{CO})$ stretching bands (far-IR, 2186 cm⁻¹ for M = Pd and X = F) point to negligible metal-to-CO π -back-bonding.

Table I. Some IR Relevant Data and Melting Points

	<i>cis</i> -M(C ₆ X ₅) ₂ L ₂	$\nu(\text{C=O})$		X-sensitive (C ₆ X ₅) ^b	$\nu(\text{MC}_2)^{10}$ (R = C ₆ Cl ₅)	mp, °C
		sym	asym			
I	Pd(C ₆ F ₅) ₂ (OC ₄ H ₈) ₂			802, 792		100 dec
II	Pd(C ₆ Cl ₅) ₂ (OC ₄ H ₈) ₂			841, 832	627, 617	94 dec
III	Pt(C ₆ F ₅) ₂ (OC ₄ H ₈) ₂			818, 806		139 dec
IV	Pt(C ₆ Cl ₅) ₂ (OC ₄ H ₈) ₂			a	637, ^b 631	144 dec
V	Pd(C ₆ F ₅) ₂ (CO) ₂	2186	2163	798, 786		
VI	Pd(C ₆ Cl ₅) ₂ (CO) ₂	2173	2152	840, 833	619, 614	
VII	Pt(C ₆ F ₅) ₂ (CO) ₂	2174	2143	804, 792 ^b		205 ^c
VIII	Pt(C ₆ Cl ₅) ₂ (CO) ₂	2160	2126	847, 842	629, 623	208 dec

^aThe presence of a very strong absorption due to the OC₄H₈ precludes the assignment. ^bShoulder. ^cSublimes.

Organometallics, 1985, 4 (10), pp 1912–1914

DOI: 10.1021/om00129a047

Publication Date: October 1985



From the ACS Legacy Archives

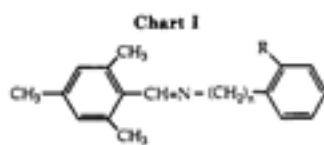
Cyclopalladation of *N*-Mesitylbenzylideneamines. Aromatic versus Aliphatic C–H Activation

Joan Albert, Rosa Maria Ceder, Montserrat Gómez, Jaume Granell, and Joaquim Sales*

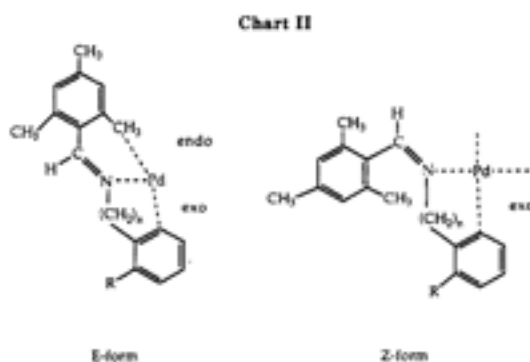
Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647, 08028 Barcelona, Spain

Received September 11, 1991

The action of $\text{Pd}(\text{AcO})_2$ on the imines 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}=\text{N}(\text{CH}_2)_n\text{-2'-RC}_6\text{H}_4$ ($\text{R} = \text{H}$, $n = 0\text{--}2$ (**1a-c**); $\text{R} = \text{CH}_3$, $n = 1$ (**1d**)), in refluxing acetic acid, affords six-membered endo metallacycles possessing an aliphatic carbon-metal bond, in preference to four-, five-, or six-membered exo metallacycles with an aromatic carbon-metal bond. The five-membered exo metallacycles can be obtained by working under milder conditions and isomerize to the more stable six-membered endo metallacycles in refluxing acetic acid. The action of $\text{Pd}(\text{AcO})_2$ on the imines 2- CH_3 -3- R^1 -4- $\text{R}^2\text{C}_6\text{H}_2\text{CH}=\text{NC}_6\text{H}_5$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$ (**1f**); $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{CH}_3\text{O}$ (**1g**)) affords the five-membered endo metallacycles with an aromatic carbon-metal bond, but with the imine 2,5- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{CH}=\text{NC}_6\text{H}_5$ (**1e**) the methyl group at carbon 5 prevents the metalation of the ortho carbon atom and the endo six-membered metallacycle with an aliphatic carbon-metal bond is formed. The reasons for the preference to form endo compounds and the high stability of six-membered derivatives containing Pd–C benzylic bonds are discussed.



1a ($n=0$, $\text{R}=\text{H}$)
1b ($n=1$, $\text{R}=\text{H}$)
1c ($n=2$, $\text{R}=\text{H}$)
1d ($n=1$, $\text{R}=\text{CH}_3$)



Organometallics, **1992**, *11* (4), pp 1536–1541

DOI: 10.1021/om00040a025

Publication Date: April 1992



From the ACS Legacy Archives

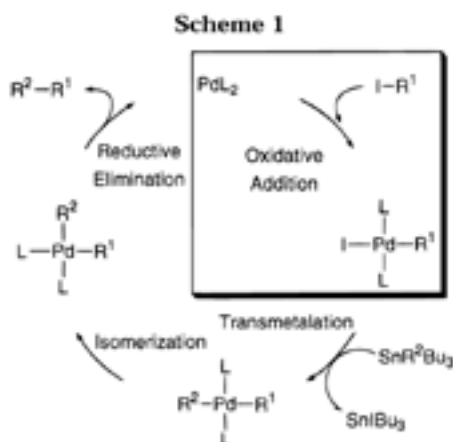
On the Configuration Resulting from Oxidative Addition of RX to Pd(PPh₃)₄ and the Mechanism of the *cis-to-trans* Isomerization of [PdRX(PPh₃)₂] Complexes (R = Aryl, X = Halide)[†]

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Received October 31, 1997

The oxidative addition of RI to Pd(0) and further *cis-to-trans* isomerization, which are involved in the Stille reaction and other Pd-catalyzed syntheses, have been studied. C₆Cl₂F₃I (**1**, C₆Cl₂F₃ = 3,5-dichlorotrifluorophenyl) adds to Pd(PPh₃)₄ in THF at room temperature giving *cis*-[Pd(C₆Cl₂F₃)I(PPh₃)₂] (**2**), which could be isolated before isomerization to the more stable *trans*-[Pd(C₆Cl₂F₃)I(PPh₃)₂] (**3**). A ¹⁹F NMR kinetic study of the isomerization of **2** in THF at 322.6 K reveals a first-order law $r_{\text{iso}} = k_{\text{iso}}[\mathbf{2}]$, with $k_{\text{iso}} = f + g[\mathbf{2}]_0 + (h + i[\mathbf{2}]_0)/([\text{PPh}_3] + j)$ ($f = (1.66 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$, $g = (2.5 \pm 0.2) \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$, $h = (1.3 \pm 0.7) \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$, $i = (4 \pm 2) \times 10^{-7} \text{ s}^{-1}$, and $j = (1.4 \pm 0.7) \times 10^{-5} \text{ mol L}^{-1}$). A four-pathway mechanism accounts for these results: Two are assigned to the associative replacements of PPh₃ coordinated to **2** by an iodide ligand of I-[Pd] (I-[Pd] = **2** or **3**), both THF-assisted (coefficient h) or direct (coefficient i), leading to a monoiodide-bridged intermediate *cis*-{Pd(C₆Cl₂F₃)I(PPh₃)(μ -I)-[Pd]}. The later rearranges via terminal-for-bridging iodide exchange to *trans*-{Pd(C₆Cl₂F₃)I(PPh₃)(μ -I)-[Pd]}, which is finally cleaved by PPh₃ yielding complex **3**. The other two concurrent pathways are assigned to the isomerization via two consecutive Berry pseudorotations in the pentacoordinated species derived from **2** by coordination of THF (coefficient g) or I-[Pd] (coefficient f). The apparent activation entropy associated with k_{iso} is negative ($\Delta S^\ddagger = -21 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$), in agreement with the proposed bimolecular mechanisms.



Organometallics, **1998**, 17 (5), pp 954–959

DOI: 10.1021/om9709502

Publication Date (Web): February 10, 1998

Study of the Reactivity of 2-Acetyl-, 2-Cyano-, 2-Formyl-, and 2-Vinylphenyl Palladium(II) Complexes. Mono- and Triinsertion of an Isocyanide into the Pd–C Bond. A 2-Cyanophenyl Palladium Complex as a Ligand

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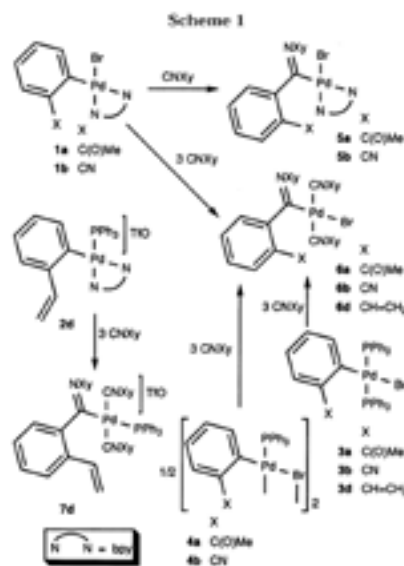
Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Aptdo. 4021, E-30071 Murcia, Spain

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We have studied the reactivity of the complexes $[\text{Pd}(\text{C}_6\text{H}_4\text{X}-2)\text{Br}(\text{bpy})]$ ($\text{bpy} = 2,2'$ -bipyridine; $\text{X} = \text{C}(\text{O})\text{Me}$ (**1a**), CN (**1b**), CHO (**1c**)), $[\text{Pd}\{\text{C}_6\text{H}_4\text{CH}=\text{CH}_2-2\}(\text{PPh}_3)(\text{bpy})](\text{TfO})$ ($\text{TfO} = \text{CF}_3\text{SO}_3^-$; **2d**), *trans*- $[\text{Pd}(\text{C}_6\text{H}_4\text{X}-2)\text{Br}(\text{PPh}_3)_2]$ ($\text{X} = \text{C}(\text{O})\text{Me}$ (**3a**), CN (**3b**), $\text{CH}=\text{CH}_2$ (**3d**)), and $[\text{Pd}(\mu\text{-Br})(\text{C}_6\text{H}_4\text{X}-2)(\text{PPh}_3)_2]$ ($\text{X} = \text{C}(\text{O})\text{Me}$ (**4a**), CN (**4b**)). Their reactions with XyNC ($\text{Xy} = 2,6$ -dimethylphenyl) depend on the nature of X and the other ligands and on the reaction conditions. The products of these reactions are mono- and triinserted complexes. Among the former are $[\text{Pd}\{\text{C}(\text{=NXy})\text{C}_6\text{H}_4\text{X}-2\}\text{Br}(\text{L}_2)]$ ($\text{L}_2 = \text{bpy}$, $\text{X} = \text{C}(\text{O})\text{Me}$ (**5a**), CN (**5b**); $\text{L} = \text{CNXy}$, $\text{X} = \text{C}(\text{O})\text{Me}$ (**6a**), CN (**6b**), $\text{CH}=\text{CH}_2$ (**6d**)) and *trans*- $[\text{Pd}\{\text{C}(\text{=NXy})\text{C}_6\text{H}_4\text{CH}=\text{CH}_2-2\}(\text{CNXy})_2(\text{PPh}_3)](\text{TfO})$ (**7d**). The reaction of **1c** with XyNC (1:5 molar ratio) gives **10**, a product resulting after substitution of bpy , coordination of two molecules of XyNC , triinsertion of XyNC , and a cyclization resulting after the attack of the nitrogen of the first inserted molecule at the carbon atom of the formyl group. The complexes $[\text{Pd}\{\kappa^2\text{C}, \text{N}^3\text{-C}(\text{=NXy})\text{C}(\text{=NXy})\text{C}_6\text{H}_4\text{X}-2\}\text{Br}(\text{CNXy})]$ ($\text{X} = \text{C}(\text{O})\text{Me}$ (**8a**), CN (**8b**)) were obtained by reacting (i) **3a** or **3b** with XyNC (1:4 molar ratio) or (ii) $\text{Pd}(\text{dba})_2$ ($\text{dba} = \text{dibenzylideneacetone}$) with $\text{BrC}_6\text{H}_4\text{X}-2$ and XyNC (1:1:4 molar ratio). When this oxidative addition reaction was carried out with $\text{BrC}_6\text{H}_4\text{CHO}-2$, the resulting product decomposed to give the Pd(I) complex $[\text{Pd}_2\text{Br}_2(\text{CNXy})_4]$ (**9**). $\text{Ti}(\text{TfO})$ was reacted with (i) **8a** and **8b** (1:1 molar ratio) to give the corresponding triflate complexes **11a** and **11b**, (ii) **4a** (1:2 molar ratio) in the presence of moisture to give the cyclopalladated aquo complex $[\text{Pd}\{\kappa^2\text{C}, \text{O-C}_6\text{H}_4\{\text{C}(\text{O})\text{Me}-2\}(\text{OH}_2)(\text{PPh}_3)\}](\text{TfO})$ (**12a**), and (iii) **4b** (3:1 molar ratio) to give $[\text{Pd}(\text{C}_6\text{H}_4\text{CN}-2)(\kappa^2\text{N}, \text{N}-4\text{b})(\text{PPh}_3)](\text{TfO})$ (**13b**), in which **4b** behaves as a ligand through the two cyano groups. The crystal structures of **5b**, **6b**, **7d**, **8a,b**, **9**, **10**, **11a,b**, **12a**, and **13b** have been determined by X-ray diffraction studies.



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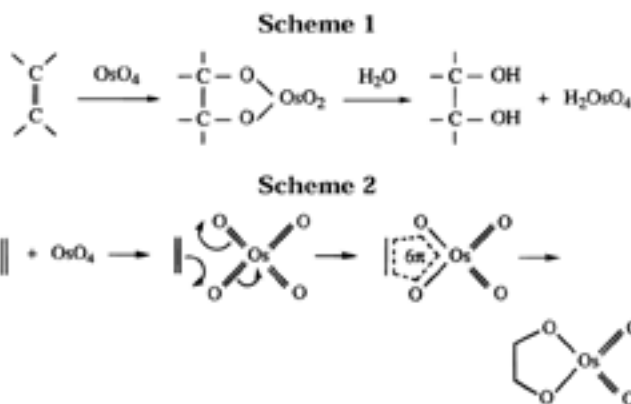
Density Functional Study of the [2+2]- and [2+3]-Cycloaddition Mechanisms for the Osmium-Catalyzed Dihydroxylation of Olefins

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Received September 12, 1996[®]

The postulated intermediates in the base-free and base-assisted addition of OsO₄ to olefins have been optimized using density functional theory (DFT). Ammonia was chosen as the base and ethylene as the olefin. The corresponding transition states have been characterized fully. Further, the activation barriers have been computed at the nonlocal level, and special attention has been given to the two different mechanistic hypothesis proposed for this reaction. In particular, the hypothesis by Sharpless of a [2+2]-cycloaddition pathway involving the formation of a four-member ring as an intermediate has been ruled out since the corresponding activation barrier was calculated to be as high as 39 kcal mol⁻¹. The addition of a NH₃ ligand to the osmium catalyst does not reduce significantly the [2+2] energy barrier. By contrast, it seems perfectly feasible that the dihydroxylation reaction proceeds through a [2+3] mechanism leading to the formation of a five-member ring intermediate as claimed by Corey. Such a process is found to be clearly exothermic and to involve a very small activation barrier of less than 2 kcal mol⁻¹. A detailed analysis of the sequence describing exactly how the cycloaddition proceeds along the reaction path has also been performed by means of intrinsic reaction coordinate (IRC) calculations for the two studied mechanisms.



Organometallics, **1997**, *16* (1), pp 13–19

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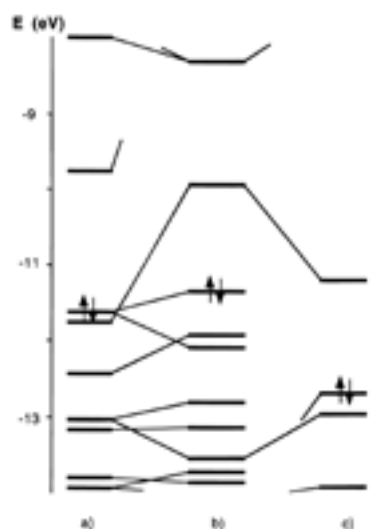
Addition of Carbon Nucleophiles to the Allenylidene Ligand of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$: Synthesis of New Organic Ligands by Formal C–C Coupling between Mutually Inert Fragments

Miguel A. Esteruelas,* Angel V. Gómez, Ana M. López, Javier Modrego, and Enrique Oñate

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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EHT-MO Calculations on the model cation $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CH}_2)(\text{CO})(\text{PH}_3)]^+$ (**1a**) suggest that 23% and 31% of the LUMO and 26% of the HOMO of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**1**) are located on C_α , C_γ , and C_β of the allenylidene ligand, respectively. On the basis of these results, we report a new synthetic strategy for the preparation of compounds resulting from the formal addition of phenylacetylene, acetone, and methane to the allenylidene of **1**. Treatment of **1** with $\text{LiC}\equiv\text{CPh}$ leads to the allenyl complex $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{C}=\text{CPh})=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**2**) and the alkynyl derivative $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{C}=\text{C}(\text{Ph})_2\text{C}=\text{CPh}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**3**). The reaction of **2** with HBF_4 affords the substituted carbene compound $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{C}=\text{CPh})\text{CH}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**4**), which is a result from the formal addition of phenylacetylene to the $\text{C}_\alpha\text{-C}_\beta$ double bond of the allenylidene of **1**. The molecular structure of **4** has been determined by X-ray crystallography. The geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face. The $\text{Ru}=\text{C}$ bond length is 2.004(5) Å. In the presence of KOH , complex **1** reacts with acetone to give $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{C}-\text{C}(\text{Ph})_2\text{CH}_2\text{C}(\text{O})\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**5**). The reaction of **5** with HBF_4 leads to the unsaturated cyclic carbene complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{CCH}_2\text{C}(\text{Ph})_2\text{CH}=\text{C}(\text{CH}_3)\text{O}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**6**). Complex **5** also reacts with 2 equiv of $\text{CF}_3\text{CO}_2\text{D}$ to give $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{CCD}_2\text{C}(\text{Ph})_2\text{CH}=\text{C}(\text{CH}_3)\text{O}\}(\text{CO})(\text{P}^i\text{Pr}_3)](\text{CF}_3\text{CO}_2)$ (**6-d₂**) and $\text{CF}_3\text{CO}_2\text{H}$, and the reaction of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{C}-\text{C}(\text{Ph})_2\text{CD}_2\text{C}(\text{O})\text{CD}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**5-d₃**) with 2 equiv of HBF_4 affords $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{CCH}_2\text{C}(\text{Ph})_2\text{CD}=\text{C}(\text{CD}_3)\text{O}\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**6-d₄**) and DBF_4 . On the basis of these isotope labeling experiments, the mechanism for the addition of acetone to the allenylidene ligand of **1** is discussed. Complex **1** also reacts with $\text{Na}(\text{acac})$ and CH_3Li . The reaction with $\text{Na}(\text{acac})$ leads to $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{C}-\text{C}(\text{Ph})_2\text{CH}[\text{C}(\text{O})\text{CH}_3]_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**7**), while the treatment of **1** with CH_3Li gives a mixture of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{CH}_3)=\text{C}=\text{CPh}_2\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**8**) and $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{C}-\text{C}(\text{Ph})_2\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (**9**). Complex **9** reacts with HBF_4 to afford $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}=\text{CHC}(\text{Ph})_2\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**10**), which is a result of the formal addition of a C–H bond of methane to the $\text{C}_\beta\text{-C}_\gamma$ double bond of the allenylidene of **1**.



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Divergent Behavior of Palladium(II) and Platinum(II) in the Metalation of 1,3-Di(2-pyridyl)benzene

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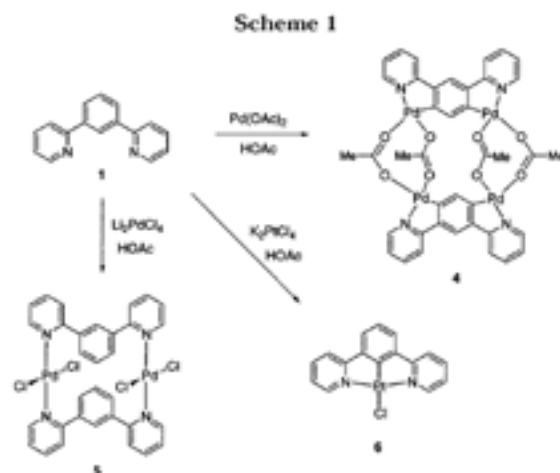
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1,3-Di(2-pyridyl)benzene undergoes regioselective orthometalation with Pd(OAc)₂ on the central aryl ring, giving rise to a dimeric complex in which four acetate units act as bridges between two doubly metalated ligands and each pyridine ligand coordinates to a different metal atom. The reaction with chloride-containing Pd(II) complexes does not lead to C–H activation but to coordination complexes without Pd–C bonds. Cycloplatination of 1,3-di(2-pyridyl)benzene takes place at C-2 of the benzene ring, generating a terdentate ligand. This behavior is the same as that previously observed for Ru and Os. Both orthometalated complexes have been structurally characterized by X-ray diffraction.

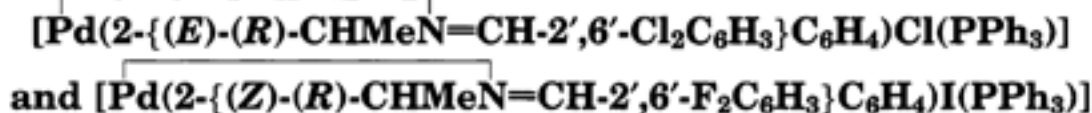


Organometallics, **1999**, *18* (17), pp 3337–3341

DOI: 10.1021/om990125g

Publication Date (Web): July 20, 1999

Optically Active Exocyclic Cyclopalladated Derivatives of Benzylidene-(*R*)-(1-phenylethyl)amines: Syntheses and X-ray Molecular Structures of



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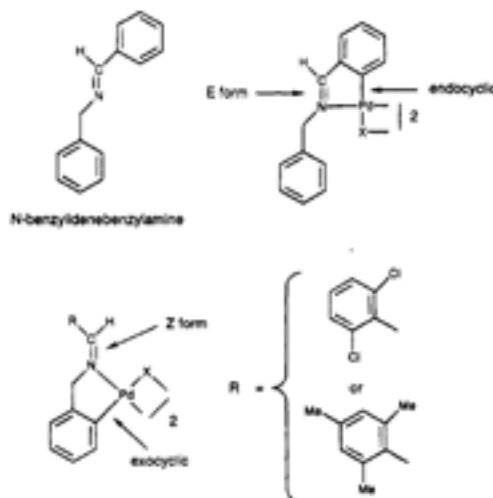
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The action of $\text{Pd}(\text{AcO})_2$ on benzylidene-(*R*)-(1-phenylethyl)amines, $\text{RCH}=\text{NCHMePh}$ ($\text{R} = 2,6\text{-Cl}_2\text{C}_6\text{H}_3$ (**1a**), $2,6\text{-F}_2\text{C}_6\text{H}_3$ (**1b**), $2,4,6\text{-(MeO)}_3\text{C}_6\text{H}_2$ (**1c**)), and subsequent treatment with LiCl , LiBr , or KI gives the corresponding halogen-bridged exocyclic cyclopalladated dimers $[\text{Pd}(\text{C}=\text{N})\text{X}]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in which the $\text{C}=\text{N}$ bond is not included in the metallacycle (compounds **2–4**, respectively). In relation to the *Z* or *E* form adopted by the imines in these cyclopalladated dimers, **2a,b–4a,b** consist of a mixture of (*Z,Z*), (*Z,E*), and (*E,E*) isomers, whereas **2c–4c** consist of only the (*E,E*) isomer. The equilibrium (*Z,Z*) + (*E,E*) \rightleftharpoons 2(*Z,E*) is observed in chloroform solutions of **2a,b–4a,b**. According to this equilibrium, when **2a,b** and **3a,b** are eluted through a column of SiO_2 with CHCl_3 , the initial band which contains a mixture of (*Z,Z*), (*Z,E*), and (*E,E*) isomers splits into two bands: the first contains the (*Z,Z*) isomer and the second the (*E,E*) isomer. The action of PPh_3 on **2a,b–4a,b** yields the corresponding cyclopalladated monomers $[\text{Pd}(\text{C}=\text{N})\text{X}(\text{PPh}_3)]$. When this reaction is carried out with dimers **2c–4c**, demethylation of one of the *ortho* methoxy groups is also observed, giving the tridentate species $[\text{Pd}(\text{C}=\text{N}-\text{O})(\text{PPh}_3)]$. The X-ray crystal structure of two monomers with PPh_3 has been determined. $[\text{Pd}(2-\{(E)-(R)\text{-CHMeN=CH-}2',6'\text{-Cl}_2\text{C}_6\text{H}_3\}\text{C}_6\text{H}_4)\text{Cl}(\text{PPh}_3)]$ crystallizes in the monoclinic space group $P2_1$ with $a = 16.996(4)$ Å, $b = 9.006(2)$ Å, $c = 9.655(2)$ Å, $\beta = 91.63(3)^\circ$, and $Z = 2$. $[\text{Pd}(2-\{(Z)-(R)\text{-CHMeN=CH-}2',6'\text{-F}_2\text{C}_6\text{H}_3\}\text{C}_6\text{H}_4)\text{I}(\text{PPh}_3)]$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 18.017(3)$ Å, $b = 14.204(2)$ Å, $c = 11.978(2)$ Å, and $Z = 4$.

Chart 1



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From the ACS Legacy Archives

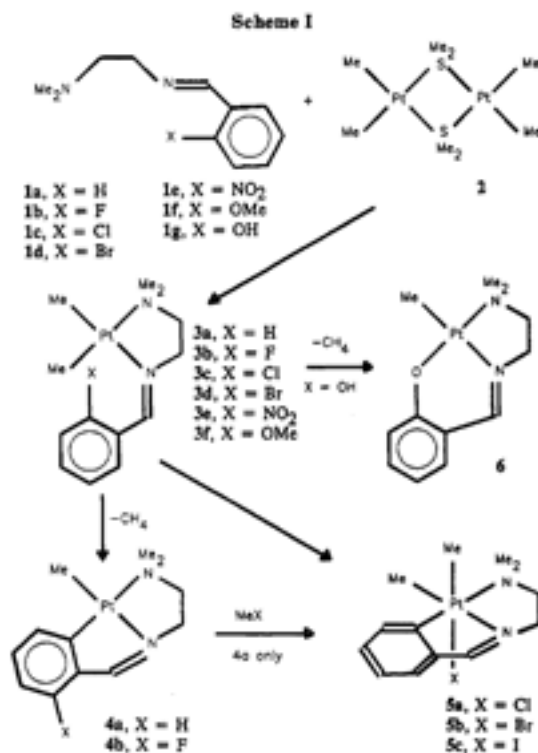
Competition between Intramolecular Oxidative Addition and Ortho Metalation in Organoplatinum(II) Compounds: Activation of Aryl-Halogen Bonds

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The ligands $2\text{-XC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2$ (**1**) react with $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ (**2**) to give $[\text{PtMe}_2(2\text{-XC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ (**3**), which then react either by ortho metalation to give CH_4 and $[\text{PtMe}(\text{2-XC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ (**4**) or undergo oxidative addition of the C-X bond to give $[\text{PtXMe}_2(\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ (**5**). These complexes, and related compounds with modified aryl substituents, have been characterized by NMR spectroscopy, and the derivative $[\text{PtClMe}_2(\text{ClC}_6\text{H}_3\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ (**7b**) has been characterized crystallographically. The complex $[\text{PtMe}(\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ reacts with CD_3Br or MeI to give $[\text{PtBrMe}(\text{CD}_3)(\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ or $[\text{PtIMe}_2(\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NMe}_2)]$, respectively, initially by trans oxidative addition. The ligands $2\text{-XC}_6\text{H}_4\text{CH}=\text{NR}$ ($\text{R} = \text{Ph}, \text{Pr}$) react with $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ to give similar products of ortho metalation, $[\text{PtMe}(\text{2-XC}_6\text{H}_4\text{CH}=\text{NR})(\text{SMe}_2)]$, or oxidative addition, $[\text{PtXMe}_2(\text{C}_6\text{H}_4\text{CH}=\text{NR})(\text{SMe}_2)]$. The kinetics of the reaction of **3** to give **4** or **5** have been studied, and the reactions each follow first-order kinetics. The activation parameters for both types of reaction are similar, and since the ortho metalation is presumed to occur by concerted C-H oxidative addition followed by rapid reductive elimination of methane, it is suggested that the oxidative addition of aryl-bromide or aryl-chloride bonds also occurs by a concerted mechanism. The rates of reaction are $\text{C-Br} > \text{C-Cl} > \text{C-H}$, and internal competition reactions give the sequence $\text{C-Cl} > \text{C-H} > \text{C-F}$. Hence, the overall reactivity series is $\text{C-Br} > \text{C-Cl} > \text{C-H} > \text{C-F}$, the series of increasing C-X bond energies. These are the first examples of aryl-halogen bond activation by platinum(II) complexes.



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Publication Date: August 1991



From the ACS Legacy Archives

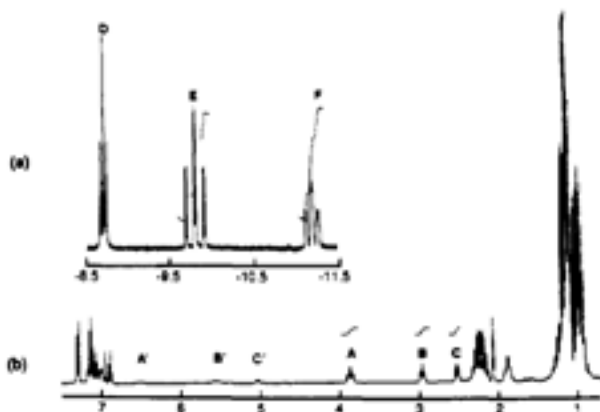
Reactivity of $\text{OsH}_4(\text{CO})(\text{PiPr}_3)_2$ toward Terminal Alkynes: Synthesis and Reactions of the Alkynyl–Dihydrogen Complexes $\text{OsH}(\text{C}_2\text{R})(\eta^2\text{-H}_2)(\text{CO})(\text{PiPr}_3)_2$ ($\text{R} = \text{Ph}, \text{SiMe}_3$)

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The tetrahydrido $\text{OsH}_4(\text{CO})(\text{PiPr}_3)_2$ (**1**) reacts with the stoichiometric amount of phenylacetylene under hydrogen atmosphere to give $\text{OsH}(\text{C}_2\text{Ph})(\eta^2\text{-H}_2)(\text{CO})(\text{PiPr}_3)_2$ (**2**). After several hours, under hydrogen atmosphere, **2** is converted into $\text{OsH}_2(\eta^2\text{-H}_2\text{C=CHPh})(\text{CO})(\text{PiPr}_3)_2$ (**4**), which subsequently evolves to **1** and styrene. **4** and acetone are produced from the reaction of **2** with 2-propanol. The dihydrogen ligand of **2** is easily displaced by neutral ligands such as CO, $\text{P}(\text{OMe})_3$, and Hpz to give the complexes $\text{OsH}(\text{C}_2\text{Ph})(\text{CO})\text{L}(\text{PiPr}_3)_2$ (**5–7**). The reaction of **2** with phenylacetylene affords $\text{Os}(\text{C}_2\text{Ph})_2(\text{CO})(\text{PiPr}_3)_2$ (**8**), which reacts with hydrogen to give **2** and styrene. The reaction of **8** with pyrazole gives rise to $\text{Os}(\text{C}_2\text{Ph})_2(\text{CO})(\text{Hpz})(\text{PiPr}_3)_2$ (**9**). The complexes $\text{OsH}(\text{C}_2\text{SiMe}_3)(\eta^2\text{-H}_2)(\text{CO})(\text{PiPr}_3)_2$ (**10**), $\text{OsH}(\text{C}_2\text{SiMe}_3)(\text{CO})\text{L}(\text{PiPr}_3)_2$ ($\text{L} = \text{P}(\text{OMe})_3$ (**11**), Hpz (**12**)), $\text{Os}(\text{C}_2\text{SiMe}_3)_2(\text{CO})(\text{PiPr}_3)_2$ (**13**), and $\text{Os}(\text{C}_2\text{SiMe}_3)_2(\text{CO})\text{L}(\text{PiPr}_3)_2$ ($\text{L} = \text{P}(\text{OMe})_3$ (**14**), Hpz (**15**)) were prepared similarly to the related 2–9 starting from **1** and (trimethylsilyl)acetylene. The reaction of **1** with methylpropiolate gives $\text{Os}(\text{C}_2\text{CO}_2\text{Me})(\text{CH}=\text{C}(\text{H})\text{C}(\text{OMe})=\text{O})(\text{CO})(\text{PiPr}_3)_2$ (**16**). The molecular structure of complex **16** has been determined. Crystals of **16** are orthorhombic, space group $Pna2_1$, with unit cell dimensions $a = 14.9009$ (6) Å, $b = 14.6152$ (5) Å, and $c = 14.0339$ (6) Å. The structure was solved and refined to the following R and R_w values: 0.022 and 0.022 on 4589 observed ($F \geq 5.0\sigma(F)$) data. The molecular structure determination has confirmed the σ -alkynyl coordination of a $\sigma\text{-C}\equiv\text{CCO}_2\text{Me}$ ligand, together with the reduction of a second alkyne molecule to give the corresponding vinylic ligand, which is bonded as a chelate group through the terminal vinylic carbon and the ketonic oxygen, generating a five-membered metallacycle ring. Two triisopropylphosphine molecules coordinated in relative trans positions and a carbonyl ligand, trans to the vinylic carbon, complete the osmium coordination sphere.



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DOI: 10.1021/om00027a016

Publication Date: March 1993



From the ACS Legacy Archives

Orthometalation of Primary Amines. 4.¹ Orthopalladation of Primary Benzylamines and (2-Phenylethyl)amine[†]

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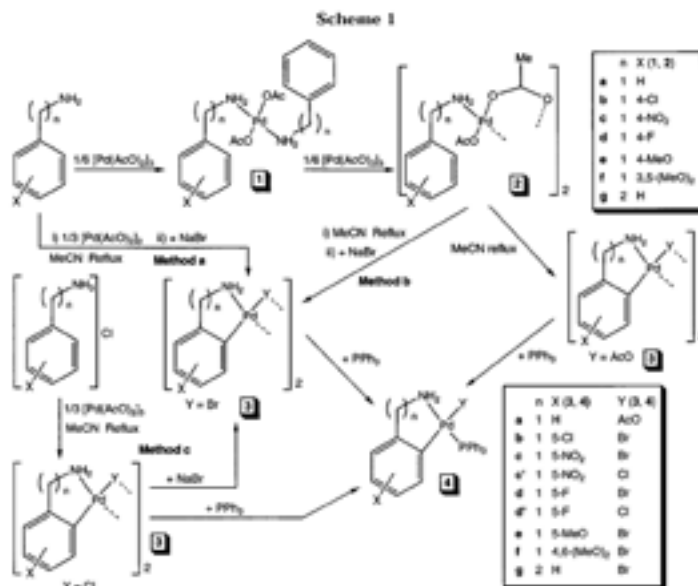
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Received November 12, 1996[®]

By the refluxing of an acetonitrile solution of $[\text{Pd}(\text{OAc})_2]_3$ and primary amines $4\text{-XC}_6\text{H}_4\text{-CH}_2\text{NH}_2$ (F, Cl, NO_2 , OMe), $3,5\text{-X}_2\text{C}_6\text{H}_3\text{CH}_2\text{NH}_2$ (X = OMe), or $\text{PhCH}_2\text{CH}_2\text{NH}_2$ (Pd:amine = 1:1) and subsequent addition of excess NaBr, the corresponding orthometalated complexes $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)\text{-}2,\text{X}\text{-}5\}(\mu\text{-Br})_2]_2$, $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)\text{-}2,\text{(OMe)}_2\text{-}4,6\}(\mu\text{-Br})_2]_2$, or $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)\text{-}2\}(\mu\text{-Br})_2]_2$ are obtained. Alternatively, the hydrochloride of $4\text{-XC}_6\text{H}_4\text{CH}_2\text{NH}_2$ (X = F, NO_2) can also be used to prepare the corresponding $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)\text{-}2,\text{X}\text{-}5\}(\mu\text{-Cl})_2]_2$ complexes. These results show that primary benzylamines can be orthometalated even if the substituents are electron-withdrawing groups and that 2-(phenyl)ethylamine can be orthometalated in spite of the six-membered ring that it forms. These reactions occur *via* intermediate complexes $[\text{Pd}(\text{OAc})_2\text{L}_2]$, which react with $[\text{Pd}(\text{OAc})_2]_3$ to give the dimeric species $[\text{Pd}(\text{OAc})(\mu\text{-OAc})\text{L}]_2$ (L = amine), from which in turn the orthometalated complexes are formed. Each of these steps has been studied, and both types of intermediates have been isolated for all the amines. PPh_3 reacts with the orthometalated complexes to give the corresponding products of the bridge splitting. The crystal structures of $[\text{Pd}(\text{OAc})(\mu\text{-OAc})\text{L}]_2$ (L = $4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{NH}_2$) and $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{CH}_2\text{NH}_2)\text{-}2\}\text{Br}(\text{PPh}_3)]$ have been determined by X-ray diffraction.



Organometallics, 1997, 16 (5), pp 826–833

DOI: 10.1021/om9609574

Publication Date (Web): March 4, 1997

Fluorous Phase Soluble Palladium Nanoparticles as Recoverable Catalysts for Suzuki Cross-Coupling and Heck Reactions

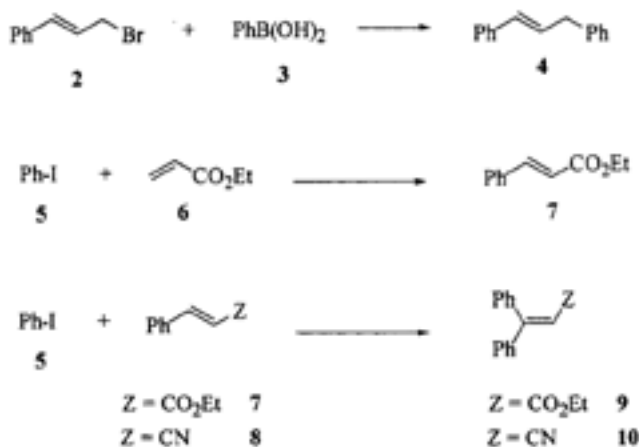
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1,5-Bis(4,4'-bis(perfluorooctyl)phenyl)-1,4-pentadien-3-one stabilizes palladium(0) nanoparticles (transmission electron microscopy) formed in the reduction of palladium dichloride with methanol. These palladium colloids are soluble in perfluorinated solvents, and they are efficient recoverable catalysts for Suzuki cross-couplings and Heck reactions under fluorous biphasic conditions.

Scheme 1. Suzuki and Heck Reactions Tested^a



Organometallics, **2001**, 20 (22), pp 4524–4528

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Publication Date (Web): September 27, 2001

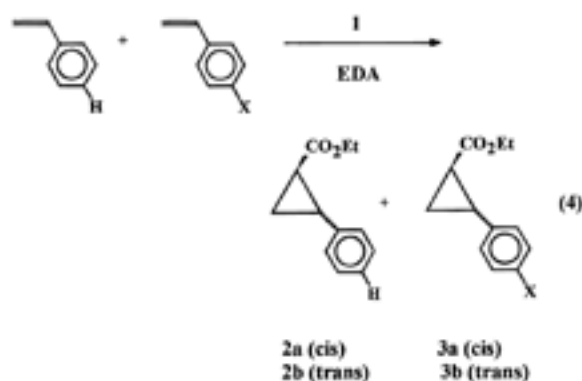
Substituent Effects on the Reaction Rates of Copper-Catalyzed Cyclopropanation and Aziridination of *para*-Substituted Styrenes[†]

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Relative rates of cyclopropanation and aziridination of a series of *para*-substituted styrenes have been determined using Tp'Cu(C₂H₄) (Tp' = hydridotris(3,5-dimethyl-1-pyrazolyl)borate) as the copper precatalyst in combination with N₂CHCO₂CH₂CH₃ and C₆H₅INSO₂C₆H₄CH₃ (PhI=NTs), respectively. For the cyclopropanation reaction, a linear plot of the experimental data is obtained by means of the Hammett equation, $\log(k_X/k_H) = \rho\sigma$ ($\rho = -0.85 \pm 0.07$). This correlation supports earlier mechanistic proposals of an electrophilic metal-carbene complex intermediate. In the case of the aziridination reaction, the experimental data can be fit with a two term equation of the type $\log(k_X/k_H) = \rho^+\sigma^+ + \rho^-\sigma^-$ (σ^+ are Jackson's radical substituent constants) leading to the values $\rho^+ = -0.28 \pm 0.06$ (polar contribution) and $\rho^- = +0.34 \pm 0.13$ (radical contribution). A paramagnetic copper nitrene species which behaves as an electrophilic, nitrogen-centered radical is proposed as the intermediate for the aziridination reaction.



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Publication Date (Web): September 30, 1997

Regioselective Nucleophilic Additions on Indenyl–Ruthenium(II)–Allenylidene Complexes. X-ray Crystal Structure of the Alkynyl Complex $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{C}\equiv\text{CH})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]^\dagger$

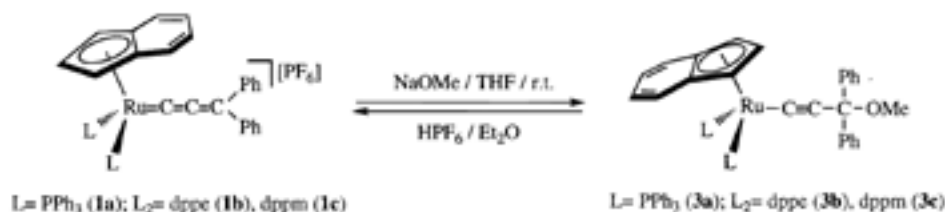
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The diphenylallenylidene complexes $[\text{Ru}(\text{=C=C=CPh}_2)(\eta^5\text{-C}_9\text{H}_7)\text{L}_2][\text{PF}_6]$ ($\text{L} = \text{PPh}_3$; $\text{L}_2 = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$ (dppe), bis(diphenylphosphino)methane (dppm)) (**1a–c**) react with NaOMe to yield the methoxyalkynyl derivatives $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{OMe})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)\text{L}_2]$ (**3a–c**). Protonation of these species gives back the starting allenylidene derivatives. Regioselective additions on the C_γ are also observed when **1a,b** are treated with LiR ($\text{R} = \text{Me}$, ^tBu), giving the alkynyl complexes $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{R})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)\text{L}_2]$ (**4a,b**, **5a,b**). Vinylidene derivatives $[\text{Ru}\{\text{=C=C}(\text{H})\text{C}(\text{R})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$ (**6a**, **7a**) can be prepared by protonation of complexes **4a** and **5a** with HBF_4 . The diphenylallenylidene compound **1c** reacts with Li^tBu to yield the metallacycle complex $[\text{Ru}\{\kappa^3(\text{C},\text{P},\text{P})\text{-C=C=CPh}_2(\text{Ph}_2\text{PCHPPH}_2)\}(\eta^5\text{-C}_9\text{H}_7)]$ (**8c**). The alkynyl complexes $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{C}=\text{CR})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ ($\text{R} = \text{Ph}$, ^nPr , H) (**9a–11a**) have been obtained by reaction of **1a** with lithium or sodium acetylides. Protonation of these derivatives yields the vinylidene complexes $[\text{Ru}\{\text{=C=C}(\text{H})\text{C}(\text{C}=\text{CR})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$ (**12a–14a**). The crystal structure of $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{C}=\text{CH})\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ (**11a**) was determined by X-ray diffraction methods. In the structure the alkynyl chain is nearly linear ($\text{Ru-C}(1)\text{-C}(2) = 175.0(2)^\circ$) with $\text{Ru-C}(1)$ and $\text{C}(1)\text{-C}(2)$ distances of 1.993(2) and 1.209(3) Å, respectively. The monosubstituted allenylidene complex $[\text{Ru}\{\text{=C=C=C}(\text{H})\text{Ph}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ (**2a**) reacts with PMe_3 , PMe_2Ph , PMePh_2 , and PPh_3 to yield the cationic alkynyl–phosponio derivatives $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{PR}_3)(\text{H})\text{Ph}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ (**17a–20a**) in a regioselective way. Similarly, allenylidene complexes **1a–c** add PMe_3 to give the corresponding alkynyl–phosponio derivatives **15a–c**. $[\text{Ru}\{\text{C}\equiv\text{CC}(\text{PMe}_3)\text{Ph}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{dppm})][\text{PF}_6]$ (**15c**) undergoes an isomerization process to yield the thermodynamically more stable allenyl–phosponio complex $[\text{Ru}\{\text{C}(\text{PMe}_3)=\text{C=CPh}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{dppm})][\text{PF}_6]$ (**21c**). $[\text{Ru}\{\text{C}(\text{PMe}_2\text{Ph})=\text{C=CPh}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{dppm})][\text{PF}_6]$ (**22c**) can be obtained directly by addition of PMe_2Ph to the C_α atom of **1c**. The behavior of the diphenylallenylidene complexes **1a–c** toward sodium 2-methylthiophenolate is also discussed.

Scheme 1



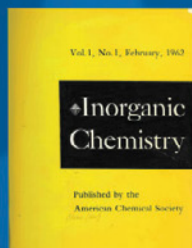
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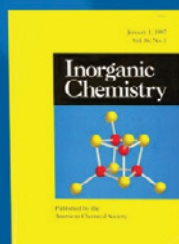
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