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Special Issue: New Organometallic Compounds for Applications in Homogeneous Catalysis

Foreword 3113

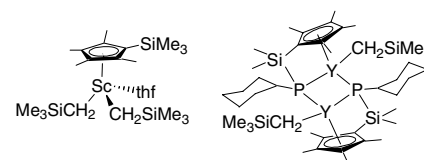
Review

Zhaomin Hou, Yunjie Luo, Xiaofang Li

J. Organomet. Chem. 691 (2006) 3114

Cationic rare earth metal alkyls as novel catalysts for olefin polymerization and copolymerization

The cationic rare earth metal alkyl species, generated by the reaction of a half-sandwich rare earth metal bis(alkyl) complex with 1 equiv. of a borate compound $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, acts as an excellent catalyst system for the regio- and stereospecific polymerization and copolymerization of various olefins, affording a series of new polymers which are difficult to be prepared previously.



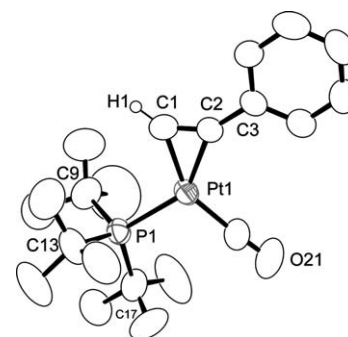
Regular papers

Richard D. Adams, Burjor Captain, Lei Zhu

J. Organomet. Chem. 691 (2006) 3122

The importance of cluster fragmentation in the catalytic hydrogenation of phenylacetylene by PtRu_5 carbonyl cluster complexes

$\text{PtRu}_5(\text{CO})_{13}(\text{PBU}_3)_2(\mu_3\text{-PhC}_2\text{H})(\mu_5\text{-C})$ (**2**) has been shown to be a catalyst precursor for the hydrogenation of PhC_2H to styrene and ethylbenzene. Three new organometallic products have been found in the catalyst solutions. These are $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-C})[\text{PtPBU}_3](\mu_3\text{-PhC}_2\text{H})(\mu\text{-H})_2$ (**4**), $\text{Pt}(\text{PBU}_3)_2(\text{PhC}_2\text{H})(\text{CO})$ (**5**) and $\text{Ru}_5(\text{CO})_{11}(\mu_4\text{-CCHCPh})(\mu_4\text{-HC}_2\text{Ph})(\mu_3\text{-PhC}_2\text{H})$ (**6**). Compounds **4–6** have been synthesized independently and structurally characterized and each compound has been tested independently for its ability to produce hydrogenation of PhC_2H catalytically. Compound **5** is significantly more active than **4** or **6**.

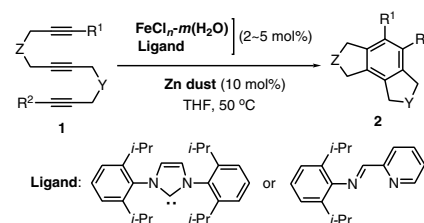


Naoko Saino, Daisuke Kogure, Kouki Kase, Sentaro Okamoto

J. Organomet. Chem. 691 (2006) 3129

Iron-catalyzed intramolecular cyclotrimerization of triynes to annulated benzenes

An iron species derived from FeCl_2 or FeCl_3 by in situ reduction with zinc powder in the presence of imidazol-2-ylidene or bidentate nitrogen ligand could effectively catalyze intramolecular cycloisomerization of triynes to annulated benzenes.

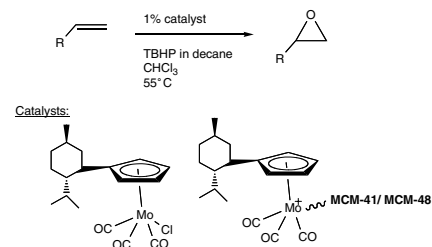


Marta Abrantes, Ayyamperumal Sakthivel, Carlos C. Romão, Fritz E. Kühn

J. Organomet. Chem. 691 (2006) 3137

A chiral menthyl cyclopentadienyl molybdenum tricarbonyl chloro complex: Synthesis, heterogenization on MCM-41/MCM-48 and application in olefin epoxidation catalysis

The chiral complex $[(-)\text{-menthylCp}]\text{Mo}(\text{CO})_3\text{Cl}$ is synthesized and tested as catalyst for the epoxidation of *cis*-cyclooctene, styrene and *trans*- β -methylstyrene in the presence of *tert*-butyl hydroperoxide (TBHP). The complex is also immobilized on mesoporous MCM-41 and MCM-48 surfaces leading to the grafted new materials AM-41CpMoChi and AM-48CpMoChi and examined as heterogeneous catalyst.

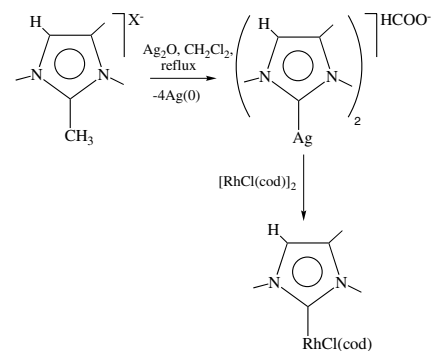


Robert H. Crabtree

J. Organomet. Chem. 691 (2006) 3146

Some chelating C-donor ligands in hydrogen transfer and related catalysis

Recent work throws light on synthetic, steric, and electronic aspects of NHC complexes and on outer sphere reactivity effects.

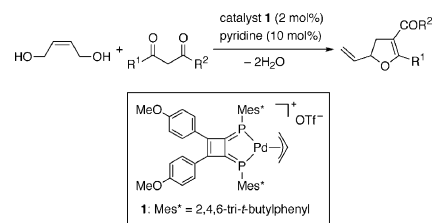


Hiroki Murakami, Yukio Matsui, Fumiyuki Ozawa, Masaaki Yoshifuji

J. Organomet. Chem. 691 (2006) 3151

Cyclodehydration of *cis*-2-butene-1,4-diol with active methylene compounds catalyzed by a diphosphinidene-cyclobutene-coordinated palladium complex

Complex **1** coordinated with 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*t*-butylphenyl)phosphinidene)cyclobutene (DPCB-OMe) efficiently catalyzes cyclodehydration of *cis*-2-butene-1,4-diol with active methylene compounds to give 2-vinyl-2,3-dihydrofurans in good to high yields.

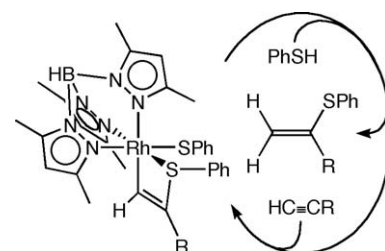


Yoshiyuki Misumi, Hidetake Seino, Yasushi Mizobe

J. Organomet. Chem. 691 (2006) 3157

Addition of benzenethiol to terminal alkynes catalyzed by hydrotris(3,5-dimethylpyrazolyl)borate-Rh(III) bis(thiolate) complex: Mechanistic studies with characterization of the key intermediate

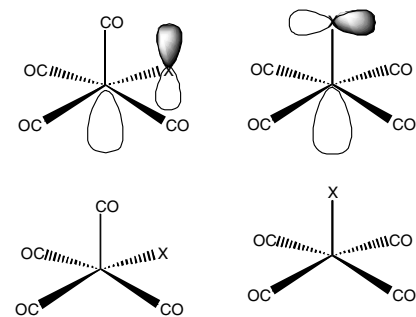
Reaction of the Rh(III)-thiolate complex $[\text{Tp}^*\text{Rh}(\text{SPh})_2(\text{MeCN})]$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate) with terminal alkynes $\text{RC}\equiv\text{CH}$ (R = aryl, alkyl) forms a rhodathiacyclobutene complex $[\text{Tp}^*\text{Rh}(\text{SPh})\{\eta^2\text{-CH}=\text{CR}(\text{SPh})\}]$. The former complex as well as $[\text{Tp}^*\text{Rh}(\text{cyclooctene})(\text{MeCN})]$ catalyze regioselective addition of PhSH to $\text{RC}\equiv\text{CH}$, yielding $\text{R}(\text{PhS})\text{C}=\text{CH}_2$, via the rhodathiacyclobutene complex as an intermediate.



D. Michael P. Mingos*J. Organomet. Chem.* 691 (2006) 3165

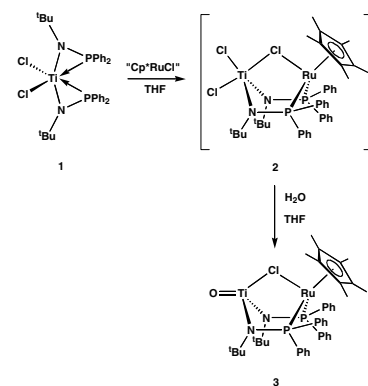
The relevance of the complementary spherical electron density model to organometallic intermediates involved in homogeneous catalysis

The implications of the Complementary Spherical Electron Density Model to co-ordinatively unsaturated intermediates in homogeneous catalytic processes are discussed. The geometric consequences of the model for 16 and 14 electron complexes are particularly important and are supported by numerous recent X-ray crystallographic investigations.

**Yusuke Sunada, Takashi Sue, Taisuke Matsumoto, Hideo Nagashima***J. Organomet. Chem.* 691 (2006) 3176

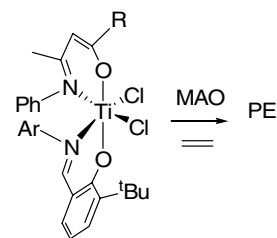
Titanium(IV) phosphinoamide as a unique bidentate ligand for late transition metals II: Ti–Ru heterobimetallics bearing a bridging chlorine atom

Treatment of titanium phosphinoamide, $(\text{Ph}_2\text{PN}^t\text{Bu})_2\text{TiCl}_2$ (**1**), with $[\text{Cp}^*\text{RuCl}]_4$ afforded $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{Ph}_2\text{PN}^t\text{Bu})_2\text{Ti}=\text{O}$ (**3**) through $\text{Cp}^*\text{Ru}(\mu\text{-Cl})(\text{Ph}_2\text{PN}^t\text{Bu})_2\text{TiCl}_2$ (**2**) as an intermediate. The molecular structure of **3** indicated the existence of intramolecular donor–acceptor interaction between the lone pair electrons of $\mu\text{-Cl}$ atom and the Lewis acidic titanium center.

**Dale A. Pennington, Ross W. Harrington, William Clegg, Manfred Bochmann, Simon J. Lancaster***J. Organomet. Chem.* 691 (2006) 3183

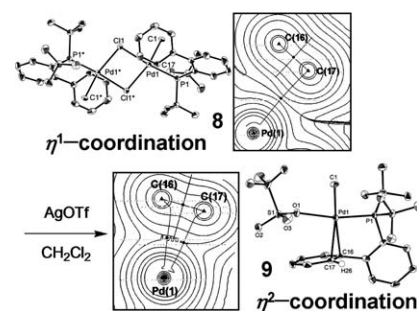
The synthesis, structure and ethene polymerization activity of octahedral heteroligated (salicylaldiminato)(β -enamino-ketonato)titanium complexes: The X-ray crystal structure of $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(Ph)}\}\{\text{(Ph)NC(Me)C(H)-C(Me)O}\}\text{TiCl}_2$

Treatment of the mono(salicylaldiminato)titanium complexes $\{3\text{-Bu}^t\text{-2-(O)C}_6\text{H}_3\text{CHN(Ar)}\}\text{TiCl}_2(\text{THF})$ ($\text{Ar} = \text{C}_6\text{H}_5, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ or C_6F_5) with the potassium β -enamino-ketonates $(\text{C}_6\text{H}_5)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{R})\text{OK}$ ($\text{R} = \text{CH}_3, \text{CF}_3$) yielded the first examples of heteroligated (salicylaldiminato) (β -enamino-ketonato)titanium dichloride complexes. These complexes polymerize ethene when activated with MAO, giving productivities up to $5650 \text{ kg PE (mol metal)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$.

**Makoto Yamashita, Ikuko Takamiya, Koichiro Jin, Kyoko Nozaki***J. Organomet. Chem.* 691 (2006) 3189

Syntheses and characterizations of methylpalladium complexes bearing a biphenyl-based bulky phosphine ligand: Weak interactions suggested by NBO and QTAIM analyses

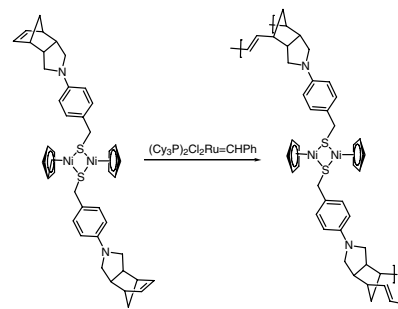
Two methylpalladium complexes $[\text{Pd}(\text{I})(\text{Me})\text{-Cl}]_2$ (**8**) and $\text{Pd}(\text{I})(\text{Me})\text{OTf}$ (**9**) where **1** is $^t\text{Bu}_2\text{P}(\text{biphenyl-2-yl})$ were synthesized and fully characterized by NMR and X-ray crystallography. In the solid state of **8**, the terminal phenyl ring of ligand **1** coordinates to the palladium through a weak η^1 -coordination. On the other hand, in the case of **9**, the terminal phenyl ring of **1** plays as η^2 -coordinating ligand. Theoretical calculations also supported the existence of these weak interactions.



Hui-Chun Yang, Shiu-Mei Lin, Yi-Hung Liu,
Yu Wang, Mei-Man Chen, Hwo-Shuenn Sheu,
Der-Lii Tsou, Chih-Hsiu Lin, Tien-Yau Luh
J. Organomet. Chem. 691 (2006) 3196

Ring opening metathesis polymerization of
bisnorbornene derivatives linked by Cp_2Ni_2 -
($\mu\text{-S}$)₂ bridge

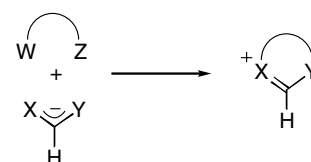
ROMP of **2** with Grubbs I catalyst in CH_2Cl_2
furnished the corresponding polymer **5** which
was characterized by spectroscopic means,
particularly, MAS ¹³NMR. The EXAFS of **5**
results were compared with those of the
monomeric starting material **2** and the X-ray
data of **2**.



Rodolphe Jazzar, Hongze Liang,
Bruno Donnadieu, Guy Bertrand
J. Organomet. Chem. 691 (2006) 3201

A new synthetic method for the preparation of
protonated-NHCs and related compounds

The protonated form of NHCs and a variety
of related heterocyclic salts, of various ring
sizes, are readily prepared by addition of (di)-
hetero-allyl anions to compounds featuring
two leaving groups.



Note

Geert-Jan M. Meppelder, Thomas P. Spaniol,
Jun Okuda
J. Organomet. Chem. 691 (2006) 3206

A binaphtholate titanium complex featuring a
linear tetradentate [OSSO]-bis(phenolato)
ligand: Synthesis and partial hydrolysis to a
homochiral dinuclear complex

The chiral-at-metal complex $[(\text{R})\text{-C}_{20}\text{H}_{12}\text{-O}_2\text{Ti}\{(\text{C}_6\text{H}_2\text{O-}^t\text{Bu-6-Me-4})_2\text{S}(\text{CH}_2)_2\text{S}\}]$ is
available from reaction of $[(\text{R})\text{-C}_{20}\text{H}_{12}\text{-O}_2\text{Ti}(\text{O}^i\text{Pr})_2]$ with 1,4-dithiaalkanediy-2,
2'-bis(6-*tert*-butyl-4-methyl-phenol) in low
diastereomeric excess. Partial hydrolysis of this
complex results in the formation of a dinuclear
species $[\mu\text{-}\{(\text{R})\text{-C}_{20}\text{H}_{12}\text{O}_2\}\text{-}\mu\text{-O}\text{-}\{(\Lambda)\text{-Ti}\{(\text{C}_6\text{H}_2\text{O-}^t\text{Bu-6-Me-4})_2\text{S}(\text{CH}_2)_2\text{S}\}_2]$, in which the two tita-
nium centres are homochiral.

