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Chemistry

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## Contents

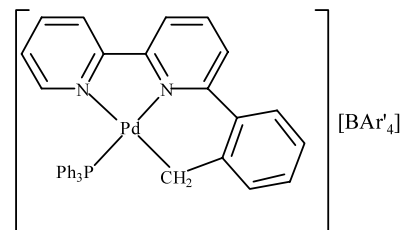
### Regular Papers

**Sergio Stoccoro, Barbara Soro,  
Giovanni Minghetti, Antonio Zucca,  
Maria A. Cinellu**

*J. Organomet. Chem. 679 (2003) 1*

Reactivity of 6-(2-tolyl)- and 6-(2,6-xylyl)-2,2'-bipyridines with palladium(II) derivatives. Selective C(sp<sup>3</sup>)-H vs. C(sp<sup>2</sup>)-H activation

The reaction of 6-(2-tolyl) and 6-(2,6-xylyl)-2,2'-bipyridine, L, with Na<sub>2</sub>[PdCl<sub>4</sub>], {Pd(OAc)<sub>2</sub>} and [Pd(COD)(Me)Cl] has been investigated. Besides adducts and N,N,C(sp<sup>2</sup>)-cyclometallated species, selective C(sp<sup>3</sup>)-H activation is achieved from [Pd(L)(Me)Cl] with loss of methane. The 6-membered N,N,C(sp<sup>3</sup>) species have been isolated as [Pd(L-H)(PPh<sub>3</sub>)] [BAr'<sub>4</sub>] (Ar' = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).

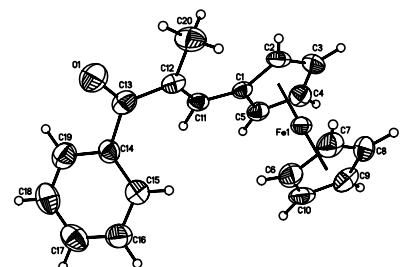


**Daniel I. Méndez, Elena Klimova,  
Tatiana Klimova, León Fernando,  
Simón O. Hernández, Marcos G. Martínez**

*J. Organomet. Chem. 679 (2003) 10*

Solvent-free aldol condensations: synthesis of ferrocenyldienones

The aldol condensation of ferrocenecarbaldehyde and acetylferrocene with aldehydes and ketones proceeded more efficiently and stereoselectively in the absence of a solvent than in solution. In all the cases, *E*-configured enones were obtained, which was confirmed by X-ray crystallographic studies of one of the products.

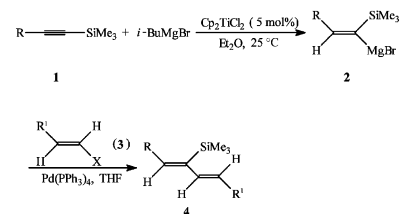


**Mingzhong Cai, Wenyan Hao, Hong Zhao,  
Caisheng Song**

*J. Organomet. Chem. 679 (2003) 14*

Novel stereoselective synthesis of 1,3-dienylsilanes via hydromagnesiation reaction of alkynylsilanes

Hydromagnesiation of alkynylsilanes **1** gives (*Z*)- $\alpha$ -silylvinyl Grignard reagents **2**, which undergo palladium-catalyzed cross-coupling reactions with alkenyl halides **3** to afford stereoselectively 1,3-dienylsilanes **4** in good yields.

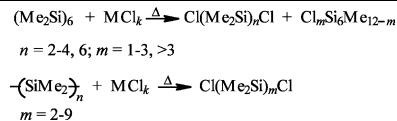


**A.I. Chernyavskii, D.Yu. Larkin, N.A. Chernyavskaya**

*J. Organomet. Chem.* 679 (2003) 17

Reactions of dodecamethylcyclohexasilane and polydimethylsilane with metal chlorides

The reactions of dodecamethylcyclohexasilane and high-molecular-weight polydimethylsilane with chlorides of I, II, IV–VI and VIII Group metals at high temperature in the absence of a solvent were studied. The influence of the reaction conditions (temperature, reaction time and the reagent ratio) on the composition and yields of the reaction products was examined.

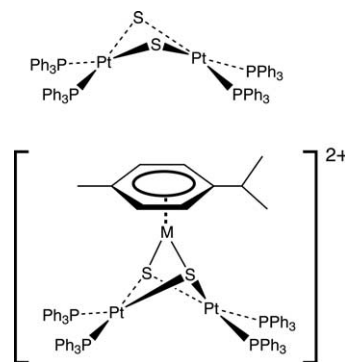


**S.-W. Audi Fong, T.S. Andy Hor, William Henderson, Brian K. Nicholson, Stephen Gardyne, Sarah M. Devoy**

*J. Organomet. Chem.* 679 (2003) 24

Coordination chemistry of the  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  metalloligand with  $\pi$ -hydrocarbon derivatives of  $d^6$  ruthenium(II), osmium(II), rhodium(III) and iridium(III)

The metalloligand  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$  forms a range of complexes  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{-ML}]^{2+}$  ( $\text{M} = \text{Ru}$ ,  $\text{L} = p$ -cymene,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{Me}_6$ ;  $\text{M} = \text{Os}$ ,  $\text{L} = p$ -cymene;  $\text{M} = \text{Rh}$ ,  $\text{Ir}$ ,  $\text{L} = \text{C}_5\text{Me}_5$ ) by reaction with the appropriate  $[\text{LMCl}_2]_2$  complexes. The compound  $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\text{Ru}(p\text{-cymene})][\text{BPh}_4]_2$  was characterised by an X-ray diffraction study.

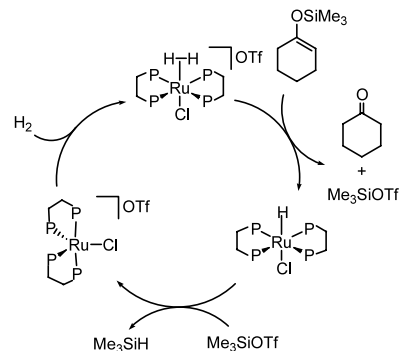


**Izuru Takei, Yoshiaki Nishibayashi, Youichi Ishii, Yasushi Mizobe, Sakae Uemura, Masanobu Hidai**

*J. Organomet. Chem.* 679 (2003) 32

Novel catalytic hydrogenolysis of silyl enol ethers by the use of acidic ruthenium dihydrogen complexes

The heterolytic cleavage of  $\text{H}_2$  is the key to the novel catalytic hydrogenolysis of silyl enol ethers to afford ketones and silanes by acidic ruthenium dihydrogen complexes,  $[\text{RuCl}(\eta^2\text{-H}_2)(\text{diphosphine})_2]\text{X}$ . In addition, stoichiometric enantioselective protonation of a prochiral lithium enolate is performed by using a chiral  $[\text{Ru}(\eta^2\text{-H}_2)]$  complex.

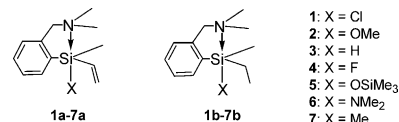


**Hyeon Mo Cho, Jung Im Jang, Chang Hwan Kim, Sueg-Geun Lee, Myong Euy Lee**

*J. Organomet. Chem.* 679 (2003) 43

Syntheses and NMR study of [(2-dimethylaminomethyl)phenyl]vinylsilane derivatives and [(2-dimethylaminomethyl)phenyl]ethylsilane derivatives

Various vinylsilanes,  $\text{SiX}(\text{CH}=\text{CH}_2)(\text{CH}_3)[2\text{-}(\text{CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4]$ , and ethylsilanes,  $\text{SiX}(\text{CH}_2\text{CH}_3)(\text{CH}_3)[2\text{-}(\text{CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4]$  [ $\text{X} = \text{Cl}$  (1);  $\text{OMe}$  (2);  $\text{H}$  (3);  $\text{F}$  (4);  $\text{OSiMe}_3$  (5);  $\text{NMe}_2$  (6);  $\text{Me}$  (7)], were synthesized in order to investigate the electronic effect of vinyl group on silicon atom having an intramolecular coordination arm. The differences of  $^{29}\text{Si}$  chemical shifts between vinylsilanes and ethylsilanes increased in the following order:  $\text{X} = \text{Me}$ ,  $\text{NMe}_2 < \text{H} < \text{OSiMe}_3 < \text{OMe} < \text{F} < \text{Cl}$ .

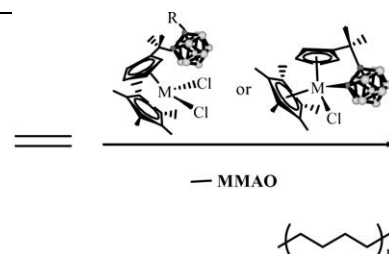


**Yonggyu Han, Eunkee Hong, Youngjo Kim,  
Min Hyung Lee, Jingdong Kim,  
Jeong-Wook Hwang, Youngkyu Do**

*J. Organomet. Chem.* 679 (2003) 48

Group 4 complexes derived from *o*-carborane: synthesis, structures and ethylene polymerization properties

A set of Group 4 metallocene-based homogeneous catalysts containing orthocarboranyl or 1-methylorthocarboranyl group as a substituent or an ancillary ligand has been synthesized and their polymerization behavior for ethylene has been explored in the presence of modified methylaluminumoxane cocatalyst, affording high-density polyethylenes.

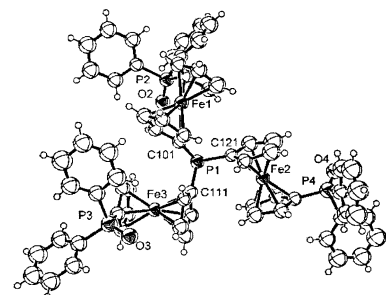


**Ian R. Butler, Michael G.B. Drew,  
Alfonso G. Caballero, Pascal Gerner,  
Christopher H. Greenwell**

*J. Organomet. Chem.* 679 (2003) 59

The design and synthesis of a new potentially  $C_3$ -symmetric ferrocenylphosphine

New triferrocenyltetraphosphine ligands and substituted triferrocenylphosphine ligands have been prepared and characterised using a simple lithiation and quench methodology. The methodology uses the now well established mono-lithiation of 1,1'-dibromoferrocene followed by the reaction of the quenched product with phosphorus trichloride.

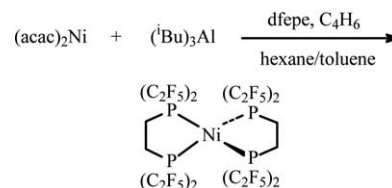


**Byron L. Bennett, Shannon White,  
Brittany Hodges, Dane Rodgers, Ade Lau,  
Dean M. Roddick**

*J. Organomet. Chem.* 679 (2003) 65

(Fluoroalkyl)phosphine complexes of nickel(0) and cobalt(I)

The synthesis of a series of (fluoroalkyl)phosphine complexes of nickel (dfepe) $Ni(L)_2$  (dfepe =  $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ ; L = CO, MeCN;  $L_2$  = dfepe, bipy) and of (dfepe) $Co(CO)_2H$  is reported. In contrast to  $(R_3P)_4Ni(0)$  phosphine and phosphite complexes, which undergo protonation by strong anhydrous acids to give  $(R_3P)_4Ni(H)^+$  products, treatment of (dfepe) $_2Ni$  with neat  $CF_3CO_2H$  or excess HOTf in dichloromethane does not produce (dfepe) $_2Ni(H)^+$  but instead leads to eventual dfepe loss and decomposition to Ni(II) products.

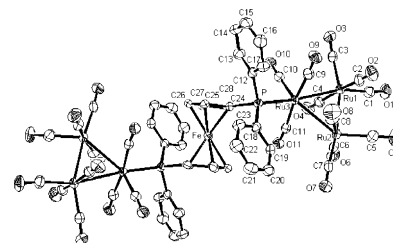


**Abby R. O'Connor, Chip Nataro,  
Arnold L. Rheingold**

*J. Organomet. Chem.* 679 (2003) 72

Ruthenium cluster compounds containing 1,1'-bis(diphenylphosphino)ferrocene (dppf): an electrochemical analysis and the crystal structure of  $[Ru_3(CO)_{11}]_2(\mu-dppf)$

The electrochemistry of 1,1'-bis(diphenylphosphino)ferrocene (dppf) derivatives of  $Ru_3(CO)_{12}$  was investigated.

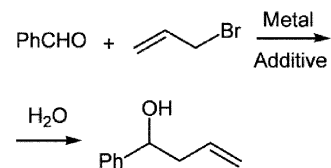


Jacques Augé, Nadège Lubin-Germain,  
Sylvain Marque, Latifa Seghrouchni

*J. Organomet. Chem.* 679 (2003) 79

Indium-catalyzed Barbier allylation reaction

Barbier allylation reaction of carbonyl compounds with allyl bromide was investigated using a catalytic amount of indium (0), indium (I) or indium (III) salts in the presence of a reducer and chlorotrimethylsilane (TMSCl). The Mn/TMSCl couple turned out to be the most efficient system to regenerate active indium in the allylation reaction of various carbonyl compounds including  $\alpha$ - and  $\beta$ -oxygenated aldehydes.

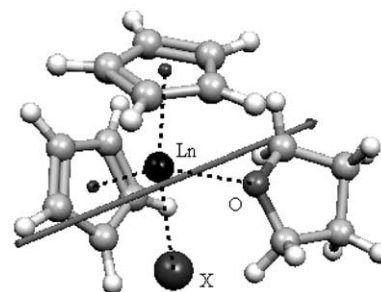


Yi Luo, Parasuraman Selvam, Yuki Ito,  
Akira Endou, Momoji Kubo,  
Akira Miyamoto

*J. Organomet. Chem.* 679 (2003) 84

Density functional study of lanthanide complexes ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>LnX·OC<sub>4</sub>H<sub>8</sub> (Ln = La–Lu; X = F, Cl, Br and I)

The mixed-ligand complexes ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>LnX·OC<sub>4</sub>H<sub>8</sub> ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub> = Cp; Ln = La–Lu; X = halide; OC<sub>4</sub>H<sub>8</sub> = THF) were investigated by density functional calculation. The lanthanide contraction and the metal–ligand interaction energy follow the sequence of Ln–X > Ln–Cp > Ln–O. The vector dipole moment didn't take the axial direction of Ln–X bond and the dipole moment magnitudes of complex molecules decreased in the order of I > Br > Cl > F. The charge population and orbital composition were also discussed.

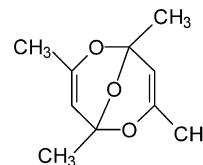


Vincenzo G. Albano, Magda Monari,  
Achille Panunzi, Giuseppina Roviello,  
Francesco Ruffo

*J. Organomet. Chem.* 679 (2003) 93

Absolute configuration, coordination and stereochemical influence of 1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3,3,1]nona-3,7-diene in Rh(I) and cationic Pd(II) complexes

Relevant stereochemical and coordination features of 1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3,3,1]nona-3,7-diene (TOND), a chiral molecule of C<sub>2</sub> symmetry, are described. The X-ray crystal structure of [RhCl{(S)-CHMePhNH<sub>2</sub>}{(+)-TOND}] has ascertained that the absolute configuration of (+)-TOND is R,R. The ability of this ligand to afford stereoselective coordination of prochiral ligands has been assessed by preparing complexes of formula [Pd( $\eta^3$ -allyl)(TOND)][BF<sub>4</sub>] and [Rh(chelate)(TOND)][BF<sub>4</sub>]. The molecular structure of the representative compound [Pd( $\eta^3$ -crotyl)(TOND)][BF<sub>4</sub>] has also been determined.

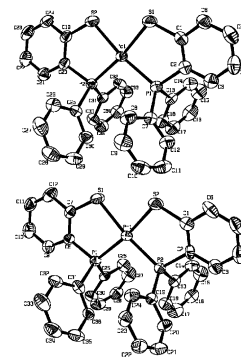


Daniel Canseco-González,  
Valente Gómez-Benítez,  
Simón Hernández-Ortega,  
Rubén A. Toscano, David Morales-Morales

*J. Organomet. Chem.* 679 (2003) 101

Transmetalation reactions of [Sn(R)<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] with metal complexes of the Group 10  
Stereoselective synthesis of *cis*-[M(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] (M = Ni, Pd, Pt)

The stereoselective synthesis of *cis*-[M(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] (M = Ni, Pd, Pt) has been achieved by transmetalation reactions of [M(Cl)<sub>2</sub>(NCC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] (M = Pd, Pt or NiCl<sub>2</sub>·6H<sub>2</sub>O) with [Sn(R)<sub>2</sub>(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>-2-S)<sub>2</sub>] (R = Ph, <sup>n</sup>Bu or <sup>t</sup>Bu) and the crystal structures of the Pd and Pt derivatives determined. The single crystal X-ray diffraction studies show both structures to have metal centers into a slightly distorted square planar environment, the main distortion being due to the steric hindrance caused by the aromatic rings in the phosphine moiety.

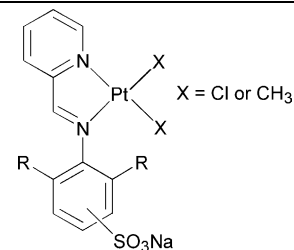


**George J.P. Britovsek, Grace Y.Y. Woo, Nitinan Assavathorn**

*J. Organomet. Chem.* 679 (2003) 110

Synthesis and reactivity of water-soluble platinum(II) complexes containing nitrogen ligands

A series of water-soluble platinum(II) dichloro and dialkyl complexes have been prepared. Whereas the dichloro complexes are stable in strongly polar solvents such as water or dimethyl sulfoxide, the dialkyl complexes decompose slowly, typically within a day at room temperature. These findings may have important ramifications for their application in catalysis.

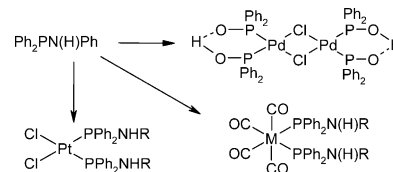


**Srinivasan Priya, Maravanji S. Balakrishna, Joel T. Mague**

*J. Organomet. Chem.* 679 (2003) 116

Transition metal (Group 6, Ru and Group 10) derivatives of aminophosphines,  $\text{Ph}_2\text{PN}(\text{H})\text{R}$  ( $\text{R} = \text{Ph}, \text{C}_6\text{H}_{11}$ )

The reactions of aminophosphines with Group 6 metal carbonyls, ruthenium and Group 10 derivatives are described. With palladium, chloro-bridged dimeric complex,  $[\text{Pd}(\text{PPh}_2\text{O})(\text{PPh}_2\text{OH})(\mu\text{-Cl})_2]$  is obtained as a result of P–N bond hydrolysis.

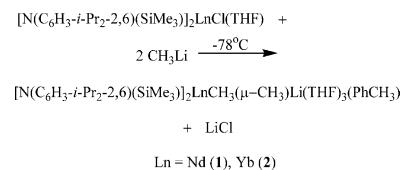


**Yunjie Luo, Yingming Yao, Wenjing Li, Jinglei Chen, Zhenqin Zhang, Yong Zhang, Qi Shen**

*J. Organomet. Chem.* 679 (2003) 125

Synthesis, crystal structure of bis(arylamido)lanthanide methyl complexes and their catalytic behavior for the polymerization of methyl methacrylate

Reactions of  $[\text{N}(\text{C}_6\text{H}_3\text{-}i\text{-Pr}_2\text{-}2,6)(\text{SiMe}_3)_2\text{LnCl}(\text{THF})]$  ( $\text{Ln} = \text{Nd}, \text{Yb}$ ) with two equivalents of MeLi in a mixture solution of toluene and Et<sub>2</sub>O gave  $[\text{N}(\text{C}_6\text{H}_3\text{-}i\text{-Pr}_2\text{-}2,6)(\text{SiMe}_3)_2\text{LnCH}_3(\mu\text{-CH}_3)\text{Li}(\text{THF})_3 \cdot \text{PhCH}_3]$  ( $\text{Ln} = \text{Nd}$  (**1**),  $\text{Yb}$  (**2**)) in good isolated yields as crystalline solids. The single-crystal structural analysis of **2** revealed that the coordination geometry of ytterbium ion is best described as a distorted pseudo-tetrahedron. Both **1** and **2** are active for the polymerization of methyl methacrylate to give syndiotactic-rich and high molecular weight polymers ( $M_n > 10^4$ ) with relatively narrow molecular weight distributions ( $M_w/M_n < 2$ ).

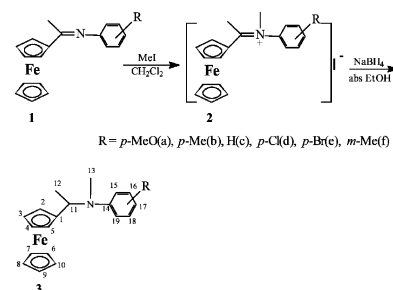


**Hong Xing Wang, Li Ding, Yang Jie Wu**

*J. Organomet. Chem.* 679 (2003) 130

Synthesis, characterization and the crystal structure of 1-[(*N*-methyl-*N*-aryl)amino]ethylferrocenes

Ferrocenylketimines  $[(\eta^5\text{-C}_5\text{H}_4\text{CCH}_3=\text{NAr})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$  reacted with methyl-iodide in  $\text{CH}_2\text{Cl}_2$  followed by reduction with sodium borohydride in abs.  $\text{C}_2\text{H}_5\text{OH}$  led to corresponding 1-[(*N*-methyl-*N*-aryl)amino]ethylferrocenes  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}(\text{CH}_3)\text{N}(\text{CH}_3)\text{Ar})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ .

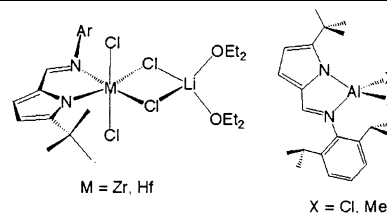


Lan-Chang Liang, Chih-Wei Yang,  
Michael Y. Chiang, Chen-Hsiung Hung,  
Pei-Ying Lee

*J. Organomet. Chem.* 679 (2003) 135

Syntheses and X-ray structures of some  
pyrrolylaldimine metal complexes

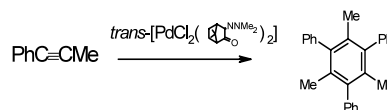
Several metal complexes supported by the sterically demanding pyrrolylaldimine ligand  $L^-$  have been synthesized; among them  $MCl_2(\mu-Cl)_2Li(OEt)_2$  ( $M = Zr, Hf$ ) and  $AlX_2$  ( $X = Cl, Me$ ) have been structurally characterized by X-ray crystallography.



M. Fernanda N.N. Carvalho,  
Fernanda M.T. Almeida,  
Adelino M. Galvão, Armando J.L. Pombeiro  
*J. Organomet. Chem.* 679 (2003) 143

Benzene ring assembly promoted by a camphor derived palladium complex

The camphorimine derived complex *trans*- $[PdCl_2L_2]$  ( $L = 3\text{-}NNMe_2C_{10}H_{14}O$ ) is an effective catalyst for the cyclic trimerization of alkynes. The activity is higher for internal than for terminal alkynes. The best results were obtained for  $PhC\equiv CMe$  (TON = 7.4, for a maximum of 10). Furthermore, the process is high selective for  $PhC\equiv CMe$  and  $t\text{-}BuC\equiv CH$  (ca. 99%).



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