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Contents

Special Issue: Atom Efficient Organic Syntheses

Papers

John T. Dixon, Mike J. Green, Fiona M. Hess, David H. Morgan

J. Organomet. Chem. 689 (2004) 3641

Advances in selective ethylene trimerisation – a critical overview

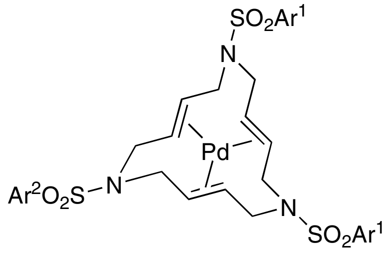
Over the past fifteen years there has been considerable interest in the selective trimerisation of ethylene to 1-hexene: This article provides an overview of all developments in the patent and open literature, paying special attention to catalyst activity, reaction selectivity and relative catalyst cost. Mechanistic aspects are discussed in detail and the article concludes with a discussion on the major findings of recent theoretical studies.

Marcial Moreno-Mañas, Roser Pleixats, Rosa M. Sebastián, Adelina Vallribera, Anna Roglans

J. Organomet. Chem. 689 (2004) 3669

Organometallic chemistry of 15-membered tri-olefinic macrocycles: catalysis by palladium(0) complexes in carbon–carbon bond-forming reactions

Compounds **4** are formed from the corresponding 15-membered macrocycles. Preparation, structures, and catalytic properties of **4** and related compounds are reviewed.



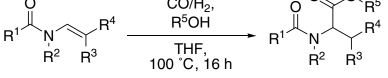
4

S. Klaus, H. Neumann, H. Jiao, A. Jacobi von Wangelin, D. Gördes, D. Strübing, S. Hübner, M. Hateley, C. Weckbecker, K. Huthmacher, T. Riermeier, M. Beller

J. Organomet. Chem. 689 (2004) 3685

Selective hydroalkoxycarbonylation of enamides to *N*-acyl amino acid esters: synthetic applications and theoretical studies

Atom efficient transformations of different enamides, CO, and alcohols into *N*-acyl amino acids catalyzed by dicobaltoctacarbonyl were performed in moderate to excellent yields under mild conditions. DFT calculations of the full catalytic cycle and relevant side reactions agree widely with the experimental results.



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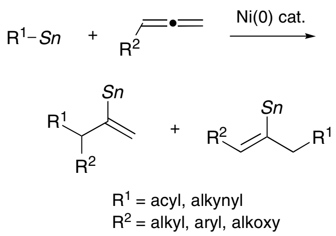
doi:10.1016/S0022-328X(04)00833-2

Yoshiaki Nakao, Eiji Shirakawa, Teruhisa Tsuchimoto, Tamejiro Hiyama

J. Organomet. Chem. 689 (2004) 3701

Nickel-catalyzed acylstannylation and alkynylstannylation of 1,2-dienes

Acylstannanes and alkynylstannanes were found to add across 1,2-dienes to give various alkenylstannanes in the presence of a nickel(0) catalyst. The regiochemistry of the reaction is switchable by proper choice of a ligand. Resulting carbostannylation products were found to be versatile precursors for various conjugated compounds and polycyclic frameworks.

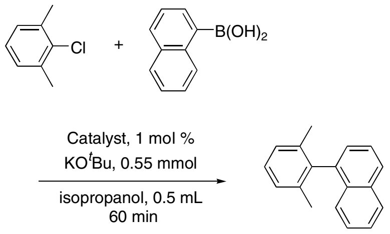


Oscar Navarro, Yosihiro Oonishi, Roy A. Kelly, Edwin D. Stevens, Oliver Briel, Steven P. Nolan

J. Organomet. Chem. 689 (2004) 3722

General and efficient methodology for the Suzuki–Miyaura reaction in technical grade 2-propanol

The reactivity of a series of well-defined palladium catalysts was tested using a simple experimental protocol enabling the Suzuki–Miyaura reaction to be carried out under mild conditions in isopropanol. The nature of the ancillary ligands has important effects on catalyst activation.

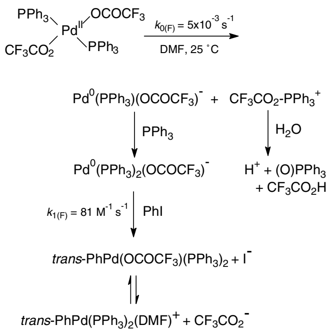


Christian Amatore, Anny Jutand, Frédéric Lemaître, Jean Luc Ricard, Sebastian Kozuch, Sason Shaik

J. Organomet. Chem. 689 (2004) 3728

Formation of anionic palladium(0) complexes ligated by the trifluoroacetate ion and their reactivity in oxidative addition

Anionic Pd^0 complexes $Pd^0(PAr_3)_n(OCOCF_3)^-$ (n = 2 or 3) are generated from $Pd(OCOCF_3)_2$ and PAr_3. $Pd^0(PAr_3)_2(OCOCF_3)^-$ is the reactive species involved in the oxidative addition to PhI.

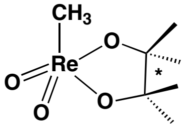


Joachim J. Haider, Roland M. Kratzer, Wolfgang A. Herrmann, Jin Zhao, Fritz E. Kühn

J. Organomet. Chem. 689 (2004) 3735

On the way to chiral epoxidations with methyltrioxorhenium(VII) derived catalysts

Methyltrioxorhenium(VII) (MTO) is successfully applied as chiral epoxidation catalyst in the presence of excess H_2O_2 and chiral Lewis base at low temperatures. Glycolate complexes of MTO are also applied under the same conditions. The results, despite displaying only moderate enantiomeric excesses and yields, are among the best observed for MTO derived chiral catalysts to date.

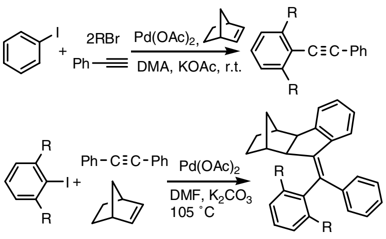


**Elena Motti, Manuela Rossetti,
Gabriele Bocelli, Marta Catellani**

J. Organomet. Chem. 689 (2004) 3741

Palladium catalyzed multicomponent reactions in ordered sequence: new syntheses of *o*,*o*′-dialkylsubstituted diarylacetylenes and diarylalkylidenehexahydromethanofluorenes

Selectively substituted diarylacetylenes and diarylalkylidenehexahydromethanofluorenes are obtained, the former from aryl iodides, alkyl bromides and phenylacetylene in the presence of palladium acetate and norbornene as catalysts, the latter from di-*ortho* substituted aryl iodides, diphenylacetylene and norbornene under the catalytic action of palladium acetate.

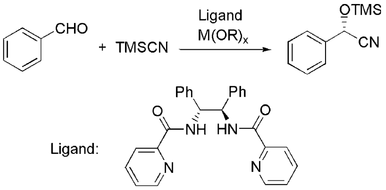


**Oscar Belda, Sophie Duquesne,
Andreas Fischer, Christina Moberg**

J. Organomet. Chem. 689 (2004) 3750

Chiral bispyridylamide metal complexes as catalysts for the enantioselective addition of TMSCN to aldehydes

The use of (1*R*,2*R*)-*N*,*N*′-bis(2-pyridinecarboxyamido)-1,2-diphenylethane metal complexes as catalysts for the enantioselective addition of trimethylsilyl cyanide to aldehydes is described. Enantioselectivities up to 70% ee were obtained with a Ti(IV) catalyst. Complexes with Zr(IV), Sc(III), Yb(III) and Cu(II) afforded less selective catalysts.

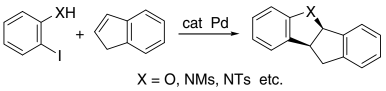


Daniel E. Emrich, Richard C. Larock

J. Organomet. Chem. 689 (2004) 3756

Palladium-catalyzed heteroannulation of cyclic alkenes by functionally substituted aryl iodides

Indolines and 2,3-dihydrobenzofurans are produced in good yields by the Pd(0)-catalyzed heteroannulation of cyclic and bicyclic alkenes by *o*-amino- and *o*-hydroxyaryl iodides. These processes are successful with cyclic olefins in which the key alkylpalladium intermediate cannot undergo facile palladium β-hydride elimination.

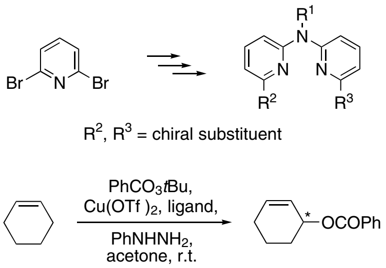


**Carsten Bolm, Jean-Cédric Frison,
Jacques Le Paih, Christian Moessner,
Gerhard Raabe**

J. Organomet. Chem. 689 (2004) 3767

Synthesis of C_2-symmetric and unsymmetrically substituted 2,2′-dipyridylamines and crystal structure of a chiral 2,2′-dipyridylamine copper(II) complex

Sequential Buchwald–Hartwig aminations of halo-pyridines lead to C_2-symmetric and unsymmetrically substituted 2,2′-dipyridylamines. The X-ray crystal structure of a copper dichloride complex bearing a C_2-symmetric 2,2′-dipyridylamine and preliminary experiments describing the use of such nitrogen chelates in asymmetric catalysis are reported.

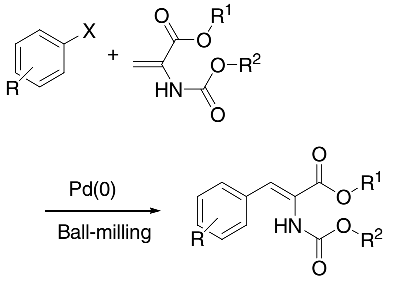


Erik Tullberg, Dan Peters, Torbjörn Frejd

J. Organomet. Chem. 689 (2004) 3778

The Heck reaction under ball-milling conditions

Ball milling provides a mild, solvent free and efficient alternative to the conventional Heck–Jeffery protocol for the synthesis of unnatural dehydro amino acids. Reproducibility, scalability and complementary reactivity patterns are discussed.

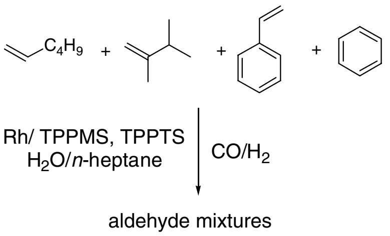


P.J. Baricelli, E. Lujano, M. Modroño, A.C. Marrero, Y.M. García, A. Fuentes, R.A. Sánchez-Delgado

J. Organomet. Chem. 689 (2004) 3782

Rhodium-catalyzed hydroformylation of C6 alkenes and alkene mixtures – a comparative study in homogeneous and aqueous-biphasic media using PPh_3, TPPTS and TPPMS ligands

The complexes $RhH(CO)L_3$ (L = TPPTS, TPPMS) are efficient catalysts for the hydroformylation of C6 alkenes and alkene mixtures in a water/*n*-heptane biphasic medium under moderate reaction conditions. These systems can be recycled without significant loss of activity and are interesting for naphtha upgrading and related applications.

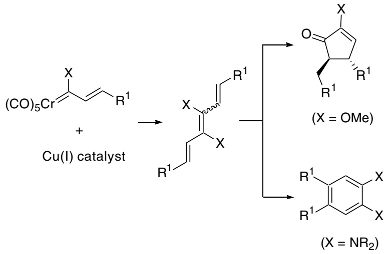


José Barluenga, Pablo Barrio, Rubén Vicente, Luis A. López, Miguel Tomás

J. Organomet. Chem. 689 (2004) 3793

Copper-catalyzed dimerization of chromium Fischer carbene complexes: synthesis of dialkoxytrienes and their Nazarov-type cyclization to 2-alkoxy-2-cyclopentenones

Fischer carbene complexes underwent a clean ligand dimerization reaction yielding functionalized olefins and trienes. The trienes resulting from alkenylcarbene complexes produce substituted cyclopentenones and arenes via Nazarov-type cyclization or electrocyclic ring closure/aromatization, respectively.

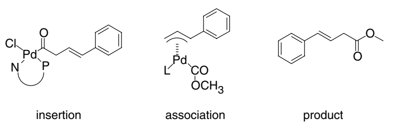


Richard J. van Haaren, Henk Oevering, Paul C.J. Kamer, Kees Goubitz, Jan Fraanje, Piet W.N.M. van Leeuwen, Gino P.F. van Strijdonck

J. Organomet. Chem. 689 (2004) 3800

The mechanism for palladium catalyzed carbonylation of cinnamyl chloride

In the palladium catalyzed alkoxycarbonylation of cinnamyl chloride an associative mechanism was observed at low pressure, while an insertion mechanism was observed at high pressure or when an excess of ligand was used. Several putative intermediates of the catalytic alkoxycarbonylation have been synthesized and characterized, such as acyl complex **5c** of which an X-ray crystal structure could be obtained.

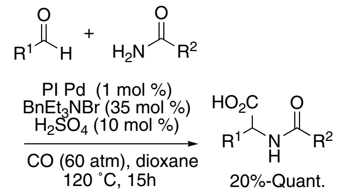


Ryo Akiyama, Takahiro Sagae, Masaharu Sugiura, Shū Kobayashi

J. Organomet. Chem. 689 (2004) 3806

Efficient synthesis of *N*-acyl-α-amino acids via polymer incarcerated palladium-catalyzed amidocarbonylation

A novel polymer incarcerated Pd catalyst (PI Pd) was synthesized from an amide-containing polymer. The catalyst was shown to be effective in amidocarbonylation, which is a versatile one-pot method for the preparation of *N*-acyl-α-amino acids. The reactions proceeded smoothly with a wide variety of substrates, and no leaching of the Pd metal to the reaction mixture was detected.

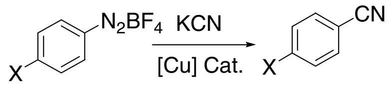


Irina P. Beletskaya, Alexander S. Sigeev, Alexander S. Peregudov, Pavel V. Petrovskii

J. Organomet. Chem. 689 (2004) 3810

Catalytic Sandmeyer cyanation as a synthetic pathway to aryl nitriles

Aryl nitriles ArCN were obtained by the Cu(I)/ Cu(II) catalysed reaction of aryl diazonium salts with KCN in good yields.

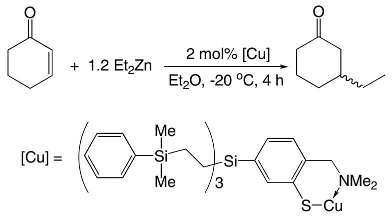


Anne M. Arink, Rob van de Coevering, Birgit Wieczorek, Judith Firet, Johann T.B.H. Jastrzebski, Robertus J.M. Klein Gebbink, Gerard van Koten

J. Organomet. Chem. 689 (2004) 3813

A recyclable nanosize aminoarenethiolato copper(I) catalyst for C–C coupling reactions

The attachment of an aminoarenethiolato copper(I) catalyst to a carbosilane dendritic wedge is described. This new catalyst is comparable in activity for the 1,4-addition of diethylzinc to 2-cyclohexenone as the parent catalyst but more robust. In addition, the new catalytic material can be easily recovered by dialysis from the reaction products and subsequently reused.

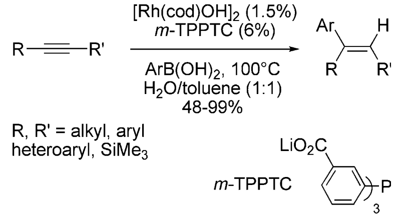


Emilie Genin, Véronique Michelet, Jean-Pierre Genêt

J. Organomet. Chem. 689 (2004) 3820

Rh-catalyzed addition of boronic acids to alkynes for the synthesis of trisubstituted alkenes in a biphasic system - Mechanistic study and recycling of the Rh/*m*-TPPTC catalyst

The use of $[Rh(cod)OH]_2$ associated with the water-soluble ligand *m*-TPPTC is highly efficient for the preparation of trisubstituted alkenes via arylation of alkynes. Aryl, heteroaryl, silylated and alkyl substituted alkynes reacted equally well with various boronic acids, leading regioselectively to functionalized alkenyl derivatives in high yields. The efficient recycling of the system and the mechanism are disclosed.

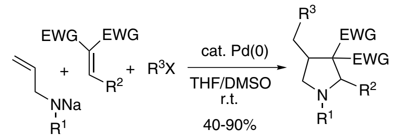


Luc Martinon, Stéphane Azoulay, Nuno Monteiro, E. Peter Kündig, Geneviève Balme

J. Organomet. Chem. 689 (2004) 3831

Pd-catalyzed one-pot coupling of allylamines, activated alkenes, and unsaturated halides (or triflate): an atom efficient synthesis of highly functionalized pyrrolidines

A Pd-catalyzed three-component assembling of highly functionalized 4-benzyl-(and allyl-) pyrrolidines was achieved based on a combination of allylic amines, *gem*-diactivated alkenes, and unsaturated halides (or triflate).



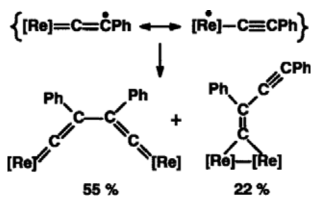
EWG = CO_2R, SO_2Ph
R^1 = Me, allyl
R^2 = (hetero)aryl, CO_2Me
R^3 = aryl, vinyl
X = I, Br, OTf

Dmitry A. Valyaev, Oleg V. Semeikin, Mikhail G. Peterleitner, Yuri A. Borisov, Viktor N. Khrustalev, Andrei M. Mazhuga, Evgeny V. Kremer, Nikolai A. Ustynyuk

J. Organomet. Chem. 689 (2004) 3837

Oxidative dehydrodimerization of rhenium vinylidene complex $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph$: two competitive routes of coupling of σ-phenylethynyl intermediate $[(\eta^5\text{-}C_5H_5)(CO)_2Re{-}C{\equiv}CPh]^{\cdot}$. X-ray structures of rhenium mononuclear $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph$ and binuclear $[(\eta^5\text{-}C_5H_5)(CO)_2Re]_2(\mu_2\text{-}C{=}C(Ph)C{\equiv}CPh)$ vinylidene compounds

The oxidation of the rhenium vinylidene complex $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph$ (**2**) with one equivalent of $AgBF_4$ or $(C_5H_5)_2FeBF_4$ leads to the radical cation $[(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph]^{+\cdot}$ ($\mathbf{2}^{+\cdot}$) which undergoes dehydrodimerization only in the presence of triethylamine affording a mixture of the binuclear compounds $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(Ph)C(Ph){=}C{=}Re(CO)_2(\eta^5\text{-}C_5H_5)$ (**6**, 55%) and $[(\eta^5\text{-}C_5H_5)(CO)_2Re]_2(\mu_2\text{-}C{=}C(Ph)C{\equiv}CPh)$ (**9**, 22%).



[Re] = $(\eta^5\text{-}C_5H_5)(CO)_2Re$

Tao Tu, Xue-Long Hou, Li-Xin Dai

J. Organomet. Chem. 689 (2004) 3847

Ligand electronic effects in the palladium catalyzed asymmetric allylic alkylation reaction with planar chiral diphosphine-oxazoline ferrocenyl ligands

A series of planar chiral diphosphineoxazoline ferrocenyl ligands with different electronic nature were applied in the asymmetric allylic substitutent reaction. When the electronic effect was coincident with the steric effect of ligand, a higher ee value could be observed.