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## Contents

## Regular Papers

Francis O. Ogini, Yanick Ortin,
Amir H. Mahmoudkhani,
Anthony F. Cozzolino, Michael J. McGlinchey, Ignacio Vargas-Baca
J. Organomet. Chem. 693 (2008) 1957

An investigation of the formation of 1,3,5heterosubstituted benzene rings by cyclocondensation of acetyl-substituted organometallic complexes

The condensation reaction of acetylferrocene and acetylcymantrene affords heterometallic 1,3,5-benzenes and (E)-1,3-disubstituted-2-bu-ten-1-ones.

## Kozo Fukumoto, Hiroshi Nakazawa

J. Organomet. Chem. 693 (2008) 1968

Geometrical isomerization of fac/mer$\mathrm{Mo}(\mathrm{CO})_{3}(\text { phosphite })_{3}$ and cis/trans$\mathrm{Mo}(\mathrm{CO})_{4}(\text { phosphite })_{2}$ catalyzed by $\mathrm{Me}_{3} \mathrm{SiOSO}_{2} \mathrm{CF}_{3}$

Geometrical isomerization of $\mathrm{fac}-\mathrm{Mo}(\mathrm{CO})_{3} \mathrm{~L}_{3}$ $\left(\mathrm{L}=\mathrm{P}(\mathrm{OPh})_{3}, \mathrm{P}(\mathrm{OMe})_{3}, \mathrm{P}(\mathrm{OEt})_{3}\right)$ to the mer form and that of cis- $\mathrm{Mo}(\mathrm{CO})_{4} \mathrm{~L}_{2}$ $\left(\mathrm{L}=\mathrm{P}(\mathrm{OPh})_{3}, \mathrm{P}(\mathrm{OMe})_{3}, \mathrm{PPh}_{2}(\mathrm{OMe})\right)$ to the trans form were observed in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at room temperature in the presence of a catalytic amount of $\mathrm{Me}_{3} \mathrm{SiOSO}_{2} \mathrm{CF}_{3}$ (TMSOTf).




Flaviana T. Vieira, Geraldo M. de Lima,
James L. Wardell, Solange M.S.V. Wardell, Klaus Krambrock, Antônio F. de C. Alcântara
J. Organomet. Chem. 693 (2008) 1986

Synthesis and characterization of [chloro$\{2(1 \mathrm{H})$-pyridinethione- $S\}\{$ tris(pyridin-2-ylthi-olato)methyl- $\left.\left.C, N, N^{\prime}, N^{\prime \prime}\right]\right\}$ nickel(II)], [Ni(TPT$\mathrm{M})(\mathrm{SPyH}) \mathrm{Cl}]$

Synthesis and characterization of [chloro$\{2(1 \mathrm{H})$-pyridinethione- $S\}$ \{tris(pyridin-2-ylthio-lato)methyl- $\left.\left.C, N, N^{\prime}, N^{\prime \prime}\right]\right\}$ nickel(II)], $\quad[\mathrm{Ni}(\mathrm{TPTM})-$ $(\mathrm{SPyH}) \mathrm{Cl}]$ is reported.


Stefan Köcher, Bernhard Walfort,
Allison M. Mills, Anthony L. Spek,
Gerard P.M. van Klink, Gerard van Koten, Heinrich Lang
J. Organomet. Chem. 693 (2008) 1991

Synthesis and reaction chemistry of 4-nitrilesubstituted NCN-pincer palladium(II) and platinum(II) complexes $\quad(\mathrm{NCN}=[\mathrm{N} \equiv \mathrm{C}-4-$ $\left.\left.\mathrm{C}_{6} \mathrm{H}_{2}\left(\mathrm{CH}_{2} \mathrm{NMe}_{2}\right)_{2}-2,6\right]^{-}\right)$

The synthesis, reaction chemistry and properties of mononuclear $\quad[\mathrm{MBr}(\mathrm{N} \equiv \mathrm{C}-4-$ $\left.\left.\mathrm{C}_{6} \mathrm{H}_{2}\left(\mathrm{CH}_{2} \mathrm{NMe}_{2}\right)_{2}-2,6\right)\right] \quad(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ and polymeric $\quad\left\{\left[\mathrm{Pt}\left(\mathrm{N} \equiv \mathrm{C}-4-\mathrm{C}_{6} \mathrm{H}_{2}\left(\mathrm{CH}_{2} \mathrm{NMe}_{2}\right)_{2}-\right.\right.\right.$ $\left.2,6)]\left(\mathrm{ClO}_{4}\right)\right\}_{n}$ is discussed. The solid state structures of the mononuclear systems are reported.


Martin Pošta, Jan Cermák, Jan Sýkora, Pavel Vojtísek, Ivana Císař̌ová, Radek Fajgar
J. Organomet. Chem. 693 (2008) 1997

Square planar diphosphinoazine rhodium(I) amido carbonyl complexes with an unsymmetrical PNP' pincer-type coordination

Kazem D. Safa, Soleiman Paymard Samani, Shahin Tofangdarzadeh, Akbar Hassanpour
J. Organomet. Chem. 693 (2008) 2004

Study of the reaction of 1,1-bis(trimethylsilyl)-2-phenylethylene with some acyl chlorides in the presence of $\mathrm{AlCl}_{3}$

A series of novel diphosphinoazine rhodium amido carbonyl complexes $\left[\left\{\mathrm{R}_{2} \mathrm{PCH}=\mathrm{C}\left(\mathrm{Bu}^{t}\right)-\right.\right.$ $\left.\left.\mathrm{NN}=\mathrm{C}\left(\mathrm{Bu}^{t}\right) \mathrm{CH}_{2} \mathrm{PR}_{2}\right\} \mathrm{Rh}(\mathrm{CO})\right] \quad\left(R=\mathrm{Ph}, \mathrm{Pr}^{i}\right.$, $\mathrm{c}-\mathrm{C}_{6} \mathrm{H}_{11}, \mathrm{Bu}^{t}$ ) was prepared. Measurement of valence vibration frequencies of CO in the complexes allowed to estimate the electron density on the rhodium. An unusual diphosphinoazine bond cleavage was observed. Four X-ray crystal structures are reported.


1,1-Bis(trimethylsilyl)-2-phenylethylene (1), reacts with various acyl chlorides $(\mathrm{RCOCl}$, $\mathrm{R}=\mathrm{Me}$, Et , iso -Pr , $n-\mathrm{Bu}$, iso -Bu , iso $-\mathrm{C}_{5} \mathrm{H}_{11}$, $\mathrm{PhCH}_{2}, \mathrm{PhCH}_{2} \mathrm{CH}_{2}$ ) in the presence of $\mathrm{AlCl}_{3}$ to give $\alpha$-silyl- $\alpha, \beta$-unsaturated enones 3 with high $E$ stereoselectivity along with trans- $\alpha, \beta$ unsaturated ketones.
(1)
(2)
(3)

$\mathrm{R}=\mathrm{Me}$, Et,iso- $\mathrm{Pr}, \mathrm{Bu}$, iso-Bu, $\mathrm{n}-\mathrm{C}_{5} \mathrm{H}_{11}, \mathrm{PhCH}_{2}, \mathrm{PhCH}_{2} \mathrm{CH}_{2}$

## M. Dolores Santana, Gabriel García, Consuelo Vicente-Hernández, Luís García, José Pérez, Teófilo Rojo, Luís Lezama

J. Organomet. Chem. 693 (2008) 2009
$N, N^{\prime}$-bis(substituted-phenyl)oxamides and their dinuclear pentacoordinate nickel(II) complexes

New $\quad N, N^{\prime}$-bis(substituted-phenyl)oxamides have been prepared and their dinuclear nickel(II) complexes $\left\{\left[\mathrm{Ni}\left(\mathrm{N}_{3}-\mathrm{mc}\right)\right]_{2}(\mu\right.$-oxamidate $)\}\left(\mathrm{PF}_{6}\right)_{2} \quad$ characterized by X-ray crystallography and spectroscopic and magnetic studies.


## Miroslav Genov, Gorka Salas, Pablo Espinet

J. Organomet. Chem. 693 (2008) 2017

Effect of microwave heating in the asymmetric addition of dimethylzinc to aldehydes

Microwave-heated enantioselective additions of dimethylzinc to various aldehydes are reported. Dramatically reduced reaction times and lower catalyst loadings ( $5 \%$ ), can be achieved, with excellent yields and just small loss of enantioselectivity (up to $83 \%$ enantioselectivity is achieved) compared to room temperature conditions.

$\mathrm{Me}_{2} \mathrm{Zn}$ (2 eq.)

## Rachana Singh, Thakohari Goswami

J. Organomet. Chem. 693 (2008) 2021

Synthesis and evaluation of thermal, photophysical and magnetic properties of novel starlike fullerene-organosilane macromolecules

Fullerene core starlike organosilane macromolecules have been synthesized and tested for their photophysical and magnetic properties. Two different reaction methods have been utilized (displacement and transesterification reactions) using fullerenol as the substrate and different chloro/alkoxy vinyl silane as reagents for the synthesis. Photophysical and magnetic properties are drastically influenced by the presence of fullerene moiety.

A variety of (hex-5-ynyl)silanes was prepared from readily available materials and converted in the corresponding 2-methylidene-1-silacyclohexanes via intramolecular hydrosilylation. Among the catalytic system tested, Speier's catalyst was found to be the most suitable for this transformation.


by intramolecular hydrosilylation

## Silvia Díez-González, Luis Blanco

J. Organomet. Chem. 693 (2008) 2033

Synthesis of 2-methylidene-1-silacyclohexanes


Majid Moghadam, Shahram Tangestaninejad, Valiollah Mirkhani,
Iraj Mohammadpoor-Baltork,
Shahin Chahardahcheric, Ziba Tavakoli
J. Organomet. Chem. 693 (2008) 2041

Rapid and highly efficient trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS) catalyzed by reusable zirconyl triflate, $\left[\mathrm{ZrO}(\mathrm{OTf})_{2}\right]$

In this paper, rapid and efficient trimethylsilylation of alcohols and phenols with hexamethyldisilazane catalyzed by $\mathrm{ZrO}(\mathrm{OTf})_{2}$ is reported. Primary, secondary and tertiary alcohols as well as phenols were efficiently converted to their corresponding TMS ethers in short reaction times at room temperature. This method can be used for chemoselective silylation of primary alcohols in the presence of secondary and tertiary alcohols and phenols.

$$
2 \mathrm{R}-\mathrm{OH}+\mathrm{Me}_{3} \mathrm{SiNHSiMe}_{3} \xrightarrow[\mathrm{CH}_{3} \mathrm{CN}]{\mathrm{ZrO}(\mathrm{OTf})_{2}} 2 \mathrm{R}-\mathrm{OSiMe}_{3}+\mathrm{NH}_{3}
$$

Neutral salicylaldiminato $\mathrm{Ni}(\mathrm{II})$ complexes bearing a single $N$-heterocyclic carbene (NHC) ligand (1 and 2) have been synthesized and characterized by X-ray structural analysis. Complex 1 can catalyze the dimerization of ethylene in the presence of MMAO with a moderate activity of $3.05 \times 10^{4} \mathrm{~g}(\mathrm{~mol} \mathrm{Ni})^{-1}$ -$\mathrm{h}^{-1} \mathrm{~atm}^{-1}$ in a highly selective fashion.


The mechanisms for both the side-insertion and the central-insertion of cis-2-butene into the $\mathrm{Zr}-\mathrm{H}$ bond of $\mathrm{Cp}_{2} \mathrm{ZrH}_{2}$ to give $\mathrm{Cp}_{2} \mathrm{Zr}(\mathrm{H})\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$ are theoretically investigated with the aid of DFT calculations.


## Notes

James R. Hermanson, Timothy M. Figley, Anna L. Seibert, Allan R. Pinhas
J. Organomet. Chem. 693 (2008) 2061

The reactivity of a nucleophilic nickel acylate complex

The reactivity of a nucleophilic nickel acylate complex with a tungsten carbene complex, $\mathrm{Fe}(\mathrm{CO})_{5}, \mathrm{Cr}(\mathrm{CO})_{6}, \mathrm{PPh}_{3}$, and CO was investigated. With the tungsten carbene complex, a methyl transfer occurred. With the metal carbonyl complexes, the acylate group on the nickel and a carbonyl on the iron or chromium traded places. With the $\mathrm{PPh}_{3}$ and CO , the acylate anion was replaced by the phosphine or CO ligand.



Amir Kohner-Kerten, Edit Y. Tshuva
J. Organomet. Chem. 693 (2008) 2065

Preparation and X-ray characterization of two-coordinate $\mathrm{Cu}(\mathrm{I})$ complex of aliphatic thiolato ligand: Effect of steric bulk on coordination features
$\mathrm{Cu}(\mathrm{I})$ complexes of aliphatic thiolato ligands were prepared, where the steric bulk of the ligand impacts the coordination number and nuclearity. Whereas the isopropylthiolato ligand leads mainly to a $\mathrm{Cu}_{4} \mathrm{~S}_{6}$ cluster where all $\mathrm{Cu}(\mathrm{I})$ centers are three coordinated, the tert-butylthiolato ligand leads under proper conditions to a mononuclear two-coordinate complex.


