

Available online at www.sciencedirect.com



Volume 689, issue 20, 29 September 2004



www.elsevier.com/locate/jorganchem

Contents

Short communication

Donatella Banti, Johannes C. Mol

J. Organomet. Chem. 689 (2004) 3113

Degradation of the ruthenium-based metathesis catalyst $[RuCl_2(=CHPh)(H_2IPr)-(PCy_3)]$ with primary alcohols

Hydride 4 was isolated via a ligand exchange reaction from hydride 8 and tested for isomerisation and hydrogenation catalytic activity. Its presence in the degradation mixture of the "Ru-Isopropylidene" metathesis catalysts when treated with an alcohol/base mixture constitutes a step forward in the realization of efficient and simple tandem metathesis/isomerisation or metathesis/hydrogenation reactions.

$$\begin{array}{c} PCy_3 \\ R^{in} - H \\ PCy_3 \\ \hline \\ 8 \end{array} \begin{array}{c} [IPr] \\ \hline \\ PCy_3 \\ \hline \\ A \end{array}$$

Regular papers

M. Ahlmann, O. Walter

J. Organomet. Chem. 689 (2004) 3117

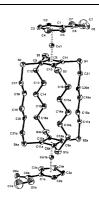
Syntheses and coordination behaviour of 2-(ortho-phosphinophenyl)-functionalised 1,3dioxolanes and 1,3-dioxanes towards a [(COD)Rh]-complex fragment – models for immobilised complexes The syntheses of 2-(ortho-phosphinophenyl)-1,3-dioxolanes or -dioxanes are reported as well as their coordination behaviour towards a [(COD)Rh] complex fragment. The ligands and complexes described act as model compounds for via trans acetalation on a polyvinylalcohol matrix bound pre-catalysts. First catalytic results on the hydrofomylation of 1-octene are presented.

Daniel B. Werz, J. Hilko Schulte, Rolf Gleiter, Frank Rominger

J. Organomet. Chem. 689 (2004) 3132

Donor-substituted CpCo-stabilized cyclobutadienes and superphanes

 $RCpCoL_2$ complexes ($L_2 = (CO)_2$ or COD, R = H, CO_2Me , TMS) were reacted with various alkynes substituted with chalcogen atoms adjacent to the triple bonds. These reactions yielded hetero-substituted CpCocapped cyclobutadienes and superphanes dependent on the ring size of the corresponding cyclic diene used as starting material.



iv *Contents*

Stefan Jank, Hauke Reddmann, Hanns-Dieter Amberger, Christos Apostolidis

J. Organomet. Chem. 689 (2004) 3143

Zur Elektronenstruktur metallorganischer Komplexe der f-Elemente LIX. Spektrochemische und nephelauxetische Effekte sowie experimentorientierte MO-Schemata (im f-Bereich) pseudo-trigonal-planarer (substituierter) Tris(η^5 -cyclopentadienyl)neodym(III)-Komplexe und eines THF-Monoaddukts

The parameters used in the fits of the crystal field splitting patterns of pseudo (ψ) trigonal planar (substituted) tris(η^5 -cyclopentadienyl)neodymium(III) compounds allowed the calculation of the global ligand field strengths experienced by the Nd^{3+} central ions and the set-up of their experimentally based nonrelativistic and relativistic molecular orbital schemes in the f range.

György Keglevich, Melinda Sipos, Dénes Szieberth, György Petőcz, László Kollár

J. Organomet. Chem. 689 (2004) 3158

4-Chloro-5-methyl-3-diphenylphosphino-1-phenyl-1,2,3,6-tetrahydrophosphinine as a bidentate P-ligand in a *cis* chelate Pt(II) complex

Bidentate phosphine ligand (**B**) obtained from 3-diphenylphosphinoxido-1,2,3,6-tetrahydrophosphinine 1-oxide (**A**) by deoxygenation involving inversion at the ring P was useful in the preparation of a *cis* chelate platinum complex (**C**). The outcome of the deoxygenation was interpreted on the basis of quantum chemical calculations. The stereostructure of the chelate complex (**C**) was confirmed by B3LYP calculations.

Michael S. Hill, Peter B. Hitchcock

J. Organomet. Chem. 689 (2004) 3163

Three-coordinate bis(phosphinimino)methanide derivatives of 'open shell' [M(II)] (M = Mn, Fe, Co) transition metals

Facile syntheses of three-coordinate derivatives of divalent manganese, iron and cobalt ligated by a sterically demanding bis(phosphinimino)methanide anion are reported.

Masashi Shiotsuki, Yasuyuki Ura, Takashi Ito, Kenji Wada, Teruyuki Kondo, Take-aki Mitsudo

J. Organomet. Chem. 689 (2004) 3168

Ruthenium-catalyzed formal [4+2] cycloaddition of alkynes with alkenes: formation of cyclohexenedicarboxylates via isomerization of alkynes and successive Diels-Alder reaction Formal [4+2] cycloaddition of alkynes with electron-deficient alkenes, which affords 3, 6-dialkyl-4-cyclohexene-1,2-dicarboxylates, was achieved using $Ru(\eta^6\text{-}1,3,5\text{-cyclooctatriene})(\eta^2\text{-dimethyl fumarate})_2$ as a catalyst. The reaction mechanism consists of two steps, isomerization of an alkyne to conjugated dienes and successive Diels–Alder reaction of the generated dienes with an electron-deficient alkene.

Pr — "Pr Ru catalyst 1 DMF 110 °C, 48 h
$$\mathbb{R}^2$$
 \mathbb{E} \mathbb{R}^2 \mathbb{E} \mathbb{R}^2 \mathbb

1: Ru(1,3,5-cyclooctatriene)(dimethyl fumarate)₂

Contents

Shiau-Yi Jin, Chih-Yu Wu, Chen-Shiang Lee, Amitabha Datta, Wen-Shu Hwang

J. Organomet. Chem. 689 (2004) 3173

Endo and exo cyclometallated iron carbonyl complexes derived from N-(N'-methyl-2-pyrrolylmethylidene)-2-thienylmethylamine

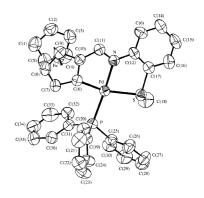
Reaction of N-(N'-methyl-2-pyrrolylmethylidene)-2-thienylmethylamine with $Fe_2(CO)_9$ in toluene yields endo and exo cyclometallated iron carbonyl complexes. These complexes were characterized spectrally and their structures were determined by means of X-ray diffraction. Reactions of the major product were studied.

Sonia Pérez, Concepción López, Amparo Caubet, Xavier Solans, Mercè Font-Bardia

J. Organomet. Chem. 689 (2004) 3184

Factors affecting the lability of the (M-X) bond in cycloplatinated and cyclopalladated complexes containing [C(sp ferrocene),N,X] or [C(sp phenyl),N,X] (X = S, N) terdentate ligands

The reactions of the cyclometallated complexes $[M\{[(\eta^5\text{-}C_5H_3)\text{-}CH=N\text{-}(C_6H_4\text{-}2\text{-}SMe)]\text{-}Fe(\eta^5\text{-}C_5H_5)\}\text{Cl}]$ [with M = Pt (5a) or Pd (5b)] with PPh3 have allowed the isolation and characterisation of $[M\{[(\eta^5\text{-}C_5H_3)\text{-}CH=N\text{-}(C_6H_4\text{-}2\text{-}SMe)]\text{Fe}(\eta^5\text{-}C_5H_5)\}(PPh_3)]X$ [M = Pt and X = Cl - (6a) or BF _4 (7a) or M = Pd and X = Cl - (6b) or BF _4 (7b)] and [Pd\{[(\eta^5\text{-}C_5H_3)\text{-}CH=N\text{-}(C_6H_4\text{-}2\text{-}SMe)]\text{Fe}(\eta^5\text{-}C_5H_5)\}\text{-}Cl(PPh_3)] (8b).



Habib Firouzabadi, Nasser Iranpoor, Sara Sobhani, Soheila Ghassamipour

J. Organomet. Chem. 689 (2004) 3197

Magnesium triflate [Mg(OTf)₂] a highly stable, non-hygroscopic and a recyclable catalyst for the high yielding preparation of diethyl α -trimethylsilyloxyphosphonates from diethyl α -hydroxyphosphonates by HMDS under solventless conditions

A broad, adaptable, high yielding and convenient procedure for the easy conversion of various α -hydroxyphosphonates to α -trimethylsilyloxyphosphonates under mild conditions with HMDS in the presence of a catalytic amount of magnesium triflate as a highly stable and a non-hygroscopic recyclable catalyst in neat conditions is described. In order to show the general applicability of this method, we have also applied this procedure successfully for the silylation of ordinary alcohols and phenols.

$$R \xrightarrow[]{P(OEt)_2} \frac{Mg(OTf)_2 (0.1 \text{ equiv.})}{HMDS (0.7 \text{ equiv.})} R \xrightarrow[]{P(OEt)_2} OTMS$$

$$1a \text{-} 0 \qquad rt, neat \qquad 2a \text{-} 0$$

Daryl P. Allen, Cathleen M. Crudden, Larry A. Calhoun, Ruiyao Wang

J. Organomet. Chem. 689 (2004) 3203

Irreversible cleavage of a carbene–rhodium bond in Rh-N-heterocyclic carbene complexes: implications for catalysis Cleavage of the Rh–C bond takes place upon treatment of the complex with dichloroethane. The same product is observed when free IMes reacts with dichloroethane at 60 °C

vi Contents

Victor Wee Lin Ng, Weng Kee Leong, Lip Lin Koh, Geok Kheng Tan, Lai Yoong Goh

J. Organomet. Chem. 689 (2004) 3210

Synthetic, X-ray structural and protonation studies of $CpCr(CO)_2SPy$ and $CpCr(CO)_2SPy$ ($SPy = C_3H_4NS$, $SPym = C_4H_3N_2S$)

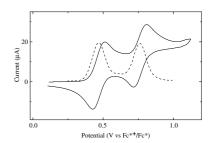
Complexes $CpCr(CO)_2(\eta^2-SPy)$ (2) and $CpCr(CO)_2(\eta^2-SPym)$ (4) were prepared from the reaction of $[CpCr(CO)_3]_2$ with 2,2′-dithiodipyridine and 2-mercaptopyrimidine, respectively. Treatment with HCl converts 2 quantitatively to $CpCrCl_2(\eta^1-SPyH)$ (3) and 4 to $CpCrCl_2(CH_3CN)$.

Avelina Arnanz, Maria-Luisa Marcos, Consuelo Moreno, David H. Farrar, Allan J. Lough, Joanne O. Yu, Salomé Delgado, Jaime González-Velasco

J. Organomet. Chem. 689 (2004) 3218

Synthesis, structures and comparative electrochemical study of 2,5-bis(trimethylsilylethynyl)thiophene coordinated cobalt carbonyl units

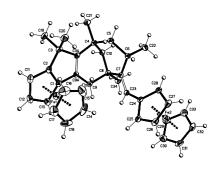
New complexes containing one or two $Co_2(CO)_6$ or $Co_2(CO)_4(X)$ units (X = dppa, dppm) and the 2,5-bis(trimethylsilylethynyl)thiophene bridge have been prepared and characterized. Electronic communication in the dinuclear compounds has been proved by electrochemical means. A comparative electrochemical study is presented by means of the cyclic and square-wave voltammetry techniques.



Elena I. Klimova, Tatiana Klimova Berestneva, José Manuel Méndez Stivalet, Ruben Alfredo Toscano, Cecilio Alvarez Toledano, Marcos Martínez García

J. Organomet. Chem. 689 (2004) 3232

Cross-conjugated 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene in cationic cycloaddition and proton-catalyzed cyclodimerization reactions Cationic cycloaddition of cross-conjugated 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene to 1-ferrocenyl-2-isopropenyl-3,3-dimethylallylium tetrafluoroborate and its proton-catalyzed cyclodimerization result in diferrocenylbicyclo[3.3.1]nonene derivatives. The spatial structure of one of the reaction products, viz., ferroceno[4,5]-{9-ferrocenylmethylidene-1,3,3,8,10-pentamethyltricyclo-[6.3.1.0^{2,6}]dodec-2(6)-ene}, was established based on the data from X-ray diffraction analysis.



Afaf R. Genady, Mohamed E. El-Zaria, Detlef Gabel

J. Organomet. Chem. 689 (2004) 3242

Non-covalent assemblies of negatively charged boronated porphyrins with different cationic moieties

A new series of electrostatically linked dimeric and pentameric porphyrins was synthesized by interaction of novel anionic boron containing porphyrins such as *meso* mono- and tetra-(benzamidodecahydro-closo-dodecaborate)phenylporphyrin and a variety of cationic *meso*-tetraarylporphyrin units. A bipyridine linked dimer was also prepared as a spacer between two mono-anionic porphyrins. A quinone-porphyrin dyad for electron or energy transfer demonstration was also synthesized.

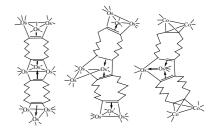
Contents vii

Tsun-Wei Shiue, Wen-Yann Yeh, Gene-Hsiang Lee, Shie-Ming Peng

J. Organomet. Chem. 689 (2004) 3251

Syntheses of double- and triple-decker clusters of osmium and cobalt metals linked by cyclotetradeca-1,8-diyne ligands

The reactions of $Os_3(CO)_{10}(NCMe)_2$ or $Co_2(CO)_8$ with $Os_3(CO)_{10}(C_{14}H_{20})$, $Os_3(CO)_9(C_{28}H_{40})$ and $Os_3(CO)_8(C_{14}H_{20})_2$ have lead to several double- and triple-decker clusters linked by cyclodiyne ligands.



Joji Ohshita, Ryosuke Taketsugu, Yuki Nakahara, Atsutaka Kunai

J. Organomet. Chem. 689 (2004) 3258

Convenient synthesis of alkoxyhalosilanes from hydrosilanes

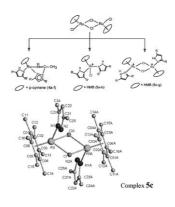
PdCl₂- or NiCl₂-catalyzed selective alkoxylation of dihydro- and trihydrosilanes, followed by halogenation, gave alkoxyhalo and dialkoxyhalosilanes in good yield, respectively.

P. Govindaswamy, Yurij A. Mozharivskyj, Mohan Rao Kollipara

J. Organomet. Chem. 689 (2004) 3265

Reactivity studies of $(\eta^6$ -arene)ruthenium dimeric complexes towards pyrazoles: isolation of amidines, bis pyrazoles and chloro bridged pyrazole complexes

The complex $[Ru(\eta^6-p\text{-cymene})(\mu\text{-Cl})Cl]_2$ 1 reacts with 3,5-disubstituted pyrazoles and gives amidine complexes, whereas the complex $[Ru(\eta^6\text{-}C_6Me_6)(\mu\text{-Cl})Cl]_2$ 2 gives chloro bridged disubstituted pyrazole complexes. The structures of representative complexes are confirmed by single crystal X-ray study.



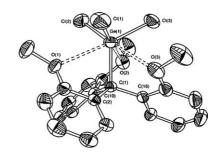
Note

Yoshito Takeuchi, Yutaka Takase

J. Organomet. Chem. 689 (2004) 3275

A new heptacoordinated organogermanium compound; trichlorogermyl[tris(2-methoxy-phenyl)]methane

A new hypercoordinated organogermanium compound, trichlorogermyl[tris(2-methoxyphenyl)]methane (4) was prepared, and its tricapped tetrahedral structure was confirmed by X-ray crystallographic analysis. All interatomic oxygen···germanium distances are shorter than the sum of van der Waals radii of O and Ge (3.62 Å).



Contents viii

The Publisher encourages the submission of articles in electronic form thus saving time and avoiding rekeying errors. Please refer to the online version of the Guide for Authors at http://www.elsevier.com/locate/jorganchem



Full text of this journal is available, on-line from ScienceDirect. Visit www.sciencedirect.com for more information.



CONTENTS This journal is part of **ContentsDirect**, the *free* alerting service which sends tables of contents by e-mail for Elsevier books and journals. You can register for ContentsDirect online at: www.elsevier.com/locate/contentsdirect