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Regular papers

Saim Özkar, Richard G. Finke

J. Organomet. Chem. 689 (2004) 493

The hydrogenphosphate complex of (1,5-cy-clooctadiene)iridium(I), {[Bu₄N][(1,5-COD)Ir · HPO₄]}_n: synthesis, spectroscopic characterization, and ES-MS of a new, preferred precursor to HPO₄²⁻ and Bu₄N⁺ stabilized Ir(0)_n nanoclusters

The synthesis and characterization of a previously unknown, rare organometallic-phosphate complex, {[Bu₄N][(1,5-COD)Ir · HPO₄]}_n (1), is described. Complex 1 is significant since it is known to be the preferred, compositionally precise precursor to the prototype example of a recently discovered class of novel, HPO₄²⁻ and Bu₄N⁺ stabilized nanoclusters, (Bu₄N)₂^{n²ⁿ⁺}[Ir(0)_n (HPO₄)₁]²ⁿ⁻.

$$\begin{split} & [(1,5-\text{COD})\text{Ir}(\text{NCCH}_3)_2]\text{BF}_4 + [\text{Bu}_4\text{N}]_2\text{HPO}_4 \\ & \xrightarrow[\text{CH}_3\text{CN}]{} \rightarrow \frac{1}{n} \left\{ [\text{Bu}_4\text{N}][(1,5-\text{COD})\text{Ir} \bullet \text{HPO}_4] \right\}_n \\ & + [\text{Bu}_4\text{N}]\text{BF}_4 + 2\text{CH}_3\text{CN} \end{split}$$

Folami T. Ladipo, Vallipuram Sarveswaran, Jesudoss V. Kingston, Rebecca A. Huyck, Sergei Y. Bylikin, Shana D. Carr, Randy Watts, Sean Parkin

J. Organomet. Chem. 689 (2004) 502

Synthesis, characterization, and alkyne cyclotrimerization chemistry of titanium complexes supported by calixarene-derived bis(aryloxide) ligation

Titananorbornadiene complex formation and catalytic alkyne cyclotrimerization occur when titanium dichloride complexes containing calix[4]arene-derived bis(aryloxide) ligands are reduced by magnesium in the presence of excess alkyne. Our results indicate that steric properties of the R_2Si bridging group of calixarene-derived bis (aryloxide) ligands affect reactivity of the titanium complexes.



Brian K. Nicholson, Sam K. Whitley

J. Organomet. Chem. 689 (2004) 515

 $Characterisation \ of \ the \ first \ authenticated \\ organomercury \ hydroxide, \ 4-Me_2NC_6H_4-HgOH$

 $4-Me_2NC_6H_4HgOH$ has been characterised spectroscopically and crystallographically as a true organomercury hydroxide.



Harry Adams, Michael J. Morris, Sarah A. Morris, Jeffrey C. Motley

J. Organomet. Chem. 689 (2004) 522

Dithiolene transfer from nickel to a dimolybdenum centre: the first dithiolene alkyne complex

The first example of a dithiolene alkyne complex, $[Mo_2(\mu-C_2R_2)(\mu-S_2C_2Ph_2)_2C_2P_2]$ (R = CO₂Me, Cp = η -C₃H₅) has been prepared by the transfer of dithiolene ligands from [Ni(S₂C₂Ph₂)₂] to the dimolybdenum alkyne complex [Mo₂(μ -C₂R₂)(CO)₄Cp₂].



Vincenzo G. Albano, Luigi Busetto, Fabio Marchetti, Magda Monari, Stefano Zacchini, Valerio Zanotti

J. Organomet. Chem. 689 (2004) 528

Stereochemistry of the insertion of disubstituted alkynes into the metal aminocarbyne bond in diiron complexes

Alkynes (R'C=CR") insert into the μ -carbon-metal bond of diiron complexes affording μ - σ : η^3 vinyliminium species. Several isomers have been found arising from: (i) the iminium moiety configuration (*E*, *Z*), (ii) mutual Cp position (*cis*-*trans* isomers), (iii) head-head or head-tail insertion mode of R'C=CR". These isomeric forms have been investigated by NMR and X-ray diffraction.



R. Lalrempuia, Hemant Yennawar, Yurij A. Mozharivskyj, Mohan Rao Kollipara

J. Organomet. Chem. 689 (2004) 539

Synthesis, characterization and molecular structures of allenylidene, vinylidene–alkylidene complexes containing $[CpOs(PPh_3)_2]^+$ fragment

The complex $[CpOs(PPh_3)_2Br]$ reacts with the alkynols $HC \equiv CCR_2(OH)$ to form a cationic osmiumallenylidene complex $[CpOs-(=C=CPCh_2)(PPh_3)_2][PF_6]$ (1) when R = Phand a metallacumulene, a dicationic diosmium vinylidene–alkylidene complex $[(CpOs)_2(\mu-C_{10}H_{12})(PPh_3)_4][PF_6]_2$ (2) was obtained when R = Me. The structures of these complexes have been determined by X-ray diffraction.



Fu-Chen Liu, Yow-Chuan Sheu, Jo-Ju She, Yu-Chang Chang, Fung-E Hong, Gene-Hsian Lee, Shie-Ming Peng

J. Organomet. Chem. 689 (2004) 544

Syntheses and characterizations of group 6 metal cyanotrihydroborate complexes

The anionic complexes, $[M(CO)_{6-n}$ (NCBH₃)_n]ⁿ⁻ (n = 2, M = Cr; n = 3, M = Cr, Mo, W), were prepared and characterized. The cyanotrihydroborate ligand bonds to the metal through a nitrogen atom. A *cis* configuration is found in $[Cr(CO)_4(NCBH_3)_2]^{2-}$. Molecular structures of $[M(CO)_3-(NCBH_3)_3]^{3-}$ (M = Cr, Mo, W) are similar and a *facial* configuration is observed.



M. Isabel Alcalde, Esther Delgado, Bruno Donnadieu, Elisa Hernández, M. Paz Martín, Félix Zamora

J. Organomet. Chem. 689 (2004) 552

Asymmetric acetylenic thioethers in ruthenium cluster chemistry The compounds $[Ru_3(CO)_9(\mu,\eta^2-SC\equiv CR)$ $(\mu_3,\eta^2-C\equiv CR')]$ (R = SiMe₃, R' = Si'Pr₃ (1); R = Si'Pr₃, R' = SiMe₃ (2); R = Si'Pr₃, R' = H (3); R = H, R' = Si'Pr₃ (4)) have been obtained by cleavage of one S–C bond of the thioethers 'Pr₃SiC=CSC=CR (R = H, SiMe₃) in the presence of Ru₃(CO)₁₂.



Antonio Rodríguez, J. Arturo García-Vázquez, Antonio Sousa-Pedrares, Jaime Romero, Antonio Sousa

J. Organomet. Chem. 689 (2004) 557

On the influence of the heterocyclic ring substituents on the structure of dimethy-lthallium pyrimidine-2-thionato complexes. Crystal structure of dimethyl-(4-trifluoro-methylpyrimidine-2-thionate)thallium(III): a compound with intermolecular C-H $\cdots \pi$ interactions

The reaction of 4-trifluoromethylpyrimidine-2-thione (4-CF₃pymSH) with dimethylthallium(III) hydroxide afforded the complex [Me₂Tl(4-CF₃pymS)]_n. This compound consists of polymeric chains which are joined by intermolecular C–H··· π interactions between an hydrogen atom of each methyl group and one of the pyrimidine rings of a neighbouring chain.



U. Herzog, H. Borrmann

J. Organomet. Chem. 689 (2004) 564

Organosilicon chalcogenides with trisilane units – bicyclo[3.3.1]nonanes, bicyclo [3.2.2]nonanes and spiro[4.4]nonanes Treatment of 1,2,3-trichloropentamethyltrisilane (1) with H₂S/NEt₃ results in the formation of a mixture of two isomers of (Me₅Si₃)₂S₃ with a bicyclo[3.3.1]nonane (**2a**) and a bicyclo[3.2.2]nonane (**2b**) skeleton, while the reaction of I with Li₂Se yields one product only, (Me₅Si₃)₂Se₃ (**3a**), with a bicyclo[3.3.1]nonane structure. Compounds Si(SiMe₂EMR₂E)₂ (**5a**–h: MR₂: SiMe₂, SiPh₂, GeMe₂, SnMe₂: E = S, Se, Te) with a spiro[4.4]nonane skeleton have been obtained in mixture with varying amounts of the corresponding six-membered rings (R₂ME)₃ by reactions of mixtures of 1,2,2, 3-tetrachlorotetramethyltrisilane (**4**) and diorganodichlorosilanes, Me₂GeCl₂ or Me₂SnCl₂, with H₂S/NEt₃, Li₂Se or Li₂Te. All products have been characterized by multinuclear NMR spectroscopy (¹H, ¹³C, ²⁹Si, ¹¹⁹Sn, ⁷⁷Se, ¹²⁵Te). The molecular structure of **3a** is reported.



Rainer Schobert, Anett Mangold, Thomas Baumann, Wolfgang Milius, Frank Hampel

J. Organomet. Chem. 689 (2004) 575

Reactions of chelated $\eta^3\mbox{-}pentadienyl$ iron complexes with nucleophiles

Metallacyclic $(1-3-\eta^3)$ pentadienyl iron complexes **2** and **3** with conjugated though electronically decoupled allyl and vinyl moieties were reacted with various heteroatom and carbon nucleophiles. Amines selectively attacked neutral complexes **2** on the allylic end C-6; S'_N-like reaction with its coplanar vinyl residue was not observed. Depending on electronic and sterical factors, nucleophiles regio- and diastereoselectively attacked the cationic complex **3** either on the allylic terminus C-6, or on the vinyl residue which is part of an activated Michael system, or they abstracted a proton H⁸.



Daniel Dönnecke, Joachim Wunderle, Wolfgang Imhof

J. Organomet. Chem. 689 (2004) 585

Ligand properties of aromatic azines: C–H activation, metal induced disproportionation and catalytic C–C coupling reactions

Aromatic azines by treatment with Fe₂(CO)₉ show two typical reaction pathways. C–H activation reactions regioselectively occur in *ortho*-position with respect to the imine moiety. In addition, products from a disproportionation reaction of the azine into a primary imine and a nitrile were observed and structurally characterized. The same reaction principles are found in catalytic C–C coupling reactions in the presence of Ru₃(CO)₁₂ as the precatalyst.



Dmitrii P. Krut'ko, Maxim V. Borzov, Roman S. Kirsanov, Mikhail Yu. Antipin, Andrei V. Churakov

J. Organomet. Chem. 689 (2004) 595

Mono- and bis-(2-dimethylaminoethyl) tetramethylcyclopentadienyl zirconium(IV) complexes: synthesis and structural studies in crystalline state and in solutions A novel half-sandwich Zr(IV) complex $[\eta^5:\eta^1\text{-}N\text{-}C_5(CH_3)_4CH_2CH_2N(CH_3)_2]ZrCl_3$ together with zirconocene dichlorides $[\eta^5\text{-}C_5(CH_3)_4CH_2CH_2N(CH_3)_2][\eta^5\text{-}C_5(CH_3)_3]$ ZrCl₂ and $[\eta^5\text{-}C_5(CH_3)_4CH_2CH_2N(CH_3)_2]_2$ ZrCl₂ have been prepared. Complex **6** has been isolated and characterized as an adduct with THF, an adduct with tetrahydrothiophene, and a solvent-free form. The dynamic behavior of the THF adduct in CD_2Cl_2 has been studied by the variable-temperature 1H and $^{13}C\{^1H\}$ NMR spectroscopy.



Clifton E.F. Rickard, Warren R. Roper, George R. Whittell, L. James Wright

J. Organomet. Chem. 689 (2004) 605

Four isomers from the oxidative addition of Me_3SnH to $Os(CO)_2(PPh_3)_3$ and the crystal structure of $Os(SnMeI_2)I(CO)_2(PPh_3)_2$, in which the pairs of CO and PPh₃ ligands are mutually *trans*

In solution $Os(SnMe_3)H(CO)_2(PPh_3)_2$ and $Os(SnMe_2Cl)H(CO)_2(PPh_3)_2$ exist as a mixture of four isomers whereas $Os(SnMeI_2)H(CO)_2(PPh_3)_2$ exists as a single isomer. The preferred isomer depends on the substituents on the stannyl ligand in these compounds.



sinale isome

Yoshinori Takashima, Yuushou Nakayama, Toshikazu Hirao, Hajime Yasuda, Akira Harada

J. Organomet. Chem. 689 (2004) 612

Bis(amido)titanium complexes having chelating diaryloxo ligands bridged by sulfur or methylene and their catalytic behaviors for ring-opening polymerization of cyclic esters A series of titanium bis(dialkylamido) complexes coordinated by O–E–O (E = S, CH₂) chelating bis(aryloxo) ligands, Ti[E(4-Me-6-'BuC₆H₂O)₂](NR₂)₂ (E = S, CH₂, R = Me, Et), were synthesized by the reaction of Ti(NR₂)₄ (R = Me, Et) with 2,2'-E(4-Me-6-'BuC₆H₂OH)₂ (E = S, E = CH₂). The crystal structures of complexes were determined by X-ray diffraction. These complexes were found to initiate the polymerization of *ɛ*caprolactone in toluene at 100 °C affording quantitative polymer yields.



José S. Casas, Alfonso Castiñeiras, Félix Condori, María D. Couce, Umberto Russo, Agustín Sánchez, José Sordo, José M. Varela, Ezequiel M. Vázquez-López

J. Organomet. Chem. 689 (2004) 620

Diorganotin(IV) complexes of dideprotonated pyridoxine (PN, vitamin B_6). The crystal structures of [SnEt₂(PN-2H)] \cdot CH₃OH, [Sn-Et₂(PN-2H)(DMSO)] and [SnBu₂(PN-2H)] By reacting the appropriate SnR_2O oxide (R = Me, Et, Bu) with pyridoxine (PN) we prepared and characterized [$SnR_2(PN-2H)$] complexes which contain dimeric [$SnR_2(PN-2H)$]₂ units. The structure of [$SnEt_2(PN-2H)$] (DMSO)] shows the ability of these units to accept electron pairs.



Daniel B. Werz, Rolf Gleiter, Frank Rominger

J. Organomet. Chem. 689 (2004) 627

An alkynyltelluronium iodide and its solid state structure: evidence for $p\to\sigma^*$ interactions

The synthesis of the first alkynyltelluronium salt is presented. X-ray investigations of this species reveal a two-dimensional polymeric structure, assembled through various secondary Te···Te and Te···I interactions. The structure itself can be rationalized in terms of $p \to \sigma^*$ interactions.



Petr Štěpnička, Ivana Císařová, Jiří Ludvík

J. Organomet. Chem. 689 (2004) 631

Acid-base and counter ion dependent solidstate assembly of a ferrocene β -aminoalcohol and the corresponding ammonium salt The solid-state structure of 2-(ferrocenylmethyl)amino-2-methylpropan-1-ol (1) and the ammonium salts [1H]Br (2) and [1H]H₂PO₄·1/6Et₂O (**3a**) have been determined with the aim of determining the potential of 1 as an organometallic building block for crystal engineering. The solid-state assemblies of 1 and 2 consist of infinite ladder-like arrays interconnected by hydrogen bonds, while that **3a** is formed by infinite hydrogen-bonded dihydrogenphosphate chains, which are interlinked by hydrogen bonds to cations [1H]⁺.



Guido Marconi, Paolo Pertici, Claudio Evangelisti, Anna Maria Caporusso, Giovanni Vitulli, Gustavo Capannelli, Manh Hoang, Terence W. Turney

J. Organomet. Chem. 689 (2004) 639

Nanostructured ruthenium on $\gamma\text{-}Al_2O_3$ catalysts for the efficient hydrogenation of aromatic compounds

Free and trioctylamine (TOA)-stabilized ruthenium nanoparticles, generated by treatment of Ru(η^6 -cycloocta-1,3,5-triene)(η^4 -cycloocta-1,5-diene) with hydrogen, have been deposited on γ -Al₂O₃ supports having different surface area. The resulting systems are efficient and long lived catalysts in the hydrogenation of aromatic rings, considerably more active than analogous commercial catalysts. A new pathway to synthesize 4-carbomethoxyformylcyclohexane, important starting material in the preparation of pharmaceutical products, has been set up in the presence of Ru(TOA) on high surface area γ -Al₂O₃ catalyst.



Barbara Binotti, Carla Carfagna, Elisabetta Foresti, Alceo Macchioni, Piera Sabatino, Cristiano Zuccaccia, Daniele Zuccaccia

J. Organomet. Chem. 689 (2004) 647

Cationic olefin Pd(II) complexes bearing α -iminoketone N,O-ligands: synthesis, intramolecular and interionic characterization and reactivity with olefins and alkynes Complexes $[Pd(\eta^1, \eta^2-5-OMe-C_8H_{12})(N,O)]$ -BF₄ (N,O = 2,6-(*i*-Pr)₂(C₆H₃)N=C(Ph)-C(Ph)=O, **1**; 2,6-(*i*-Pr)₂(C₆H₃)N=C(Me)-C(Ph)=O, **2**; 2-benzoylpyridine, **3**; were synthesized by the reactions of $[Pd(\eta^1, \eta^2-5-OMe-C_8H_{12})Cl]_2$ with the suitable N,Oligand.



Sensuke Ogoshi, Masaki Morita, Katsuharu Inoue, Hideo Kurosawa

J. Organomet. Chem. 689 (2004) 662

Convenient synthesis of Pt(0) olefin complexes by colorimetric reduction of Pt(II) complexes with SmI_2

Homoleptic olefin platinum(0) complexes, Pt(C_7H_{10})₃ and Pt(cod)₂, were synthesized by the colorimetric reduction of platinum(II) complexes with SmI₂ in the presence of 2norbornene or COD.



Bing Luo, Wayne L. Gladfelter

J. Organomet. Chem. 689 (2004) 666

Synthesis and X-ray crystallographic structures of $[HGa(NMe_2)_2]_2$ and $[PhGa(NHNMe_2)_2]_2$, and room-temperature conversions of $[HGa(NMe_2)_2]_2$ to $(HGaNH)_n$ and $(HGaNMe)_n$

Bis(dimethylamido) complexes of phenyl and hydrido gallium were found to be useful sources of " RGa^{2+} " synthons, where R = Phand H. Solid state structures of $[HGa(NMe_2)_2]_2$ and $[PhGa(NH-NMe_2)_2]_2$ were determined.



Allan J. Canty, Melanie C. Denney, Jim Patel, Huailin Sun, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 689 (2004) 672

Reversible oxidative addition of a diaryl diselenide to a diorganopalladium(II) complex, carbon–selenium bond formation at palladium(IV), and structural studies of palladium(II) and platinum(IV) selenolates

Methyl(4-methoxyphenyl)(2,2'-bipyridine)palladium(II) (1) reacts with bis(4-chlorophenyl) diselenide to form an equilibrium with a Pd(IV) complex (2), and organopalladium(II) complexes of 1,2-bis(diphenylphosphino) ethane react with cleavage of Pd–C bonds to form C–Se bonds.



Guangrong Tang, Guo-Xin Jin, Linhong Weng

J. Organomet. Chem. 689 (2004) 678

Self-immobilized metallocene catalysts bearing an allyl group for ethylene polymerization, X-ray crystal structure of [(CH₂=CHCH₂)CH₃Si(C₁₃H₈)₂]ZrCl₂

The ansa-metallocene complexes with an allyl substituted silane bridge have been synthesized and used as self-immobilized catalysts for ethylene polymerization. The results showed that the self-immobilized catalysts 1-4, 6 kept high ethylene polymerization activities of ca. 10⁶ g PE mol⁻¹ M h⁻¹ and high molecular weight $(M_{\rm w} \approx 10^5)$ of polyethylene.



Notes

Rehan Basta, Atta M. Arif, Richard D. Ernst

J. Organomet. Chem. 689 (2004) 685

Formation and structural study of a mixed ene/enyl ligand on reaction of [Ru(C5Me5)-Cl₂]₂ with 1,3-cyclononadiene

The incorporation of 1,3-cyclononadiene into a Ru(C₅Me₅) complex occurs in conjunction with its deprotonation and subsequent isomerization to an η^{5} -1,2,3,6,7cyclononadienyl ligand, having isolated allyl and olefin fragments rather than a contiguous $\eta^{5}\text{-dienyl}$ ligand. This formulation has been supported spectroscopically and by a single crystal structural study.



OSi(CH₃)₂H

OSi(CH₃)₂H

OSi(CH₃)₂H

OSi(CH₃)₂H

H(H₃C)₂SiO

H(H₃C)₂SiO

H(H₃C)₂SiO

Guoping Cai, Jonathan R. Sargent, William P. Weber

J. Organomet. Chem. 689 (2004) 689

six- and eight-membered cyclic silicates

Six- and eight-membered cyclic silicates with reactive Si-H or Si-vinyl functional groups have been synthesized. These are generally resistant to either strong acid or base catalyzed ring opening.

Preparation and reactivity of polyfunctional

Michael P. Coogan, Robert L. Jenkins, Eva Nutz

J. Organomet. Chem. 689 (2004) 694

Carbonylative dimerisation of norbornene by cobalt carbonyl: an overlooked byproduct of the Pauson-Khand reaction

Dicobaltoctacarbonyl or dicobalthexacarbonyl-alkyne complexes react with norbornene in inert solvents and in the absence of activation to give an enol-lactone 3.

H(H₃C)₂SiO

i) Co₂(CO)₈ or RC(Co(CO)₃)₂CR

Michael I. Bruce, Benjamin G. Ellis, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 689 (2004) 698

Preparation and molecular structure of a pyrazolyl-ruthenium complex, Ru{C₃H₂NN-(SO2tol)}(dppe)Cp*

The reaction between RuCl(dppe)Cp* and Me₃SiC=CC(SiMe₃)=NNHTs has given the pyrazole derivative Ru(C=CHNTsN=CH)(dppe)Cp* (1), which was characterised by a singlecrystal X-ray structure determination.



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