Available online at www.sciencedirect.com

SCIENCE DIRECT®

Volume 689, issue 21, 15 October 2004

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Contents

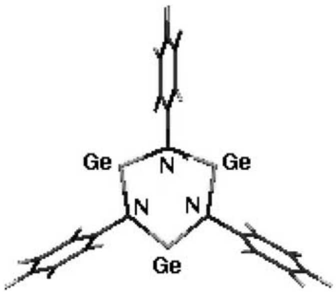
Regular papers

Salima Boughdiri, Khansaa Hussein, Bahoueddine Tangour, Mohamed Dahrouch, Monique Rivière-Baudet, Jean-Claude Barthelat

J. Organomet. Chem. 689 (2004) 3279

Aromaticity or non aromaticity in germanazenes? Theoretical studies on germanazenes, the *N*-cyano analogs and their carbodiimide isomers

DFT/B3LYP studies of germanazene rings $[(\mathrm{Ge_{II}}{-}\mathrm{NR})_{2,3}$; $\mathrm{R = H}$, Me, CN, Ph] have been performed. The fully optimized geometrical structures display four or six-membered planar rings of alternating germanium and nitrogen. Although this planar conformation could indicate some degree of delocalization, the homodesmotic reaction energy indicates very little or no aromatic character.

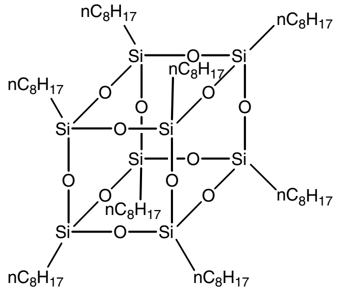


Alan R. Bassindale, Huiping Chen, Zhihua Liu, Iain A. MacKinnon, David J. Parker, Peter G. Taylor, Yuxing Yang, Mark E. Light, Peter N. Horton, Michael B. Hursthouse

J. Organomet. Chem. 689 (2004) 3287

A higher yielding route to octasilsesquioxane cages using tetrabutylammonium fluoride, Part 2: further synthetic advances, mechanistic investigations and X-ray crystal structure studies into the factors that determine cage geometry in the solid state

The recently-reported reaction of triethoxysilanes with tetrabutylammonium fluoride in the presence of scarce water provides a higher yielding route to substituted octasilsesquioxane cages. Further cages have now been prepared in good yield and their X-ray crystal structures examined. The mechanism of cage formation has been probed and the proposed mechanism further validated. By careful choice of reaction conditions, dramatic increases in rate and yield have been demonstrated.

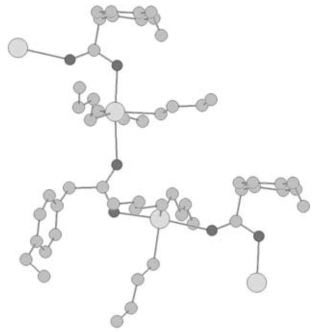


Luigi Angiolini, Daniele Caretti, Laura Mazzocchetti, Elisabetta Salatelli, Cristina Femoni

J. Organomet. Chem. 689 (2004) 3301

Tri-*n*-butyltin carboxylate derivatives of *para*-substituted phenyl-ethanoic acids: synthesis, characterization and X-ray structure determination

The tributyltin esters of 4-(ethyl)-phenyl-ethanoic acid and 4-(isopropyl)-phenyl-ethanoic acid have been prepared. The supramolecular arrangement of the products in the solid state confirms pentacoordination at tin in both the products as predicted by FT-IR and indicates a different spatial arrangement of the alkylated aryl groups, as evidenced also by the slightly different thermal properties.



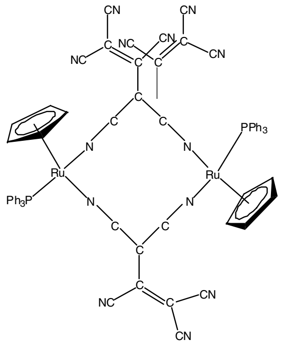
Elsevier B.V.
doi:10.1016/S0022-328X(04)00686-2

**Michael I. Bruce, Mark A. Buntine,
Karine Costuas, Benjamin G. Ellis,
Jean-Franois Halet, Paul J. Low,
Brian W. Skelton, Allan H. White**

J. Organomet. Chem. 689 (2004) 3308

Some ruthenium complexes containing cyanocarbon ligands: syntheses, structures and extent of electronic communication in binuclear systems

The syntheses, structures and redox properties of a series of mono- and bi-nuclear complexes containing various cyanocarbon ligands and Ru(PP)Cp′ [PP = $(PPh_3)_2$, Cp′ = Cp; PP = dppe, Cp′ = Cp*] are reported. Evidence for electronic interactions between metal centres mediated by the cyanocarbon bridge is presented, together with computational studies of the conformations of isomers present in solution.

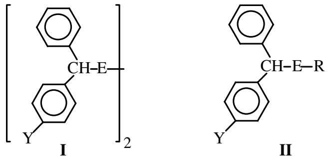


**K.K. Bhasin, Neelam Singh, Rajeev Kumar,
D. Gupta Deepali, S.K. Mehta,
Thomas M. Klapoetke, M. Crawford**

J. Organomet. Chem. 689 (2004) 3327

A convenient synthesis of some symmetrical and unsymmetrical diarylmethyl sulfur and selenium compounds: X-ray crystal structure of diphenylmethylseleno-2-propene and bis[*p*-chlorophenyl(phenyl)methyl] diselenide

The synthesis and characterization of various symmetrical (I) and unsymmetrical (II) diarylmethyl sulfur and selenium compounds have been reported. The decomposition behaviour and reactivity of these compounds have also been investigated. The molecular structure of bis[*p*-chlorophenyl(phenyl)-methyl] diselenide and diphenylmethylseleno-2-propene is briefly discussed.



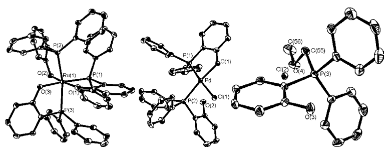
E = S, Se; R = alkyl, benzyl, allyl, 2,2,2-trifluoroethyl and aryl etc.; Y = H, Cl.

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

J. Organomet. Chem. 689 (2004) 3335

Mononuclear and heterodinuclear transition metal complexes of functionalized phosphines. Crystal and molecular structures of $[Mo(CO)_5(RPC_6H_4OCH_2OCH_3\text{-}o)]$ (R = Ph, $C_6H_4OCH_2OCH_3\text{-}o$), $[Ru(Ph_2PC_6H_4O\text{-}o)_3]$, $[Pd(Ph_2PC_6H_4O\text{-}o)_2]$ and $[PdCl(Ph_2PC_6H_4O\text{-}o)(Ph_2PC_6H_4OH\text{-}o)]$

Reactions of functionalized phosphine, $Ph_2PC_6H_4OCH_2OCH_3$ with ruthenium and palladium compounds gave interesting metallacycles through the elimination of methoxymethylchloride.

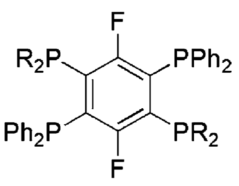


**Natcharee Kongprakaiwoot, Rudy L. Luck,
Eugenijus Urnezius**

J. Organomet. Chem. 689 (2004) 3350

New synthetic route to polyphosphine ligands bearing 1,2,4,5-tetrakis(phosphino)-benzene framework: structural characterizations of 1,4-$(PPh_2)_2$-2,5-$(PR_2)_2$-C_6F_2 (R = Ph, ^{i}Pr, Et)

Three 1,2,4,5-tetrakis(phosphino)-3,6-difluorobenzenes 1,4-$(PPh_2)_2$-2,5-$(PR_2)_2$-C_6F_2 (R = Ph, ^{i}Pr and Et) have been synthesized. The compounds are obtained starting from 1,4-dibromo-2,5-difluorobenzene utilizing low temperature dilithiation reactions followed by $ClPR_2$ quenches. All three tetrakis (phosphino)benzenes 1,4-$(PPh_2)_2$-2,5-$(PR_2)_2$-C_6F_2 have been characterized by spectroscopic methods, elemental analyses, and single crystal X-ray diffraction methods.



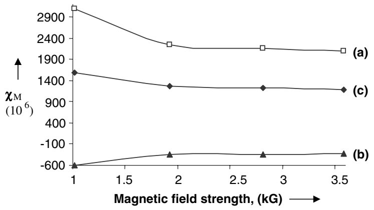
R = Ph, ^{i}Pr, Et

B.N. Achar, K.S. Lokesh

J. Organomet. Chem. 689 (2004) 3357

Studies on tetra-amine phthalocyanines

Metal(II) tetranitro phthalocyanines of cobalt, nickel and copper are synthesized in pure state by a novel modified method. The complexes are characterized using elemental, electronic and IR spectral studies. Pure metal(II) tetra-amino phthalocyanines of cobalt, nickel and copper are synthesized by reducing the nitro groups of the above complexes using sodium sulphide. These complexes are also characterized by elemental, electronic, IR spectral and magnetic susceptibility measurements. The nature of the electrical conductivities of the above three metal(II) tetra-amino phthalocyanine derivatives are studied in the temperature range 303–473 K and the data are presented. Among the effect of various substituent groups on the electrical conducting property of phthalocyanine, amine group substituent on the peripheral benzene ring of the phthalocyanine molecule has been found to increase electrical conductivity to a greatest extent. These complexes showed about 10^5–10^6 times higher electrical conductivities compared to their parent phthalocyanine compounds.

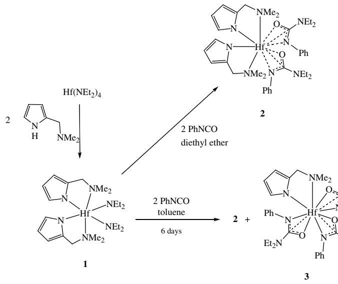


Kun-Chun Hsieh, Wen-Yi Lee, Chun-Liang Lai, Ching-Han Hu, Hon Man Lee, Jui-Hsien Huang, Shie-Ming Peng, Gene-Hsing Lee

J. Organomet. Chem. 689 (2004) 3362

Insertion reactions of phenyl isocyanate into hafnium nitrogen bonds: synthesis and reactivity of hafnium complexes bearing substituted pyrrolyl ligands

A bis(diethylamido)hafnium compound $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(NEt_2)_2$ (**1**) has been prepared in 79% yield by reacting $Hf(NEt_2)_4$ with 2 equiv. of $[C_4H_3NH\text{-}(CH_2NMe_2)\text{-}2]$ in heptane via deamination. Reacting compound **1** with 2 equiv. of phenyl isocyanate at room temperature in diethyl ether results in the PhNCO being inserted seletively into hafnium–NEt_2 bonds to generate $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf[PhN\text{-}C(NEt_2)O]_2$ (**2**) in 56% yield.

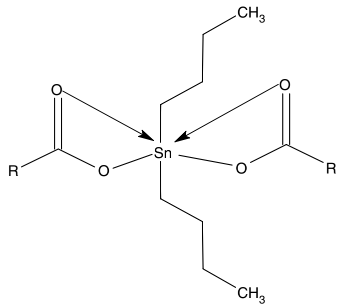


M.I. Khan, Musa Kaleem Baloch, Muhammad Ashfaq

J. Organomet. Chem. 689 (2004) 3370

Biological aspects of new organotin(IV) compounds of 3-maleimidopropionic acid

Organotin(IV) esters of the general formulae R'_2SnR_2, $R'_8Sn_4R_4$ and R'_3SnR, (R: 3-maleimidopropionic acid and R′: n-butyl, phenyl and cyclohexyl) have been synthesized. These compounds were characterized by %CHN analyses, FT IR, multinuclear (^1H, ^{13}C, ^{119}Sn) NMR, ^{119m}Sn Mössbauer and mass spectrometry. Compound R'_2SnR_2 exhibited an octahedral arrangement while R'_3SnR were tetrahedral in solution. Biological screenings like anti-bacterial, anti-fungal, anti-yeast, anti-inflammatory and *in vivo* anti-tumour were performed to establish their biological activity.

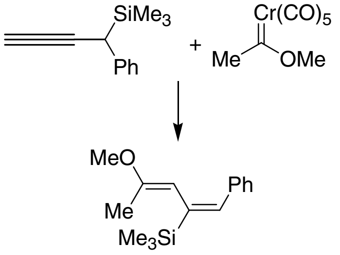


Paren P. Patel, Yixin Zhu, Lei Zhang, James W. Herndon

J. Organomet. Chem. 689 (2004) 3379

Coupling of propargylsilanes with Fischer carbene chromium complexes: a new synthesis of conjugated dienes

The reaction of secondary propargylsilanes with Fischer carbene complexes affords conjugated dienes through a process involving alkyne insertion, followed by a 1,2-silicon shift, followed by decomplexation. If a primary propargylsilane is employed, the silicon does not shift and normal alkyne-Fischer carbene coupling processes are observed.

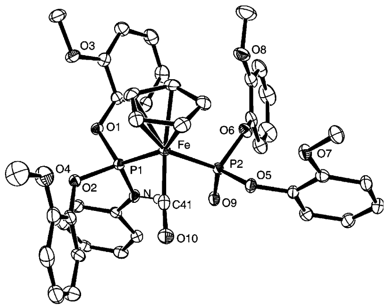


Maravanji S. Balakrishna, P.P. George, Joel. T. Mague

J. Organomet. Chem. 689 (2004) 3388

Synthesis and derivatization, structures and transition metal (Mo(0), Fe(II), Pd(II) and Pt(II)) complexes of phenylaminobis-(diphosphonite), PhN{P(OC$_6$H$_4$OMe-*o*)$_2$}$_2$

The synthesis, derivatization and transition metal complexes of PhN{P(OC$_6$H$_4$O-Me-*o*)$_2$}$_2$ (**1**) is presented. P–N bond cleavage was observed in the reaction of **1** with [FeCp(CO)$_2$]$_2$. Crystals structures of **1**, its diselenide derivative, Mo(0) and Fe(II) complexes are also presented.

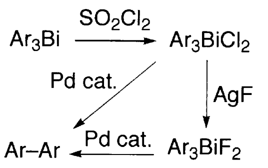


A.F.M. Mustafizur Rahman, Toshihiro Murafuji, Motoko Ishibashi, Youhei Miyoshi, Yoshikazu Sugihara

J. Organomet. Chem. 689 (2004) 3395

Effect of π-accepting substituent on the reactivity and spectroscopic characteristics of triarylbismuthanes and triarylbismuth dihalides

The electronic effect of the *p*-substituents on the oxidative chlorination of triarylbismuthanes, Pd-catalyzed coupling reaction of triarylbismuth dihalides and spectroscopic characteristics of these organobismuth compounds was studied. The π-accepting substituents were revealed to markedly affect their reactivity and spectroscopic properties.



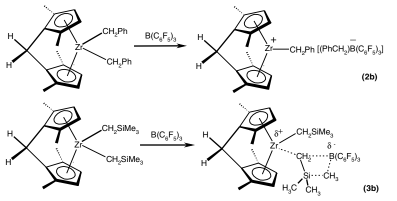
Ar=*p*-XC$_6$H$_4$; X=OMe, H, Cl, CO$_2$Et, CF$_3$, CN, NO$_2$

Hyosun Lee, Sung-Don Hong, Young-Whan Park, Boong-Goon Jeong, Dae-Woo Nam, Hye Young Jung, Min Whan Jung, Kwang Ho Song

J. Organomet. Chem. 689 (2004) 3402

Control of symmetry in active cationic *ansa*-zirconocene species: catalyst preparation, characterization and ethylene–norbornene copolymerization

Four novel hydrocarbyl methylene bridged *ansa*-zirconocenes have been synthesized which form ionic systems with B(C$_6$F$_5$)$_3$, [Me$_2$PhHN]$^+$[B(C$_6$F$_5$)$_4$]$^-$ or [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$. Interestingly, C$_{2v}$ symmetric hydrocarbyl complexes become C$_S$ symmetric zwitterions when activated by borane. The complex [H$_2$C(Me$_2$C$_5$H$_2$)$_2$]Zr(CH$_2$Ph)$_2$ with [Me$_2$PhHN]$^+$[B(C$_6$F$_5$)$_4$]$^-$ shows the highest ethylene/norbornene copolymerzation of the systems studied.

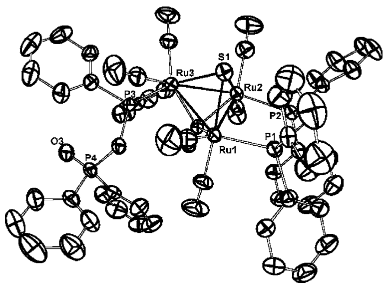


Shariff E. Kabir, Syed J. Ahmed, Md. Iqbal Hyder, Md. Arzu Miah, Dennis W. Bennett, Daniel T. Haworth, Tasneem A. Siddiquee, Edward Rosenberg

J. Organomet. Chem. 689 (2004) 3412

Triruthenium clusters containing bridging dppm and capping sulfido and selenido ligands: X-ray structures of [Ru$_3$(CO)$_5$(μ$_3$-CO)(μ$_3$-Se)(μ-dppm)$_2$], [Ru$_3$(CO)$_6$(μ$_3$-CO)-(μ$_3$-Se)(μ-dppm)(η^1-Ph$_2$PCH$_2$P(O)Ph$_2$)] and [Ru$_2$(CO)$_4$(μ-SePh)$_2$(μ-dppm)]

Four new compounds, [Ru$_3$(CO)$_5$(μ$_3$-CO)(μ$_3$-Se)-(μ-dppm)$_2$] (**4**), [Ru$_3$(CO)$_6$(CO)(μ$_3$-Se)(μ-dppm)-(η^1-Ph$_2$PCH$_2$P(=O)Ph$_2$)] (**5**), [Ru$_3$(CO)$_5$(μ$_3$-CO)-(μ$_3$-S)(μ-dppm)$_2$] (**8**), and [Ru$_3$(CO)$_6$(μ$_3$-CO)(μ$_3$-Se) (μ-dppm)(η^1-Ph$_2$PCH$_2$P (=O)Ph$_2$)] (**9**) along with some previously reported compounds have been synthesized and characterized from the reactions of [Ru$_3$(CO)$_{10}$(μ-dppm)] (**1**) with dppmSe and dppmS. Treatment of **1** with PhSeSePh at 66 °C affords the dinuclear compound [Ru$_2$(CO)$_4$(μ-SePh)$_2$(μ-dppm)] (**10**). Thermolysis of **5** and **9** in refluxing toluene at 110 °C gives **4** and **8**, respectively, by the cleavage of the P=O bond of the dangling oxygenated dppm ligands.



Reuben D. Rieke, Jun-sik Lee, Young-Sik Kye, Gerard S. Harbison

J. Organomet. Chem. 689 (2004) 3421

Preparation of lithium stannide mixtures in organic solvents. A alternate source of lithium in organolithium chemistry

Lithium stannides were prepared from lithium naphthalenide and tin (II) chloride or tin (0) powder in THF solvent at room temperature under dry argon atmosphere and their chemical applications were studied.

$$SnCl_2 + Li^{+}Np^{\bullet -} \xrightarrow[\text{RT, 10 min}]{\text{THF}} Li_xSn$$

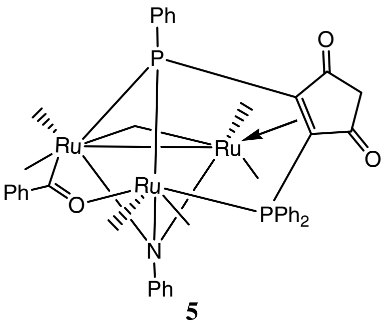
$x = 0.5, 1.0, 2.5, 3.5$

Simon G. Bott, Huafeng Shen, Michael G. Richmond

J. Organomet. Chem. 689 (2004) 3426

Thermally induced dual P–C bond cleavage routes from the imido-capped cluster $Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}NPh)(bpcd)$: synthesis, spectroscopic properties, and X-ray diffraction structures of $Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}NPh)(bpcd)$, $Ru_3(CO)_5(\mu_2\text{-}CO)_2(\mu_3\text{-}NPh)(\mu_2\text{-}PPh_2)[\mu,\eta^1,\eta^1\text{-}C{=}C(PPh_2)C(O)CH_2C(O)]$, $Ru_3(CO)_6(\mu_2\text{-}CO)(\mu_3\text{-}NPh)(\mu\text{-}PhCO)$ $[\mu_2,\eta^2,\eta^1\text{-}PPhCC(PPh_2)C(O)CH_2C(O)]$, and $Ru_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}PPh)$

The imido-capped clusters $Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}NPh)(bpcd)$ (**2**) and $Ru_3(CO)_5(\mu_3\text{-}CO)(\mu_3\text{-}NPh)(bpcd)_2$ (**3**) have been isolated from the reaction of $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NPh)$ (**1**) with the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) under thermal and Me_3NO activation. Thermolysis of the former product furnishes the new clusters $Ru_3(CO)_5(\mu_2\text{-}CO)_2(\mu_3\text{-}NPh)(\mu_2\text{-}PPh_2)[\mu,\eta^1,\eta^1\text{-}CC(PPh_2)\ C(O)CH_2C(O)]$ (**4**), $Ru_3(CO)_6(\mu_2\text{-}CO)(\mu_3\text{-}NPh)(\mu\text{-}PhCO)[\mu_2,\eta^2,\eta^1\text{-}PPhCC(PPh_2)C(O)CH_2C(O)]$ (**5**), and $Ru_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}PPh)$ (**6**).



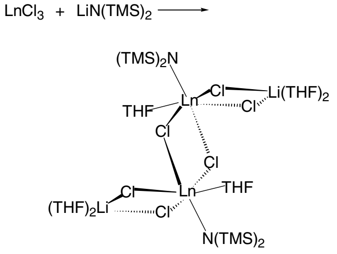
5

Hong-Xi Li, Qing-Feng Xu, Jin-Xiang Chen, Mei-Ling Cheng, Yong Zhang, Wen-Hua Zhang, Jian-Ping Lang, Qi Shen

J. Organomet. Chem. 689 (2004) 3438

Syntheses, crystal structures and catalytic properties of a series of lanthanide(III) bis(trimethylsilyl)amide chloride complexes: $[\{((Me_3Si)_2N)_2Nd(\mu'\text{-}Cl)Li(THF)_3\}(\mu\text{-}Cl)]_2$, $[\{((Me_3Si)_2N)_2Ln(\mu'\text{-}Cl)Li(THF)_2\}(\mu_3\text{-}Cl)]_2$ (Ln = Eu, Ho), and $[\{(Me_3Si)_2NLn(\mu'\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$ (Ln = Nd, Sm, Eu, Ho, Yb)

A family of lanthanide(III) bis(trimethylsilyl) amide chloride complexes, $[\{((Me_3Si)_2N)_2Nd(\mu'\text{-}Cl)Li(THF)_3\}(\mu\text{-}Cl)]_2$ (**1**), $[\{((Me_3Si)_2N)_2Ln(\mu'\text{-}Cl)Li(THF)_2\}(\mu_3\text{-}Cl)]_2$ (Ln = Eu (**2**); Ln = Ho (**3**)), and $[\{(Me_3Si)_2NLn(\mu'\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$ (Ln = Nd (**4**); Ln = Sm (**5**); Ln = Eu (**6**); Ln = Ho (**7**); Ln = Yb (**8**)) were produced from reactions of $LnCl_3$ (Ln = Nd, Sm, Eu, Ho, Yb) with one or two equiv. of $LiN(SiMe_3)_2$ in THF. These complexes were characterized by melting point determination, elemental analysis, IR spectra and single-crystal X-ray analysis. They exhibited catalytic activity for the ring-opening polymerization of ε-caprolactone.



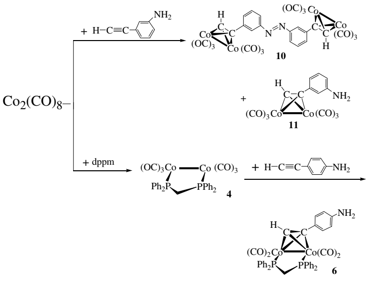
Ln= Nd, Sm, Eu, Ho, Yb

Fung-E Hong ,Yi-Luen Huang, Hsueh-Liang Chen

J. Organomet. Chem. 689 (2004) 3449

Observations on reaction pathways of dicobalt octacarbonyl with alkynyl amines

Direct treatment of 3-ethynlaniline with $Co_2(CO)_8$ gave an alkyne bridged dicobalt complex **11** plus a coupling product, an azobenzene derivative **10**. Only alkynyl amines bridged dicobalt complex **6** was obtained while treatment of a dppm bridged dicobalt complex **4** with 4-ethynylaniline.

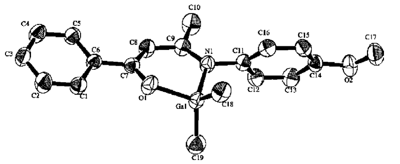


Yingzhong Shen, Jianlin Han, Hongwei Gu, Yu Zhu, Yi Pan

J. Organomet. Chem. 689 (2004) 3461

Synthesis, characterization and luminescence study of dimethyl(β-ketoiminato)gallium (-indium) complexes: crystal structure of dimethyl[1-phenyl-3-*N*-(4-methoxyphenylimino)-1-butanonato]gallium

Six new dimethylgallium (indium) complexes of type Me_2ML [M = Ga, L = 1-phenyl-3-*N*-(phenylimino)-1-butanonato (**1**), 1-phenyl-3-*N*-(*p*-methoxyphenylimino)-1-butanonato (**2**), 1-phenyl-3-*N*-(*o*-chlorophenylimino)-1-butanonato (**3**); M = In, L = 1-phenyl-3-*N*-(phenylimino)-1-butanonato (**4**), 1-phenyl-3-*N*-(*p*-methoxyphenylimino)-1-butanonato (**5**), 1-phenyl-3-*N*-(*o*-chlorophenylimino)-1-butanonato (**6**)] have been prepared. Structure of **2** has been determined by X-ray single crystal analysis. The electroluminescent (EL) properties of **1**–**6** were examined by fabricating EL devices using them as emitter. The EL bands are located in the green region (509–522 nm).



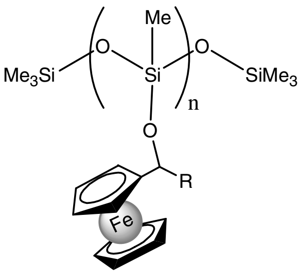
Note

Philip Boudjouk, Zoha M.H. AL-Badri, Bhanu P.S. Chauhan

J. Organomet. Chem. 689 (2004) 3468

Dehydrogenative coupling as an efficient route to ferrocene functionalized siloxanes

Ferrocene grafted siloxanes were prepared in high yields (~79–97%) via Rh-catalyzed dehydrogenative coupling of a series of monomeric, polymeric, and cyclic hydrosiloxanes with ferrocenemethanol. Wilkinson's catalyst was the most efficient of those surveyed (Karstedt's catalyst, H_2PtCl_6, $Co_2(CO)_8$, 10% Pd/C, 10% Pt/C, 5% Rh/C) with respect to yield and selectivity. Benzene and toluene were better solvents than tetrahydrofuran and methylene chloride.



R = H, Me

Erratum 3472