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Contents

Regular Papers

Douglas Hoffmann, Helmut Reinke, Clemens Krempner

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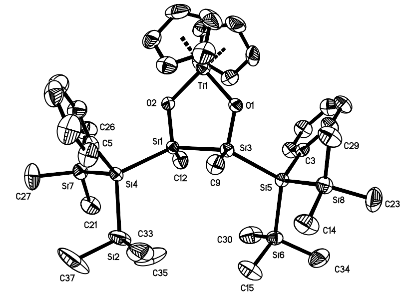
Dihydroxyoligosilanes as novel ligands in coordination chemistry—first synthesis of 2,5-dioxa-3,4-disilatitanacyclopentanes

The synthesis of vicinale dihydroxyhexasilanes, a novel class of stable anionic disiloxide ligands for the preparation of metal containing five-membered ring compounds, is reported. The molecular structures of dicyclopentadienyltitanium complexes are determined by single crystal X-ray analysis. The structural features of the five-membered rings are strongly influenced by the arrangement and the space demand of the surrounding $(Me_3Si)_2RSi$ substituents [R = $SiMe_3$, Ph].

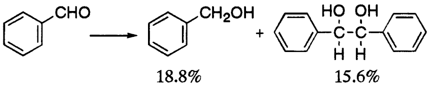


Yoshitomo Kashiwagi, Chikara Kikuchi, Futoshi Kurashima, Jun-ichi Anzai

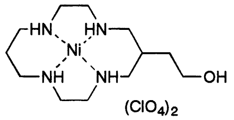
J. of Organomet. Chem. 662 (2002) 9

Electrocatalytic reduction of aldehydes and ketones on nickel(II) tetraazamacrocyclic complex-modified graphite felt electrode

The **1**-modified GF electrode was active for reduction of aldehydes and ketones, and led to the corresponding alcohol and pinacol compounds in the adequate current efficiency, conversion and turnover number of the Ni cayalyst.



conversion: 52.9%
current efficiency: 50.6%
turnover number of **1**: 1147



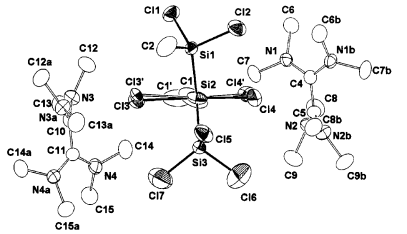
: **1**

C. Knopf, U. Herzog, G. Roewer, E. Brendler, G. Rheinwald, H. Lang

J. of Organomet. Chem. 662 (2002) 14

Interactions of chloromethyldisilanes with tetrakis(dimethylamino)ethylene (TDAE), formation of $[TDAE]^{\bullet +}$ $[Si_3Me_2Cl_7]^-$

The chlorodisilanes $SiClMe_2$–$SiClMe_2$ (**1**), $SiCl_2Me$–$SiCl_2Me$ (**2**), $SiCl_3$–$SiCl_3$ (**3**) and a 9:1 mixture of **2** and $SiCl_3$–$SiCl_2Me$ (**4**) were reacted with the electron-rich alkene tetrakis(dimethylamino)ethylene (TDAE) in *n*-hexane as well as in polar solvents. A mixture of crystals of $Si_3Me_3Cl_6 \cdot TDAE$ (**5a**) plus $Si_3Me_2Cl_7 \cdot TDAE$ (**5b**) was obtained by reaction of a 9:1 mixture of **2** and **4** with TDAE in *n*-hexane as well as in 1,2-dimethoxyethane. The reaction of **2** with TDAE in acetonitrile (MeCN) led to a crystalline precipitation of $[TDAE]Cl_2 \cdot MeCN$ (**6**·MeCN) in addition to $MeSiCl_3$ and methylchlorooligosilanes. The structures of **5b** and **6**·MeCN were determined by X-ray analysis beside their NMR and IR spectroscopic characterization.



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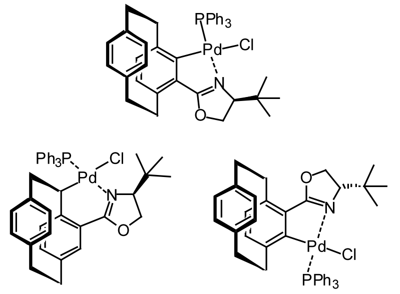
Carsten Bolm, Kirsten Wenz, Gerhard Raabe

J. of Organomet. Chem. 662 (2002) 23

Regioselective palladation of 2-oxazolinyl-[2.2]paracyclophanes.
Synthesis of planar-chiral phosphines

When 4-(4-*tert*-butyl-2-oxazolinyl)-[2.2]-paracyclophanes are treated with Pd(OAc)$_2$ palladated complexes stemming from either metallation in the *ortho* or the benzylic position of the [2.2]paracyclophane skeleton are obtained. The regioselectivity can be influenced by the reaction conditions. The solid state structures of two palladacycles have been determined by X-ray diffraction analysis.

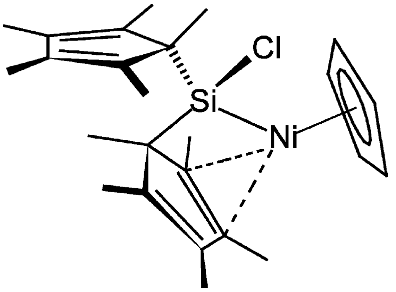


Martin Theil, Peter Jutzi, Beate Neumann, Anja Stammler, Hans-Georg Stammler

J. of Organomet. Chem. 662 (2002) 34

Zur Insertion von Decamethylsilicocen in Nickel- und Gold-Chlor-Bindungen

Reaction of decamethylsilicocene (Cp^*_2Si, **1**) with CpNiCl(PPh$_3$) leads to the silylnickel complex $[Cp^*_2(Cl)Si]NiCp$, in which one of the Si-bonded Cp* substituents is π-coordinated to the nickel atom. Similarly, silylgold complexes $[Cp^*_2(Cl)Si]AuL$ are formed in the reaction of **1** with compounds of the type ClAuL.

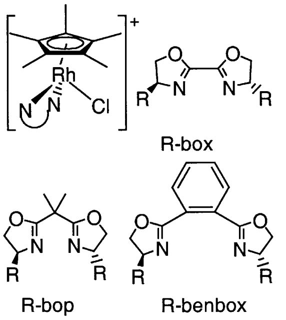


David L. Davies, John Fawcett, Shaun A. Garratt, David R. Russell

J. of Organomet. Chem. 662 (2002) 43

Cp*rhodium and iridium complexes with bisoxazolines: synthesis, fluxionality and applications as asymmetric catalysts for Diels–Alder reactions

A number of half-sandwich complexes [MCl(N–N)Cp*][EF$_6$] (M = Rh, Ir; N–N = a bis-oxazoline; E = P or Sb) have been synthesised. Treatment of some of these with AgSbF$_6$ generates dications [Rh(OH$_2$)(N–N)Cp*]$^{2+}$, some of which are fluxional at room temperature. One of these is an enantioselective catalyst for the Diels–Alder reaction of methacrolein and cyclopentadiene. Three complexes, [RhCl(^{i}Pr-box)Cp*][SbF$_6$], [RhCl(^{i}Pr-bop)Cp*][SbF$_6$] and [RhCl(Et-benbox)Cp*][SbF$_6$] have been characterised by X-ray crystallography.



Li-Cheng Song, Jin-Ting Liu, Qing-Mei Hu

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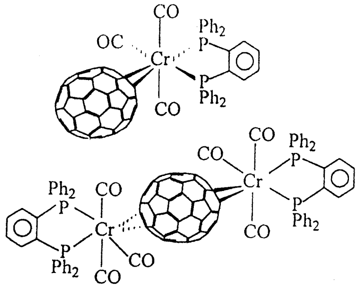
Synthesis and characterization of Group 6 transition-metal [70]fullerene derivatives containing dppb ligands.
Crystal structure of *fac*-Mo(CO)$_3$(dppb)-(CH$_3$CN)

A series of Group 6 transition-metal [70]fullerene complexes *fac*/*mer*-Mo(CO)$_3$(dppb)(η^2-C$_{70}$), *mer*-M(CO)$_3$(dppb)(η^2-C$_{70}$) (M = W, Cr) and [*mer*-M(CO)$_3$(dppb)]$_2$(η^2,η^2-C$_{70}$) (M = Mo, Cr) have been synthesized by thermal reaction of *fac*-M(CO)$_3$ (dppb)(CH$_3$CN) (M = Mo, W) with C$_{70}$, and photochemical reaction of M(CO)$_6$ (M = Mo, Cr), dppb and C$_{70}$. The crystal structure of *fac*-Mo(CO)$_3$(dppb)-(CH$_3$CN) is described.



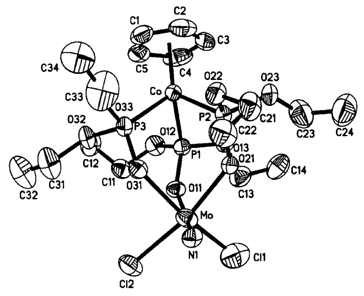
Note

Francisco Montilla, Agustín Galindo, Ángeles Monge, Enrique Gutiérrez-Puebla

J. of Organomet. Chem. 662 (2002) 59

Synthesis and molecular structure of the nitride $(L_{OEt})Mo(N)Cl_2$ [$L_{OEt} = (\eta\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$]

Interaction of $MoCl_4(THF)_2$ with trimethylsilylazide, N_3SiMe_3, and the sodium salt of the Kläui's ligand, NaL_{OEt} ($L_{OEt} = (\eta\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$) affords complex $(L_{OEt})Mo(N)Cl_2$ (**1**). The molecular structure of **1** has been determined by X-ray crystallography. The apparently long molybdenum–nitride bond distance was interpreted on the basis of the existence of rotational disorder.



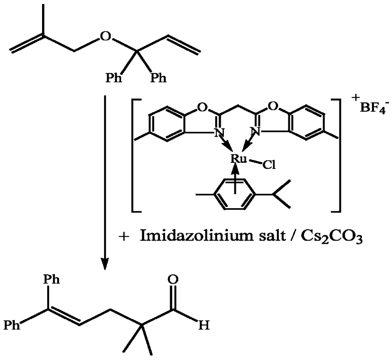
Regular Papers

Hamed Ben Ammar, Jérôme Le Nôtre, Mansour Salem, Mohamed T. Kaddachi, Pierre H. Dixneuf

J. of Organomet. Chem. 662 (2002) 63

Synthesis of bis-oxazoline-ruthenium(II)-arene complexes.
Combined catalytic isomerisation and Claisen rearrangement of bis-allyl ether

Bis-oxazolines react with $[RuCl_2(p\text{-cymene})]_2$ to give $[RuCl(bisoxazoline)(p\text{-cymene})][BF_4]$ complexes that are easily deprotonated at the methylene bridge and show irreversible redox process in cyclic voltammetry. Combined with 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride and Cs_2CO_3, they catalyse allyl to vinyl isomerisation of bis-allyl ether and lead to Claisen rearrangement affording γ,δ-unsaturated aldehydes.

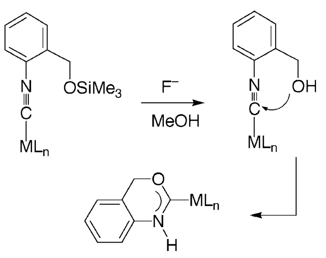


Giacomo Facchin, Rino A. Michelin, Mirto Mozzon, Augusto Tassan

J. of Organomet. Chem. 662 (2002) 70

Synthesis, coordination and reactivity of 2-(trimethylsiloxymethyl)phenyl- and 2-(hydroxymethyl)phenyl isocyanides

The synthesis of the new *O*-functionalized isocyanides 2-(trimethylsiloxymethyl)phenyl- and 2-(hydroxymethyl)phenyl isocyanides is reported. Their coordination ability has been tested towards some Pt(II), Pd(II) and M(0) (M = Cr, W) complexes. The 2-(hydroxymethyl)phenyl isocyanide is stable as free ligand, but undergoes spontaneous intramolecular cyclization to benzoxazin-2-ylidene upon coordination to electron poor metal centers.



Koichi Mikami, Shiho Ohba, Hirofumi Ohmura

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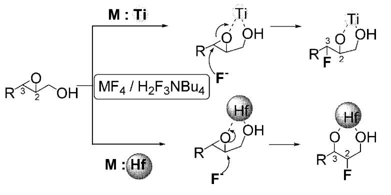
Regioselective, stereospecific, and chemoselective fluorination of epoxy alcohols: development of fluorinating hybrid reagents, associated with Lewis acid metal fluoride

Lewis acid metal fluoride/ammonium hydrogen fluoride hybrid reagents are developed for regio-, stereo-, and chemoselective ring opening fluorination of epoxy alcohols.

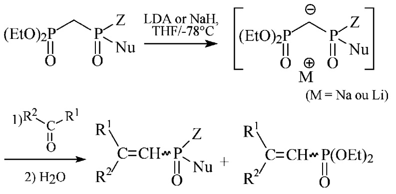


Claude Grison, Corinne Comoy, David Chatenet, Philippe Coutrot

J. of Organomet. Chem. 662 (2002) 83

Synthesis of P-chiral enephosphonic acid derivatives

Synthesis of P-chiral enephosphonic acid derivatives. A synthesis of chiral enephosphonic acid derivatives (enephosphonates, enephosphonamides, enephosphinates) was reported by a two-step procedure involving alkylidene diphosphorylation of nucleophiles followed by a Horner–Emmons olefination. Depending on the selected strategy, the synthesis could be executed according to a one-pot or a two-step reaction sequence. Regioselectivity of Horner–Emmons reaction and ^{31}P-NMR study of diphosphorylated anions were described.

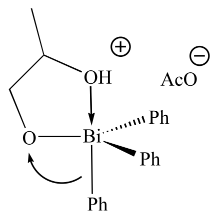


Simon J. Coles, James F. Costello, Michael B. Hursthouse, Stephen Smith

J. of Organomet. Chem. 662 (2002) 98

A structural and mechanistic investigation of the mono-*O*-phenylation of diols with BiPh$_3$(OAc)$_2$

The mono-*O*-phenylation of pinanediol using BiPh$_3$(OAc)$_2$ has been investigated. Mechanistic and crystallographic studies suggest that reductive elimination at the trigonal bipyramidal bismuth (V) centre upon exposure to ambient light affects the transfer of an apical phenyl ligand to the least sterically encumbered hydroxyl group of the diol.



Luís F. Veiros, Manuel E. Minas da Piedade

J. of Organomet. Chem. 662 (2002) 105

On the transferability of Ir–I bond enthalpies between [Ir(μ-S^{t}Bu)(I)$_2$(CO)$_2$]$_2$ and *trans*-[Ir(X)(I)$_2$(CO)(PPh$_3$)$_2$] (X = F, Cl, Br, I) complexes

The transferability of the Ir–I bond snap enthalpy E_s(Ir–I) in [Ir(μ-S^{t}Bu)(I)$_2$(CO)$_2$]$_2$ and *trans*-[Ir(X)(I)$_2$(CO)(PPh$_3$)$_2$] (X = halogen) complexes was investigated by theoretical calculations based on the B3LYP HF/DFT hybrid functional. It was concluded that the E_s(Ir–I) is not transferable between both types of molecules and that, in this case, two widely used indicators of 'bond strength'—bond distances and Wiberg indexes—do not seem to be sensitive to significant changes in the Ir–I bond snap enthalpy.

$$\begin{tikzcd} X_nIrL \arrow[r, "E_s(Ir\text{-}L)"] \arrow[dr, "DH(Ir\text{-}L)"'] & X_nIr^* + L^* \arrow[d, "ER_1"] \\ & X_nIr + L \end{tikzcd}$$

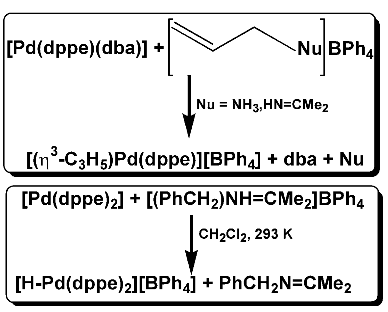
ER_2

Michele Aresta, Eugenio Quaranta

J. of Organomet. Chem. 662 (2002) 112

Reactivity of ammonium and iminium tetraphenylborates towards Pd(0)-complexes: selective allyl or proton transfer to Pd(0). Evidence of formation of the species [HPd(dppe)$_2$][BPh$_4$]

[CH$_2$=CHCH$_2$NH$_3$]BPh$_4$ and [(CH$_2$=CH-CH$_2$)HN=CMe$_2$]BPh$_4$ react with [Pd(dppe)-(dba)] to afford [(η^3-C$_3$H$_5$)Pd(dppe)][BPh$_4$] through selective transfer of allyl group from the *primary* ammonium or iminium cation to the Pd center. The proton transfer from [(PhCH$_2$)HN=CMe$_2$]BPh$_4$ to [Pd-(dppe)$_2$] to afford the five-coordinated cationic Pd–hydride [HPd(dppe)$_2$][BPh$_4$] is also documented.

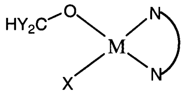


Sze Ming Ng, Cunyuan Zhao, Zhenyang Lin

J. of Organomet. Chem. 662 (2002) 120

Theoretical studies on the β-hydrogen elimination reactions of palladium and platinum alkoxide complexes containing bidentate ligands

Density functional theory calculations have been employed to examine the effect of *cis*-ligand X, transition metal M, bidentate ligand L_2 and alkoxy group OCY_2H on the selection of reaction pathways between the β-hydrogen elimination and σ-bond metathesis for palladium and platinum alkoxide complexes containing bidentate ligands.

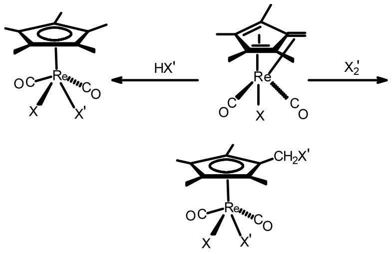


Fernando Godoy, A. Hugo Klahn,
Beatriz Oelckers

J. of Organomet. Chem. 662 (2002) 130

Reactions of the tetramethylfulvene ligand coordinated to rhenium with hydrohalic acids and halogens: synthesis of dicarbonyl complexes with a 'four-legged piano-stool' structure containing mixed-halide ligands

The syntheses of new tetramethylfulvene complexes $(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2X$ (X = I (**2a**), Br (**2b**) and Cl (**2c**)) are reported. Complexes **2a** and **2b** reacts with HX′ and X'_2 to yield the first examples of pentamethylcyclopentadienyl dicarbonyl rhenium derivatives containing mixed-halide ligands *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2XX'$ and *cis*-$(\eta^5\text{-}C_5Me_4CH_2X')Re(CO)_2XX'$.

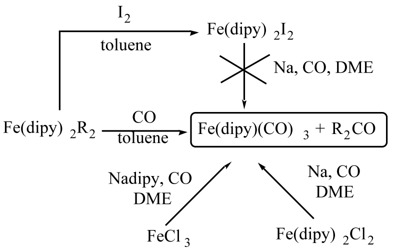


Fausto Calderazzo, Silvia Falaschi,
Fabio Marchetti, Guido Pampaloni

J. of Organomet. Chem. 662 (2002) 137

Carbonyl derivatives of iron(0) from the reaction of $FeR_2(bipy)_2$ (R = Me, Et) with carbon monoxide

The reaction of $FeR_2(bipy)_2$, R=Me, Et, with CO proceeds with reductive elimination of acetone or diethylketone and formation of carbonyl derivatives of iron(0). The nature of the carbonyl derivatives depends on the solvent, $Fe_2(bipy)_2(CO)_5$ and $Fe(bipy)(CO)_3$ being isolated in heptane and toluene, respectively. Conversion of $Fe_2(bipy)_2(CO)_5$ to $Fe(bipy)(CO)_3$ takes place in toluene under a CO atmosphere. The tricarbonyl derivative $Fe(bipy)(CO)_3$, alternatively prepared by reaction of $FeCl_3$ with Nabipy in DME under a CO atmosphere, was studied by X-ray diffraction methods.

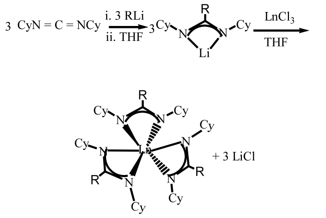


Yunjie Luo, Yingming Yao, Qi Shen,
Jie Sun, Linhong Weng

J. of Organomet. Chem. 662 (2002) 144

Synthesis, characterization of homoleptic lanthanide amidinate complexes and their catalytic activity for the ring-opening polymerization of ε-caprolactone

A series of homoleptic amidinate lanthanide complexes with the general formula $[CyNC(R)NCy]_3Ln\cdot n\text{THF}$ (R = methyl, Ln = Nd (**1**), Gd (**2**), Yb (**3**), $n = 0$; R = phenyl, Ln = Nd (**4**), Y (**5**), Yb (**6**), $n = 2$) were synthesized. The X-ray crystal structural determination of **3** and **6** revealed that the ytterbium ions in both complexes are coordinated by three bidentate amidinate moieties with a trigonal planar geometry. These amidinate lanthanide complexes showed extremely high activity for the ring-opening polymerization of ε-caprolactone at room temperature.



Cy = cyclohexyl, R = Me, Ln = Nd (**1**), Gd (**2**), Yb (**3**)
R = Ph, Ln = Nd (**4**), Y (**5**), Yb (**6**)

Wilhelm Keim, Stefan Killat, Cosimo F. Nobile, Gian Paolo Suranna, Ulli Englert, Ruimin Wang, Stefan Mecking, Dirk Lucas Schröder

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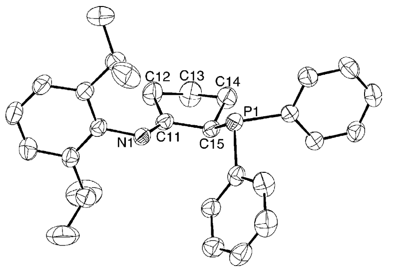
Synthesis, characterisation and catalytic activity of Pd(II) and Ni(II) complexes with new cyclic α-diphenylphosphino-ketoimines. Crystal structure of 2,6-diisopropyl-*N*-(2-diphenylphosphino-cyclopentylidene)aniline and of 2,6-diisopropyl-*N*-(2-diphenylphosphino-cyclohexylidene)aniline

Neutral complexes of new α-(diphenylphosphino)-ketoimines have been obtained by cyclooctadiene displacement from (cod)Pd-$(CH_3)(Cl)$. Reaction of the neutral complexes with $AgSbF_6$ yielded the corresponding cationic complexes. Neutral Ni(II) complexes have been obtained by reaction with (1,2-dimethoxyethane)$NiBr_2$. Cationic Pd-(II) complexes and MAO-activated neutral Ni(II) complexes are active olefin oligomerisation catalysts.



Moncef Bellassoued, Jérôme Grugier, Nathalie Lensen

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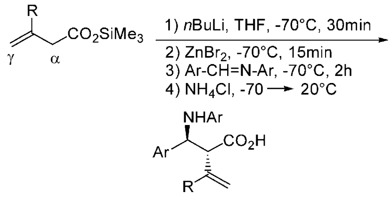
Direct synthesis of unsaturated β-amino acids

Unsaturated β-amino acids were prepared by addition of trimethysilyl butenoate lithium enolates to aldimines in the presence of zinc bromide.

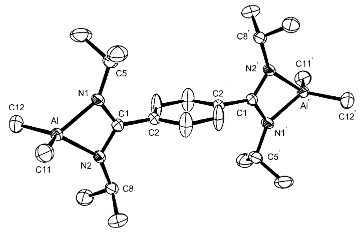


Joanna Grundy, Martyn P. Coles, Peter B. Hitchcock

J. of Organomet. Chem. 662 (2002) 178

A new class of linked-bis(*N*,*N*′-dialkylamidinate) ligand: applications in the synthesis of bimetallic aluminium complexes

1,4-Benzenebis(*N*,*N*′-dialkylamidine) compounds have been synthesised by quenching the in situ generated dilithio-salt with stoichiometric water; the *N*-silylated derivatives are accessed via a Me_3SiCl quench. Structural investigations show an *E-syn*:*E-syn* configuration for the N*H* compounds and *E-anti*:*E-anti* for the N*SiMe*$_3$. The monomeric, bimetallic aluminium complexes 1,4-$C_6H_4[C\{N^iPr\}_2AlMeX]_2$ (X = Me, Cl) are synthesised by protonolysis or salt metathesis.



Jorge Forniés-Cámer, Carmen Claver, Anna M. Masdeu-Bultó, Christine J. Cardin

J. of Organomet. Chem. 662 (2002) 188

New half-sandwich heterobimetallic CpMPt (M = Rh, Ir) dithiolato bridged complexes. X-ray structure of $[(PPh_3)_2Pt(\mu\text{-}S(CH_2)_2S)\text{-}RhCl(\eta^5\text{-}C_5H_5)]BF_4$

Cationic heterobimetallic complexes $[(PPh_3)_2Pt(\mu\text{-}S(CH_2)_2S)MClCp')]BF_4$ (M = Rh, Ir) were prepared. The crystalline structure of $[(PPh_3)_2Pt(\mu\text{-edt})RhClCp)]BF_4$ was determined by X-ray diffraction methods.