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Volume 672, Issues 1–2, 14 April 2003

Journal of Organometallic Chemistry

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Regular Papers

Sarah E. d'Arbeloff–Wilson,
Peter B. Hitchcock, John F. Nixon,
Hiroyuki Kawaguchi, Kazuyuki Tatsumi

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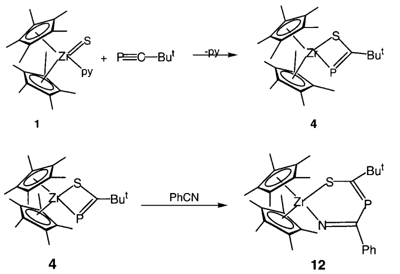
[2+2] Cyclo-addition reactions of bis-pentamethylcyclopentadienyl zirconium metal complexes containing terminal chalcogenide ligands with the phospha-alkyne PC^{t}Bu. Syntheses, crystal and molecular structures of the four complexes [Zr(η^5-(C$_5$Me$_5$)$_2$(SC-(^{t}Bu)=P))], [Zr(η^5-(C$_5$Me$_5$)$_2$(SeC(^{t}Bu)=P))], [Zr(η^5-(C$_5$Me$_5$)$_2$(SC(^{t}Bu)=PSe))] and [Zr-(η^5-(C$_5$Me$_5$)$_2$(SC(^{t}Bu)=PC(Ph)=N))]

[2+2] Cyclo-addition reactions of chalcogenide (S, Se and Te) complexes of zirconium with the phospha-alkyne ^{t}BuCP are reported and further ring expansions with chalcogens and PhCN are described. NMR and single crystal data of the products are presented.



Bob De Clercq, Francis Verpoort

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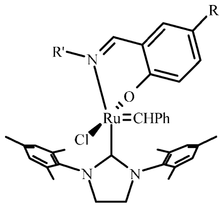
Synthesis and evaluation of a new class of ruthenium-based catalytic systems for atom transfer radical addition and enol ester synthesis

We succeeded in synthesizing and characterizing a new class of N-heterocyclic carbene (NHC) and Schiff base containing ruthenium carbene complexes. These systems are highly active for the ATRA of CCl$_4$ to terminal alkenes. Moreover, dependent on the reaction conditions, they also allow the stereoselective formation of enol esters or enynes in excellent yields.



a. R = H, R' = Me
b. R = NO$_2$, R' = Me
c. R = H, R' = 2,6-Me-4-BrC$_6$H$_2$
d. R = NO$_2$, R' = 2,6-Me-$_4$-BrC$_6$H$_2$
e. R = H, R' = 2,6-iPrC$_6$H$_3$
f. R = NO$_2$, R' = 2,6-iPrC$_6$H$_3$

Christopher S. Griffith,
George A. Koutsantonis,
Brian W. Skelton, Allan H. White

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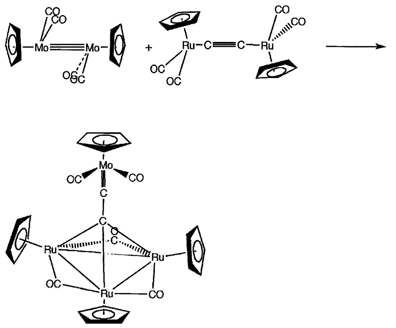
Structural characterization of [Ru$_3$Mo(μ$_3$-η^1-CC}(μ-CO)$_3$(CO)$_2$(η-C$_5$H$_5$)$_5$]: a revisitation

The reinvestigation of the single crystal X-ray structural determination of the product of the reaction between [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-C≡C)] and [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] has confirmed the stoichiometry but the connectivity has been reformulated. While it was previously modelled with a Ru(CO)$_2$(η-C$_5$H$_5$) group pendant, in the revised structure, now Mo(CO)$_2$(η-C$_5$H$_5$) is pendant. The new formulation better fits the available spectroscopic data.



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Graeme Hogarth, Matthew O'Brien,
Derek A. Tocher

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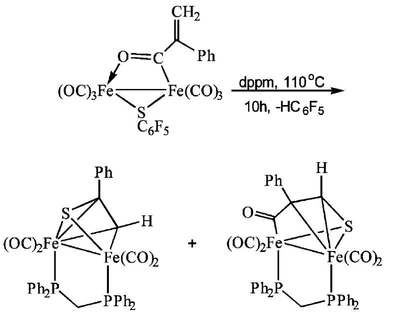
Thiocarbyl ligands via elimination of pentafluorobenzene at a diiron centre: crystal structures of $[Fe_2(CO)_4\{\mu\text{-}SC(Ph){=}CH\}(\mu\text{-}dppm)]$ and $[Fe_2(CO)_4\{\mu\text{-}SCH{=}C(Ph)C(O)\}(\mu\text{-}dppm)]$

Addition of dppm to $[Fe_2(CO)_6\{\mu\text{-}O{=}C{-}C(Ph){=}CH_2\}(SC_6F_5)]$ at 110 °C results in elimination of pentafluorobenzene giving thiocarbamyl complexes $[Fe_2(CO)_4\{\mu\text{-}SC(Ph){=}CH\}(\mu\text{-}dppm)]$ and $[Fe_2(CO)_4\{\mu\text{-}SCH{=}C(Ph)C(O)\}(\mu\text{-}dppm)]$. The former exists as fluxional *cis* and *trans* isomers which interconvert at higher temperatures.



Graeme Hogarth, Matthew O'Brien,
Derek A. Tocher

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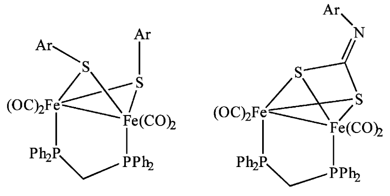
Crystal and molecular structures of dppm-bridged diiron dithiolate complexes $[Fe_2(CO)_4(\mu\text{-}SAr)_2(\mu\text{-}dppm)]$ (Ar = Ph, *p*-tol; $Ar_2 = C{=}N{-}p\text{-}tol$)

Crystallographic studies have been carried out on three bis(diphenylphosphino)-methane (dppm) bridged diiron dithiolate complexes. Both $[Fe_2(CO)_4(\mu\text{-}SAr)_2(\mu\text{-}dppm)]$ (Ar = Ph, *p*-tol) adopt the expected *anti* configuration, while $[Fe_2(CO)_4\{\mu\text{-}SC({=}N{-}p\text{-}tol)S\}(\mu\text{-}dppm)]$ is constrained to be *syn*. In each the diphosphine lies *trans* to one of the bridging sulfurs but this has no significant effect on the iron–sulfur bond lengths.



Ar = Ph, p-tol

Ar = p-tol

Concepción López, Ramón Bosque,
Javier Arias, Emilia Evangelio,
Xavier Solans, Mercè Font-Bardía

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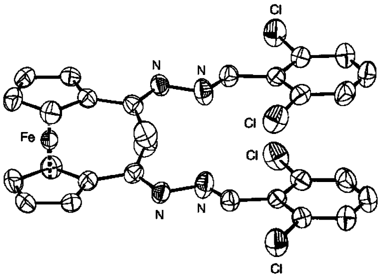
Activation of σ(C–H) bonds of $[Fe\{(\eta^5\text{-}C_5H_4){-}C(Me){=}N{-}N{=}C(H)(C_6H_3{-}2,6\text{-}R)\}_2]$ (with R = Cl or H) promoted by palladium(II)

The activation of the $\sigma(Csp^2$,ferrocene–H) bond of the novel bifunctional ferrocenyl Schiff bases $[Fe\{(\eta^5\text{-}C_5H_4){-}C(Me){=}N{-}N{=}C(H)(C_6H_3{-}2,6\text{-}R_2)\}_2]$ (with R = Cl or H) promoted by palladium(II) salts is reported. This process has allowed the isolation of the two isomers (*meso*- and d,l- forms) of the heterotrimetallic complexes of general formula $[Pd_2\{Fe[(\eta^5\text{-}C_5H_3){-}C(Me){=}N{-}N{=}C(H)(C_6H_5{-}2.6\text{-}R_2)]_2Cl_2(PPh_3)_2]$, (with R = Cl or H).



Zbigniew Grobelny, Andrzej Stolarzewicz,
Barbara Morejko-Buż, Adalbert Maercker,
Stanisław, Krompiec, Tadeusz Bieg

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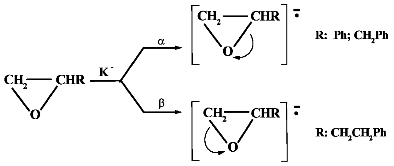
Regioselectivity of the ring opening in the reaction of phenyloxirane, (phenylmethy-l)oxirane and (2-phenylethyl)oxirane with K^-, $K^+(15\text{-crown-}5)_2$

The electron from potassium anion of K^-, $K^+(15\text{-crown-}5)_2$ is initially transferred to the aromatic ring of phenyloxirane and (phenylmethyl)oxirane. The oxirane ring is then opened exclusively in the α-position. However, introduction of the second CH_2 group into the substituent results in the β-opening of the oxirane ring in (2-phenylethyl)oxirane. Organometallic intermediates take part in all these processes.



Nan-Yan Fu, Yao-Feng Yuan, Mei-Li Pang, Ji-Tao Wang, Clovis Peppe

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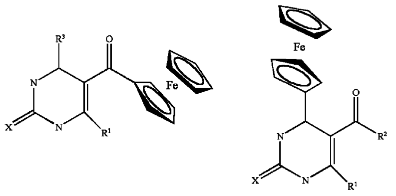
Indium(III) halides-catalyzed preparation of ferrocene-dihydropyrimidinones

Indium(III) halides catalyse the three component Biginelli coupling of ferrocenyl-1,3-diketones, aldehydes and urea (or thiourea) to give 5-ferrocenoyl-3,4-dihydropyrimidinones. 4-Ferrocenyl-3,4-dihydropyrimidinones were obtained from alkyl-acetoacetates, formylferrocene and urea.



Carolina López, Miguel Angel Muñóz-Hernández, David Morales-Morales, Federico del Rio, Simón Hernández-Ortega, Ruben A. Toscano, Juventino J. García

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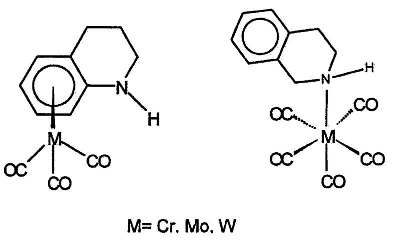
Synthesis of (η^6-arene)tricarbonylmetal and (σ-nitrogen)pentacarbonylmetal complexes of 1,2,3,4-tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline with chromium, molybdenum and tungsten

The hexacarbonyls of chromium, molybdenum and tungsten react with 1,2,3,4-tetrahydroquinoline (THQ) and 1,2,3,4-tetrahydroisoquinoline (THIQ), to yield in the case of THQ the η^6-arene-tricarbonylmetal type complexes and in the case of THIQ gave mainly σ-N-pentacarbonylmetal compounds of molybdenum and tungsten; but in the case of THIQ and chromium both type of compounds where isolated.



Norio Nakata, Nobuhiro Takeda, Norihiro Tokitoh

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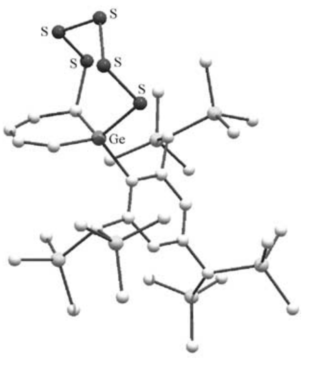
Reaction of a stable germabenzene with chalcogens: synthesis and structure of a novel germanium analog of pentathiepane, 1,2,3,4,5,6-pentathiagermepane

A novel cyclic pentasulfide containing a germanium atom in the seven-membered ring, 1,2,3,4,5,6-pentathiagermepane, was synthesized together with the corresponding 1,2,3,4-trithiagermolane by the reaction of a kinetically stabilized germabenzene with elemental sulfur. Structures of these cyclic polysulfides were determined by X-ray crystallographic analysis.



Joji Ohshita, Hidetoshi Takayama, Mitsuo Ishikawa, Atsutaka Kunai

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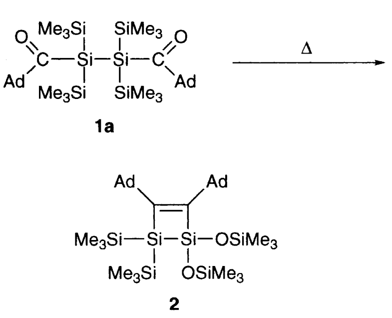
Thermal isomerization of 1,2-diadamantoyltetrakis(trimethylsilyl)disilane via a 2,3-disilabutadiene intermediate

Heating a benzene solution of 1,2-diadamantoyltetrakis(trimethylsilyl)disilane (**1a**) at 120 °C gave an isomerization product (**2**) in 24% yield. A mechanistic interpretation including a 2,3-disiladiene intermediate is described for the formation of **2**, on the basis of the trapping experiment with methanol.



Isabelle Saur, Ghassoub Rima, Karinne Miqueu, Heinz Gornitzka, Jacques Barrau

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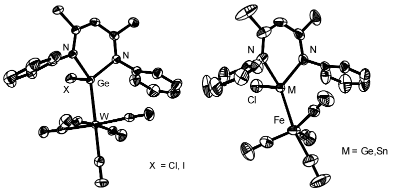
Heteronuclear bonding between heavier Group 14 elements and transition-metals: novel halogermylene- and stannylene transition-metal complexes $L^2(X)MM'L'_n$ [$L^2 =$ PhNC(Me)CHC(Me)NPh; X = Cl, I; M = Ge, Sn; $M'L'_n = W(CO)_5$, $Fe(CO)_4$]

The new halogermylene- or stannylenetungsten- and iron-complexes $L^2(X)MM'L'_n$ [$M'L'_n = W(CO)_5$, M = Ge, X = Cl (**3**) and I (**4**); $M'L'_n = Fe(CO)_4$, X = Cl, M = Ge (**6**) and Sn (**7**)] have been synthesized, starting from the divalent species $L^2(X)M$, and characterized by analytical and spectroscopic methods, including X-ray structures. The MM′ bonds are very short. The nature of the MM′ bond is discussed.



Jie Han, Liang Fu Zhang, Wen Wan

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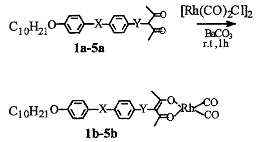
Synthesis and mesomorphic properties of γ-substituted β-diketones and their dicarbonylrhodium(I) complexes

The synthesis, characterization and mesomorphic properties of five series of γ-substituted pentane-2,4-diones and their dicarbonylrhodium(I) complexes have been reported. The effect of the bridging groups of X and Y on the mesogenic properities has also been investigated by DSC and UV-visible data.



X= -CH=CHCO$_2$-, -CO$_2$-, -N=N-, CH$_2$O, Y = -CH=CHCO$_2$-, -CO$_2$-,

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Jie Zhang, Ruifang Cai, Linhong Weng, Xigeng Zhou

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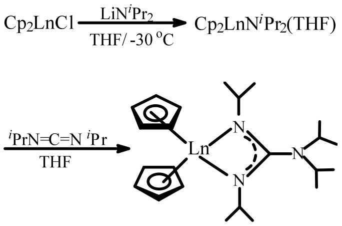
Insertion of carbodiimide into the Ln–N σ-bond of organolanthanide complexes. Synthesis and characterization of organolanthanide guanidinates $(C_5H_5)_2Ln[^iPrN{\because}C(N^iPr_2){\because}N^iPr]$ (Ln = Yb, Dy, Gd)

N,N′-Di-*isopropyl*-carbodiimide can be inserted into the Ln–N σ-bond of $Cp_2LnN^iPr_2$, which provides an efficient method for synthesis of lanthanide guanidinate complexes.



Ln = Yb, Dy, Gd

Masato Nanjo, Takashi Oda, Kunio Mochida

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Preparation and structural characterization of trimethylsilyl-substituted germylzinc halides, $(Me_3Si)_3GeZnX$ (X = Cl, Br, and I) and silylzinc chloride, $R(Me_3Si)_2SiZnCl$ (R = $SiMe_3$ and Ph)

$(Me_3Si)_3GeZnX$ (X = Cl, Br, and I) and $R(Me_3Si)_2SiZnCl$ (R = Me_3Si, Ph) have been prepared, and their structures have been determined by single-crystal X-ray diffraction. The germylzinc halides and silylzinc chlorides have dimeric structures consisiting of two μ-halogen atoms. The reactivity of germylzinc chloride with substrates is also examined.

$$R(Me_3Si)_2ELi(thf)_3 \; + \; ZnX_2 \longrightarrow$$

$$R(Me_3Si)_2EZnX\,(thf)$$

E = Ge, R = Me_3Si, X = Cl, Br, I
E = Si, R = Me_3Si, Ph, X = Cl

Gregory C. Turpin, Arnold L. Rheingold, Richard D. Ernst

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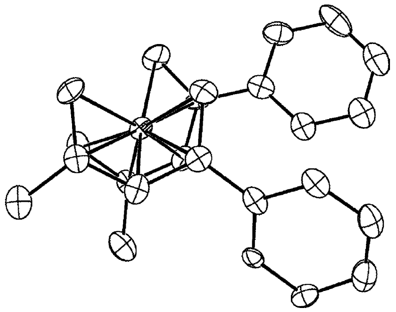
Synthetic, spectroscopic, and structural studies of bis(2-methyl-4-phenylpentadienyl)-ruthenium, Ru(2-CH_3-4-$C_6H_5C_5H_5$)$_2$: characterization of isomeric open ruthenocenes

The reaction of $RuCl_3$ hydrate with 2-methyl-4-phenyl pentadienes leads to diastereomeric Ru(2-methyl-4-phenylpentadienyl)$_2$ complexes, which have been found to possess significantly different physical, spectral, and structural properties.



Elizabeth Gómez, Rosario Flores, Gloria Huerta, Cecilio Alvarez-Toledano, Rubén A. Toscano, Víctor Santes, Noel Nava, Pankaj Sharma

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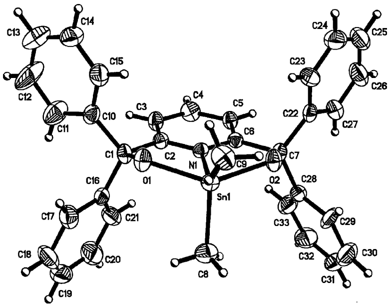
Dimethyltin(IV) 2,6-disubstituted pyridine complexes

The synthesis and characterization of hypervalent pentacoordinated dimethyltin complexes obtained from the reaction of 2,6-disubstituted pyridine ligands with dichlorodimethyltin are reported. The complexes were characterized by mass spectrometry, ^{1}H-, ^{13}C- and ^{119}Sn-NMR and Mössbauer spectroscopy, additionally the structures for two compounds were established by X-ray diffraction.



Angelo Maspero, Stefano Brenna, Simona Galli, Andrea Penoni

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Synthesis and characterisation of new polynuclear copper(I) pyrazolate complexes and their catalytic activity in the cyclopropanation of olefins

The homoleptic [Cu(dcsbpz)]$_4$ and [Cu(dtbpz)]$_4$ copper(I) pyrazolate derivatives have been found to catalytically promote cyclopropanation reactions of alkenes, the *trans*-diastereoisomeric products being, in all cases, favoured.