20 Catalysis and organometallic chemistry of monometallic species

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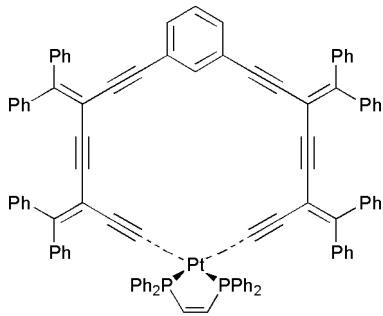
Organometallic chemistry reported in 2003 again demonstrated the breadth of interest and application of this core chemical field. Significant discoveries and developments were reported particularly in the application and understanding of organometallic compounds in catalysis. Highlights include the continued development of catalytic reactions incorporating C–H activation processes, the demonstration of inverted electronic dependence in ligand substitution of palladium(0),[1] and the synthesis of the first early-transition metal perfluoroalkyl complexes.[2]

1 Introduction

A number of relevant reviews and collections of research papers spanning the transition metal series were published in 2003. The 50th anniversary of Ziegler catalysis was commemorated[3,4] and a survey of metal mediated polymerisation using non-metallocene catalysts surveyed.[5] Journal issues dedicated to selected topics included metal–carbon multiple bonds and related organometallics,[6] developments in the reactivity of metal allyl and alkyl complexes,[7] metal alkynyls,[8] and carbon rich organometallic compounds including **1**.[9]



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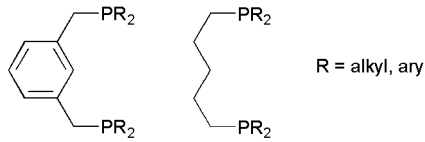
Reviews of catalytic reactions using well-defined precatalyst complexes include alkene ring-closing and opening methathesis using molybdenum and tungsten imido

alkylidene precatalysts,[10] chiral organometallic half-sandwich complexes with defined metal configuration,[11] rhodium-catalysed carbon–carbon bond forming reactions of organometallic compounds,[12] advances in functional group tolerant alkyl–alkyl cross-coupling reactions,[13] asymmetric catalytic hydrogenation,[14] and ring-opening reactions of oxabicyclic alkenes.[15] The relative importance of steric and electronic effects of chelating diphosphines on catalytic hydroformylation[16] and cyclometalated phosphine-based pincer complexes derived from **2** and **3** were reviewed.[17] A collection of papers[18] describing various facets of modern homogenous catalysis and organometallic chemistry includes the use of diffusion and NOE NMR spectroscopy for the study of ion interactions in solution,[19] and picosecond time-resolved infrared spectroscopy for the study of excited states and reaction intermediates in inorganic systems.[20]



2 **3**

In the field of C–H activation an account of the intricacies of kinetic and equilibrium isotope effects in several C–H activation processes[21] and a study of the temperature dependence of isotope effects were published.[22] C–H activation and functionalisation with platinum complexes,[23] transition-metal catalysed borylation of alkanes and arenes *via* C–H activation,[24] and thermal activation of C–H bonds by molybdenum and tungsten nitrosyl complexes were also reviewed.[25] High-resolution X-ray diffraction and DFT calculations were employed to study agostic bonding in d^0 metal alkyl complexes,[26] and using experimental gas phase reactions coupled with theoretical treatments the competition between transition metal C–C and C–H activation of cyclopropane investigated.[27]

Reviews of particular organometallic ligand sets include N-confused porphyrins,[28] cyclopentadienyl-carboranyl hybrids,[29] chiral mono- and bidentate ligands derived from chromium arene complexes,[30] and metal alkynyl σ-complexes.[31]

Theoretical studies include *de novo* design of ligands suitable for stabilising iridium(v),[32] an investigation into the structure and neutral homoaromaticity of metallocyclopentene, -pentadiene, -pentyne, and -pentatriene complexes,[33] and the relative stability of metallobenzene *versus* metal cyclopentadienyl complexes.[34] The properties of organometallic complexes predicted using an effective group potential methodology was developed[35] and spin forbidden chemical reactions of transition metals reviewed.[36]

Apropos the organometallic chemistry of transition metals a simple one-pot synthesis of sodium and potassium cyclopentadienides was developed.[37]

2 Titanium, zirconium, hafnium

The study and application of group 4 metallocene complexes to alkene oligomerisation and polymerisation catalysis was intensively investigated in 2003. For example, a

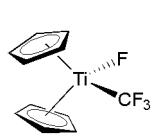
fully-integrated high-throughput screening methodology for the discovery of new alkene copolymerisation catalysts was successfully applied to the copolymerisation of ethene and 1-octene.[38] Other copolymerisation studies using well-defined group 4 organometallics include dual-site alternating copolymerisation of 1,3-butadiene and ethene,[39] and stereoselective copolymerisations of styrene and methyl methacrylate,[40] and cyclopentene and ethene.[41] Degenerative transfer living polymerisation has also been applied to the synthesis of monomodal stereoblock polyolefins[42] and reactions between vinyl chloride and various alkene polymerisation catalysts investigated.[43]

New polymerisation catalyst systems include those derived from reaction between butadiene complexes[44,45] or bis(trimethylsilyl)acetylene complexes[46] and $B(C_6F_5)_3$, and C–H activation of the trimethylsilyl substituents of a zirconocene complexes using $B(C_6F_5)_3$[47] or magnesium.[48] Titanium alkyne complexes[49] prepared *via* transfer epimetalation of alkenes and alkynes also exhibit stereoselective polymerisation.[50]

Several theoretical studies have been reported including the origin of polymerisation activity with chloride and alkoxy ligands,[51] regiochemistry of propene insertion,[52] ethene trimerisation catalysed by titanium complexes,[53] and the effect of borate counterion on the kinetics and mechanism of styrene polymerisation.[54] Experimental mechanistic work has been performed using quench-flow kinetics for zirconocene propene polymerisation,[55] ion pair aggregation investigated using cryoscopy and pulsed field gradient spin-echo NMR diffusion experiments,[56] and by modelling polymer microstructure.[57] NMR spectroscopy has also been employed to probe oscillating conformations that affect stereoselectivity of zirconocene catalysts,[58] and insertion of α-olefins using a zirconocene catalyst has been observed directly by NMR spectroscopy.[59] The electron density distribution of a zirconocene precatalyst derived from synchrotron X-ray diffraction indicates that potential agostic interactions are not present.[60]

Several reports investigating coupling reactions include stereoselective tricyclisation of a dienyne,[61] regioselective coupling of C_6F_5 substituted alkynes,[62] and cross-coupling of titanium alkyne complexes with aryl halides.[63]

Novel complexes include the first example of an early transition metal perfluoroalkyl **4**, synthesised using Me_3SiCF_3 as the fluoroalkyl transfer agent,[2] a zwitterionic zirconium sandwich complex **5** incorporating η^5- and η^6-indenyl ligands,[64] and a rare example of a fully characterised titanium *N*-heterocyclic carbene complex.[65] Boron containing ligands such as boratocyclooctatetraenes that are isoelectronic with dianionic cyclooctatetraene have been coordinated to titanium,[66] and a zirconium complex **6** of an allyl-like zwitterionic ligand has been reported.[67] The first example of a four coordinate titanium alkylidene complex was also prepared.[68]



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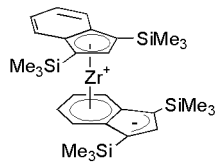

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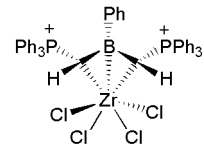

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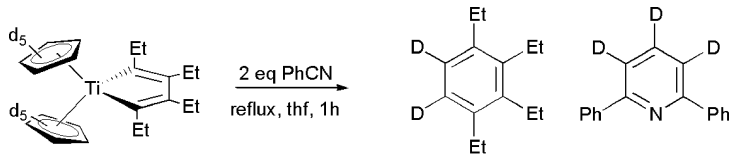
Reactivity studies include double C–C bond cleavage of a cyclopentadienyl ligand in reaction between **7** and PhCN,[69] a survey of C–F activation using zirconocenes,[70] allene stereoinversion by zirconium imido complexes,[71] cyclopentadienyl substituent effects on reductive elimination of alkyl hydrides from zirconocenes[72,73] and Si–C and Si–H activation by hafnocene complexes.[74,75]



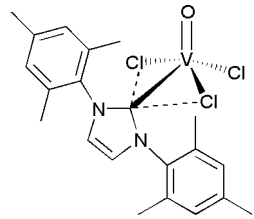
7 59% 49%

3 Vanadium, niobium, tantalum

The challenges, problems and promise of vanadium based Ziegler–Natta catalysis has been reviewed.[76] Dynamic NMR methods and DFT calculations have been used to study hydrogen exchange in *ansa*-niobocene and tantalocene ethene hydride complexes,[77] and in substituted derivatives the preferred stereochemistry for propene and styrene insertion.[78] Of relevance to alkene polymerisation a DFT study of the stereochemistry of alkene insertion and β-X elimination from reaction between $Ta(H)_2(OH)_3$ and β-substituted alkenes was published,[79] and of the origin of selective trimerisation of ethene catalysed by $[TaCl_3(CH_3)_2]$.[80]

A convenient single step synthesis of $[Ta(CH_2Ph)_5]$ and an X-ray structure determination showed that $[Ta(CH_2Ph)_5]$ exhibits distorted square-pyramidal geometry.[81] The reactivity of a (Cp*)Ta benzylidene complex to small unsaturated hydrocarbon molecules gives a range of organometallic products.[82] Complexes resulting from substitution chemistry of tantalum alkynes of the type $[TaCl_3(RCCR)L_2]$ (*e.g.* R = Me, Et, Ph; L_2 = bipy, tmen) have been applied to the isomerisation of 3-phenylpropanal to the corresponding allylic alcohol.[83] The synthesis and characterisation of paramagnetic open vanadocenes has also been investigated.[84]

Bonding in group 5 organometallic complexes has shown some interesting developments including unprecedented α-C–C agostic interactions in the cyclopropyl complex $[(Tp)NbCl(CH_3)_2(MeCCMe)(c\text{-}C_3H_5)]$[85] and related compounds,[86] the usefulness of *J*(Si–H) coupling constants in the search of nonclassical Si–H interactions,[87] and a highly stable *N*-heterocyclic carbene complex **8** that exhibits evidence of Cl–carbene bonding.[88]



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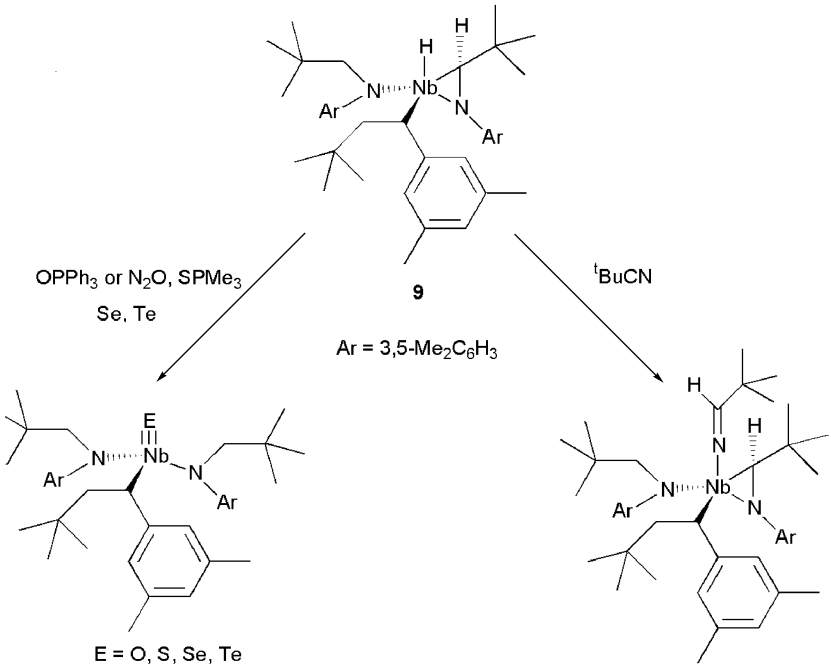
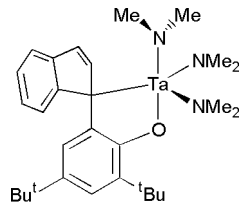
Diverse reactivity includes catalytic C=N bond metathesis of carbodiimides by group 5 imido complexes,[89] and the niobaziridine-hydride **9** that exhibits both insertion and atom transfer chemistry.[90] Reaction between niobocene hydrides and halogermanes leads to dehydrohalogenation to give rapid access to niobocene germanes[91] and cyclometallation of tantalum naphthyl and indenyl aryloxide ligands gives complexes including **10**.[92]





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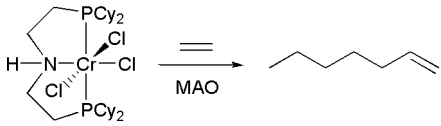
4 Chromium, molybdenum, tungsten

Intermolecular C–H activation chemistry includes thermal activation of $SiMe_3$, mesitylene and benzene by tungsten[93] and molybdenum[94] allyl complexes. Normal and inverse primary kinetic deuterium isotope effects in benzene reductive elimination and oxidative addition to molybdocene and tungstenocene complexes,[95]

and the temperature dependence of equilibrium isotope effects have been measured and interpreted.[22] Aromatic binding and C–H activation by a molybdenum π-base,[96] and experimental and computational studies on the mechanism of Cp molybdenum and tungsten catalysed alkane borylation were also reported.[97]

New precatalysts for alkene oligomerisation include chromium complexes derived from a bis(tertiary phosphine)amine **11** for trimerisation of ethene,[98] and a bis(*N*-heterocyclic carbene)pyridine for oligomerisation of ethene.[99] Of relevance to radical chain polymerisation the kinetics and thermodynamics of H$^{\bullet}$ transfer from $[CpCr(CO)_3H]$ to methyl methacrylate and styrene was investigated.[100] An unusually stable chromium(IV) alkyl complex **12**,[101] and chromium(II) alkyl hydride[102] were also prepared.



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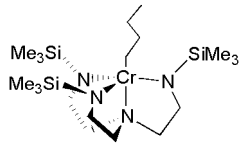

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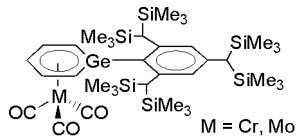
The bonding and synthesis of arenes and heteroatom derivatives was of interest in 2003 leading to some interesting conclusions. An energy portioning scheme resulting from DFT calculations was used to determine the bonding in $[Cr(\eta^6\text{-}C_6H_6)_2]$ and $[Fe(\eta^5\text{-}C_5H_5)_2]$ concluding that in $[Cr(\eta^6\text{-}C_6H_6)_2]$ the most important orbital contribution to metal–ligand bonding is Cr–C_6H_6 δ-back-donation whereas for $[Fe(\eta^5\text{-}C_5H_5)_2]$ the dominant orbital contribution is C_5H_5–Fe π donation.[103] Laser flash photolysis was also employed to estimate the bond dissociation enthalpy of benzene in the complex $[(CO)_5Cr(\eta^2\text{-}C_6H_6)]$ (lower estimate 11.4(1.1) kcal mol^{-1}).[104] The first stable germabenzenes have been stabilised by coordination to chromium as shown in complex **13**,[105] and unusual π-coordination of 2,6-substituted aryl thiolates to molybdenum observed for the first time.[106] η^3-Pyranyl and pyridinyl π-complexes were used as chiral scaffolds for the first stereoselective and regioselective [5 + 3] cycloaddition reactions.[107]



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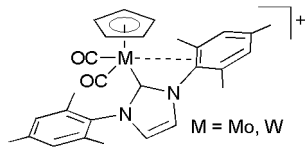
Alkyne and acetylide chemistry includes enediyne synthesis *via* sequential acetylide reductive coupling and alkyne metathesis using a molybdenum amido complex,[108] and insertion of alkynes into Fischer carbene complexes.[109,110] Alkylidene and alkylidyne chemistry include a new enantiomerically pure adamantylimido molybdenum alkylidene complex for enantioselective alkene metathesis,[111] a DFT analysis of the ligand influences on hydrogen migration of $[WH(CH)(CO)_2(PH_3)_2]$ to $[W(CH_2)(CO)_2(PH_3)_2]$,[112] and association of molybdenum and tungsten alkynylcarbyne complexes in solution prior to crystallisation.[113]

Unusual ligand sets include benzannulated *N*-heterocyclic carbene complexes of chromium and tungsten that are synthesised at the metal atom *via* templating from an isocyanide ligand,[114] and hemilabile behaviour of a C=C moiety in mesitylene substituted *N*-heterocyclic carbene complexes such as **14**.[115]



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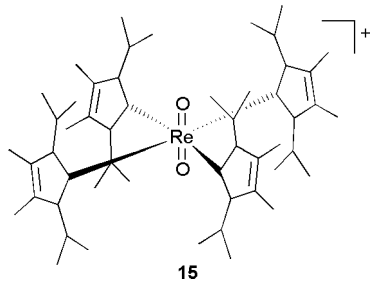
Paramagnetic complex chemistry includes the electronic structure and spectrum of $[Mo(CN)_8]^{3-}$, calculations on which substantiate the spin ground states of clusters and networks that contain the $[Mo(CN)_8]^{3-}$ moiety.[116] Magnetic properties of tungsten(IV) complexes of the type $[(Cp^*)W(bipy)Cl_2]^+$ that show different behaviour in the solid state from solution is accounted for by ligand effects on a thermally accessible excited triplet state.[117] The reactivity between the $[(Cp^*)Cr(CO)_3]$ radical and N,S 2-pyridinethiones has been investigated,[118] and the ability of the cationic complex $[(Cp)W(CO)_3]^+$ to reduce H_2 to dihydride is ascribed to a low lying triplet state.[119]

Solvent free migratory insertion reactions of molybdenum and tungsten complexes $[(Cp)M(CO)_3Me]$ using tertiary phosphines have been shown to occur with similar kinetic profiles to solution chemistry with diffusional effects detected at low temperature.[120]

5 Manganese, technetium, rhenium

The organometallic chemistry of oxo complexes includes the synthesis of cationic technetium and rhenium *N*-heterocyclic carbenes such as **15**,[121] the structures of which indicate a lack of π-back donation to these ligands. Rhenium catalysed oxygen atom transfer from epoxides to PPh_3 catalysed by $[(Tp)Re(O)_3]$ has been shown to occur *via* a complex combination of mechanisms.[122] C–O bond formation to give propargyl ethers is catalysed by $[(dppm)Re(O)Cl_3]$,[123] and the mechanism of aldehyde olefination by $[(2,2'\text{-bipy})Re(O)_3]^+$ has been investigated in the gas phase by mass spectrometry.[124]



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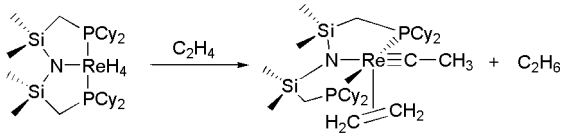
The formation constants of mono- and bidentate nitrogen donor adducts of $[Re(O)_3Me]$ have been determined[125] and new methyloxorhenium(v) compounds derived from tridentate SSS, SOS, and ONO ligands synthesised and their oxidation chemistry investigated.[126] DFT calculations and variable photon energy photoelectron spectroscopy have also been used to elucidate the electronic structure of $[Re(O)_3Me]$ and allow comparison to $[TiCl_3Me]$.[127] Reactivity of the rhenium amido complex $[(2,2'\text{-bipy})Re(CO)_3(NH(p\text{-}C_6H_4Me))]$ toward organic electrophiles such as thiocyanates gives insertion into Re–N and N–H bonds.[128] The rhenium amido polyhydride **16** led to conversion of ethene to a hydrido ethylidyne **17**,[129] and in a related study also gave cyclohexene isomerisation to a β-agostic carbene ligand.[130]



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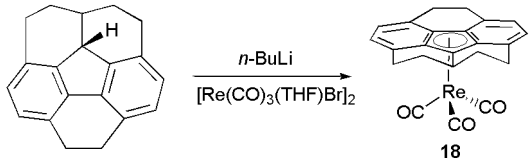
C–H and C–F activation using cyclopentadienyl carbonyl complexes of group 7 includes a comparative computational study of methane activation by $[(Cp)Re(CO)_2]$ and $[(Tp)Re(CO)_2]$ complexes indicating significant differences occur mainly as a consequence of steric factors.[131] *ortho*-C–F activation of arylfluorides has been investigated experimentally and by DFT for $[(Cp/Cp^*)Re(CO)_2]$ derived complexes showing that Re–C bond strengths play the dominant role in thermodynamic and kinetic correlations.[132,133] The reactivity of related fulvene complexes $[(\eta^6\text{-}C_5Me_4CH_2)Re(CO)_2C_6F_5]$ has also been explored allowing access to functionalised Cp derivatives.[134]

Substituted Cp rhenium and technetium carbonyl complexes of the type $[(RC(O)Cp)M(CO)_3]$ have also been developed for radiopharmaceutical application.[135,136] Time resolved infrared spectroscopy was used to probe the substitution kinetics of $[(Cp)Mn(CO)_2(\text{cyclohexane})]$,[137] and a ring-slip mechanism for CO substitution for an alkyne in indenyl rhenium carbonyls such as $[(\eta^5\text{-}C_9H_7)Re(CO)_2\text{-}(MeCCMe)]$ is promoted by the alkyne.[138]

Unusual ligand sets include managanese N-confused porphyrins,[139] and a rhenium complex **18** of a corannulene-based ligand.[140] Metal bound ligand transformations include the synthesis of cyclic *cis*-enediynes from manganese carbyne complexes and α,ω-diynes,[141] borohydride reduction of a rhenium bound acetonitrile to give a

chelating iminoborane,[142] rhenium catalysed coupling of propargyl alcohols and allyl silanes,[143] and stereoselective aldehyde addition to rhenium coordinated furans.[144]



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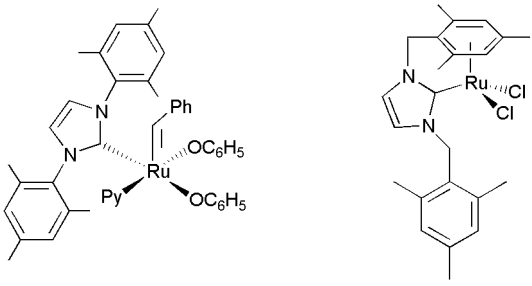
6 Iron, ruthenium, osmium

The organometallic chemistry of group 8 was again dominated by the application of ruthenium complexes to catalytic and stoichiometric organic transformations. Reviews include design of new chiral ruthenium catalysts for asymmetric hydrogenation and their transition from laboratory to industrial applications,[14] the catalytic applications of coordinatively unsaturated ruthenium amidinates,[145] and the reactivity and catalytic applications of [Ru(cod)(cot)].[146]

Alkene metathesis was again very prominent in 2003. DFT studies investigated the mechanism of ruthenium catalysed metathesis[147,148] and several new precatalysts were reported. These include the first highly active halide free example **19**,[149] ruthenium indenylidenes,[150] and *N*-heterocyclic carbene ligand derivatives of Grubb's type catalysts,[151–153] including chiral derivatives.[154] The importance of trace linear contaminants in ROMP catalysis was also highlighted for the synthesis of cyclic polybutadiene.[155] Ring-closing metathesis and cycloisomerisation reactions are catalysed by *N*-heterocyclic carbene complexes such as **20**.[156] An experimental and theoretical study examined the binding of *N*-heterocyclic carbenes to {(Cp*)RuCl} in order to quantify and clarify the bonding of these ligands to complexes relevant to alkene metathesis and other catalytic reactions.[157]



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Atom transfer radical polymerisation of alkenes using ruthenium *N*-heterocyclic carbene complexes,[158] iron salicylaldiminato ligands,[159] and indenylidene ruthenium complexes[150] was also reported.

Other studies relevant to catalysis include chemoselective *N*-allyl bond cleavage using Grubb's type catalysts,[160] a DFT study on the mechanism, regiochemistry and stereochemistry of ruthenium catalysed hydrosilylation,[161] ruthenium silylenes for

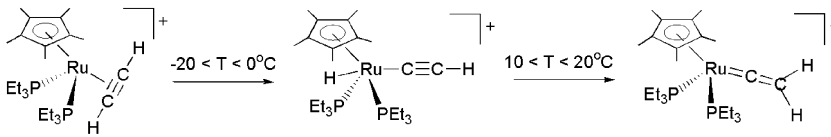
hydrosilylation that provides evidence for a new hydrosilylation mechanism,[162] cleavage of a C–C triple bond to give an alkene and carbon monoxide,[163] and asymmetric transfer hydrogenation.[164]

The moiety {(Cp/Cp*)RuCl} has been used to catalyse hydrophosphination of propargyl alcohols,[165] stereoselective synthesis of substituted 1,3-dienes,[166] intramolecular [2 + 2 + 2] alkyne cyclotrimerisations,[167] and has been the focus of DFT studies for bis-Diels–Alder cycloaddition of 1,5-cyclooctadiene with alkynes,[168] and cyclotrimerisation of alkynes.[169] The complex [(Cp*)Ru(2,2′-bipy)(MeCN)][PF_6] was used to catalyse regioselective allylic substitution,[170] and aminocyclopentadienylruthenium complexes the catalytic dynamic resolution of (*S*)-secondary alcohols.[171] PGSE and NOE NMR spectroscopy were employed to probe higher order aggregation of some cationic ruthenium complexes relevant to catalysis in both protic and aprotic sovents.[172]

Other interesting catalytic reactions include the use of C–H activation products for the arylation of aromatic compounds with arylboronates using [$RuH_2(CO)(PPh_3)_3$],[173] and the addition of arenes to ethylene and propene catalysed by [(Tp)Ru(CO)Me(CNMe)].[174] A DFT study on the borylation of methane and benzene by Cp iron and ruthenium complexes was also undertaken.[175]

The thermodynamics and kinetics of oxidation of aromatic C–H bonds by [Ru(2,2′-bipy)(py)O]$^+$ was investigated showing that C–H activation occurs by hydrogen abstraction,[176] and tandem C–H activation/Si–H elimination in a ruthenium phosphine hydride leads to stabilisation of C–H activation products by an unusual β-agostic Si–H interaction.[177]

The first X-ray and theoretical study of π-alkyne, alkynyl hydride and vinylidene isomers for the same transition metal fragment **21–23** was reported,[178] and related isomerisations are observed in osmium hydrido-vinylidene-π-alkyne *vs.* hydride osmacyclopropene,[179] and the coupling of phenylacetylene with an osmium trihydride.[180]

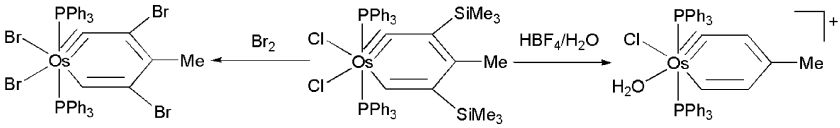


Carbene and cumulene studies include those of {Cp*Ru},[181] electronic structure calculations of [$RuCl(PH_3)_4C_nH_n$] (n = 1–8),[182] the osmium-carbene complex [(Cp)Os(CHPh)Cl(P^iPr_3)] that exhibits Fischer–Schrock ambivalent behaviour,[183] and ruthenium alkynyl complexes for nonlinear optical applications.[184] In a similar vein new rigid rod-like structures were synthesised based on ruthenium acetylides,[185] and ferrocenyl-fluorenes.[186]

Chemistry directed toward medicinal applications of group 8 organometallics includes the synthesis of water soluble ruthenium arene complexes and their screening for antibiotic and antiviral activity,[187] and kinetics of aquation of ruthenium(II) arene anticancer complexes.[188]

The first example of a structurally characterised octahedral Tp iron methyl complex [(Tp)Fe(CO)(Me)(PMe_3)] was reported,[189] and methane σ-bond metathesis

in related complexes was investigated by DFT.[190] Novel zerovalent ruthenium arene complexes bearing two dimethylfumarate ligands that could potentially serve as useful precursors to ruthenium complexes have been prepared from substitution of [Ru(cot)(dimethyfumarate)$_2$].[191] Protonation and bromination of an osmabenzyne **24** was investigated,[192] and theoretical studies used to probe their stability.[193] The first photochromic organometallic derivative of a diarylethene **25** was prepared and photon induced valence isomerisation investigated.[194] The molecular turnstile **26**,[195] that exhibits a ratchet motion, was also synthesised.



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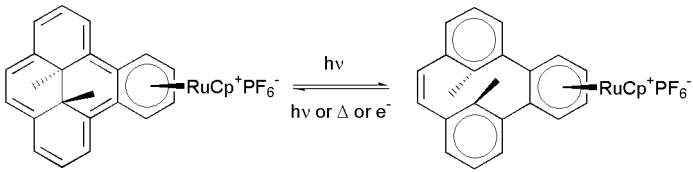

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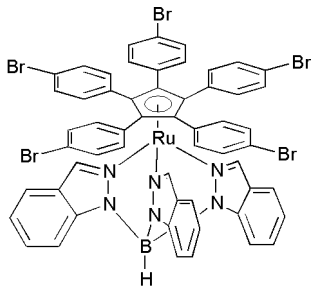

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7 Cobalt, rhodium, iridium

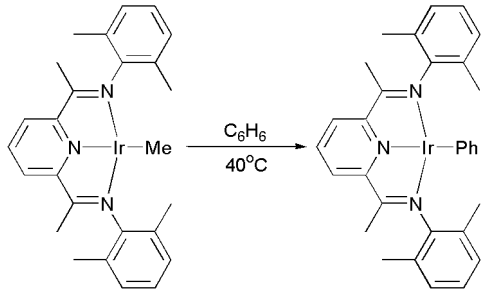
The ligand effects in rhodium-catalysed carbonylation of methanol were surveyed and placed in the context of current industrial processes,[196] and iridium-catalysed alkane dehydrogenation investigated by DFT was reviewed.[197]

Catalytic reactions performed employing well defined metal complexes include asymmetric hydrogenation of aryl alkenes catalysed by *N*-heterocyclic carbene-oxazoline hybrid ligand complexes of iridium,[198] novel axially chiral

rhodium-*N*-heterocyclic carbene complexes derived from BINAM for enantioselective hydrosilylation,[199] rhodium catalysed Mizoroki–Heck arylation between alkenes and aroyl chlorides without the need for ligand or base,[200] and coupling of internal alkynes in {(Tp)IrMe$_2$} derivatives.[201] Studies on the mechanism of cobalt catalysed hydroformylation were reported,[202,203] and insights into rhodium catalysed hydroformylation were achieved using *in situ* high-pressure IR and polymer matrix techniques.[204]

Inter- and intramolecular C–H activation and its application to organic chemistry were prevalent in 2003. Selective *ortho*-C–H activation of haloarenes by an iridium(I) complex was achieved,[205] oxidative addition of benzene to [Rh(H)(PMe$_3$)$_3$] under photochemical conditions observed,[206] addition of *ortho*-C–H bonds of phenol across norbornene catalysed by a chiral iridium(I) diphosphine complex,[207] and a DFT study made of the direct conversion of methane into acetic acid by $RhCl_3$.[208]

Iridium complexes of N-donors were particularly prominent in C–H activation. For example competitive α *vs.* β C–H activation of (Tp)iridium(III) alkyls relevant to intermolecular C–H activation of ethers and amines,[209] H/D exchange between CH_4 and deuterated solvents including perdeutero-benzene, thf, diethyl ether and 1,4-dioxane catalysed by [(Tp)Ru(H)(PPh$_3$)(CH$_3$CN)],[210] DFT analysis of room temperature benzene activation using the iridium complex **27**,[211] and room temperature borylation of arenes and heteroarenes using a complex generated from 4,4′-di-*tert*-butyl-2,2′-bipyridine and [Ir(OMe)(cod)]$_2$.[212,213] Alkane C–H activation using an O-donor ligand complex **28** was also reported for the first time.[214]



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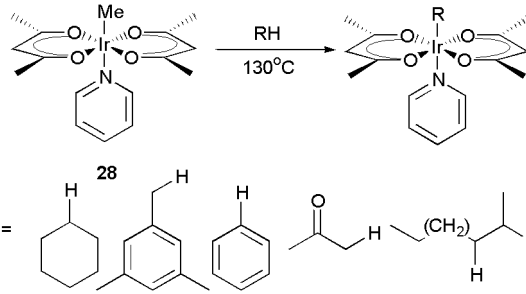

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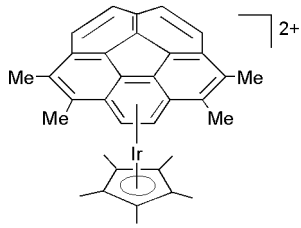
Various phosphino pincer ligands have been investigated for C–H activation including a mechanistic study of transfer dehydrogenation catalysed by an iridium complex,[215] rhodium catalysed H/D exchange between alkenes and methanol or water,[216] synthesis of enamines by iridium-catalysed dehydrogenation of tertiary amines,[217] and competitive intramolecular C–H *vs.* C–C activation *vs.* C–C agostic interaction of a PCN pincer ligand coordinated to rhodium(I).[218,219]

C–F activation and hydrodefluorination of fluorinated alkenes at rhodium by $[Rh(H)(PEt_3)_3]$ was investigated,[220] and intramolecular dehydrofluorinative coupling of an asymmetric diphosphine and Cp* ligands in a rhodium complex observed.[221]

Stoichiometric C–C bond activation includes iridium assisted C–C alkyne cleavage by water to give alkyl derivatives,[222] and a mechanistic investigation into the C–C cleavage of aryl and alkyl cyanides using $[(Cp^*)Rh(PMe_3)(SiPh_3)(CH_2Cl_2)][BAr^f_4]$ (Ar^f = 3,5-$(CF_3)_2C_6H_3$).[223]

New ligand sets include η^6-corrannulene complexes of iridium **29**,[224] and η^2-corrannulene complexes of rhodium,[225] asymmetrically substituted saturated *N*-heterocyclic carbenes of rhodium,[226] 6-membered *N*-heterocycles for carbene complex formation,[227] the first monophosphacobaltocene **30**,[228] TROPDAD a tetradentate ligand based on cycloheptenyl and diazobutadiene moieties for the stabilisation of paramagnetic rhodium and iridium complexes in water,[229] and the first example of a phosphinidene incorporating a *N*-heterocyclic carbene was also prepared.[230] Of relevance to catalysis a DFT study compared the bonding in rhodium(I) carbene and tertiary phosphine complexes.[231]



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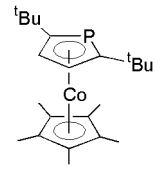

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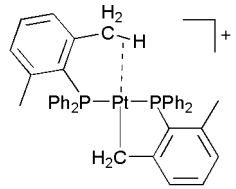
Unusual structures include rhodium(II) and (I) two-legged piano-stool complexes incorporating a bis-phosphine-η^6-arene ligand,[232] several examples of carbon rich cyclyne complexes of cobalt,[233,234] iridabenzene and naphthalene complexes containing electron withdrawing substituents,[235] and the chemistry of an iridium benzyne.[236]

8 Nickel, palladium, platinum

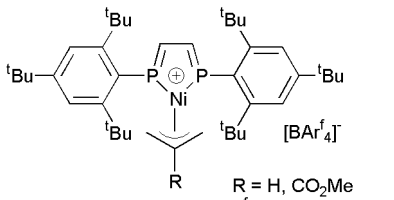
Reviews of group 10 organometallic chemistry include the catalytic design and mechanistic aspects of alternating copolymerisation of ethene and carbon monoxide using palladium catalysts,[237] the use of phosphapalladacycles and *N*-heterocyclic carbene palladium complexes for C–C coupling reactions,[238] and C–H activation and functionalisation with platinum.[23]

C–H activation has again been a focus of much effort in group 10. For example arene C–H activation and arene oxidative coupling by cationic diimine palladium(II) complexes,[239] palladium catalysed activation of benzylic *gem*-dialkyl groups,[240] and dehydrohalogenation of haloarenes by [(dcpe)Ni(η^2-C_2H_4)] [dcpe = 1,2-bis(dicyclohexylphosphino)ethane].[241] Several reports of C–H activation mediated by platinum complexes of N-donor ligands were published including β-diiminate platinum complexes for alkane activation,[242] alcoholysis of tetramethylsilane,[243] the geometric effects on the reactivity of unsymmetrical 2-(*N*-arylimino)pyrrolide platinum complexes,[244] mechanistic studies of reductive elimination/oxidative addition of [(Tp)Pt$(CH_3)_2$H],[245] and synthesis and acid/base properties of [(2,2′-bipy)Pt$(CH_3)_2$-$(OH)_{2-x}(OCH_3)_x$] (x = 0,1).[246] Reductive elimination from bis-phosphineplatinum alkyl complexes,[247] and zwitterionic complexes containing a bis-phosphine borate for C–H activation of benzene were investigated.[248] In related studies a novel T-shaped 14-electron platinum cation **31** stabilized by an agostic interaction was synthesised.[249]



31

Group 10 mediated polymerisation and oligomerisation studies include new nickel complexes incorporating ligand sets derived from arenes,[250] chiral anilines giving C_2 symmetric complexes,[251] sp^2 hybridised bis-phosphines to give **32**,[252] anilinoperinaphthalenone,[253] and salicylaldiminato.[254] Diimine palladium(II) complexes for copolymerisation of ethene and norbornene were also reported.[255] In related studies mechanistic aspects of ethene polymerisation have been aided by the synthesis of nickel(II) alkyl agostic cations and alkyl ethene complexes,[256] a DFT study of ethene polymerisation and branching catalysed by a nickel anilinopropene complex,[257] and the selective cyclotrimerisation of 1,3-butadiene using Ni(0) complexes.[258]



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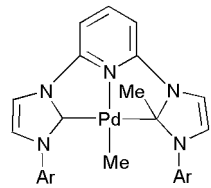
The mechanism and kinetics of solvolysis of a range of bis-phosphine acylpalladium(II) complexes relevant to the copolymerisation of ethene and CO

indicate that polymerisation is favoured by less bulky phosphines,[259] and η^1-allyl complexes of palladium(II) have been prepared and insertion of CO observed to give 3-butenoyl derivatives.[260] Reaction between vinyl chloride and various late metal alkene polymerisation catalysts has shown that β-Cl elimination to give a metal chloride and propene is the main barrier to coordination polymerisation,[261] and the formation of stable palladacycles prevents copolymerisation of vinyl chloride with CO.[262]

Carbene complexes, particularly those of *N*-heterocyclic carbenes (NHC), and their application to various catalytic reactions were very prominent. Catalytic reactions include palladium NHC catalysed room temperature Suzuki coupling reactions of aryl chlorides,[263] transfer hydrogenation of imines catalysed by nickel NHC,[264] chiral palladium NHC complexes for Mizoroki-Heck[265] and asymmetric allylic alkylation,[266] selective hydrosilylation of styrene,[267] palladium catalysed CO/ethene copolymerisation using a chelating NHC-tertiary phosphine,[268] and telomerisation of amines and 1,3-butadiene.[269]

Relevant work to catalysis using NHC complexes includes migratory insertion of a methyl group in a palladium NHC complex shown in **33**,[270] experimental determination of nickel–NHC bond enthalpies in $Ni(NHC)(CO)_2$ complexes,[271] and palladium–NHC bond enthalpies in $[Pd(NHC)_2(Ar)Cl]$,[272] effect of counteranion on the mechanism of conformer interconversion in cationic chelating di-NHC complexes,[273] and fluxionality in palladium imino-NHC hybrid ligands.[274] C–H activation of imidazolium salts by platinum(0)[275] and palladium(0)[276] gives NHC complexes that may indicate that NHC complexes are active in reactions performed in ionic liquids derived from imidazolium salts.



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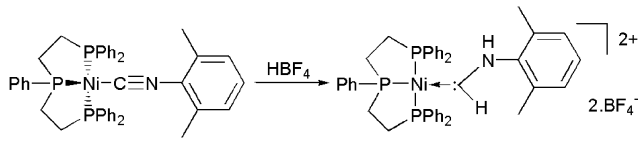
Non-NHC carbenes include the synthesis of an acyclic aminocarbene **34** by protonation of an isocyanide that catalyses the transfer hydrogenation of ketones,[277] and inserts alkenes into the C–H bond of the carbene.[278] An unusual tris-carbene pincer complex **35** containing a carbonyl and three bound carbene centres was also prepared.[279]



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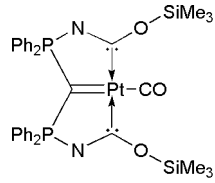

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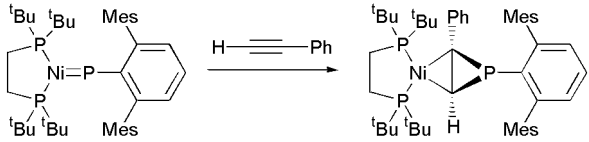
Other molecules of interest include a pseudo-tetrahedral bromotris(1-norbornyl)-nickel(IV) complex,[280] formation of a phosphirene **36** by phosphinidene group transfer,[281] a nickel(III) complex of an N-confused porphyrin,[282] platinum acetylide macrocycles,[283] and the observation of five different fluxional process in $[(Tp)Pt(C_6F_5)_2]$.[284]



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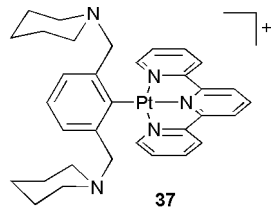
Interesting electronic phenomena include the synthesis of an outer-sphere two-electron platinum reagent **37**,[285] and 'inverse electron demand' that has been determined from kinetic measurements in the ligand substitution chemistry of palladium(0) alkene complexes. The kinetic data are interpreted in terms of a metal 'electrophile' and alkene 'nucleophile', an observation that could have important ramifications for reactions catalysed by transition metal complexes.[1]



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References

1 S. S. Stahl, J. L. Thorman, N. de Silva, I. A. Guzei and R. W. Clark, *J. Am. Chem. Soc.*, 2003, **125**, 12.
2 F. L. Taw, B. L. Scott and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2003, **125**, 14712.
3 G. Wilke, *Angew. Chem., Int. Ed.*, 2003, **42**, 5000.
4 L. L. Bohm, *Angew. Chem., Int. Ed.*, 2003, **42**, 5010.
5 V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
6 Special issue of *J. Organomet. Chem.*, 2003, **684**, 1–391.
7 Special issue of *J. Organomet. Chem.*, 2003, **683**, 1–266.
8 Special issue of *J. Organomet. Chem.*, 2003, **670**, 1–264.
9 Special issue of *J. Organomet. Chem.*, 2003, **683**, 267–445.
10 R. R. Schrock and A. H. Hoveyda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4592.
11 C. Ganter, *Chem. Soc. Rev.*, 2003, **32**, 130.
12 K. Fagnou and M. Lautens, *Chem. Rev.*, 2003, **103**, 169.

13 D. J. Cardenas, *Angew. Chem., Int. Ed.*, 2003, **42**, 384.
14 J. P. Genet, *Acc. Chem. Res.*, 2003, **36**, 908.
15 M. Lautens, K. Fagnou and S. Hiebert, *Acc. Chem. Res.*, 2003, **36**, 48.
16 Z. Freixa and P. van Leeuwen, *Dalton Trans.*, 2003, 1890.
17 M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759.
18 R. N. Perutz and D. J. Cole-Hamilton, *Dalton Trans.*, 2003(21), IX.
19 P. S. Pregosin, E. Martinez-Viviente and P. G. A. Kumar, *Dalton Trans.*, 2003, 4007.
20 M. K. Kuimova, W. Z. Alsindi, J. Dyer, D. C. Grills, O. S. Jina, P. Matousek, A. W. Parker, P. Portius, X. Z. Sun, M. Towrie, C. Wilson, J. X. Yang and M. W. George, *Dalton Trans.*, 2003, 3996.
21 W. D. Jones, *Acc. Chem. Res.*, 2003, **36**, 140.
22 K. E. Janak and G. Parkin, *J. Am. Chem. Soc.*, 2003, **125**, 6889.
23 U. Fekl and K. I. Goldberg, *Adv. Inorg. Chem.*, 2003, **54**, 259.
24 T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2003, **680**, 3.
25 C. B. Pamplin and P. Legzdins, *Acc. Chem. Res.*, 2003, **36**, 223.
26 W. Scherer, P. Sirsch, D. Shorokhov, M. Tafipolsky, G. S. McGrady and E. Gullo, *Chem. Eur. J.*, 2003, **9**, 6057.
27 R. Z. Hinrichs, J. J. Schroden and H. F. Davis, *J. Am. Chem. Soc.*, 2003, **125**, 860.
28 J. D. Harvey and C. J. Ziegler, *Coord. Chem. Rev.*, 2003, **247**, 1.
29 Z. W. Xie, *Acc. Chem. Res.*, 2003, **36**, 1.
30 A. Salzer, *Coord. Chem. Rev.*, 2003, **242**, 59.
31 N. J. Long and C. K. Williams, *Angew. Chem., Int. Ed.*, 2003, **42**, 2586.
32 C. E. Webster and M. B. Hall, *Coord. Chem. Rev.*, 2003, **238**, 315.
33 E. D. Jemmis, A. K. Phukan, H. J. Jiao and U. Rosenthal, *Organometallics*, 2003, **22**, 4958.
34 M. A. Iron, J. M. L. Martin and M. E. van der Boom, *J. Am. Chem. Soc.*, 2003, **125**, 13020.
35 F. Alary, J. L. Heully, R. Poteau, L. Maron, G. Trinquier and J. P. Daudey, *J. Am. Chem. Soc.*, 2003, **125**, 11051.
36 R. Poli and J. N. Harvey, *Chem. Soc. Rev.*, 2003, **32**, 1.
37 T. K. Panda, M. T. Gamer and P. W. Roesky, *Organometallics*, 2003, **22**, 877.
38 T. R. Boussie, G. M. Diamond, C. Goh, K. A. Hall, A. M. LaPointe, M. Leclerc, C. Lund, V. Murphy, J. A. W. Shoemaker, U. Tracht, H. Turner, J. Zhang, T. Uno, R. K. Rosen and J. C. Stevens, *J. Am. Chem. Soc.*, 2003, **125**, 4306.
39 T. N. Choo and R. M. Waymouth, *J. Am. Chem. Soc.*, 2003, **125**, 8970.
40 T. R. Jensen, S. C. Yoon, A. K. Dash, L. B. Luo and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 14482.
41 A. R. Lavoie, M. H. Ho and R. M. Waymouth, *Chem. Commun.*, 2003, 864.
42 Y. H. Zhang, R. J. Keaton and L. R. Sita, *J. Am. Chem. Soc.*, 2003, **125**, 9062.
43 R. A. Stockland, S. R. Foley and R. F. Jordan, *J. Am. Chem. Soc.*, 2003, **125**, 796.
44 G. Erker, *Chem. Commun.*, 2003, 1469.
45 S. Venne-Dunker, G. Kehr, R. Frohlich and G. Erker, *Organometallics*, 2003, **22**, 948.
46 P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, V. V. Burlakov and V. B. Shur, *Angew. Chem., Int. Ed.*, 2003, **42**, 1414.
47 R. Choukroun, F. Wolff, C. Lorber and B. Donnadieu, *Organometallics*, 2003, **22**, 2245.
48 M. Horacek, P. Stepnicka, J. Kubista, K. Fejfarova, R. Gyepes and K. Mach, *Organometallics*, 2003, **22**, 861.
49 U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann and A. Spannenberg, *Organometallics*, 2003, **22**, 884.
50 J. J. Eisch and J. N. Gitua, *Organometallics*, 2003, **22**, 4172.
51 S. Bhaduri, S. Mukhopadhyay and S. A. Kulkarni, *J. Organomet. Chem.*, 2003, **671**, 101.
52 G. Talarico, V. Busico and L. Cavallo, *J. Am. Chem. Soc.*, 2003, **125**, 7172.
53 T. J. M. de Bruin, L. Magna, P. Raybaud and H. Toulhoat, *Organometallics*, 2003, **22**, 3404.
54 I. E. Nifant'ev, L. Y. Ustynyuk and D. V. Besedin, *Organometallics*, 2003, **22**, 2619.
55 F. Q. Song, R. D. Cannon and M. Bochmann, *J. Am. Chem. Soc.*, 2003, **125**, 7641.
56 N. G. Stahl, C. Zuccaccia, T. R. Jensen and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 5256.
57 M. Mohammed, M. Nele, A. Al-Humydi, S. X. Xin, R. A. Stapleton and S. Collins, *J. Am. Chem. Soc.*, 2003, **125**, 7930.
58 V. Busico, V. V. A. Castelli, P. Aprea, R. Cipullo, A. Segre, G. Talarico and M. Vacatello, *J. Am. Chem. Soc.*, 2003, **125**, 5451.
59 C. R. Landis, K. A. Rosaaen and D. R. Sillars, *J. Am. Chem. Soc.*, 2003, **125**, 1710.
60 S. Pillet, G. Wu, V. Kulsomphob, B. G. Harvey, R. D. Ernst and P. Coppens, *J. Am. Chem. Soc.*, 2003, **125**, 1937.
61 R. A. Himes, P. E. Fanwick and I. P. Rothwell, *Chem. Commun.*, 2003, 18.
62 S. A. Johnson, F. Q. Liu, M. C. Suh, S. Zurcher, M. Haufe, S. S. H. Mao and T. D. Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 4199.
63 Y. Obora, H. Moriya, M. Tokunaga and Y. Tsuji, *Chem. Commun.*, 2003, 2820.
64 C. A. Bradley, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 8110.

65 H. Aihara, T. Matsuo and H. Kawaguchi, *Chem. Commun.*, 2003, 2204.
66 X. D. Fang, D. Woodmansee, X. H. Bu and G. C. Bazan, *Angew. Chem., Int. Ed.*, 2003, **42**, 4510.
67 F. L. Jiang, P. J. Shapiro, F. Fahs and B. Twamley, *Angew. Chem., Int. Ed.*, 2003, **42**, 2651.
68 F. Basuli, B. C. Bailey, J. Tomaszewski, J. C. Huffman and D. J. Mindiola, *J. Am. Chem. Soc.*, 2003, **125**, 6052.
69 Z. F. Xi, K. Sato, Y. Gao, J. M. Lu and T. Takahashi, *J. Am. Chem. Soc.*, 2003, **125**, 9568.
70 W. D. Jones, *Dalton Trans.*, 2003, 3991.
71 F. E. Michael, A. P. Duncan, Z. K. Sweeney and R. G. Bergman, *J. Am. Chem. Soc.*, 2003, **125**, 7184.
72 J. A. Pool, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 2241.
73 J. A. Pool, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2003, **22**, 2797.
74 A. D. Sadow and T. D. Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 9462.
75 A. D. Sadow and T. D. Tilley, *Organometallics*, 2003, **22**, 3577.
76 S. Gambarotta, *Coord. Chem. Rev.*, 2003, **237**, 229.
77 L. J. Ackerman, M. L. H. Green, J. C. Green and J. E. Bercaw, *Organometallics*, 2003, **22**, 188.
78 P. J. Chirik, D. L. Zubris, L. J. Ackerman, L. M. Henling, M. W. Day and J. E. Bercaw, *Organometallics*, 2003, **22**, 172.
79 T. R. Cundari and C. D. Taylor, *Organometallics*, 2003, **22**, 4047.
80 Z. X. Yu and K. N. Houk, *Angew. Chem., Int. Ed.*, 2003, **42**, 808.
81 S. Groysman, I. Goldberg, M. Kol and Z. Goldschmidt, *Organometallics*, 2003, **22**, 3793.
82 K. Mashima, H. Yonekura, T. Yamagata and K. Tani, *Organometallics*, 2003, **22**, 3766.
83 T. Oshiki, K. Tanaka, J. Yamada, T. Ishiyama, Y. Kataoka, K. Mashima, K. Tani and K. Takai, *Organometallics*, 2003, **22**, 464.
84 F. H. Kohler, R. Molle, W. Strauss, B. Weber, R. W. Gedridge, R. Basta, W. Trakarnpruk, R. Tomaszewski, A. M. Arif and R. D. Ernst, *Organometallics*, 2003, **22**, 1923.
85 J. Jaffart, M. Etienne, M. Reinhold, J. E. McGrady and F. Maseras, *Chem. Commun.*, 2003, 876.
86 J. Jaffart, M. L. Cole, M. Etienne, M. Reinhold, J. E. McGrady and F. Maseras, *Dalton Trans.*, 2003, 4057.
87 S. R. Dubberley, S. K. Ignatov, N. H. Rees, A. G. Razuvaev, P. Mountford and G. I. Nikonov, *J. Am. Chem. Soc.*, 2003, **125**, 642.
88 C. D. Abernethy, G. M. Codd, M. D. Spicer and M. K. Taylor, *J. Am. Chem. Soc.*, 2003, **125**, 1128.
89 T. G. Ong, G. P. A. Yap and D. S. Richeson, *Chem. Commun.*, 2003, 2612.
90 J. S. Figueroa and C. C. Cummins, *J. Am. Chem. Soc.*, 2003, **125**, 4020.
91 G. I. Nikonov, A. V. Churakov and M. Y. Antipin, *Organometallics*, 2003, **22**, 2178.
92 M. G. Thorn, J. R. Parker, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 2003, **22**, 4658.
93 S. H. K. Ng, C. S. Adams, T. W. Hayton, P. Legzdins and B. O. Patrick, *J. Am. Chem. Soc.*, 2003, **125**, 15210.
94 K. Wada, C. B. Pamplin, P. Legzdins, B. O. Patrick, I. Tsyba and R. Bau, *J. Am. Chem. Soc.*, 2003, **125**, 7035.
95 D. G. Churchill, K. E. Janak, J. S. Wittenberg and G. Parkin, *J. Am. Chem. Soc.*, 2003, **125**, 1403.
96 S. H. Meiere, J. M. Keane, T. B. Gunnoe, M. Sabat and W. D. Harman, *J. Am. Chem. Soc.*, 2003, **125**, 2024.
97 C. E. Webster, Y. B. Fan, M. B. Hall, D. Kunz and J. F. Hartwig, *J. Am. Chem. Soc.*, 2003, **125**, 858.
98 D. S. McGuinness, P. Wasserscheid, W. Keim, C. H. Hu, U. Englert, J. T. Dixon and C. Grove, *Chem. Commun.*, 2003, 334.
99 D. S. McGuinness, V. C. Gibson, D. F. Wass and J. W. Steed, *J. Am. Chem. Soc.*, 2003, **125**, 12716.
100 L. H. Tang, E. T. Papish, G. P. Abramo, J. R. Norton, M. H. Baik, R. A. Friesner and A. Rappe, *J. Am. Chem. Soc.*, 2003, **125**, 10093.
101 A. C. Filippou and S. Schneider, *Organometallics*, 2003, **22**, 3010.
102 L. A. MacAdams, G. P. Buffone, C. D. Incarvito, J. A. Golen, A. L. Rheingold and K. H. Theopold, *Chem. Commun.*, 2003, 1164.
103 V. M. Rayon and G. Frenking, *Organometallics*, 2003, **22**, 3304.
104 A. A. Bengali and T. F. Stumbaugh, *Dalton Trans.*, 2003, 354.
105 N. Nakata, N. Takeda and N. Tokitoh, *Angew. Chem., Int. Ed.*, 2003, **42**, 115.
106 T. Komuro, T. Matsuo, H. Kawaguchi and K. Tatsumi, *J. Am. Chem. Soc.*, 2003, **125**, 2070.
107 R. M. Arrayas and L. S. Liebeskind, *J. Am. Chem. Soc.*, 2003, **125**, 9026.
108 J. M. Blackwell, J. S. Figueroa, F. H. Stephens and C. C. Cummins, *Organometallics*, 2003, **22**, 3351.
109 S. Unaldi, R. Aumann and R. Frohlich, *Chem. Eur. J.*, 2003, **9**, 3300.
110 H. Wang, J. Huang, W. D. Wulff and A. L. Rheingold, *J. Am. Chem. Soc.*, 2003, **125**, 8980.
111 W. C. P. Tsang, J. A. Jernelius, G. A. Cortez, G. S. Weatherhead, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2003, **125**, 2591.
112 H. Jacobsen, *J. Organomet. Chem.*, 2003, **674**, 50.
113 B. Schwenzer and H. Fischer, *J. Organomet. Chem.*, 2003, **667**, 16.
114 F. E. Hahn, V. Langenhahn, N. Meier, T. Lugger and W. P. Fehlhammer, *Chem. Eur. J.*, 2003, **9**, 704.
115 V. K. Dioumaev, D. J. Szalda, J. Hanson, J. A. Franz and R. M. Bullock, *Chem. Commun.*, 2003, 1670.

116 M. F. A. Hendrickx, L. F. Chibotaru and A. Ceulemans, *Inorg. Chem.*, 2003, **42**, 590.
117 C. Cremer and P. Burger, *J. Am. Chem. Soc.*, 2003, **125**, 7664.
118 K. Sukcharoenphon, D. Moran, P. V. Schleyer, J. E. McDonough, K. A. Abboud and C. D. Hoff, *Inorg. Chem.*, 2003, **42**, 8494.
119 H. Lesnard, I. Demachy, Y. Jean and A. Lledos, *Chem. Commun.*, 2003, 850.
120 O. G. Adeyemi and N. J. Coville, *Organometallics*, 2003, **22**, 2284.
121 H. Braband, T. I. Zahn and U. Abram, *Inorg. Chem.*, 2003, **42**, 6160.
122 K. P. Gable and E. C. Brown, *J. Am. Chem. Soc.*, 2003, **125**, 11018.
123 B. D. Sherry, A. T. Radosevich and F. D. Toste, *J. Am. Chem. Soc.*, 2003, **125**, 6076.
124 X. Y. Zhang and P. Chen, *Chem. Eur. J.*, 2003, **9**, 1852.
125 S. M. Nabavizadeh, *Inorg. Chem.*, 2003, **42**, 4204.
126 X. P. Shan, A. Ellern, I. A. Guzei and J. H. Espenson, *Inorg. Chem.*, 2003, **42**, 2362.
127 M. de Simone, M. Coreno, J. C. Green, S. McGrady and H. Pritchard, *Inorg. Chem.*, 2003, **42**, 1908.
128 E. Hevia, J. Perez and V. Riera, *Organometallics*, 2003, **22**, 257.
129 O. V. Ozerov, J. C. Huffman, L. A. Watson and K. G. Caulton, *Organometallics*, 2003, **22**, 2539.
130 O. V. Ozerov, L. A. Watson, M. Pink and K. G. Caulton, *J. Am. Chem. Soc.*, 2003, **125**, 9604.
131 R. G. Bergman, T. R. Cundari, A. M. Gillespie, T. B. Gunnoe, W. D. Harman, T. R. Klinckman, M. D. Temple and D. P. White, *Organometallics*, 2003, **22**, 2331.
132 E. Clot, M. Besora, F. Maseras, C. Megret, O. Eisenstein, B. Oelckers and R. N. Perutz, *Chem. Commun.*, 2003, 490.
133 E. Clot, B. Oelckers, A. H. Klahn, O. Eisenstein and R. N. Perutz, *Dalton Trans.*, 2003, 4065.
134 F. Godoy, A. H. Klahn, F. J. Lahoz, A. I. Balana, B. Oelckers and L. A. Oro, *Organometallics*, 2003, **22**, 4861.
135 J. Bernard, K. Ortner, B. Spingler, H. J. Pietzsch and R. Alberto, *Inorg. Chem.*, 2003, **42**, 1014.
136 F. Le Bideau, J. Henique, P. Pigeon, J. M. Joerger, S. Top and G. Jaouen, *J. Organomet. Chem.*, 2003, **668**, 140.
137 S. Lugovskoy, J. Lin and R. H. Schultz, *Dalton Trans.*, 2003, 3103.
138 C. P. Casey, T. E. Vos, J. T. Brady and R. K. Hayashi, *Organometallics*, 2003, **22**, 1183.
139 J. D. Harvey and C. J. Ziegler, *Chem. Commun.*, 2003, 2890.
140 R. M. Chin, B. Baird, M. Jarosh, S. Rassman, B. Barry and W. D. Jones, *Organometallics*, 2003, **22**, 4829.
141 C. P. Casey, T. L. Dzwiniel, S. Kraft and I. A. Guzei, *Organometallics*, 2003, **22**, 3915.
142 A. C. Hillier, T. Fox, H. W. Schmalle and H. Berke, *J. Organomet. Chem.*, 2003, **669**, 14.
143 M. R. Luzung and F. D. Toste, *J. Am. Chem. Soc.*, 2003, **125**, 15760.
144 M. A. Schiffler, L. A. Friedman, B. C. Brooks, M. Sabat and W. D. Harman, *Organometallics*, 2003, **22**, 4966.
145 H. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondo, S. Masuda, K. Miyazaki, K. Matsubara and K. Kirchner, *Coord. Chem. Rev.*, 2003, **245**, 177.
146 S. Komiya and M. Hirano, *Dalton Trans.*, 2003, 1439.
147 F. Bernardi, A. Bottoni and G. P. Miscione, *Organometallics*, 2003, **22**, 940.
148 S. Fomine, S. M. Vargas and M. A. Tlenkopatchev, *Organometallics*, 2003, **22**, 93.
149 J. C. Conrad, D. Amoroso, P. Czechura, G. P. A. Yap and D. E. Fogg, *Organometallics*, 2003, **22**, 3634.
150 T. Opstal and F. Verpoort, *Angew. Chem., Int. Ed.*, 2003, **42**, 2876.
151 M. B. Dinger, P. Nieczypor and J. C. Mol, *Organometallics*, 2003, **22**, 5291.
152 T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T. L. Choi, S. Ding, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 2546.
153 J. C. Conrad, G. P. A. Yap and D. E. Fogg, *Organometallics*, 2003, **22**, 1986.
154 J. J. Van Veldhuizen, D. G. Gillingham, S. B. Garber, O. Kataoka and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2003, **125**, 12502.
155 C. W. Bielawski, D. Benitez and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 8424.
156 B. Cetinkaya, S. Demir, I. Ozdemir, L. Toupet, D. Semeril, C. Bruneau and P. H. Dixneuf, *Chem. Eur. J.*, 2003, **9**, 2323.
157 A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo and S. P. Nolan, *Organometallics*, 2003, **22**, 4322.
158 L. Delaude, S. Delfosse, A. Richel, A. Demonceau and A. F. Noels, *Chem. Commun.*, 2003, 1526.
159 R. K. O'Reilly, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2003, **125**, 8450.
160 B. Alcaide, P. Almendros and J. M. Alonso, *Chem. Eur. J.*, 2003, **9**, 5793.
161 L. W. Chung, Y. D. Wu, B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2003, **125**, 11578.
162 P. B. Glaser and T. D. Tilley, *J. Am. Chem. Soc.*, 2003, **125**, 13640.
163 S. Datta, C. L. Chang, K. L. Yeh and R. S. Liu, *J. Am. Chem. Soc.*, 2003, **125**, 9294.
164 A. H. Ell, J. B. Johnson and J. E. Backvall, *Chem. Commun.*, 2003, 1652.
165 F. Jerome, F. Monnier, H. Lawicka, S. Derien and P. H. Dixneuf, *Chem. Commun.*, 2003, 696.
166 J. Le Paih, F. Monnier, S. Derien, P. H. Dixneuf, E. Clot and O. Eisenstein, *J. Am. Chem. Soc.*, 2003, **125**, 11964.
167 Y. Yamamoto, T. Arakawa, R. Ogawa and K. Itoh, *J. Am. Chem. Soc.*, 2003, **125**, 12143.

168 X. Huang and Z. Y. Lin, *Organometallics*, 2003, **22**, 5478.
169 K. Kirchner, M. J. Calhorda, R. Schmid and L. F. Veiros, *J. Am. Chem. Soc.*, 2003, **125**, 11721.
170 M. D. Mbaye, B. Demerseman, J. L. Renaud, L. Toupet and C. Bruneau, *Angew. Chem., Int. Ed.*, 2003, **42**, 5066.
171 M. J. Kim, Y. I. Chung, Y. K. Choi, H. K. Lee, D. Kim and J. Park, *J. Am. Chem. Soc.*, 2003, **125**, 11494.
172 D. Zuccaccia, S. Sabatini, G. Bellachioma, G. Cardaci, E. Clot and A. Macchioni, *Inorg. Chem.*, 2003, **42**, 5465.
173 F. Kakiuchi, S. Kan, K. Igi, N. Chatani and S. Murai, *J. Am. Chem. Soc.*, 2003, **125**, 1698.
174 M. Lail, B. N. Arrowood and T. B. Gunnoe, *J. Am. Chem. Soc.*, 2003, **125**, 7506.
175 W. H. Lam and Z. Y. Lin, *Organometallics*, 2003, **22**, 473.
176 J. R. Bryant and J. M. Mayer, *J. Am. Chem. Soc.*, 2003, **125**, 10351.
177 V. K. Dioumaev, P. J. Carroll and D. H. Berry, *Angew. Chem., Int. Ed.*, 2003, **42**, 3947.
178 E. Bustelo, J. J. Carbo, A. Lledos, K. Mereiter, M. C. Puerta and P. Valerga, *J. Am. Chem. Soc.*, 2003, **125**, 3311.
179 P. Barrio, M. A. Esteruelas and E. Onate, *Organometallics*, 2003, **22**, 2472.
180 T. B. Wen, Z. Y. Zhou and G. C. Jia, *Organometallics*, 2003, **22**, 4947.
181 T. Braun, G. Munch, B. Windmuller, O. Gevert, M. Laubender and H. Werner, *Chem. Eur. J.*, 2003, **9**, 2516.
182 N. Auger, D. Touchard, S. Rigaut, J. F. Halet and J. Y. Saillard, *Organometallics*, 2003, **22**, 1638.
183 M. A. Esteruelas, A. I. Gonzalez, A. M. Lopez and E. Onate, *Organometallics*, 2003, **22**, 414.
184 C. E. Powell, M. P. Cifuentes, J. P. Morrall, R. Stranger, M. G. Humphrey, M. Samoc, B. Luther-Davies and G. A. Heath, *J. Am. Chem. Soc.*, 2003, **125**, 602.
185 S. Rigaut, J. Perruchon, L. Le Pichon, D. Touchard and P. H. Dixneuf, *J. Organomet. Chem.*, 2003, **670**, 37.
186 W. Y. Wong, K. Y. Ho and K. H. Choi, *J. Organomet. Chem.*, 2003, **670**, 17.
187 C. S. Allardyce, P. J. Dyson, D. J. Ellis, P. A. Salter and R. Scopelliti, *J. Organomet. Chem.*, 2003, **668**, 35.
188 F. Wang, H. M. Chen, S. Parsons, L. D. H. Oswald, J. E. Davidson and P. J. Sadler, *Chem. Eur. J.*, 2003, **9**, 5810.
189 O. Graziani, L. Toupet, J. R. Hamon and M. Tilset, *J. Organomet. Chem.*, 2003, **669**, 200.
190 W. H. Lam, G. C. Jia, Z. Y. Lin, C. P. Lau and O. Eisenstein, *Chem. Eur. J.*, 2003, **9**, 2775.
191 Y. Ura, M. Shiotsuki, K. Sadaoka, T. Suzuki, T. Kondo and T. Mitsudo, *Organometallics*, 2003, **22**, 1863.
192 T. B. Wen, S. M. Ng, W. Y. Hung, Z. Y. Zhou, M. F. Lo, L. Y. Shek, I. D. Williams, Z. Y. Lin and G. C. Jia, *J. Am. Chem. Soc.*, 2003, **125**, 884.
193 S. M. Ng, X. Huang, T. B. Wen, G. C. Jia and Z. Y. Lin, *Organometallics*, 2003, **22**, 3898.
194 R. H. Mitchell, Z. Brkic, V. A. Sauro and D. J. Berg, *J. Am. Chem. Soc.*, 2003, **125**, 7581.
195 A. Carella, J. Jaud, G. Rapenne and J. P. Launay, *Chem. Commun.*, 2003, 2434.
196 C. M. Thomas and G. Suss-Fink, *Coord. Chem. Rev.*, 2003, **243**, 125.
197 M. B. Hall and H. J. Fan, *Adv. Inorg. Chem.*, 2003, **54**, 321.
198 M. C. Perry, X. H. Cui, M. T. Powell, D. R. Hou, J. H. Reibenspies and K. Burgess, *J. Am. Chem. Soc.*, 2003, **125**, 113.
199 W. L. Duan, M. Shi and G. B. Rong, *Chem. Commun.*, 2003, 2916.
200 T. Sugihara, T. Satoh, M. Miura and M. Nomura, *Angew. Chem., Int. Ed.*, 2003, **42**, 4672.
201 E. Alvarez, M. Gomez, M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendon, L. L. Santos, S. Rojas-Lima, V. Salazar, K. Mereiter and C. Ruiz, *J. Am. Chem. Soc.*, 2003, **125**, 1478.
202 C. F. Huo, Y. W. Li, M. Beller and H. Jiao, *Organometallics*, 2003, **22**, 4665.
203 S. M. Massick, T. Buttner and P. C. Ford, *Inorg. Chem.*, 2003, **42**, 575.
204 J. Zhang, M. Poliakoff and M. W. George, *Organometallics*, 2003, **22**, 1612.
205 E. Ben-Ari, M. Gandelman, H. Rozenberg, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2003, **125**, 4714.
206 J. C. Choi and T. Sakakura, *J. Am. Chem. Soc.*, 2003, **125**, 7762.
207 R. Dorta and A. Togni, *Chem. Commun.*, 2003, 760.
208 I. H. Hristov and T. Ziegler, *Organometallics*, 2003, **22**, 3513.
209 E. Carmona, M. Paneque and M. L. Poveda, *Dalton Trans.*, 2003, 4022.
210 S. M. Ng, W. H. Lam, C. C. Mak, C. W. Tsang, G. C. Jia, Z. Y. Lin and C. P. Lau, *Organometallics*, 2003, **22**, 641.
211 S. Nuckel and P. Burger, *Angew. Chem. Int. Ed.*, 2003, **42**, 1632.
212 T. Ishiyama, Y. Nobuta, J. F. Hartwig and N. Miyaura, *Chem. Commun.*, 2003, 2924.
213 H. Tamura, H. Yamazaki, H. Sato and S. Sakaki, *J. Am. Chem. Soc.*, 2003, **125**, 16114.
214 A. G. Wong-Foy, G. Bhalla, X. Y. Liu and R. A. Periana, *J. Am. Chem. Soc.*, 2003, **125**, 14292.
215 K. B. Renkema, Y. V. Kissin and A. S. Goldman, *J. Am. Chem. Soc.*, 2003, **125**, 7770.
216 B. Rybtchinski, R. Cohen, Y. Ben-David, J. M. L. Martin and D. Milstein, *J. Am. Chem. Soc.*, 2003, **125**, 11041.
217 X. W. Zhang, A. Fried, S. Knapp and A. S. Goldman, *Chem. Commun.*, 2003, 2060.

218 M. Gandelman, L. Konstantinovski, H. Rozenberg and D. Milstein, *Chem. Eur. J.*, 2003, **9**, 2595.
219 M. Gandelman, L. J. W. Shimon and D. Milstein, *Chem. Eur. J.*, 2003, **9**, 4295.
220 D. Noveski, T. Braun, M. Schulte, B. Neumann and H. G. Stammler, *Dalton Trans.*, 2003, 4075.
221 R. M. Bellabarba, M. Nieuwenhuyzen and G. C. Saunders, *Organometallics*, 2003, **22**, 1802.
222 G. Albertin, S. Antoniutti, A. Bacchi, G. Pelizzi and F. Piasente, *Dalton Trans.*, 2003, 2881.
223 F. L. Taw, A. H. Mueller, R. G. Bergman and M. Brookhart, *J. Am. Chem. Soc.*, 2003, **125**, 9808.
224 C. M. Alvarez, R. J. Angelici, A. Sygula, R. Sygula and P. W. Rabideau, *Organometallics*, 2003, **22**, 624.
225 M. A. Petrukhina, K. W. Andreini, J. Mack and L. T. Scott, *Angew. Chem., Int. Ed.*, 2003, **42**, 3375.
226 F. E. Hahn, M. Paas, D. Le Van and T. Lugger, *Angew. Chem., Int. Ed.*, 2003, **42**, 5243.
227 P. Bazinet, G. P. A. Yap and D. S. Richeson, *J. Am. Chem. Soc.*, 2003, **125**, 13314.
228 C. Burney, D. Carmichael, K. Forissier, J. C. Green, F. Mathey and L. Ricard, *Chem. Eur. J.*, 2003, **9**, 2567.
229 F. Breher, C. Bohler, G. Frison, J. Harmer, L. Liesum, A. Schweiger and H. Grutzmacher, *Chem. Eur. J.*, 2003, **9**, 3859.
230 A. T. Termaten, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek and K. Lammertsma, *Chem. Eur. J.*, 2003, **9**, 3577.
231 K. Miqueu, E. Despagnet-Ayoub, P. W. Dyer, D. Bourissou and G. Bertrand, *Chem. Eur. J.*, 2003, **9**, 5858.
232 F. M. Dixon, M. S. Masar, P. E. Doan, J. R. Farrell, F. P. Arnold, C. A. Mirkin, C. D. Incarvito, L. N. Zakharov and A. L. Rheingold, *Inorg. Chem.*, 2003, **42**, 3245.
233 M. Laskoski, G. Roidl, H. L. Ricks, J. G. M. Morton, M. D. Smith and U. H. F. Bunz, *J. Organomet. Chem.*, 2003, **673**, 13.
234 M. Laskoski, W. Steffen, J. G. M. Morton, M. D. Smith and U. H. F. Bunz, *J. Organomet. Chem.*, 2003, **673**, 25.
235 M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendon, V. Salazar, E. Onate and K. Mereiter, *J. Am. Chem. Soc.*, 2003, **125**, 9898.
236 R. P. Hughes, R. B. Laritchev, A. Williamson, C. D. Incarvito, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2003, **22**, 2134.
237 C. Bianchini, A. Meli and W. Oberhauser, *Dalton Trans.*, 2003, 2627.
238 W. A. Herrmann, K. Ofele, D. Von Preysing and S. K. Schneider, *J. Organomet. Chem.*, 2003, **687**, 229.
239 L. J. Ackerman, J. P. Sadighi, D. M. Kurtz, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2003, **22**, 3884.
240 O. Baudoin, A. Herrbach and F. Gueritte, *Angew. Chem., Int. Ed.*, 2003, **42**, 5736.
241 M. A. Bennett, M. R. Kopp, E. Wenger and A. C. Willis, *J. Organomet. Chem.*, 2003, **667**, 8.
242 U. Fekl, W. Kaminsky and K. I. Goldberg, *J. Am. Chem. Soc.*, 2003, **125**, 15286.
243 A. F. Heyduk, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2003, **125**, 6366.
244 C. N. Iverson, C. A. G. Carter, R. T. Baker, J. D. Scollard, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2003, **125**, 12674.
245 M. P. Jensen, D. D. Wick, S. Reinartz, P. S. White, J. L. Templeton and K. I. Goldberg, *J. Am. Chem. Soc.*, 2003, **125**, 8614.
246 K. Thorshaug, I. Fjeldahl, C. Romming and M. Tilset, *Dalton Trans.*, 2003, 4051.
247 D. M. Crumpton-Bregel and K. I. Goldberg, *J. Am. Chem. Soc.*, 2003, **125**, 9442.
248 J. C. Thomas and J. C. Peters, *J. Am. Chem. Soc.*, 2003, **125**, 8870.
249 W. Baratta, S. Stoccoro, A. Doppiu, E. Herdtweck, A. Zucca and P. Rigo, *Angew. Chem., Int. Ed.*, 2003, **42**, 105.
250 J. Campora, M. D. Conejo, M. L. Reyes, K. Mereiter and E. Passaglia, *Chem. Commun.*, 2003, 78.
251 A. E. Cherian, E. B. Lobkovsky and G. W. Coates, *Chem. Commun.*, 2003, 2566.
252 A. Ionkin and W. Marshall, *Chem. Commun.*, 2003, 710.
253 J. C. Jenkins and M. Brookhart, *Organometallics*, 2003, **22**, 250.
254 W. H. Sun, H. J. Yang, Z. L. Li and Y. Li, *Organometallics*, 2003, **22**, 3678.
255 J. Kiesewetter and W. Kaminsky, *Chem. Eur. J.*, 2003, **9**, 1750.
256 M. D. Leatherman, S. A. Svejda, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 2003, **125**, 3068.
257 A. Michalak and T. Ziegler, *Organometallics*, 2003, **22**, 2069.
258 S. Tobisch, *Chem. Eur. J.*, 2003, **9**, 1217.
259 P. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz and A. L. Spek, *J. Am. Chem. Soc.*, 2003, **125**, 5523.
260 P. Braunstein, Z. A. Jing and R. Welter, *Dalton Trans.*, 2003, 507.
261 S. R. Foley, R. A. Stockland, H. Shen and R. F. Jordan, *J. Am. Chem. Soc.*, 2003, **125**, 4350.
262 H. Shen and R. F. Jordan, *Organometallics*, 2003, **22**, 1878.
263 G. Altenhoff, R. Goddard, C. W. Lehmann and F. Glorius, *Angew. Chem., Int. Ed.*, 2003, **42**, 3690.
264 S. Kuhl, R. Schneider and Y. Fort, *Organometallics*, 2003, **22**, 4184.
265 J. Pytkowicz, S. Roland, P. Mangeney, G. Meyer and A. Jutand, *J. Organomet. Chem.*, 2003, **678**, 166.
266 L. G. Bonnett, R. E. Douthwaite and B. M. Kariuki, *Organometallics*, 2003, **22**, 4187.

267 J. W. Sprengers, M. J. Mars, M. A. Duin, K. J. Cavell and C. J. Elsevier, *J. Organomet. Chem.*, 2003, **679**, 149.
268 N. Tsoureas, A. A. Danopoulos, A. A. D. Tulloch and M. E. Light, *Organometallics*, 2003, **22**, 4750.
269 M. S. Viciu, F. K. Zinn, E. D. Stevens and S. P. Nolan, *Organometallics*, 2003, **22**, 3175.
270 A. A. Danopoulos, N. Tsoureas, J. C. Green and M. B. Hursthouse, *Chem. Commun.*, 2003, 756.
271 R. Dorta, E. D. Stevens, C. D. Hoff and S. P. Nolan, *J. Am. Chem. Soc.*, 2003, **125**, 10490.
272 A. K. D. Lewis, S. Caddick, F. G. N. Cloke, N. C. Billingham, P. B. Hitchcock and J. Leonard, *J. Am. Chem. Soc.*, 2003, **125**, 10066.
273 J. R. Miecznikowski, S. Grundemann, M. Albrecht, C. Megret, E. Clot, J. W. Faller, O. Eisenstein and R. H. Crabtree, *Dalton Trans.*, 2003, 831.
274 M. Froseth, A. Dhindsa, H. Roise and M. Tilset, *Dalton Trans.*, 2003, 4516.
275 M. A. Duin, N. D. Clement, K. J. Cavell and C. J. Elsevier, *Chem. Commun.*, 2003, 400.
276 A. Furstner, G. Seidel, D. Kremzow and C. W. Lehmann, *Organometallics*, 2003, **22**, 907.
277 H. Y. Hou, P. K. Gantzel and C. P. Kubiak, *Organometallics*, 2003, **22**, 2817.
278 H. Y. Hou, P. K. Gantzel and C. P. Kubiak, *J. Am. Chem. Soc.*, 2003, **125**, 9564.
279 G. Y. Lin, N. D. Jones, R. A. Gossage, R. McDonald and R. G. Cavell, *Angew. Chem., Int. Ed.*, 2003, **42**, 4054.
280 V. Dimitrov and A. Linden, *Angew. Chem., Int. Ed.*, 2003, **42**, 2631.
281 R. Waterman and G. L. Hillhouse, *Organometallics*, 2003, **22**, 5182.
282 Z. W. Xiao, B. O. Patrick and D. Dolphin, *Inorg. Chem.*, 2003, **42**, 8125.
283 K. Campbell, R. McDonald, M. J. Ferguson and R. R. Tykwinski, *J. Organomet. Chem.*, 2003, **683**, 379.
284 M. C. Carrion, A. Guerrero, F. A. Jalon, B. R. Manzano, A. de la Hoz, R. M. Claramunt, V. Milata and J. Elguero, *Inorg. Chem.*, 2003, **42**, 885.
285 H. Jude, J. A. K. Bauer and W. B. Connick, *J. Am. Chem. Soc.*, 2003, **125**, 3446.