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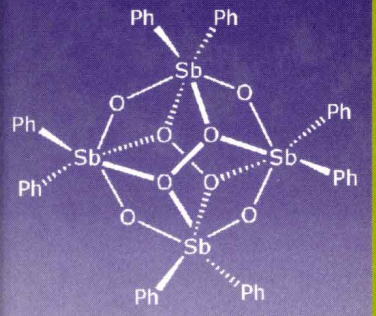

Organometallic *Chemistry*

Volume 32

senior reporter **M. GREEN**

A Specialist Periodical Report

Organometallic Chemistry

Volume 32

A Review of the Literature Published During 2002

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Preface

The interdisciplinary science known as Organometallic Chemistry continues to grow apace with important developments in catalysis, synthetic and theoretical main group, transition metal and lanthanide chemistry, all of which have possible important consequences for synthetic organic chemistry. As before it is a pleasure to thank all of this volume's contributors for capturing the excitement of this important area of science.

Michael Green

Abbreviations

Ac	acetate
acac	acetylacetonate
acacen	*N*,*N*′-ethylenebis(acetylacetone iminate)
Ad	adamantyl
AIBN	azoisobutyronitrile
ampy	2-amino-6-methylpyridine
Ar	aryl
Ar*	2,4,6-tri(*tert*-butyl)phenyl
Ar'_f	3,5-bis(trifluoromethyl)phenyl
arphos	1-(diphenylphosphino)-2-(diphenylarsino)ethane
ATP	adenosine triphosphate
Azb	azobenzene
9-BBN	9-borabicyclo[3.3.1]nonane
BHT	2,6-dibutyl-4-methylphenyl
Biim	biimidazole
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
bipy	2,2′-bipyridyl
Bis	bis(trimethylsilyl)methyl
bma	2,3-bis(diphenylphosphino)maleic anhydride
BNCT	boron neutron capture therapy
Bp	biphenyl
bpcd	4,5-bis(diphenylphosphino)cyclopent-4-ene-1,3-dione
bpk	benzophenone ketyl (diphenylketyl)
Bpz_4	tetra(1-pyrazolyl)borate
Bu^t_2bpy	4,4′-di-*tert*-butyl-2,2′-bipyridine
t-bupy	*tert*-butylpyridine
Bz	benzyl
Bzac	benzoylacetonate
cbd	cyclobutadiene
1,5,9-cdt	cyclododeca-1,5,9-triene
chd	cyclohexadiene
chpt	cycloheptatriene
CIDNP	chemically induced dynamic nuclear polarisation
[Co]	cobalamin
(Co)	cobaloxime [$Co(dmg)_2$ derivative]
cod	cycloocta-1,5-diene
coe	cyclooctene
cot	cyclooctatriene
CP/MAS	cross polarisation/magnetic angle spinning
Cp	η^5-cyclopentadienyl
Cp^R	η^5-alkylcyclopentadienyl

Cp*	η^5-pentamethylcyclopentadienyl
Cp′	trimethylsilylcyclopentadienyl
Cp″	tetramethylethylcyclopentadienyl
CV	cyclic voltammetry(ogram)
CVD	chemical vapour deposition
Cy	cyclohexyl
Cyclam	1,4,8,11-tetraazacyclotetradecane
Cym	*p*-cymene
Cyttp	$PhP(CH_2CH_2CH_2PCy_2)_2$
dab	1,4-diazabutadiene
dabco	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
dbpe	1,2-bis(dibutylphosphino)ethane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCA	9,10-dicyanoanthracene
depe	1,2-bis(diethylphosphino)ethane
depm	1,2-bis(diethylphosphino)methane
DFT	density functional theory
diars	*o*-phenylenebis(dimethyl)arsine
diarsop	{[(2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene)] bis[diphenylarsine]}
dien	diethylenetriamine
diop	{[(2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene)]bis-1-[diphenylphosphine]}
DIPAMP	1,2-bis(phenyl-*o*-anisoylphosphino)ethane
diphos	1,2-bis(diphenylphosphino)ethane
dipp	2,6-diisopropylphenyl
dipyam	di-(2-pyridyl)amine
DMAD	dimethyl acetylenedicarboxylate
DMAP	2-dimethylaminopyridine
dmbpy	dimethylbipyridine
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
dmg	dimethylglyoximate
dmgH	monoanion of dimethylglyoxime
$dmgH_2$	dimethylglyoxime
DMP	dimethylpiperazine
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	bis(dimethylphosphino)methane
dmpz	1,3-dimethylpyrazolyl
DMSO	dimethyl sulfoxide
dpae	1,2-bis(diphenylarsino)ethane
dpam	bis(diphenylarsino)methane
dppa	1,2-bis(diphenylphosphino)ethyne
dppb	1,4-bis(diphenylphosphino)butane
dppbz	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane

DSD	diamond–square–diamond
edt	ethane-1,2-dithiolate
EDTA	ethylenediaminetetraacetate
ee	enantiomeric excess
EELS	electron energy loss spectroscopy
EH MO	extended Hückel molecular orbital
ELF	electron localisation function
en	ethylene-1,2-diamine
ES	MS electrospray mass spectrometry
EXAFS	extended X-ray absorption fine structure
F_6acac	hexafluoroacetylacetonate
Fc	ferrocenyl
Fe*	$Fe(CO)_2Cp^*$
Fp	$Fe(CO)_2Cp$
Fp′	$Fe(CO)_2\eta^5$-(C_5H_4Me)
FTIR	fourier transform infrared
FVP	flash vacuum pyrolysis
glyme	ethyleneglycol dimethyl ether
GVB	generalised valence bond
HBpz3	tris(pyrazolyl)borate
HBpz*3	tris(3,5-dimethylpyrazolyl)borate
H_4cyclen	tetraaza-1,4,7,10-cyclododecane
HEDTA	*N*-hydroxyethylethylenediaminetetraacetate
hfa	hexafluoroacetone
hfacac	hexafluoroacetylacetonato
hfb	hexafluorobutyne
HMPA	hexamethyl phosphoric triamide
HNCC	high nuclearity carbonyl cluster
HOMO	highest occupied molecular orbital
IGLO	individual gauge for localised orbitals
im	imidazole
Is*	2,4,6-triisopropylphenyl
ISEELS	inner shell electron energy loss spectroscopy
KTp	potassium hydrotris(1-pyrazolyl)borate
LDA	lithium diisopropylamide
LiDBB	lithium di-*tert*-butylbiphenyl
LMCT	ligand to metal charge transfer
LNCC	low nuclearity carbonyl cluster
MAO	methyl alumoxane
Me_2bpy	4,4′-dimethyl-2,2′-bypyridyl
Me_6[14]dieneN_4	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
Me_6[14]N_4	5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
4,7-Me_2phen	4,7-dimethyl-1,10-phenanthroline
3,4,7,8-Me_4phen	3,4,7,8,-tetramethyl-1,10-phenanthroline
Mes	mesityl
Mes*	2,4,6-tributylphenyl
MeTHF	methyltetrahydrofuran
mcpba	metachloroperbenzoic acid
MLCT	metal–ligand charge transfer

MTO	methylrhenium trioxide
nap	1-naphthyl
nb	norbornene
nbd	norbornadiene
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NCT	neutron capture theory
Neo	neopentyl
Np	1-naphthyl
np_3	$N(CH_2CH_2PPh_2)_3$
nta	nitrilotriacetate
OEP	octaethylporphyrin
OTf	trifluoromethanesulfonate (triflate)
OTs	*p*-toluenesulfonate (tosylate)
Pc	phthalocyanin
PES	photoelectron spectroscopy
PMDT	pentamethylenediethylenetetramine
pd	pentane-2,4-dionate
phen	1,10-phenanthroline
pic	pyridine-2-carboxylic acid
Pin	(+)-pinanyl
Pmedta	pentamethyldiethylenetriamine
pp_3	$P(CH_2CH_2PPh_2)_3$
$[PPN]^+$	$[(Ph_3P)_2N]^+$
py	pyridine
pydz	pyridazine
pz	pyrazolyl
R-PROPHOS	(*R*)-(+)-1,2-bis(diphenylphosphino)propane
R,R-SKEWPHOS	(2*R*,4*R*)-bis(diphenylphosphino)pentane
RDF	radial distribution function
ROMP	ring opening metathesis polymerisation
sal	salicylaldehyde
salen	*N*,*N*′-bis(salicylaldehydo)ethylenediamine
saloph	*N*,*N*-bisalicylidene-o-phenylenediamine
SCF	self consistent field
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
terpy	2,2′,2″-terpyridyl
tetraphos	1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane
TFA	trifluoroacetic acid
tfbb	tetrafluorobenzobarrelene
tfacac	trifluoroacetylacetonato
THF	tetrahydrofuran
thsa	thiosalicylate (2-thiobenzoate)
tht	tetrahydrothiophen
TMBD	*NNN′N″*-tetramethyl-2-butene-1,4-diamine
TMEDA	(tmena) tetramethylethylenediamine
tmp	2,2,6-6-tetramethylpiperidino
TMS	tetramethylsilane
tol	tolyl

TP	hydrotris(1-pyrazolyl)borate
TP*	hydrotris(2,5-dimethylpyrazolyl)borate
TPP	*meso*-tetraphenylporphyrin
Trip	2,4,6-triisopropylphenyl
Triph	2,4,6-(triphenyl)phenyl
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane
TRIR	time resolved infrared (spectroscopy)
Tsi	tris(trimethylsilyl)methyl $(Me_3Si)_3C$
TTF	tetrathiafulvalene
vi	vinyl
WGSR	water gas shift reaction
XPS	X-ray photoelectron spectroscopy
Xyl	xylyl

Contents

Organometallic Chemistry, Volume 32

1
Theoretical Organometallic Chemistry

BY A.J. BRIDGEMAN

1 Introduction

This chapter aims to cover theoretical and computational studies on organometallic molecules. Section 1 covers the s and p-block elements and Section 2 covers the d- and f-block metals. Clusters, carbonyls and metal-metal bonded systems containing M-C bonds are included. Extended systems and organic species on metal surfaces are excluded except where calculations have been performed on model complexes designed to mimic solid state and surface chemistry.

A wide variety of computational methods is employed in the computational chemistry community. As in previous recent years, density functional theory (DFT) continues to grow in prominence. The vast majority of the work described in this chapter has been performed at the DFT level with the hybrid functional B3LYP being the most popular for studies of organometallic molecules and reactions. 'Traditional' *ab initio* approaches including Hartree-Fock (HF) and post-HF methods (including MP2 and MP4) continue to be used, often for comparison with DFT based methods. Semi-empirical methods now appear to have only limited use except in the molecular mechanics (MM) calculations. A relatively new use of molecular mechanics for large systems is in hybrid calculations where the transition metal and its coordination environment or the reactive centre of a molecule are treated at a higher level leaving the remainder to be treated at the MM level. These QM/MM or ONIOM calculations enable the steric bulk of organometallic molecules to be adequately but computationally efficiently treated and are becoming particularly prevalent in studies of reaction mechanisms and profiles.

Only a brief mention of the computational method is given. Standard abbreviations for computational methods are employed throughout. Given the plethora of basis sets available in modern computational chemistry programs and the variety of basis set designations employed by authors in this field, no description of basis sets is given. The reader should consult the original work for further details of the computational method and the basis set.

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