Ferrocenes

•• Homogeneous Catalysis
•• Organic Synthesis
•• Materials Science

Edited by
Antonio Togni and Tamio Hayashi

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Professor Dr. Antonio Togni
Laboratorium für Anorganische Chemie
Eidgenössische Technische Hochschule
Universitätsstrasse 6
CH-8092 Zürich
Switzerland

Professor Dr. Tamio Hayashi
Department of Chemistry
Faculty of Science
Kyoto University
Sakyo, Kyoto 606-01

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Preface

More than forty years after its serendipitous discovery in 1951 [1], ferrocene still enjoys a great deal of interest from scientists in many areas of research. Due to its high stability and the well-established methods for its incorporation into more complex structures, ferrocene has become a versatile building block for the synthesis of compounds with tailor-made properties.

The wealth of derivatives known is documented by an enormous number of publications. Despite progress in the use of electronic databases, systematic literature searches on ferrocenes still remain difficult. The most viable, useful, and comprehensive source of information about ferrocene is the ten volumes of Gmelin's *Handbook of Inorganic and Organometallic Chemistry* [2] covering the literature up to 1986. The annual reviews on ferrocene, appearing in the *Journal of Organometallic Chemistry* also provide fairly systematic and up-to-date accounts [3]. However, there is no single-volume source available delineating ferrocene chemistry and its applications.

This book is intended to provide an overview of the main areas of research where ferrocene plays a key role, because of both its chemical and physical properties. No attempt has been made to present a comprehensive work, but those areas of ferrocene research that have not been included (e.g., nonlinear-optical materials and flame retardants) either do not bear sufficient material to justify a review, or are no longer of general interest. The title of the book has been adapted from the title of a talk one of us (A. T.) gave in 1991 at an international conference and reflects the development of his own research interests. For this reason the arrangement of the chapters is somewhat arbitrary. However, the book is subdivided into three main sections: Homogeneous Catalysis, Organic Synthesis, and Materials Science, thus conveying its own logic. In order to provide, whenever possible, new perspectives in the different areas treated in the book, the majority of the authors have been recruited from the younger generation of internationally recognized authorities in their specific field. Chapter 1 (A. Hor and K. S. Gan) describes the coordination chemistry and catalytic applications of the unique ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) and serves as a background for the impressive series of successful application of chiral, enantiomerically pure ferrocenylphosphines in asymmetric catalysis, reported in Chapter 2 (T. Hayashi). In Chapter 3, Y. Butsugan and coworkers demonstrate that chiral ferrocene derivatives can not only be incorporated into phosphine ligands for late transition metals, but also into aminoalcohols, which, coordinated to zinc, can be used in catalytic reactions. More about optically active ferrocenes is to be found in Chapter 4, where

R. Herrmann and G. Wagner describe general methods for the preparation of such compounds and their application as templates in synthesis. After these first four chapters, which should be of great interest, in particular to the synthesis-oriented reader, the next three chapters mainly address coordination and electrochemical aspects. Thus, in Chapter 5, M. Herberhold reports on the synthesis and properties of ferrocenes containing heteroelements (mainly of group 16) directly attached to the metallocene core. Such compounds display interesting ligand properties. The incorporation of the redox-active ferrocene fragment into macrocyclic hosts is treated in Chapter 6 (C. D. Hall), whereas structural and electrochemical properties of ferrocene-containing ligands and their complexes are reviewed comprehensively by P. Zanello in Chapter 7. The last three chapters are more interdisciplinary in character, as they address the incorporation of ferrocenes in materials explicitly designed to possess specific physical properties. Thus, the combination of the well-known redox and structural properties of simple, for the most part highly symmetric, ferrocene derivatives allows the preparation of charge-transfer complexes having interesting magnetic behaviors (Chapter 8, A. Togni). A fairly new area of ferrocene research deals with liquid-crystalline materials, as presented in Chapter 9 by R. Deschenaux and J. W. Goodby. Last but not least, a not so novel, but still active area of research is the synthesis of polymers containing ferrocene units. This is reviewed by K. E. Gonsalves and X. Chen in Chapter 10.

We gratefully acknowledge the work done by all authors in presenting up-to-date and well-referenced contributions. Without their effort this volume would not have been possible. Furthermore, it was a pleasure to collaborate with the VCH "crew" in Weinheim. They not only did an excellent job in producing the book, but also helped us in a competent manner in all phases of its preparation. Finally, we are grateful to Dr. Peter Gölitz of *Angewandte Chemie* who originally encouraged the idea of making a book about ferrocene.

Zürich and Kyoto
October 1994

Antonio Togni
Tamio Hayashi

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List of Contributors

Shuki Araki
Department of Applied Chemistry
Nagoya Institute of Technology
Gokiso-cho, Showa-ku
Nagoya 466
Japan

Yasuo Butsugan
Department of Applied Chemistry
Nagoya Institute of Technology
Gokiso-cho, Showa-ku
Nagoya 466
Japan

Xiaohe Chen
Polymer Science Program
Institute of Materials Science, U-136
Department of Chemistry
University of Connecticut
Storrs, CT 06269
USA

Robert Deschenaux
Institut de Chimie
Université de Neuchâtel
Avenue de Bellevaux 51
2000 Neuchâtel
Switzerland

Kim-Suan Gan
Department of Chemistry
Faculty of Science
National University of Singapore
Kent Ridge
Singapore 0511

Kenneth E. Gonsalves
Polymer Science Program
Institute of Materials Science, U-136
Department of Chemistry
University of Connecticut
Storrs, CT 06269
USA

John W. Goodby
School of Chemistry
University of Hull
Hull, HU6 7RX
United Kingdom

C. Dennis Hall
Department of Chemistry
King's College
University of London, Strand
London WC2R 2LS
United Kingdom

Tamio Hayashi
Department of Chemistry
Faculty of Science
Kyoto University
Sakyo, Kyoto 606-01
Japan

Max Herberhold
Laboratorium für Anorganische Chemie
Universität Bayreuth
Universitätsstraße 30
D-95440 Bayreuth
Germany

Rudolf Herrmann
Organisch Chemisches Institut
Technische Universität München
Lichtenbergstraße 4
D-85747 Garching
Germany

T. S. Andy Hor
Department of Chemistry
Faculty of Science
National University of Singapore
Kent Ridge
Singapore 0511

Antonio Togni
Laboratorium für Anorganische Chemie
Eidgenössische Technische Hochschule
Universitätsstrasse 6
8092 Zürich
Switzerland

Gabriele Wagner
Organisch Chemisches Institut
Technische Universität München
Lichtenbergstraße 4
D-85747 Garching
Germany

Makoto Watanabe
Department of Applied Chemistry
Nagoya Institute of Technology
Gokiso-cho, Showa-ku
Nagoya 466
Japan

Piero Zanello
Dipartimento di Chimica
dell'Universita di Siena
Piano dei Mantellini, 44
53100 Siena
Italy

List of Abbreviations

A	acceptor
AIBN	azodi(isobutyronitrile)
Bct	benzene chromium tricarbonyl
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, binaphthyl
BPPFA	(*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)-ferrocenyl]ethylamine
cis-dppet	*cis*-1,2-bis(diphenylphosphino)ethylene
chiraphos	2,3-bis(diphenylphosphino)butane
CIP	Cahn-Ingold-Prelog rules
cod	1,5-cyclooctadiene
COSY	correlated spectroscopy
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethyl cyclopentadienyl
CT	charge transfer
ctb	capped trigonal biprism
CV	Cyclic voltammetry
D	donor
DAG	diacetone-2-keto-1-gluconic acid
dba	1,5-diphenylpenta-1,4-dien-3-one
DBU	1,8-diazabicyclo[5.4.0]undec-1-ene
DCNQI	*N*,*N*′-dicyanoquinonediimine
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DDQH	2,3-dichloro-5,6-dicyanobenzohydroquinone
DFPE	(−)-(*R*,*S*)-1-[2-(diphenylhydroxymethyl)-ferrocenyl]-1-piperidino ethane
DIOP	*P*,*P*′-[2,2-dimethyl-1,3-dioxolane-4,5-diylbis(methylene)]-bis[diphenylphosphane]

DIPAMP	bis[(2-methoxyphenyl)phenylphosphino]ethane
DMAP	4-dimethylaminopyridine
DME	dimethoxyethane
DMF	*N*,*N*-dimethylformamide
dmit	1,3-dithiole-2-thione-4,5-dithiolate
DMSO	dimethylsulfoxide
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
DSC	differential scanning calorimetry
dtpe	1,2-bis(di-*p*-tolylphosphino)ethane
ESR	electron spin resonance
FAB MS	fast-atom bombardment mass spectrometry
fc	1,1′-ferrocenediyl
Fc	ferrocenyl
Fc^+	ferrocenium
FcCNP	1-[(dimethylamino)methyl]-2-(diphenylphosphino)ferrocene
GPC	gel permeation chromatography
$HB(pz)_3$	hydrido-tris(*N*-pyrazolyl)borate
$HB(pz^*)_3$	hydrido-tris(3,5-dimethyl-*N*-pyrazolyl)borate
HLADH	horse liver alcohol dehydrogenase
HOMO	highest occupied molecular orbital
I	isotropic liquid
L	ligand
MDI	4,4′-methylene-bis(phenylisocyanate)
Me_2DCNQI	2,5-dimethyl-*N*,*N*′-dicyanoquinonediimine
mim	*N*-methylimidazole
M_n	number average molecular weight
MWD	molecular weight distribution
N	nematic phase
nbd	norbornadiene
NLO	non-linear optical

NOE	nuclear Overhauser effect
oc	1,1′-osmocenediyl
odppf	1,1′-bis(oxodiphenylphosphoranyl)-ferrocene
PDCI	5,12-bis(cyanoimine)pentacene-7,14-dione
PPFA	(*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]-ethylamine
PPG	poly(propylene glycol)
prophos	1,2-bis(diphenylphosphino)propane
PTCI	5,7,12,14-tetrakis(cyanoimine)pentacene
py	pyridine
QS	quadrupole splitting
rc	1,1′-ruthenocenediyl
Rc	η^1-ruthenocenyl
ROMP	ring opening metathesis polymerization
SCE	standard calomel electrode
SHG	second harmonic generator [efficiency] (sic)
SmA	smectic-A phase
SmC	smectic-C phase
SUMO	singly unoccupied molecular orbital
tbp	trigonal bipyramid
TCIDBT	5,7,12,14-tetrakis(cyanoimine)dibenzo[b,i]thianthrene
TCNE	tetracyanoethylene
TCNQ	tetracyano-*p*-quinodimethane
$TCNQF_4$	tetracyanoperfluoro-*p*-quinodimethane
T_g	glass transition temperature
T_m	melt transition temperature
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TMTSF	tetramethyltetraselenofulvalene
triphos	1,1,1-tris(diphenylphosphino)methylethane
TTF	tetrathiafulvalene
UPS	ultraviolet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy
9-BBN	borabicyclo[3.3.1]nonane

Part 1. Homogeneous Catalysis

1 1,1′-Bis(diphenylphosphino)ferrocene – Coordination Chemistry, Organic Syntheses, and Catalysis

Kim-Suan Gan and T. S. Andy Hor

1.1 Introduction

The use of ferrocenyl phosphines as ligands in coordination chemistry is well known [1 – 12]. The ability of these ligands to convey the ferrocenyl qualities to the resultant complexes without disturbing the inherent characteristics of the latter has widened the scope of metal complexes in the design of catalysts, drugs and materials. As diphosphine complexes metamorphose from their monophosphine analogues and begin to develop their individual traits [13 – 16], it is inevitable that ferrocenyl diphosphines must play a special role in the development of applied organometallic chemistry. Although the metalloligand 1,1′-bis(diphenylphosphino)ferrocene (dppf), which is probably the best developed ferrocenyl diphosphine, was first synthesized more than two decades ago, its chemical uniqueness and industrial importance were not fully appreciated until recently. In this chapter we attempt to trace its development as a coordination ligand and relate its chemistry to a variety of applications. The catalytic potential is emphasized in view of the ever growing influence of homogeneous catalysis in organic synthesis, manipulation of materials and production of fine chemicals.

Derivatives of dppf are beyond the scope of the present discussion and will be excluded. Chiral syntheses using dppf derivatives are covered in Chapter 2 and hence are also omitted. The coordination mode of dppf is usually specified in the complex formulas in the descriptions on coordination chemistry but ignored elsewhere for reasons of clarity. When reference is made to the C_5 ring of dppf, it is often, for the sake of simplicity, referred to as a cyclopentadienyl (Cp) ring, although, strictly speaking, it refers to a phosphinated cyclopentadienyl ring ($C_5H_4PPh_2$). Catalytic discussions are biased towards the complex $PdCl_2$(dppf), as it is with this catalyst that most coupling reactions are reported. Catalysts based on other phosphines are generally overlooked unless a comparison with dppf analogues merits their inclusion.

1.2 Preparation and Complexation

The synthesis of dppf was first recorded in 1965 by the lithiation of ferrocene with *n*-butyllithium, followed by condensation with chlorodiphenylphosphine [17]. A higher yield can be obtained in the presence of *N*, *N*, *N*′, *N*′-tetramethylethylene-

Table 1-1. List of ^{31}P NMR chemical and coordination shifts of some dppf complexes and their coordination geometries [dppf = $Fe(C_5H_4PPh_2)_2$] (blank entries denote unavailable data)

Complex	Coordination geometry	$\delta(^{31}P)$, ppm[a]	Δ ppm[b]	Ref.
$[Fe(C_5H_4PPh_2)_2]$ (dppf)	sandwich	-17.2(s)	–	[1]
		-16.8(s)	–	[2]
$Fe[C_5H_4P(O)Ph_2]_2$	sandwich	28.3(s)	45.5	[3]
Group 5				
$[NEt_4][V(CO)_4$(dppf-*P*, *P′*)]	octahedral	–	–	[4]
$[NEt_4][Ta(CO)_4$(dppf-*P*, *P′*)]	octahedral	–	–	[4]
Group 6				
$Cr(CO)_4$(dppf-*P*, *P′*)	octahedral	52.6(s)	69.8	[4, 5]
$Cr(CO)_5$(dppf-*P*)	octahedral	47.3(s); -17.2(s)	64.5	[5]
$[Cr(CO)_5]_2(\mu$-dppf)	octahedral	47.5(s)	64.7	[5]
$Cr(CO)_5(\mu$-dppf)$Mo(CO)_5$	octahedral	47.5(s,P_{Cr}); 28.5(s,P_{Mo})	64.7(P_{Cr}); 45.7 (P_{Mo})	[6]
$Cr(CO)_5(\mu$-dppf)$W(CO)_5$	octahedral	47.5(s,P_{Cr}); 11.3(t,P_W), J(PW) 247 Hz	64.7(P_{Cr}); 28.5(P_W)	[6]
trans-$[Cr(CO)_4\{(\mu$-dppf)$Cr(CO)_5\}_2]$	octahedral	64.8(s,$P_{Cr'}$); 46.8(s,$P_{Cr''}$)[c]	82.0($P_{Cr'}$); 64.0($P_{Cr''}$)[c]	[7]
trans-$[Cr(CO)_4\{(\mu$-dppf)$Mo(CO)_5\}_2]$	octahedral	64.8(s,P_{Cr}); 27.9(s,P_{Mo})	82.0(P_{Cr}); 45.1(P_{Mo})	[7]
trans-$[Cr(CO)_4\{(\mu$-dppf)$W(CO)_5\}_2]$	octahedral	64.8(s,P_{Cr}); 10.9(t,P_W), J(PW) 247 Hz	82.0(P_{Cr}); 28.1(P_W)	[7]
trans-$[Cr(CO)_4\{(\mu$-dppf)$Fe(CO)_4\}_2]$	octahedral	67.0(s,P_{Fe}); 65.2(s,P_{Cr})	84.2(P_{Fe}); 82.4(P_{Cr})	[7]
trans-$[Cr(CO)_4\{(\mu$-dppf)$Mn_2(CO)_9\}_2]$	octahedral	65.6(s,br,P_{Mn}); 64.6(s,P_{Cr})	82.8(P_{Mn}); 81.8(P_{Cr})	[7]
$Mo(CO)_4$(dppf-*P*, *P′*)	octahedral	33.9(s)	51.1	[4, 5, 8]
$Mo(CO)_5$(dppf-*P*)	octahedral	28.3(s); -17.10(s)	45.5	[5]
$[Mo(CO)_5]_2(\mu$-dppf)	octahedral	28.5(s)	45.7	[5]
$Mo(CO)_5(\mu$-dppf)$W(CO)_5$	octahedral	28.5(s,P_{Mo}); 11.3(t,P_W), J(PW) 247 Hz	45.7(P_{Mo}); 28.5(P_W)	[6]
cis-$[Mo(CO)_4\{(\mu$-dppf)$Mo(CO)_5\}_2]$	octahedral	27.9(s,$P_{Mo''}$); 26.8(s,$P_{Mo''}$)[c]	45.1($P_{Mo''}$); 44.0($P_{Mo'}$)[c]	[7]
cis-$[Mo(CO)_4\{(\mu$-dppf)$Cr(CO)_5\}_2]$	octahedral	46.9(s,P_{Cr}); 26.8(s,P_{Mo})	64.1(P_{Cr}); 44.0(P_{Mo})	[7]

cis-[$Mo(CO)_4\{(\mu\text{-dppf})Fe(CO)_4\}_2$]	octahedral	66.4(s,P_{Fe}); 26.7(s,P_{Mo})	83.6(P_{Fe}); 43.9(P_{Mo})	[7]
cis-[$Mo(CO)_4\{(\mu\text{-dppf})Mn_2(CO)_9\}_2$]	octahedral	65.6(s,P_{Mn}); 26.8(s,P_{Mo})	82.8(P_{Mn}); 44.0(P_{Mo})	[7]
$MoI_2(CO)_2$(dppf-*P*, *P*′)	octahedral	–	–	[9]
$MoI_2(CO)_3$(dppf-*P*, *P*′)	capped octahedral	–	–	[9]
cis-[$MoCl_2(CO)_2$(dppf-*P*, *P*′)(dppf-*P*)]	capped octahedral	–	–	[9]
$Mo_2I_4(CO)_6(\mu\text{-dppf})(XPh_3)_2$ (X = P, As, Sb)	capped octahedral	–	–	[10]
fac-[$Mo(N_2)$(dppf-*P*, *P*′)](triphos)[d]	octahedral	−19.7(d,2P),[e] $^2J(PP)$ 14 Hz	−2.5	[11]
fac-[Mo(dppf-P_a, P'_b)(dppf-P_c)(triphos)][d]	octahedral	37.0(dt,P_a); −20.9(s,P_d);[f] −21.9(d,P_b,P_c), $^2J(P_bP_c)$ 3.7 Hz	54.2(P_a); −3.7(P_d); −4.7(P_b,P_c)	[11]
$W(CO)_4$(dppf-*P*, *P*′)	octahedral	18.4(t), J(PW) 239 Hz	35.6	[4, 5]
$W(CO)_5$(dppf-*P*)	octahedral	11.3(t), J(PW) 249 Hz; −17.1(s)	28.5	[5]
$[W(CO)_5]_2(\mu\text{-dppf})$	octahedral	11.3(t), J(PW) 244 Hz	28.5	[5]
trans-[$W(CO)_4\{(\mu\text{-dppf})W(CO)_5\}_2$]	octahedral	16.2(t,$P_{W'}$), J(PW′) 283 Hz; 11.2(t,$P_{W''}$), J(PW″) 249 Hz[c]	33.4($P_{W'}$); 28.4($P_{W''}$)[c]	[7]
trans-[$W(CO)_4\{(\mu\text{-dppf})Cr(CO)_5\}_2$]	octahedral	15.6(t,P_W), J(PW) 282 Hz; 46.8(s,P_{Cr})	32.8(P_W); 64.0(P_{Cr})	[7]
cis-[$W(CO)_4\{(\mu\text{-dppf})Cr(CO)_5\}_2$]	octahedral	20.6(t,P_W), J(PW) 244 Hz; ≈47(s,br,P_{Cr})	37.8(P_W); ≈64.2(P_{Cr})	[7]
$[Et_4N][W_2(\mu\text{-H})(CO)_8(\mu\text{-dppf})]$	octahedral	10.1, J(PW) 219 Hz	27.3	[12]
$WI_2(CO)_3$(dppf-*P*, *P*′)	capped octahedral	–	–	[9]
$[W_2I_2(CO)_2(\mu\text{-dppf})$(dppm-*P*, *P*′)$_2(\eta^2\text{-}MeC_2Me)_2][BF_4]_2$	octahedral	–	–	[13]
$W_2I_4(CO)_6(\mu\text{-dppf})(XPh_3)_2$ (X = P, As, Sb)	capped octahedral	–	–	[10]
Group 7				
$[Mn_2(CO)_9]_2(\mu\text{-dppf})$	octahedral	66.4(s,br)	83.6	[14]
$Mn_2(CO)_9(\mu\text{-dppf})Cr(CO)_5$	octahedral	66.2(s,br,P_{Mn}); 47.5(s,P_{Cr})	83.4(P_{Mn}); 64.7(P_{Cr})	[6]
$Mn_2(CO)_9(\mu\text{-dppf})Mo(CO)_5$	octahedral	66.2(s,br,P_{Mn}); 28.5(s,P_{Mo})	83.4(P_{Mn}); 45.7(P_{Mo})	[6]
$Mn_2(CO)_9(\mu\text{-dppf})W(CO)_5$	octahedral	66.2(s,br,P_{Mn}); 11.3(t,P_W), J(PW) 244 Hz	83.4(P_{Mn}); 28.5(P_W)	[6]

Table 1-1. (continued)

Complex	Coordination geometry	$\delta(^{31}P)$, ppm[a]	Δ ppm[b]	Ref.
$Mn(\eta^5\text{-}MeCp)(CO)_2(dppf\text{-}P)$	3-legged piano-stool	84.7(s); −17.2(s)	101.9	[15]
$Mn(\eta^5\text{-}MeCp)(CO)(dppf\text{-}P,P')$	3-legged piano-stool	not observed due to exchange	–	[15–17]
cis-$[Mn_2Cl_2(CO)_8(\mu\text{-}dppf)]$	octahedral	40.3(s)	57.5	[15, 18]
$[Re_2(CO)_9]_2(\mu\text{-}dppf)$	octahedral	5.8(s)	23.0	[3]
$Re_2(CO)_9(dppf\text{-}P)$	octahedral	$5.7(s,P_{Re})$; $-17.0(s,P_{free})$	$22.9(P_{Re})$	[3]
$Re_2(CO)_9(dppfO\text{-}P)^g$	octahedral	$28.4(s,P{=}O)$; $5.7(s,P_{Re})$	$45.6(P{=}O)$; $22.9(P_{Re})$	[3]
fac-$[ReBr(CO)_3(dppf\text{-}P,P')]$	octahedral	0.27(s)	17.47	[3]
fac-$[ReCl(CO)_3(dppf\text{-}P,P')]$	octahedral	2.8	20.0	[19]
cis-$[Re_2Cl_2(CO)_8(\mu\text{-}dppf)]$	octahedral	−3.4(s)	13.8	[20]
cis-$[Re_2Br_2(CO)_8(\mu\text{-}dppf)]$	octahedral	−7.4(s)	9.8	[20]
$(cis\text{-}Br)(OC)_4Re(\mu\text{-}dppf)Re(trans\text{-}Br)(CO)_4$	octahedral	5.1(s,*trans*-P); −7.7(s,*cis*-P)	22.3(*trans*-P), 24.9(*cis*-P)	[20]
$Re_2(\mu\text{-}OMe)_2(CO)_6(\mu\text{-}dppf)$	octahedral	5.5(s)	22.5	[21]
$Re(MeCO_2\text{-}O)(CO)_3(dppf\text{-}P,P')$	octahedral	7.9(s)	25.1	[21]
$[Re_2(CO)_9(Ph_2P(C_5H_4)Fe(C_5H_4)PMePh_2)]I$	octahedral	$24.4(s,P_{Me})$; $5.5(s,P_{Re})$	$41.6(P_{Me})$; $22.7(P_{Re})$	[3]
Group 8				
$Fe(CO)_3(dppf\text{-}P,P')$	trigonal bipyramidal	62.0(s)	79.3	[22, 23]
$Fe(CO)_4(dppf\text{-}P)$	trigonal bipyramidal	66.8(s); −17.1(s)	84.0	[22, 23]
$[Fe(CO)_4]_2(\mu\text{-}dppf)$	trigonal bipyramidal	67.0(s)	84.2	[22, 23]
$Fe_2(CO)_7(dppf\text{-}P,P')$	octahedral	73.5(s); 64.6(s)	90.7; 81.8	[24]
$Fe(CO)_4(\mu\text{-}dppf)Cr(CO)_5$	Fe: trigonal bipyramidal Cr: octahedral	$67.0(s,P_{Fe})$; $47.4(s,P_{Cr})$	$84.2(P_{Fe})$; $64.6(P_{Cr})$	[14]

$Fe(CO)_4(\mu\text{-dppf})Mo(CO)_5$	Fe: trigonal bipyramidal Mo: octahedral	$67.0(s,P_{Fe}); 28.4(s,P_{Mo})$	$84.2(P_{Fe}); 45.6(P_{Mo})$	[22]
$Fe(CO)_4(\mu\text{-dppf})W(CO)_5$	Fe: trigonal bipyramidal W: octahedral	$67.0(s,P_{Fe}); 11.2(t,P_W)$, J(PW) 244 Hz	$84.2(P_{Fe}); 28.4(P_W)$	[14]
$Fe(CO)_4(\mu\text{-dppf})Mn_2(CO)_9$	Fe: trigonal bipyramidal Mn: octahedral	$67.1(s,P_{Fe}); 66.3(s,P_{Mn})$	$84.3(P_{Fe}); 83.5(P_{Mn})$	[14]
$RuCl(\eta^5\text{-}C_5H_5)(dppf\text{-}P,P')$	3-legged piano-stool	–	–	[25]
$Ru(\eta^5\text{-}C_5H_5)H(dppf\text{-}P,P')$	3-legged piano-stool	–	–	[25]
$[Ru(\eta^5\text{-}C_5H_5)(dppf\text{-}P,P')(CH_3CN)]X$ $[X = PF_6, BF_4, BPh_4]$	3-legged piano-stool	–	–	[26]
$[Ru(\eta^5\text{-}C_5H_5)(CO)(dppf\text{-}P,P')]X$ $[X = BF_4, PF_6]$	3-legged piano-stool	–	–	[26]
$[Ru(C{=}CHR)(\eta^5\text{-}C_5H_5)(dppf\text{-}P,P')][PF_6]$ [R = Ph, *t*Bu, Fc(ferrocenyl)]	3-legged piano-stool	–	–	[26]
$[Ru(C{\equiv}CR)(\eta^5\text{-}C_5H_5)(dppf\text{-}P,P')]$ $[R = Ph, tBu, C_6H_{13}, Fc, CO_2Me]$	3-legged piano-stool	–	–	[26]
$Ru\{C(OMe){=}CH(CO_2Me)\}(\eta^5\text{-}C_5H_5)(dppf\text{-}P,P')$	3-legged piano-stool	–	–	[26]
$Ru\{C(CO_2Me){=}CH(CO_2Me)\}(\eta^5\text{-}C_5H_5)(dppf\text{-}P,P')$	3-legged piano-stool	–	–	[25]
$Ru(\eta^3\text{-}C_3H_5)\{\eta^3\text{-}[OC(CF_3)]_2CH\}(dppf\text{-}P,P')^h$	pseudo-octahedral	58.5(d); 24.5(d), $^2J(PP)$ 34 Hz	75.7; 41.7	[27]
$[RuH(dppf\text{-}P,P')_2(\eta^2\text{-}H_2)][PF_6]$	distorted octahedral	38.2(br)	55.4	[28]
$Ru_2(\mu\text{-}pz)_2(CO)_4(dppf\text{-}P)_2{}^i$	octahedral	–	–	[29]

Table 1-1. (continued)

Complex	Coordination geometry	$\delta(^{31}P)$, ppm[a]	Δ ppm[b]	Ref.
Group 9				
$CoCl_2$(dppf-P, P')	tetrahedral	–	–	[2, 4]
[$Co(acac)_2$(dppf-P, P')][BF_4]	octahedral	–	–	[30]
[$Co(dtc)_2$(dppf-P, P')][BF_4][j]	octahedral	–	–	[30]
[Rh(dppf-P, P')$_2$][BPh_4]	distorted square planar	22.2(d), J(RhP) 144 Hz	39.4	[31]
[Rh(dppf-P, P')(nbd)][ClO_4]	square planar	14.8(d), J(RhP) 161 Hz	32.0	[8, 32, 33]
[Rh(dppf-P, P')(cod)][ClO_4]	square planar	22.0(d), J(RhP) 149 Hz	39.2	[32, 34]
Rh{(η^6-C_6H_5)B(C_6H_5)$_3$}(dppf-P, P')	2-legged piano-stool	43.0(d), J(RhP) 212 Hz	60.2	[32]
Rh_2(μ-S-*t*Bu)$_2$(CO)$_2$(μ-dppf)	square planar	27.0(d), J(Rh-P) 156 Hz	44.2	[34]
$Rh_2H_2(CO)_2$(dppf-P, P')$_2$(μ-dppf)	trigonal bipyramidal	–	–	[35]
[Ir(dppf-P, P')$_2$][BPh_4]	distorted square planar	7.7	24.9	[31]
Group 10				
NiX_2(dppf-P, P') (X = Cl, Br)	tetrahedral	–	–	[2, 4, 8, 36]
cis-[$PdCl_2$(dppf-P, P')]	square planar	34.0(s)	51.2	[2, 8, 37]
1-{(dppf-P, P')Pd}B_3H_7	square planar	12.5(s)	29.7	[38]
[Pd(μ-Cl)(dppf-P, P')]$_2$[BF_4]$_2$	square planar	46.5(s)	63.7	[39]
[Pd(μ-OH)(dppf-P, P')]$_2$[BF_4]$_2$	square planar	38.7(s)	55.9	[39]
[Pd(dppf-P, P')(PPh_3)][BF_4]$_2$	square planar	–	–	[40, 41]
trans-[$PdCl_2${(μ-dppf)Cr(CO)$_5$}$_2$]	Pd: square planar	47.5(s,P_{Cr}); 14.7(s,P_{Pd})	64.7(P_{Cr}); 31.9(P_{Pd})	[42]
trans-[$PdCl_2${(μ-dppf)Mo(CO)$_5$}$_2$]	Pd: square planar	28.5(s,P_{Mo}); 14.7(s,P_{Pd})	45.7(P_{Mo}); 31.9(P_{Pd})	[42]
trans-[$PdCl_2${(μ-dppf)W(CO)$_5$}$_2$]	Pd: square planar	14.7(s,P_{Pd}); 11.2(t,P_W), J(PW) 247 Hz	31.9(P_{Pd}); 28.4(P_W)	[42]
cis-[$PtCl_2$(dppf-P, P')]	square planar	13.1, J(PtP) 3769 Hz	30.3	[1, 2, 43, 44]