

Chemistry of Precious Metals

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Preface

Some 20 years ago, I was privileged to share in writing a book on the descriptive chemistry of the 4d, 5d, 4f and 5f metals that included these eight elements within its compass (S.A. Cotton and F.A. Hart, *The Heavy Transition Elements*, Macmillan, 1975). This volume shares the same aim of covering the descriptive chemistry of silver, gold and the six platinum metals in some detail at a level suitable for advanced undergraduate and postgraduate study.

It does not attempt to be a comprehensive treatise on the chemistry of these metals. It attempts to fill a slot between the general text and the in-depth review or monograph. The organometallic chemistry is confined to σ -bonded compounds in normal oxidation states; compounds with π -bonding ligands are generally excluded. Their inclusion would have increased the length of the book considerably and, moreover, their recent chemistry has been extensively and expertly reviewed in the new *Comprehensive Organometallic Chemistry, II*, eds G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon, Oxford, 1995.

I have concentrated upon providing information on 'essential' binary compounds and complexes of these elements – oxides, halides, aqua complexes, amines and tertiary phosphine complexes, for example – and highlighting key areas of study rather than giving comprehensive coverage (impossible outside a monograph). It is easy to be seduced by the 'latest thing' in research to the detriment of more fundamental, if prosaic, topics (in any case, there are other texts that provide up to the moment coverage of all research developments). There is still a lot of basic research waiting to be done out there and we have all heard the horror stories of students who can produce *ab initio* MO calculations at the drop of a hat yet think that sodium chloride is a green gas. The data are intended to illustrate trends in the chemistry and not to replace it; theories explain facts and not vice versa. I make no apology for this approach; a sound factual understanding is fundamental to any scientific discipline.

My first priority has, therefore, been to try to provide 'the facts' (and I hope that I have got (most of) them right) but I have tried to write the book with the needs of the teacher in mind, by providing plenty of bond lengths and also spectroscopic data (mainly vibrational, with a little NMR and ESR) that can be used as a teaching tool by hard-pressed lecturers or tutors who have not time to look up the information themselves.

The bibliography is intended to give key references (particularly to structures), not just to the recent literature (which can be hard to find because they

are not yet in compilations) but in some cases to relevant older work (which can also be hard to find because everyone assumes that you know them); it begins for each chapter with a listing of the relevant sections of Gmelin and of the various 'Comprehensive Chemistries' and monographs. I have attempted to follow the literature received up to March 1996.

Some readers may feel that I have been unduly optimistic (or just plain presumptuous) in writing this book, when I am not actually carrying out research on any of these metals. They may well be right, though I would point out that the spectator does get a different view of events on the sports fields to that obtained by the player.

Producing a book like this is impossible without access to the primary literature, for which I am mainly indebted to the Chemistry Department of the University of Cambridge, and to Mrs Cheryl Cook in particular.

Much of the background reading, especially for osmium and gold, as well as work on the bibliography was done in the course of visits to l'Abbaye N-D du Bec-Hellouin; it is again a pleasure to give thanks to Dom Philibert Zobel O.S.B., Abbot of Bec, and to the monastic community for the shelter of their roof and a calm and sympathetic environment.

I should like to take the opportunity to thank all those who have supplied information, answered questions or discussed points with me, including the late Sir Geoffrey Wilkinson; Professors S. Ahrland, K.G. Caulton, F.A. Cotton, W.P. Griffith, D.M.P. Mingos, J.D. Woollins and R.K. Pomeroy; and Drs A.J. Blake, P.R. Raithby, S.D. Robinson and P. Thornton. They are not, of course, responsible for the use I have made of the information.

I am particularly grateful to Dr John Burgess for reading the whole manuscript in (a very rough) draft and making many helpful suggestions for improvement, some of which I have been wise enough to adopt. John has also been an invaluable sounding board for ideas. I must also thank three (anonymous) reviewers for drawing my attention to a number of omissions, mistakes and ambiguities, which I hope have now been resolved.

I should finally like to thank Patricia Morrison for her encouragement in the earlier part of the project and Louise Crawford for patient, sympathetic and accurate typing.

Simon Cotton
Uppingham
December 1996

Abbreviations

acac	acetylacetonate, $\text{CH}_3\text{COCHCOCH}_3$
Ar	aryl
bipy	bipyridyl (usually 2,2'-bipyridyl)
Bu or Bu ⁿ	<i>n</i> -butyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$
Bu ^t	<i>t</i> -butyl, $(\text{CH}_3)_3\text{C}$
bz	benzyl
cod	cycloocta-1,5-diene
cy	cyclohexyl, cyclo- C_6H_{11}
cyclam	1,4,8,11-tetraazaacyclotetradecane
depe	bis(dimethylphosphino)ethane
diars	<i>o</i> -phenylenebis(dimethylarsine), $\text{C}_6\text{H}_4(\text{AsMe}_2)_2$
dien	diethylenetriamine, $\text{HN}[(\text{CH}_2)_2\text{NH}_2]_2$
dimphen	2,9-dimethylphenanthroline
dme	1,2-dimethoxyethane, glyme
DMF	<i>N,N</i> -dimethylformamide
dmg	dimethylglyoximate
dmpe	bis(dimethylphosphino)ethane
DMSO	dimethylsulphoxide, Me_2SO
dppe	1,2-bis(diphenylphosphino)ethane, $\text{Ph}_2(\text{CH}_2)_2\text{Ph}_2$
dppm	1,2-bis(diphenylphosphino)methane, $\text{Ph}_2(\text{CH}_2)\text{Ph}_2$
dppp	1,2-bis(diphenylphosphino)propane, $\text{Ph}_2(\text{CH}_2)_3\text{Ph}_2$
dppz	bis(diphenylphosphino)benzene
EDTA	ethylenediamine tetracetate (4-)
en	1,2-diaminoethane, ethylenediamine
equ	2-ethyl-8-quinolinate
Et	ethyl
Et ₄ dien	<i>N,N,N',N'</i> -tetraethyldiethylenetriamine, $\text{HN}[(\text{CH}_2)_2\text{NEt}_2]_2$
im	imidazole
M-CPBA	<i>m</i> -chloroperoxybenzoic acid
Me	methyl
mes	mesityl, 2,4,6-trimethylphenyl
MNTS	<i>N</i> -methyl- <i>N</i> -nitrosotoluene sulphonamide
ncs	<i>N</i> -chlorosuccinamide
np	naphthyl
OEP	octaethylporphyrin
Ph	phenyl
phen	1,10-phenanthroline

PP	2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene
Pr	propyl, $\text{CH}_3\text{CH}_2\text{CH}_2$
Pr ⁱ	isopropyl, $(\text{CH}_3)_2\text{CH}$
py	pyridine, $\text{C}_5\text{H}_5\text{N}$
py ₂ CH ₂	dipyridiniomethane, $(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2$
pz	pyrazole
tacn	1,4,7-triazacyclononane, [9]aneN ₃
terpy	2,2':6,2''-terpyridyl
thf	tetrahydrofuran
tht	tetrahydrothiophene
TMP	tetramesitylporphyrin
tmpp	tris(2,4,6-trimethoxyphenyl)phosphine
tmu	tetramethylthiourea
TPP	tetraphenylporphyrin
trien	triethylenetetramine, $\text{N}[(\text{CH}_2)_2\text{NH}_2]_3$
ttn	1,4,7-trithiacyclononane, 9S ₃
tu	thiourea, $(\text{H}_2\text{N})_2\text{CS}$
9S ₃	1,4,7-trithiacyclononane
10S ₃	1,4,7-trithiacyclodecane
14[ane]N ₄	1,4,8,11-tetraazaacyclotetracane, cyclam
14S ₄	1,4,8,11-tetrathiacyclotetradecane
18S ₆	1,4,8,11,14,17-hexathiacyclooctadecane

All bond lengths given in ångström units ($1 \text{ \AA} = 0.1 \text{ nm}$)