Contents

Intr	oductio	on and Survey	
1.1	Prolog	·	1
	1.1.1	From Werner to the new transition metal chemistry	1
	1.1.2	Prior to about 1963	2
1.2	How It	· All Began	3
	1.2.1	Rhenium chemistry from 1963 to 1965	3
	1.2.2	The recognition of the quadruple bond	7
	1.2.3	Initial work on other elements	8
1.3	An Ove	erview of the Multiple Bonds	12
	1.3.1	A qualitative picture of the quadruple bond	13
	1.3.2	Bond orders less than four	15
	1.3.3	Oxidation states	15
1.4.	Growth of the Field		
1.5	Going	Beyond Two	19
Com	plexes	of the Group 5 Elements	
2.1	Genera	l Remarks	23
2.2	Divana	dium Compounds	23
	2.2.1	Triply-bonded divanadium compounds	24
	2.2.2	Metal-metal vs metal-ligand bonding	27
	2.2.3	Divanadium compounds with the highly reduced V_2^{3+} core	27
2.3	Diniob	ium Compounds	29
	2.3.1	Diniobium paddlewheel complexes	29
	2.3.2	Diniobium compounds with calix[4] arene ligands and related species	31
2.4	Tantalı	ım	32

Chr	omium	Compounds				
3.1	Dichro	omium Tetracarboxylates	35			
	3.1.1	History and preparation	35			
	3.1.2	Properties of carboxylate compounds	38			
	3.1.3	Unsolvated Cr ₂ (O ₂ CR) ₄ compounds	40			
3.2	Other	Paddlewheel Compounds	43			
	3.2.1	The first 'supershort' bonds	43			
	3.2.2	2-Oxopyridinate and related compounds	47			
	3.2.3	Carboxamidate compounds	50			
	3.2.4	Amidinate compounds	52			
	3.2.5	Guanidinate compounds	56			
3.3	Miscel	laneous Dichromium Compounds	57			
	3.3.1	Compounds with intramolecular axial interactions	57			
	3.3.2	Compounds with Cr–C bonds	60			
	3.3.3	Other pertinent results	61			
3.4	Conclu	nding Remarks	65			
Mol	ybdeni	ım Compounds				
4.1	Dimol	ybdenum Bridged by Carboxylates or Other O,O Ligands	69			
	4.1.1	General remarks	69			
	4.1.2	Mo ₂ (O ₂ CR) ₄ compounds	70			
	4.1.3	Other compounds with bridging carboxyl groups	79			
	4.1.4	Paddlewheels with other O,O anion bridges	92			
4.2	Paddle	Paddlewheel Compounds with O,N, N,N and Other Bridging Ligands				
	4.2.1	Compounds with anionic O,N bridging ligands	95			
	4.2.2	Compounds with anionic N,N bridging ligands	98			
	4.2.3	Compounds with miscellaneous other anionic bridging ligands	103			
4.3	Non-P	addlewheel Mo ₂ ⁴⁺ Compounds	105			
	4.3.1	$Mo_2X_8^{4-}$ and $Mo_2X_6(H_2O)_2^{2-}$ compounds	105			
	4.3.2	$[Mo_2X_8H]^{3-}$ compounds	108			
	4.3.3	Other aspects of dimolybdenum halogen compounds	109			
	4.3.4	M ₂ X ₄ L ₄ and Mo ₂ X ₄ (LL) ₂ compounds	111			
	4.3.5	Cationic complexes of Mo ₂ ⁴⁺	130			
	4.3.6	Complexes of Mo ₂ ⁴⁺ with macrocyclic, polydentate and chelate ligands	132			
	4.3.7	Alkoxide compounds of the types Mo ₂ (OR) ₄ L ₄ and Mo ₂ (OR) ₄ (LL) ₂	134			

4.4	Other .	Aspects of Mo ₂ ⁴⁺ Chemistry	136
	4.4.1	Cleavage of Mo ₂ ⁴⁺ compounds	136
	4.4.2	Redox behavior of Mo ₂ ⁴⁺ compounds	137
	4.4.3	Hydrides and organometallics	142
	4.4.4	Heteronuclear Mo–M compounds	145
	4.4.5	An overview of Mo–Mo bond lengths in Mo ₂ ⁴⁺ compounds	148
4.5	Higher	order Arrays of Dimolybdenum Units	148
	4.5.1	General concepts	148
	4.5.2	Two linked pairs with carboxylate spectator ligands	154
	4.5.3	Two linked pairs with nonlabile spectator ligands	155
	4.5.4	Squares: four linked pairs	160
	4.5.5	Loops: two pairs doubly linked	162
	4.5.6	Rectangular cyclic quartets	164
	4.5.7	Other structural types	166
Tun	gsten (Compounds	
5.1	Multip	le Bonds in Ditungsten Compounds	183
5.2	The W	² Tetracarboxylates	183
5.3	W_{2}^{4+}	Complexes Containing Anionic Bridging Ligands Other	
	Than C	Carboxylate	189
5.4	W_{2}^{4+} C	Complexes without Bridging Ligands	191
	5.4.1	Compounds coordinated by only anionic ligands	191
	5.4.2	Compounds coordinated by four anionic ligands and	
		four neutral ligands	192
5.5	Multip	le Bonds in Heteronuclear Dimetal Compounds of	
	Molybo	denum and Tungsten	196
5.6	Paddle	wheel Compounds with W_2^{5+} or W_2^{6+} Cores	197
X_3N	I≡MX ₃	Compounds of Molybdenum and Tungsten	
6.1	Introdu	action	203
6.2	Homol	eptic $X_3M=MX_3$ Compounds	204
	6.2.1	Synthesis and characterization of homoleptic M_2X_6 compounds	204
	6.2.2	Bonding in M ₂ X ₆ compounds	208
	6.2.3	$X_3M=MX_3$ Compounds as Molecular Precursors to Extended Solids	210
6.3	M_2X_2	NMe_2) ₄ and $M_2X_4(NMe_2)_2$ Compounds	210

6.4	Other !	$M_2X_2Y_4$, M_2X_{6-n} Y_n and Related Compounds	212
	6.4.1	Mo ₂ X ₂ (CH ₂ SiMe ₃) ₄ compounds	215
	6.4.2	1,2-M ₂ R ₂ (NMe ₂) ₄ compounds and their derivatives	217
6.5	M ₄ Co	mplexes: Clusters or Dimers?	218
	6.5.1	Molybdenum and tungsten twelve-electron clusters $M_4(OR)_{12}$	218
	6.5.2	$M_4X_4(OPr')_8$ (X = Cl, Br) and $Mo_4Br_3(OPr')_9$	220
	6.5.3	$W_4(p\text{-tolyl})_2(\text{OPr}^i)_{10}$	221
	6.5.4	$W_4O(X)(OPr')_9$, $(X = Cl \text{ or } OPr')$	221
	6.5.5	$K(18\text{-crown-6})_2Mo_4(\mu_4\text{-H})(OCH_2Bu')_{12}$	221
	6.5.6	Linked M_4 units containing localized MM triple bonds	222
6.6	M_2X_6L	, $M_2X_6L_2$ and Related Compounds	223
	6.6.1	$Mo_2(CH_2Ph)_2(OPr^i)_4(PMe_3)$ and $[Mo_2(OR)_7]^{-1}$	223
	6.6.2	M ₂ (OR) ₆ L ₂ compounds and their congeners	224
	6.6.3	Amido-containing compounds	226
	6.6.4	$Mo_2Br_2(CHSiMe_3)_2(PMe_3)_4$	228
	6.6.5	Calix[4]arene complexes	228
6.7	Triple	Bonds Uniting Five- and Six-Coordinate Metal Atoms	229
6.8	Redox	Reactions at the M ₂ ⁶⁺ Unit	230
6.9	Organo	ometallic Chemistry of M ₂ (OR) ₆ and Related Compounds	232
	6.9.1	Carbonyl adducts and their products	232
	6.9.2	Isocyanide complexes	234
	6.9.3	Reactions with alkynes	234
	6.9.4	Reactions with C≡N bonds	236
	6.9.5	Reactions with C=C bonds	237
	6.9.6	Reactions with H ₂	240
	6.9.7	Reactions with organometallic compounds	241
	6.9.8	$(\eta^5-C_5H_4R)_2W_2X_4$ compounds where $R=Me, Pr^i$ and $X=Cl, Br$	241
6.10	Conclu	sion	242
Tech	netiur	n Compounds	
7.1	Synthe	sis and Properties of Technetium	251
7.2	Preparation of Dinuclear and Polynuclear Technetium Compounds 25		
7.3	Bonds	of Order 4 and 3.5	252
7.4	Tc ₂ ⁶⁺ as	nd Tc ₂ ⁵⁺ Carboxylates and Related Species with Bridging Ligands	257

7.5	Bonds of Order 3		261	
7.6	Hexan	uclear and Octanuclear Technetium Clusters	265	
Rhe	nium (Compounds		
8.1	The La	st Naturally Occurring Element to Be Discovered	271	
8.2	Synthe	sis and Structure of the Octachlorodirhenate(III) Anion	273	
8.3	Synthe	sis and Structure of the Other Octahalodirhenate(III) Anions	278	
8.4	Substi	tution Reactions of the Octahalodirhenate(III) Anions that		
	Proceed with Retention of the Re ₂ ⁶⁺ Core			
	8.4.1	Monodentate anionic ligands	280	
	8.4.2	The dirhenium(III) carboxylates	282	
	8.4.3	Other anionic ligands	292	
	8.4.4	Neutral ligands	298	
8.5	Dirhenium Compounds with Bonds of Order 3.5 and 3			
	8.5.1	The first metal-metal triple bond: Re ₂ Cl ₅ (CH ₃ SCH ₂ CH ₂ SCH ₃) ₂ and		
		related species	302	
	8.5.2	Simple electron-transfer chemistry involving the		
		octahalodirhenate(III) anions and related species that contain		
		quadruple bonds	303	
	8.5.3	Oxidation of $[Re_2X_8]^{2-}$ to the nonahalodirhenate		
		anions $[Re_2X_9]^{n-}$ (n = 1 or 2)	307	
	8.5.4	Re25+ and Re24+ halide complexes that contain phosphine ligands	309	
	8.5.5	Other Re25+ and Re24+ complexes	359	
	8.5.6	Other dirhenium compounds with triple bonds	360	
8.6	Dirher	nium Compounds with Bonds of Order Less than 3	361	
8.7	Cleavage of Re–Re Multiple Bonds by σ -donor and π -acceptor Ligands		361	
	8.7.1	σ-Donor ligands	362	
	8.7.2	π-Acceptor ligands	363	
8.8	Other Types of Multiply Bonded Dirhenium Compounds			
8.9	Postscript on Recent Developments 3			

Ruthenium Compounds 9.1 Introduction 377 Ru₂⁵⁺ Compounds 9.2 378 Ru₂⁵⁺ compounds with O,O'-donor bridging ligands 382 Ru₂⁵⁺ compounds with N,O-donor bridging ligands 9.2.2 391 Ru25+ compounds with N,N'-donor bridging ligands 9.2.3 396 9.3 Ru₂⁴⁺ Compounds 404 9.3.1 Ru2⁴⁺ compounds with O,O'-donor bridging ligands 405 Ru₂⁴⁺ compounds with N,O-donor bridging ligands 9.3.2 409 Ru24+ compounds with N,N'-donor bridging ligands 9.3.3 411 Ru₂⁶⁺ Compounds 414 9.4 9.4.1 Ru₂⁶⁺ compounds with O,O'-donor bridging ligands 415 9.4.2 Ru26+ compounds with N,N'-donor bridging ligands 416 9.5 Compounds with Macrocyclic Ligands 422 9.6 **Applications** 422 9.6.1 Catalytic activity 422 9.6.2 Biological importance 423 Osmium Compounds Syntheses, Structures and Reactivity of Os₂⁶⁺ Compounds 431 Syntheses and Structures of Os₂⁵⁺ Compounds 437 10.3 Syntheses and Structures of Other Os₂ Compounds 438 Magnetism, Electronic Structures, and Spectroscopy 10.4 439 10.5 Concluding Remarks 444 Iron, Cobalt and Iridium Compounds 11.1 General Remarks 447 11.2 Di-iron Compounds 447 11.3 Dicobalt Compounds 451 11.3.1 Tetragonal paddlewheel compounds 451 11.3.2 Trigonal paddlewheel compounds 453 11.3.3 Dicobalt compounds with unsupported bonds 454 11.3.4 Compounds with chains of cobalt atoms 455

11.4	Di-iridium Compounds				
	11.4.1	Paddlewheel compounds and related species	455		
	11.4.2	Unsupported Ir–Ir bonds	458		
	11.4.3	Other species with Ir–Ir bonds	459		
	11.4.4	Iridium blues	461		
Rho	dium C	Compounds			
12.1	Introdu	action	465		
12.2	Dirhod	ium Tetracarboxylato Compounds	466		
	12.2.1	Preparative methods and classification	466		
	12.2.2	Structural studies	469		
12.3	Other I	Dirhodium Compounds Containing Bridging Ligands	493		
	12.3.1	Complexes with fewer than four carboxylate bridging groups	493		
	12.3.2	Complexes supported by hydroxypyridinato, carboxamidato and			
		other (N, O) donor monoanionic bridging groups	505		
	12.3.3	Complexes supported by amidinato and other (N, N) donor			
		bridging groups	512		
		Complexes supported by sulfur donor bridging ligands	521		
		Complexes supported by phosphine and (P, N) donor bridging ligands	524		
	12.3.6	Complexes supported by carbonate, sulfate and phosphate			
		bridging groups	527		
12.4	Dirhod	ium Compounds with Unsupported Rh–Rh Bonds	528		
	12.4.1	The dirhodium(II) aquo ion	528		
	12.4.2	The $[Rh_2(NCR)_{10}]^{4+}$ cations	529		
	12.4.3	Complexes with chelating and macrocyclic nitrogen ligands	530		
12.5	1				
	12.5.1	Complexes with isocyanide ligands	533		
	12.5.2	Rhodium blues	536		
12.6.	Reactions of Rh ₂ ⁴⁺ Compounds				
	12.6.1	Oxidation to Rh ₂ ⁵⁺ and Rh ₂ ⁶⁺ species	540		
	12.6.2	Cleavage of the Rh–Rh bond	547		
12.7	Applica	ations of Dirhodium Compounds	547		
	12.7.1	Catalysis	547		
	12.7.2	Supramolecular arrays based on dirhodium building blocks	548		
	12.7.3	Biological applications of dirhodium compounds	555		
	12.7.4	Photocatalytic reactions	566		
	12.7.5	Other applications	567		

Chira	al Dirhodium(II) Catalysts and Their Applications	
13.1	Introduction	591
13.2	Synthetic and Structural Aspects of Chiral Dirhodium(II) Carboxamidates	591
13.3	Synthetic and Structural Aspects of Dirhodium(II) Complexes	
	Bearing Orthometalated Phosphines	599
13.4	Dirhodium(II) Compounds as Catalysts	605
13.5	Catalysis of Diazo Decomposition	607
13.6	Chiral Dirhodium(II) Carboxylates	609
13.7	Chiral Dirhodium(II) Carboxamidates	611
13.8	Catalytic Asymmetric Cyclopropanation and Cyclopropenation	613
	13.8.1 Intramolecular reactions	613
	13.8.2 Intermolecular reactions	616
	13.8.3 Cyclopropenation	617
	13.8.4 Macrocyclization	617
13.9	Metal Carbene Carbon-Hydrogen Insertion	619
	13.9.1 Intramolecular reactions	619
	13.9.2 Intermolecular reactions	624
13.10	Catalytic Ylide Formation and Reactions	624
13.11	Additional Transformations of Diazo Compounds Catalyzed by Dirhodium(II)	626
13.12	Silicon-Hydrogen Insertion	626
Nick	el, Palladium and Platinum Compounds	
14.1	General Remarks	633
14.2	Dinickel Compounds	633
14.3	Dipalladium Compounds	634
	14.3.1 A singly bonded Pd ₂ ⁶⁺ species	634
	14.3.2 Chemistry of Pd ₂ ⁵⁺ and similar species	635
	14.3.3 Other compounds with Pd–Pd interactions	636
14.4	Diplatinum Compounds	636
	14.4.1 Complexes with sulfate and phosphate bridges	642
	14.4.2 Complexes with pyrophosphite and related ligands	644
	14.4.3 Complexes with carboxylate, formamidinate and related ligands	646

	14.4.4	Complexes containing monoanionic bridging ligands with	
		N,O and N,S donor sets	648
	14.4.5	Unsupported Pt-Pt bonds	656
	14.4.6	Dinuclear Pt ₂ ⁵⁺ species	657
	14.4.7	The platinum blues	658
	14.4.6	Other compounds	661
Exte	nded I	Metal Atom Chains	
15.1	Overvi	ew	669
15.2	EMAC	s of Chromium	671
15.3	EMAC	s of Cobalt	686
15.4	EMAC	s of Nickel and Copper	694
15.5	EMAC	s of Ruthenium and Rhodium	701
15.6	Other I	Metal Atom Chains	702
Phys	sical, S	pectroscopic and Theoretical Results	
16.1	Structu	ral Correlations	707
	16.1.1	Bond orders and bond lengths	707
	16.1.2	Internal rotation	710
	16.1.3	Axial ligands	712
		Comparison of second and third transition series homologs	713
	16.1.5	Disorder in crystals	715
	16.1.6	Rearrangements of M ₂ X ₈ type molecules	718
	16.1.7	Diamagnetic anisotropy of M–M multiple bonds	720
16.2	Thermo	odynamics	721
	16.2.1	Thermochemical data	721
	16.2.2	Bond energies	722
16.3		nic Structure Calculations	724
	16.3.1	Background	724
	16.3.2	$[M_2X_8]^{n-}$ and $M_2X_4(PR_3)_4$ species	725
	16.3.3	The $M_2(O_2CR)_4$ (M = Cr, Mo, W) molecules	728
	16.3.4	$M_2(O_2CR)_4R'_2$ (M = Mo, W) compounds	729
	16.3.5	Dirhodium species	731
	16.3.6	Diruthenium compounds	732
	16.3.7	M_2X_6 molecules (M = Mo, W)	733
	16.3.8	Other calculations	738

16.4	Electro	nic Spectra	738
	16.4.1	Details of the δ manifold of states	739
	16.4.2	Observed $\delta \rightarrow \delta^*$ transitions	744
	16.4.3	Other electronic absorption bands of Mo ₂ , W ₂ , Tc ₂ and Re ₂ species	751
	16.4.4	Spectra of Rh ₂ , Pt ₂ , Ru ₂ and Os ₂ compounds	756
	16.4.5	CD and ORD spectra	758
	16.4.6	Excited state distortions inferred from vibronic structure	760
	16.4.7	Emission spectra and photochemistry	762
16.5	Photoe	lectron Spectra	766
	16.5.1	Paddlewheel molecules	766
	16.5.2	Other tetragonal molecules	772
	16.5.3	M_2X_6 molecules	773
	16.5.4	Miscellaneous other PES results	774
16.6	Vibrational Spectra		775
	16.6.1	M–M stretching vibrations	775
	16.6.2	M–L stretching vibrations	781
16.7	Other types of Spectra		783
	16.7.1	Electron Paramagnetic Resonance	783
	16.7.2	X-Ray spectra, EXAFS, and XPS	785
Abbreviations			797
Index			811