

## Contents

Preface *xi*

About the Editor *xiii*

1	Overviews of the Preparation and Reactivity of Transition Metal–Dinitrogen Complexes	1
	<i>Yoshiaki Tanabe and Yoshiaki Nishibayashi</i>	
1.1	Introduction	1
1.2	Biological Nitrogen Fixation	4
1.3	Historical Background of Transition Metal–Dinitrogen Complexes	9
1.4	Coordination Chemistry of Transition Metal–Dinitrogen Complexes	13
1.4.1	Coordination Patterns of Dinitrogen and Mononuclear Transition Metal–Dinitrogen Complexes	13
1.4.2	Multinuclear Transition Metal–Dinitrogen Complexes	16
1.5	Chemical Activation and Reactivity of Dinitrogen Using Transition Metal Complexes	21
1.5.1	Protonation of Transition Metal-bound Dinitrogen	21
1.5.2	Cleavage of Transition Metal-bound Dinitrogen	25
1.5.3	Reaction of Transition Metal-bound Dinitrogen with Dihydrogen	26
1.5.4	Functionalization of Transition Metal-bound Dinitrogen	29
1.5.5	Electrochemical and Photochemical Conversion of Dinitrogen Using Transition Metal Complexes	31
1.6	Catalytic Conversion of Dinitrogen into Ammonia Using Transition Metal Complexes	34
1.6.1	Catalytic Formation of Ammonia or Hydrazine Using Molybdenum Complexes	34
1.6.2	Catalytic Formation of Ammonia or Hydrazine Using Transition Metal Other than Molybdenum (Iron, Ruthenium, Osmium, Cobalt, and Vanadium) Complexes	40
1.6.3	Catalytic Transformation of Hydrazine into Ammonia	45
1.6.4	Catalytic Formation of Silylamine	47
1.7	Conclusion and Perspectives	50
	References	51

<b>2</b>	<b>Group 4 Transition Metal–Dinitrogen Complexes</b>	<b>79</b>
	<i>Hidetake Seino and Yuji Kajita</i>	
2.1	Introduction	79
2.2	Preparation of Group 4 Transition Metal–Dinitrogen Complexes	80
2.2.1	Dinitrogen Complexes of Bis(cyclopentadienyl)titanium Derivatives	80
2.2.2	Dinitrogen Complexes of Bis(cyclopentadienyl)zirconium and Bis(cyclopentadienyl)hafnium Derivatives	89
2.2.3	Other Dinitrogen Complexes Based on Cyclopentadienyl Ligands	98
2.2.4	Dinitrogen Complexes Supported by $\sigma$ -donor Ligands	100
2.2.5	Heterobimetallic Dinitrogen Complexes	109
2.3	Reactions of Group 4 Transition Metal–Dinitrogen Complexes	112
2.3.1	Protonation	112
2.3.2	Reduction	115
2.3.3	Reactions with Hydrogen	120
2.3.4	Reactions with Si—H and B—H Bonds	129
2.3.5	Reactions with Alkyl Halides and Their Equivalents	131
2.3.6	Reactions with Alkynes	136
2.3.7	Reactions with Carbon Dioxide and Cumulenes	138
2.3.8	Reactions with Carbon Monoxide	142
2.3.9	Dinitrogen Ligand Substitution	148
2.4	Conclusion and Perspectives	151
2.5	Addition After Acceptance of this Manuscript	151
	References	152
<b>3</b>	<b>Group 5 Transition Metal-Dinitrogen Complexes</b>	<b>159</b>
	<i>Leila M. Duman and Lawrence R. Sita</i>	
3.1	Introduction	159
3.2	Preparation of Group 5 Metal N <sub>2</sub> Complexes	160
3.2.1	Vanadium	160
3.2.2	Niobium	174
3.2.3	Tantalum	178
3.3	N≡N Bond Cleavage Within Group 5 Metal N <sub>2</sub> Complexes	187
3.3.1	Vanadium	188
3.3.2	Niobium	192
3.3.3	Tantalum	197
3.4	Nitrogen Fixation Mediated by Group 5 Transition-metal N <sub>2</sub> Complexes	201
3.4.1	Vanadium	202
3.4.2	Niobium	204
3.4.3	Tantalum	206
3.5	CPAM Group 5 Bimetallic ( $\mu$ - $\eta^1$ : $\eta^1$ -N <sub>2</sub> ) Complexes	206
3.6	Conclusions and Perspectives	212
	References	214

<b>4</b>	<b>Group 6 Transition Metal–Dinitrogen Complexes</b>	<b>221</b>
	<i>Nicolas Mézailles</i>	
4.1	Introduction	221
4.2	Preparation of Group 6 Transition Metal–Dinitrogen Complexes	222
4.2.1	End-on Dinitrogen Complexes from N <sub>2</sub>	222
4.2.1.1	Arene and Phosphine Ligands	222
4.2.1.2	Thioether Ligands	226
4.2.1.3	Nitrogen and Cp Ligands	226
4.2.2	End-on Bridging Dinitrogen Complexes from N <sub>2</sub> ; Synthesis and N <sub>2</sub> Splitting	228
4.3	Stoichiometric Reactions of Group 6 Transition Metal–Dinitrogen and Metal–Nitrido Complexes	234
4.3.1	N–H Bond Formation	234
4.3.2	N–C Bond Formation	238
4.3.3	N-element Bond Formation	241
4.4	Catalytic Reactions of Group 6 Transition Metal–Dinitrogen Complexes	247
4.4.1	Catalytic Formation of N <sub>2</sub> H <sub>4</sub> /NH <sub>3</sub> from Nonisolated M–N <sub>2</sub> Complexes	247
4.4.2	Catalytic Formation of N(SiMe <sub>3</sub> ) <sub>3</sub>	247
4.4.3	Catalytic Formation of NH <sub>3</sub>	251
4.5	Chemistry of Cr Complexes	259
4.6	Conclusion and Perspectives	261
	References	263
<b>5</b>	<b>Toward N—N Bond Cleavage: Synthesis and Reactivity of Group 7 Dinitrogen Complexes</b>	<b>271</b>
	<i>Elon A. Ison</i>	
5.1	Synthesis of Group VII N <sub>2</sub> Complexes	271
5.1.1	Syntheses of Terminal N <sub>2</sub> Complexes	271
5.1.2	Reactivity of Terminal N <sub>2</sub> Complexes	275
5.1.2.1	Synthesis of Bridged N <sub>2</sub> Complexes by Reaction with Lewis Acids	276
5.1.2.2	Alternative Syntheses of Bridged N <sub>2</sub> Complexes	279
5.2	Cleavage and Functionalization of N <sub>2</sub> Bonds	280
5.2.1	Generation of Diazomethane from CpMn(CO) <sub>2</sub> N <sub>2</sub>	280
5.2.2	Cleavage of N <sub>2</sub> in the Coordination Sphere of Rhenium	281
5.3	Conclusions and Future Outlook	281
	References	282
<b>6</b>	<b>Group 8 Transition Metal–Dinitrogen Complexes</b>	<b>285</b>
	<i>Adam D. Piascik and Andrew E. Ashley</i>	
6.1	Introduction	285
6.2	Preparation of Group 8 Transition Metal–Dinitrogen Complexes	288
6.2.1	Ligand Substitution	288
6.2.2	Precursor Reduction	292
6.2.3	Other Methods	296

6.3	Stoichiometric Reactions of Group 8 Transition Metal–Dinitrogen Complexes	297
6.3.1	Substitution Reactions and Lability of Bound N <sub>2</sub>	297
6.3.2	Cleavage and Functionalization of Coordinated N <sub>2</sub>	301
6.3.3	Other Stoichiometric Reactivity	309
6.4	Catalytic Reactions of Group 8 Transition Metal–Dinitrogen Complexes	311
6.4.1	Early Results and Fe Bis(diphosphine) Systems for Catalytic N <sub>2</sub> Fixation	311
6.4.2	Catalytic NH <sub>3</sub> Production by EP <sup>R</sup> <sub>3</sub> -supported Systems	313
6.4.3	Catalytic N <sub>2</sub> Fixation by Other Systems	317
6.4.4	Other Catalytic Reactions of Group 8 M–N <sub>2</sub> Complexes	319
6.5	Conclusion and Perspectives	327
	References	328
<b>7</b>	<b>Group 9 Transition Metal–Dinitrogen Complexes</b>	<b>337</b>
	<i>Connie C. Lu and Steven D. Prinslow</i>	
7.1	Cobalt–Dinitrogen Complexes	337
7.1.1	Monodentate Phosphine Donors	338
7.1.1.1	CoH(N <sub>2</sub> )(PR <sub>3</sub> ) <sub>3</sub> and Related Co(I) Complexes	338
7.1.1.2	Cobaltate Complexes: [Co(N <sub>2</sub> )(PR <sub>3</sub> ) <sub>3</sub> ] <sup>−</sup>	342
7.1.2	Tripodal Polyphosphine Ligands	345
7.1.2.1	Tris(phosphine) Ligands	345
7.1.2.2	Tris(phosphino)borate Ligands	346
7.1.2.3	Trisphosphine Systems with an Apical Main Group Donor	347
7.1.2.4	Trisphosphine Systems with an Apical Transition Metalloligand Donor	350
7.1.3	Ligands with Exclusively Nitrogen Donors	355
7.1.3.1	Tris(pyrazoyl)borate (Tp) Ligands	355
7.1.3.2	β-diketiminato Ligands	356
7.1.3.3	Bis(α-imino)pyridine Ligands	358
7.1.4	N-heterocyclic Carbene Ligands	359
7.1.5	Pincer Ligands	360
7.1.5.1	Monoanionic PNP-Type and PBP-Type Ligands	361
7.1.5.2	Pincer Ligands with N/P Donors	363
7.1.5.3	N-heterocyclic Carbene-Based Pincer Ligands	365
7.1.6	Other Assorted Ligands	367
7.1.7	Analysis and Summary of Cobalt–Dinitrogen Complexes	369
7.2	Rhodium–Dinitrogen Complexes	370
7.2.1	Early Rh–N <sub>2</sub> Complexes	370
7.2.2	Phosphine Ligands	372
7.2.3	Ligands with Exclusively Nitrogen Donors	374
7.2.3.1	Bis(α-imino)pyridine Ligands	374
7.2.3.2	β-diketiminato Ligands	375
7.2.4	Pincer Ligands	375
7.2.4.1	PCP Pincer Ligands	376
7.2.4.2	PNP Pincer Ligands	378

7.2.4.3	Other Pincer Ligands	380
7.2.5	<i>N</i> -heterocyclic Carbene Ligands	380
7.2.6	Summary of Rhodium–Dinitrogen Complexes	381
7.3	Iridium–Dinitrogen Complexes	381
7.3.1	Early Ir–N <sub>2</sub> Complexes	382
7.3.2	Phosphine Ligands	383
7.3.3	Ligands with Exclusively Nitrogen Donors	385
7.3.3.1	Tris(pyrazoyl)borate (Tp) Ligands	385
7.3.3.2	β-diketiminate Ligands	386
7.3.4	Pincer Ligands	386
7.3.4.1	PNP-Type Pincer Ligands	386
7.3.4.2	PCP- and PSiP-Type Pincer Ligands	388
7.3.5	<i>N</i> -heterocyclic Carbene Ligands	390
7.3.6	Miscellaneous	391
7.3.7	Summary of Iridium–Dinitrogen Complexes	391
7.4	Group 9 Catalysts for N <sub>2</sub> Functionalization	392
7.4.1	Cobalt-Based Catalysts	392
7.4.1.1	Dinitrogen Silylation	393
7.4.1.2	Dinitrogen Fixation	395
7.4.2	Outlook for Rhodium and Iridium Catalysts	396
	Acknowledgments	396
	References	396
<b>8</b>	<b>Group 10 and 11 Transition Metal–Dinitrogen Complexes</b>	<b>403</b>
	<i>Ricardo B. Ferreira and Leslie J. Murray</i>	
8.1	Introduction	403
8.2	Group 10 Transition Metal–Dinitrogen Complexes	405
8.2.1	Nickel	405
8.2.1.1	Interaction of Dinitrogen with Nickel Surfaces	406
8.2.1.2	Matrix-Assisted Isolation of Binary or Ternary Compounds	406
8.2.1.3	Coordination Compounds	408
8.2.1.4	Structural Relationships and Comparisons	420
8.2.2	Palladium and Platinum	422
8.3	Group 11 Transition Metal–Dinitrogen Complexes	423
8.3.1	Copper	423
8.3.1.1	Matrix-Assisted Isolation of Binary or Ternary Compounds	423
8.3.1.2	Coordination Compounds	425
8.3.1.3	Structural Relationships and Comparisons	427
8.3.2	Silver and Gold	429
8.4	Conclusion and Perspectives	430
	References	431
<b>9</b>	<b>Group 3 Transition Metal, Lanthanide, and Actinide–Dinitrogen Complexes</b>	<b>441</b>
	<i>Yoshiaki Tanabe</i>	
9.1	Introduction	441

- 9.2 Preparation and Characterization of Group 3 Transition Metal, Lanthanide, and Actinide–Dinitrogen Complexes 443  
9.2.1 Overviews of Preparation, Structures, and Characterization of Group 3 Transition Metal, Lanthanide, and Actinide–Dinitrogen Complexes 443  
9.2.2 Preparation and Structures of Side-on-Bound  $\{(N_2)^{2-}\}$ -Bridged Dinuclear Group 3 Transition Metal, Lanthanide, and Actinide–Dinitrogen Complexes 443  
9.2.3 Preparation and Structures of Side-on-bound  $\{(N_2)^{3-}\}$ -Bridged Dinuclear Group 3 Transition Metal and Lanthanide Complexes 456  
9.2.4 Preparation and Structures of  $\{(N_2)^{4-}\}$ -Bridged Dinuclear, Trinuclear, and Tetranuclear Lanthanide and Actinide–Dinitrogen Complexes 457  
9.2.5 Preparation and Structures of End-on-Bound Group 3 Transition Metal, Lanthanide, and Actinide–Dinitrogen Complexes 460  
9.3 Reactivity and Property of Group 3 Transition Metal, Lanthanide, and Actinide–Dinitrogen Complexes 462  
9.3.1 Cleavage, Protonation, and Functionalization of Dinitrogen upon Group 3 Transition Metal, Lanthanide, and Actinide–Dinitrogen Complexes 462  
9.3.2 Group 3 Transition Metal–Dinitrogen Complexes as Mediators for the Transformation of Small Molecules 466  
9.3.3  $\{(N_2)^{3-}\}$ -Bridged Dinuclear Group 3 Transition Metal and Lanthanide Complexes as Single-Molecule Magnets 468  
9.4 Conclusion and Perspectives 469  
References 470

**Index** 475