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Nitrido and imido transition metal complexes of Groups 6–8

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Abbreviations: [9]aneS$_3$, 1,4,7-trithiacyclononane; AA, acetic anhydride, $(CH_3CO)_2O$; Ac, acetate; Acac, pentane-2,4-dionate; Ad, adamantyl; Atp, 2-aminothiophenol; Bdt, 1,2-benzenedithiolate dianion; Bpy, 2,2′- bipyridine; Bpy,*o*-, 1,2-(bis-(2,2′-bipyridyl)-6-yl)-ethane; Brtbsalchxn, *N*,*N*′-cyclohexylenebis(3-di-*tert*-butyl-5-bromo-salicylideneaminato)dianion; Cl$_2$salophen,5,5′-, *N*,*N*′-*o*-phenylenebis(5,5′-dichloro-salicylideneaminato)dianion; Cp, cyclopentadienyl monoanion; Cp*, pentamethylcyclopentadienyl monoanion; Cp^{Cl}, (chlorodimethylsilyl)cyclopentadienyl monoanion; Cp^{Me}, methylcyclopentadienyl monoanion; Cp^{iPr}, isopropylcyclopentadienyl monoanion; Cyclam, 1,4,8,11-tetraazacyclotetradecane; Cyclam-acetato, 1,4,8,11-tetraazacyclotetradecane-1-acetate monoanion; Dadpe, 1-diphenylarsino-2-diphenylphosphinoethane; Dbabh, 2,3:5,6-dibenzo-7-azabiocylco[2.2.1]hepta-2,5-diene monoanion; Dfppe, 1,2-bis(di-4-fluorophenylphosphino)ethane; Dme, 1,2-dimethoxyethane; Dmbpb, 1,2-bis(pyridine-2-carbozamido)-4,5-dimethylbenzene dianion; Dmbpy, 4,4′-dimethyl-2,2′-bipyridine; DMBTH, 2,6-dimethylbenzenethiol; Dmeppe, 1,2-bis(di-4-methylphenylphosphino)ethane; Dmit, isotrithionedithiolate dianion; Dmp, 2,9-dimethyl-1,10-phenanthroline; Dmpe, dimethylphosphinoethane; Dmppe, 1,2-bis(di-4-methoxyphenylphosphino)ethane; Dppm, 1,2-bis(diphenylphosphino)methane; DMTPH, 2,6-dimethylthiophenol; Dpae, 1,2-bis(diphenylarsino)ethane; Dppbz, 1,2-bis(diphenylphosphino)benzene; Dppe, 1,2-bis(diphenylphosphino)ethane; Dppee, 1,2-bis(diphenylphosphino)ethene; Dppf, diphosphinoferrocyl; *R*-1,2-dppp, *R*-(+)-1,2-bis(diphenylphosphino)propane; Dtc, diethyldithiocarbamate; Et$_2$tcb, *N*,*N*-diethylthiocarbamoylbenzamidinate monoanion; Et$_2$dtc, *N*,*N*-diethyldithiocarbamate monoanion; HOMO, Highest occupied molecular orbital; In, indenyl monoanion; L$_{OEt}$, η^5-C_5H_5-Co[PO(OEt$_2$)]$_3$; LUMO, Lowest occupied molecular orbital; Mebpb, 1,2-bis(pyridine-2-carbozamido)-4-methylbenzene dianion; Mebpy,6-, 6-methyl-2,2′-bipyridine; Me$_2$dtc, *N*,*N*-dimethyldithiocarbamate monoanion; Mepy,4-, 4-methylpyridine; Me$_2$salophen,5,5′-, *N*,*N*′-*o*-phenylenebis(5,5′-dimethyl-salicylideneaminato)dianion; (MeO)$_2$salophen,5,5′-, *N*,*N*′-*o*-phenylenebis(5,5′-dimethoxy-salicylideneaminato)dianion; Mes, Mesityl or 2,4,6-trimethylphenyl; Me$_3$tacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; Metbsalchxn, *N*,*N*′-cyclohexylenebis(3-di-*tert*-butyl-5-methyl-salicylideneaminato)dianion; Mnt, 1,2-dicyanoethene-1,2-dithiolate dianion; Morphdtc, *N*-morpholinyldithiocarbamate monoanion; Morphtcb, *N*-(morpholinylthiocarbamoy)benzamidine monoanion; NBS, *N*-bromosuccinimide; Np, neopentyl; OTf, triflate or trifluoromethanesulfonate; OEP, (2,3,7,8,12,13,17,18-octaethylporphyrinato)dianion; Pc2−, phtalocyaninate dianion; PCy$_3$, tricyclohexylphosphine; Ph$_2$dtc, *N*,*N*-diphenyldithiocarbamate monoanion; Phen, 1,10-phenanthroline; PhI=O, iodosobenzene; Pic, picolinate; picdtc, *N*-picolinyldithiocarbamate monoanion; pictcb, *N*-(picolinylthiocarbamoy)benzamidine monoanion; Py, pyridine; Salchxn, *N*,*N*′-cyclohexylenebis(salicylideneaminato)dianion; Saldmpen, *N*,*N*′-dimethylpropylenebis(salicylideneaminato)dianion; Salen, *N*,*N*′-ethylenebis(salicylideneaminato)dianion; Salophen, *N*,*N*′-*o*-phenylenebis(salicylideneaminato)dianion; Salpd, *N*,*N*′-propylenebis(salicylideneaminato)dianion; Saltmen, *N*,*N*′-1,1,2,2-tetramethylethylenebis(salicylideneaminato)dianion; *syn*-Me$_8$[16]aneS$_4$, 3,3,7,7,11,11,15,15-octamethyl-1,5-9,13-tetrathiacyclohexadecane; Tacac, 2,2,6,6-tetramethylheptane-3,5-dionate; Tacn, 1,4,7-triazacyclononane; Tbsalchxn, *N*,*N*′-cyclohexylenebis(5-*tert*-butyl-salicylideneaminato)dianion; Tb$_2$salchxn, *N*,*N*′-cyclohexylenebis(3,5-di-*tert*-butyl-salicylideneaminato)dianion; Tb$_2$salen, *N*,*N*′-ethylenebis(3,5-di-*tert*-butyl-salicylideneaminato)dianion; Tbsaldphen, *N*,*N*′-1,2-diphenylethylenebis(5-*tert*-butyl-salicylideneaminato)dianion; Tcb, *N*,*N*-diethylthiocarbamoylbenzamidine; Tb$_2$saldphen, *N*,*N*′-1,2-diphenylethylenebis(3,5-di-*tert*-butyl-salicylideneaminato)dianion; Tdt, 3,4-toluenedithiolate dianion; TFA, trifuoracetic acid, CF_3CO_2H; TFAA, trifluoroacetic anhydride, $(CF_3CO)_2O$; THF, tetrahydrofuran; TMBTH, 2,3,5,6-tetramethylbenzenethiol; TMP, (5,10,15,20-tetramethylporphyrinato)dianion; TMSA, trimethylsilyl azide or TMS-N$_3$; TMS$_2$pda, *N*,*N*′-bis(trimethylsilyl)-*o*-phenylenediamine dianion; Tol, toluene; Tp, hydridotris(pyrazolyl)borate monoanion; Tp*, hydridotris(3,5-dimethylpyrazolyl)borate monoanion; Tpfc, (5,10,15-tris(pentafluorophenyl)corrole)trianion; Tpm, hydridotris(pyrazolyl)methane; TPP, (5,10,15,20-tetraphenylporphyrinato)dianion; Tpy or terpy, 2,2′:6′,2″-terpyridine; TTP, (5,10,15,20-tetratolylporphyrinato)dianion; Ts or Tos, tosyl or *p*-tolylsulfonyl; Ts$_2$O, tosyl anhydride; Tu, thiourea.

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Abstract

This review summarizes the syntheses and reactivities of Groups 6, 7, and 8 metal nitrido and imido complexes reported until August 2002. We begin with a general description of the bonding and reactivity of transition metal nitrido and imido complexes followed by a discussion of the common synthetic routes. The main focus of the review is the survey of the nitrido and imido complexes of Groups 6–8 with an emphasis on their synthesis and reactivity.

Keywords: Nitrido; Imido; Group 6 metals; Group 7 metals; Group 8 metals

1. Introduction

Transition metal complexes containing multiple bonds to nitrogen remain an important class of compounds. Such complexes have been implicated in nitrogen fixation, atom and group transfer reactions, and catalysis, such as olefin metathesis and ammonoxidation of olefins. We became interested in transition metal nitrido and imido complexes of manganese and rhenium due to their reactivity as N-atom and NR group transfer agents.

This review focuses on transition metal complexes containing multiple bonds to nitrogen, in the form of terminal nitrido (M≡N) and terminal imido (M≡NR) bonding motifs for Groups 6–8. Only mono-substituted complexes are considered here. Thus, compounds containing more than one type of multiple bond ligand, such $[Cr(N-^tBu)_2Cl_2]$, $[W(=C-^tBu)(=NPh)Cl(PEt_3)_2]$, or $[Os(N)(O)_3]^-$ are not included. Complexes containing a bridging nitrido or imido moiety, which is shared between two or more metal centers, are also not discussed. For more details on transition metal complexes containing multiple bonds to nitrogen as well as other atoms, such as carbon or oxygen, the text by Nugent and Mayer provides a thorough introduction to this area of transition metal chemistry [1].

This review is organized into the following sections: Bonding, Reactivity, Syntheses, and Survey of Complexes of Groups 6–8. The survey, which is organized by group, focuses only on those complexes made in the last ten years with an emphasis on their reactivity and synthesis. Thus, the survey of the nitrido complexes includes only complexes of Groups 6–8 prepared since 1992, which was the year of most recent review for metal nitrido compounds. Thorough accounts on the transition metal nitrido complexes made prior to 1992 can be found in reviews by Dehnicke, Strahle and Griffith [2]. Likewise, the survey for imido complexes of Groups 6–8 includes complexes made since 1994. For detailed accounts on the types of imido complexes prepared prior to 1994, reviews by Wigley, Strahle, and Nugent are most helpful [3]. All abbreviations are listed at the beginning.

2. Bonding and relationship to reactivity

In simple valence terms, the bonding between the metal and the isoelectronic nitrido and imido ligands consists of one σ and two π bonds, Fig. 1. In both cases

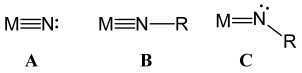


Fig. 1. Simplified representation of the bonding in metal nitrido and imido complexes.

A and B, the N-atom can be considered sp hybridized. In order for the N-atom of the imido moiety to be considered sp hybridized, the bond angle must be linear. Although linear imido complexes are more common, there are examples of bent imido ligands, which contain an sp^2 hybridized N-atom with the lone pair centered on the N-atom, case C. However, despite the linearity of the imido ligand, it is common to represent it as a double bond, M=NR. This simplification makes the assignment of oxidation states easier. As closed-shell anions, the nitrido and imido ligands are assigned as N^{3-} and NR^{2-}, respectively. The π bonding can be further understood in terms of filled nitrogen p orbitals overlapping with empty metal d orbitals. Thus, metal complexes capable of forming multiple bonds to nitrogen are usually in a high oxidation state. Furthermore, formation of a bent imido ligand can result when the d orbitals on the metal are filled, they are not the proper symmetry for π bonding, or they are in competition with other π bonding ligands [1]. In terms of molecular orbital descriptions for an octahedral complex, the triple bond can be rationalized in Fig. 2. If the z-axis is defined along the metal–nitrogen bond, then d_{xz} combines with p_x and d_{yz} combines with p_y to form both π bonds. The d_{xy} orbital, a nonbonding orbital, is sufficiently lower in energy than the π* orbitals and is mainly metal centered.

The reactivity of the ligand for transition metal terminal nitrido and imido complexes essentially depends on the following factors: the transition metal, the oxidation state of the transition metal, and the ancillary ligands [1,3a,4]. All factors contribute to the π interaction of the ligand's p orbitals with the metal's d orbitals. As a simplification of this interaction, one extreme would be when the π* orbital is mostly metal in character, case A, and the other would be when the π* orbital is mostly ligand in character, case B, Fig. 3. With a π* orbital that is mostly metal in nature, the metal is considered to be electrophilic, and hence a nucleophilic ligand is expected to result. On the other hand, the ligand is predicted to be electrophilic when the π* orbital is mostly ligand in character. Thus, typically nucleophilic behavior of the ligand is expected for early transition metal complexes in high oxidation states [1]. On the other hand, electrophilic behavior is expected for late transition metal complexes in low oxidation states [1]. Therefore, as one moves up and to the right in the periodic table for transition metals, the amount of ligand character to the π* orbital increases and the electrophilicity of the ligand increases. Of course, there are numerous examples where the π* orbital has both metal and ligand character and the nature of the ligand's reactivity is effected as a result. In reference to Fig. 3, having both the p and d orbitals at a similar energy level would represent this latter case. Thus, there are examples of nitrido complexes where the M≡N moiety

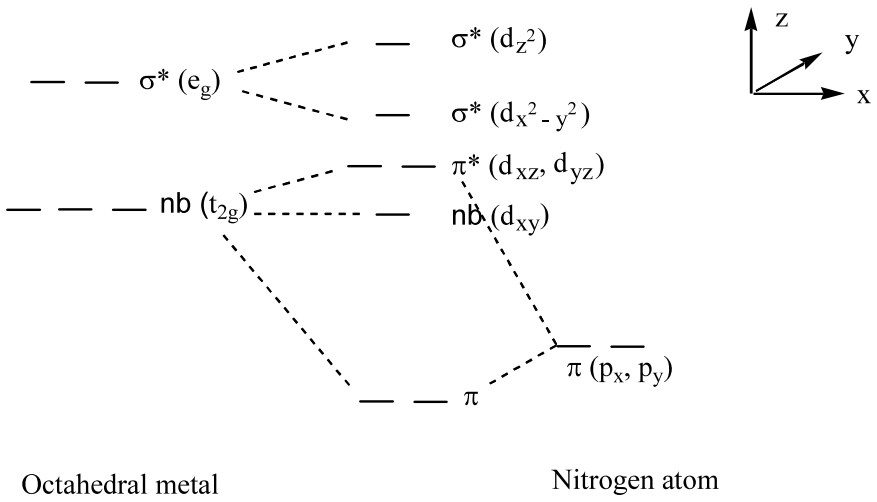


Fig. 2. The molecular orbital description of nitrido and imido bonding in an octahedral. Adapted from Ref. [1].

displays both nucleophilic and electrophilic reactivity [5].

3. Reactivity of the transition metal nitrido moiety

3.1. Nucleophilic behavior

When the transition metal is more electrophilic in nature, a nucleophilic nitrido ligand should result. More often early and middle transition metal complexes contain nucleophilic M≡N moieties. Although there are examples of late transition metal nitrido complexes reacting in nucleophilic manner, such as the organometallic osmium(VI) complexes studied by Shapley and coworkers [6]. Nucleophilic behavior has been observed with, for example, tungsten(VI) [7], manganese(V) [8,9], and rhenium(V) [10] nitrido complexes. These complexes, for example, will react with electrophiles, such as methyltriflate [7,10], trifluoroacetic anhydride [8–10], and trityl tetrafluoroborate [10] to produce the corresponding imido derivatives with no change in the oxidation state of the metal. In the complexes studied by Leung and Wong [10], it is worth noting that the isoelectronic osmium(VI) analogues do not react under the same conditions with electrophiles demonstrating the importance of the transition metal and oxidation state on the reactivity of the nitrido ligand. Further examples of nucleophilic nitrido transition metal complexes will be discussed when appropriate in the Survey of Groups 6–8 section. A simplistic representation of the nucleophilicity of the nitrido moiety is presented in Scheme 1.

Alkylation: $[M{\equiv}N{:}] + CR_3^+ \rightarrow [M(=NCR_3)]^+$

Acylation: $[M{\equiv}N{:}] + (CR_3CO)_2O \rightarrow [(OCOCR_3)M(=NC(O)CR_3)]$

General: $[M{\equiv}N{:}] + Elec \rightarrow [M(=N\text{-}Elec)]$

Where Elec = Alkyl halides, methyl triflate, anhydrides, aldehydes, ketones, CO_2, CS_2, S_2Cl_2, CR_3^+, and organic isocyanates.

Scheme 1. Simplified representations of the nucleophilic behavior of the nitrido moiety.

$$[M{\equiv}N{:}] + BR_3 \rightleftharpoons [M{\equiv}N{\rightarrow}BR_3]$$

Scheme 2. Simplified representations of the Lewis basicity of the nitrido moiety.

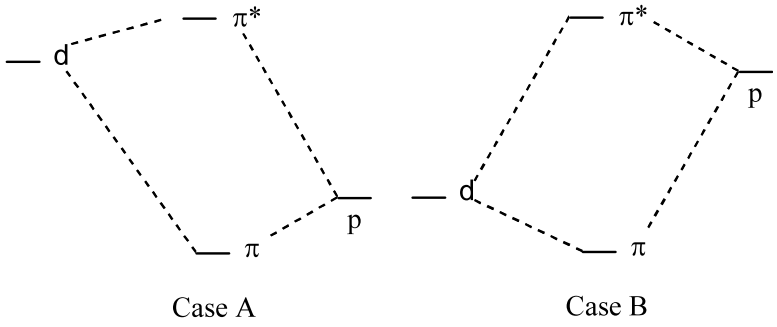


Fig. 3. Case A represents a nucleophilic ligand and Case B represents an electrophilic ligand. Adapted from Refs. [1,3a,4].

3.2. Lewis basicity

Under certain circumstances, the nitrido moiety can be considered a Lewis base [11,12]. Thus, the electron pair on the nitrogen is available for donation to the appropriate Lewis acid, such as Ag^+, $GaCl_3$, or BR_3 where R = halogen, Ph or C_6F_5. The nitrido ligands coordinate reversibly to the Lewis acids to form adducts, Scheme 2.

3.3. Electrophilic behavior

Electrophilic behavior of the nitrido moiety is observed for late transition metals. Thus, late transition metal complexes are often very good oxidants. For example, osmium(VI) complexes will react with various nucleophiles, such as carbanions, organic phosphanes, amines, azides, amine-*N*-oxides, sulfides and even alkenes [5,13–16]. The reactions with nucleophiles are expected to result in a lowered oxidation state of the metal and a reduced bond order between the metal and nitrogen atom. Ideally, these reactions could result in the complete transfer of the nitrogen to the nucleophilic substrate. However, in most cases an adduct is formed. For example, the reaction of triphenylphosphane and ruthenium(VI) complex in pyridine, $[(L)Ru^{VI}(N)Cl]$ gives the reduced iminophosphane adduct, $[(L)Ru^{IV}(N=PPh_3)Cl(py)]$ where L is the tridentate ligand, 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine [13]. As stated previously, the reactivity of the nitrido moiety is dependent on the metal, its oxidation state and the ancillary ligands. The effect of the ancillary ligands is readily apparent for osmium(VI) complexes studied by Mayer and coworkers. For example, $[TpOs(N)Cl_2]$ is much more reactive towards Grignard reagents than the organometallic analogue, $[TpOs(N)Ph_2]$ [5]. Additionally, although $[TpOs(N)Cl_2]$ does not react with electrophiles such as methyl triflate, $[TpOs(N)Ph_2]$ will react with methyl triflate [5]. Additional examples of electrophilic nitrido transition metal complexes will be discussed in the Survey of Groups 6–8 section. A simplistic representation of the electrophilicity of the nitrido moiety is given in Scheme 3.

Phosphinimidation: $[M^{(n)+}{\equiv}N:] + PR_3 \rightarrow [M^{(n-2)+}(N{=}PR_3)]$
Where R = alkyl or aryl groups

General: $[M^{(n)+}{\equiv}N:] + Nuc \rightarrow [M^{(n-2)+}(NNuc)]$ or $[M^{(n-2)+}] + NNuc$
Where Nuc = alkenes, PhMgX (X = Cl, Br), CN^-, N_3^-, LiPh, NHR_2, py-*N*-oxide, Me_3NO, S_8, propylene sulfide, and thiols.

Scheme 3. Simplified representations of the electrophilic behavior of the nitrido moiety.

General: $[M{=}NR] + Elec \rightarrow [M(\text{-}NRElec)]$

Where Elec = Alkyl halides, methyl triflate, aldehydes, ketones, CO_2, CS_2, CR_3^+, and organic isocyanates.

Scheme 4. Simplified representations of the nucleophilic behavior of the imido moiety.

General: $[M^{(n)+}{\equiv}NR] + Nuc \rightarrow [M^{(n-2)+}(NRNuc)]$
or
$[M^{(n)+}{\equiv}NR] + Nuc \rightarrow [M^{(n-2)+}] + RNNuc$

Where Nuc = alkenes, PhMgX (X = Cl, Br), CN^-, N_3^-, LiPh, CO, NHR_2, Me_3NO, S_8, propylene sulfide, thiols.

Scheme 5. Simplified representations of the electrophilic behavior of the imido moiety.

4. Reactivity of the transition metal imido moiety

4.1. Nucleophilic behavior

A bent imido ligand results in a double bond between the metal and the nitrogen atom with the lone pair centered on an sp^2 hybridized nitrogen. Thus, nucleophilic behavior is expected for this type of bonding. As mentioned previously, a bent imido ligand results when there is competition by other π bonding ligands. Hence, bent imido complexes are usually found in complexes containing other multiply bonded ligands, such as akylidene ($M{=}CR_2$) or oxo ($M{=}O$) ligands. A linear terminal imido complex of iridium(III), $[Cp^*Ir(N^tBu)]$, has been reported to react with methyl iodide [17]. A simplification of this type of reactivity is presented in Scheme 4.

4.2. Electrophilic behavior

When the imido ligand is bonded to a metal in linear fashion, the bond can be considered a triple bond and most often electrophilic reactivity of the M≡NR moiety is expected. For example, this reactivity has been observed for imido complexes of chromium(IV) [18], chromium(V) [19], and tungsten(IV) [20]. Reactions with nucleophiles result in a reduction of the metal's oxidation state and a reduced bond order between the metal and the imido ligand. Furthermore, complete transfer of the imido ligand (NR) is often a desirable goal. Further examples of electrophilic imido ligands will be discussed when appropriate in the Survey of Groups 6–8 section (Scheme 5).

4.3. Lewis acidity

Recently, it was reported that chromium(V) imido complexes will catalyze the ring opening of epoxides in the presence of trimethylsilyl azide [21]. The vicinal azido hydrins were produced in high yields. In these catalytic reactions, the (imido)chromium(V) complexes act as Lewis acids.

$$[M^{(n)+}{=}NR] + H^{+} \rightleftharpoons [M^{(n-2)+}(NRH)]$$

Scheme 6. Simplified representations of the Lewis basicity of the imido moiety.

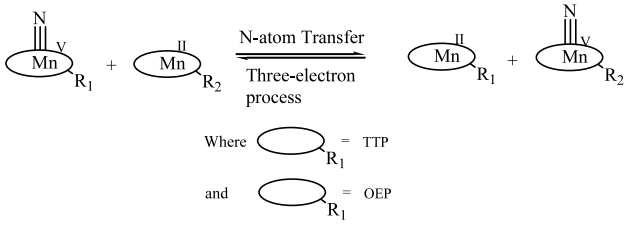
4.4. Lewis basicity

The behavior of the imido moiety also makes it viable to consider it a Lewis base (or Bronsted base) [22]. Thus, the electron pair on the nitrogen is available for donation to an appropriate Lewis acid such as H^+ to give an amido product, Scheme 6. For example, a tungsten(VI) imido complex has been observed to produce the corresponding amido upon addition of acid [23].

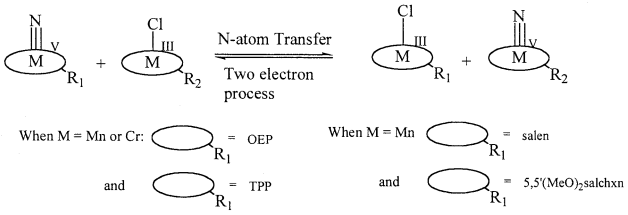
5. Intermetal N-atom transfer: nitrido complexes

Often nitrogen atom transfer is observed to occur from nucleophilic transition metal nitrido complexes to electrophilic transition metal complexes of a lower oxidation state. Although these reactions can be considered a special type of atom transfer reactions where multiple electrons are transferred along with the nitrogen atom, these reactions also clearly demonstrate the nucleophilic tendency of the nitrido moiety. The reactions can either be reversible or irreversible processes. Furthermore, depending on the transition metals and their oxidation states, these reactions may result in incomplete N-atom transfer and the formation of dimeric species containing a bridging nitrido moiety (μ-N). Although incomplete N-atom transfer type reactions provide a convenient synthetic entry for the formation of new bridging-type complexes, these reactions will not be explicitly discussed in this review. Only complete N-atom transfer reactions resulting in the formation of terminal nitrido complexes will be discussed herein.

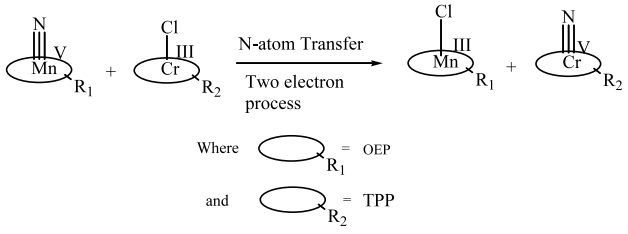
Nitrogen atom transfer involving metals with macrocyclic ligands, such as porphyrin and salen, have received considerable attention. Woo and coworkers have observed complete and reversible N-atom transfer with the transfer of three electrons, Scheme 7 [24]. Reversible two electron N-atom transfer has also been



Scheme 7. Homometallic nitrogen atom transfer as a three-electron process utilizing manganese porphyrin systems.



Scheme 8. Homometallic nitrogen atom transfer as a two-electron process utilizing both manganese and chromium porphyrin systems and manganese salen systems.



Scheme 9. Heterometallic nitrogen atom transfer as a two-electron process utilizing manganese and chromium porphyrin systems.

observed with both manganese and chromium systems, Scheme 8 [24a,24c,25]. These processes can be regarded as simplified double exchange reactions since both the nitrido and chloride ligands are exchanged between the two complexes. Although, these are not true self-exchange reactions, these reactions do contain the same metal as both the donor and acceptor. When the acceptor metal is changed, irreversible N-atom transfer has been observed. For example, irreversible complete N-atom transfer has been observed from (nitrido)manganese(V) to chromium(III), Scheme 9 [26]. In all cases, however, a nucleophilic nitrido complex attacks a cationic metal complex, a bridging species is believed to result [27], followed by rapid atom and electron transfer.

Cummins and coworkers have studied nitrogen atom transfer involving metals with simple ligands. Irreversible N-atom transfer was observed from (nitrido)molybdenum(VI), $[Mo(N)(O^tBu)_3]$, to molybdenum(III), $[Mo(NRAr)_3]$, where $R = C(CD_3)_2CH_3$ and $Ar = 3,5\text{-}C_6H_3Me_2$ [28]. This reaction was a three electron process and coupled to molybdenum–molybdenum triple bond formation to give the product, $[Mo_2(O^tBu)_6]$.

6. Common synthetic routes

6.1. Nitrido complexes

The common synthetic routes for making transition metal nitrido complexes are discussed in this section, which is divided into two parts. The first part deals with the syntheses that have been employed in creating the metal–nitrogen multiple bonds; the second part deals

NH_3 (aq)/(g) + $M^{(n)+}$ + oxidizer → $[M^{(n+2)+}{\equiv}N:]$
Where oxidizer = NaOCl, PhIO, NBS, or Cl_2

Scheme 10. The synthesis of nitrido complexes from ammonia.

$[N_3\text{-}M^{(n)+}]$ + heat/light → $[M^{(n+2)+}{\equiv}N:]$ + N_2
$M^{(n)+}$ + RN_3 → $[M^{(n+2)+}{\equiv}N:]$ + $\{RN_2\}$
Where R = Na, Mes, or TMS

Scheme 11. The synthesis of nitrido complexes from the decomposition of azidos or reaction with azides.

with the syntheses involving the formation of new complexes from known metal nitrido complexes. Specific examples of the synthetic routes used to make new nitrido complexes are presented in the Survey of Groups 6–8.

6.1.1. Syntheses that result in the formation of M≡N bond

6.1.1.1. Reactions involving NH_3 and its derivatives. Oxidation of the metal in the presence of aqueous or gaseous ammonia can result in the formation of nitrido complexes. This type of synthesis, for example, has been successfully employed in the syntheses of manganese(V) [8b,9a,9b,9e,12,74] and chromium(V) [32a] nitrido complexes (Scheme 10).

6.1.1.2. Decomposition of azides. The thermo- or photochemical-decomposition of metal azido complexes has been known to result in the formation of the corresponding metal nitrido complexes and the release of nitrogen gas. This reaction is an oxidative cleavage type reaction. For example, chromium(V) [31,32a] and manganese(V) [9,75] nitrido complexes have been prepared this way. Utilizing the decomposition of sodium azide [7a,45c], mesityl azide [46], or trimethylsilyl azide [7a,45d], the formation of the M≡N bond occurs along with oxidation of the metal. The use of an organic azide, such as mesityl azide, in creating nitrido complexes is quite rare. More often the use of organic azides results in formation of imido complexes and not nitrido [18,20,71,105] (Scheme 11).

6.1.2. Syntheses with the retention of the M≡N bond

6.1.2.1. Ligand exchange or substitution reactions. Ligand exchange reactions are a simple means of creating new complexes from existing ones. The success of these reactions will depend on the stability of the chosen

$[LM{\equiv}N]$ + L' → $[L'M{\equiv}N]$ + L
Where L' represents incoming ligand.

Example [100a]: $[Re^{V}(N)Cl_2(PPh_3)_2]$ + 2 dppm → $[Re^{V}(N)Cl(dppm)_2]Cl$ + 2 PPh_3

Scheme 12. The synthesis of nitrido complexes utilizing ligand exchange.

$[LM^{(n)+}{\equiv}N:]$ + L' → $[L'M^{(n-x)+}{\equiv}N:]$ + L (x = 1, 2)
Where L' represents incoming ligand.

Example [80]: $[AsPh_4][Tc^{VI}(N)Cl_4]$ + $2Ph_2PCH_2CH_2SH$ → $[Tc^{V}(N)(SCH_2CH_2PPh_2)_2]$

Scheme 13. The synthesis of nitrido complexes utilizing ligand exchange coupled with reduction of the metal.

starting materials. There are quite a number of new nitrido complexes created this way for rhenium(V) [10,80,90–95,97,100], technetium(V) [77b,78–86], ruthenium(VI) [123,124], and osmium(VI) [10a,123,125–135]. Ligands employed have ranged from monodentate to multidentate. For example, simple mondentate ligands such as CN^- have been used to prepare new chromium(V) and manganese(V) nitrido complexes [34a]. Some types of multidentate ligands commonly employed include phosphines, such as dppe and analogues, thiols, such as bdt^{2-}, and amine-type ligands, such as tacn. Multidentate ligands containing mixed types of donor atoms are also commonly found [79,84,90,123]. Further examples of these reactions are highlighted in the Survey of Groups 6–8. The reactions do not result in a change of oxidation state for the metal (Scheme 12).

6.1.2.2. Reduction reactions. Ligand exchange reactions can be coupled with reduction of the metal's oxidation state. The ligands can behave as the reducing agent or an exogeneous reducing agent can be added. For example, these reaction types have worked well for making new technetium(V) complexes from the starting material $[Tc(N)Cl_4]^-$ with reducing ligands such as phosphines and thiols [77b,79,80] (Scheme 13).

6.2. Imido complexes

The common synthetic routes for making transition metal imido complexes are discussed in this section, which is divided into two parts. The first part deals with the syntheses that have been employed in creating the metal–nitrogen multiple bonds; the second part deals with the syntheses involving the formation of new complexes from known metal imido complexes.

6.2.1. Syntheses that result in the formation of M≡NR bond

6.2.1.1. Reactions involving primary amines, RNH_2. Reactions of the metal chlorides, $[M^{V}Cl_4Cp]$ with primary amines can result in formation of imido complexes. This synthetic strategy has worked well to make terminal imido complexes of molybdenum(V) and tungsten(V) [61a,62,63]. Metal oxo complexes can also be transformed into imido compounds with primary

$[MCl_4Cp]$ + H_2NR → $[M(NR)Cl_2Cp]$ + 2HCl
$[M(O)L_n]$ + H_2NR → $[M(NR)L_n]$ + H_2O

Scheme 14. The synthesis of imido complexes from primary amines.

$$[LM^{(n)+}] + LiNHR \rightarrow [LM^{(n+2)+}{\equiv}NR]$$
Where R = alkyl or aryl

Scheme 15. The synthesis of imido complexes utilizing amine bases.

$$[RN_3\text{-}M^{(n)+}] + \text{heat/light} \rightarrow [M^{(n+2)+}{\equiv}NR] + N_2$$
$$M^{(n)+} + RN_3 \rightarrow [M^{(n+2)+}{\equiv}NR] + N_2$$
Where R = Me_3Si, aryl or alkyl groups

Scheme 16. The synthesis of imido from the decomposition of azides.

$$[RHN\text{-}M^{(n)+}] + base \rightarrow [M^{(n+2)}{\equiv}NR]$$

Scheme 17. The synthesis of imido complexes by deprotonation of coordinated amines.

$$[M{\equiv}N{:}] + R^+ \rightarrow [M{=}NR]^+$$
Sources of R^+: MeOTf, $PhCH_2Br$, $(RCO)_2O$ (R = CH_3 or CF_3), $[CPh_3][BF_4]$

Scheme 18. The synthesis of imido complexes by alkylation or acylation of the nitrido ligand.

amines, such as derivatives of aniline [56a,65,111,112e,113a,117,118] (Scheme 14).

6.2.1.2. Reactions utilizing amine bases, [NHR]$^-$. Utilization of lithium amide reagents for generating the imido moiety has worked well with chromium [48,49] and ruthenium 137. The R group can be either aryl or alkyl substituents. The bulk of the R-group can play a significant role in the isolation of late transition metal imido complexes [137] (Scheme 15).

6.2.1.3. Decomposition of azides. Utilizing thermal and photochemical decomposition of trimethylsilyl azide [71] or various organic azides [18,20,71,105] containing aryl or alky substituents, results in the formation of the M≡NR bond along with the oxidation of the metal. Recently, Bergman and coworker isolated an organoazido complex that upon heating releases nitrogen gas and produces the imido product [29] (Scheme 16).

6.2.1.4. Deprotonation of coordinated amides. The deprotonation of coordinated amides can be a convenient synthesis of the corresponding imido products. Oxidation of the metal results as well. This strategy works well for amido transition metal complexes that are susceptible to oxidation [20,23,139] (Scheme 17).

6.2.1.5. Alkylation or acylation of nitrido complexes. The alkylation or acylation of the nitrido ligand has provided another synthetic route to imido complexes. Nucleophilic M≡N moieties can be alkylated or acylated with electrophiles such as methyltriflate, anhydrides and trityl tetrafluoroborate [7a,10,93b,110,126,141] (Scheme 18).

$$[LM{\equiv}NR] + L' \rightarrow [L'M{\equiv}NR] + L$$
Where L' represents incoming ligand.

Example [68a]: $[W(NPh)(CO)_2(THF)I_2] + 2\,PMe_3 \rightarrow [W(NPh)(CO)_2(PMe_3)_2I_2] + THF$

Scheme 19. The synthesis of imido complexes ultilizing ligand exchange.

6.2.2. Syntheses with the retention of the M≡NR bond

6.2.2.1. Ligand exchange or substitution reactions. Ligand exchange reactions are a simple means of creating new complexes from existing ones. The success of these reactions will depend on the stability of the chosen starting materials. The chemistry of tungsten(VI), for example, has largely been built on these types of reactions [20,56,63,68,72,73]. These reactions have also been applied to molybdenum(IV) and (VI) [58,59,61], technetium(V) [77,107], and rhenium(V) [83a,90,91b,91h,100,112,118] (Scheme 19).

7. Survey of Groups 6–8

7.1. Group 6: chromium, molybdenum, tungsten

7.1.1. Nitrido complexes of Group 6

7.1.1.1. Chromium nitrido complexes. The nitrido complexes of chromium(V) and (VI) are considered a rare class of complexes due to their limited numbers. The trans influence of the nitrido ligand is often very pronounced in both chromium(V) and (VI) nitrido compounds, which contain very short Cr≡N bonds ($\sim$1.5–1.6 Å). Thus, five-coordinate complexes usually result; and, six-coordinate complexes display elongated bonds trans to the Cr≡N moiety.

Chromium(V) nitrido complexes are paramagnetic and usually rather stable. These complexes are commonly formed via photolysis of the corresponding (azido)chromium(III) which results in a two-electron oxidation and formation of the CrN triple bond. Although, this synthetic strategy has been known and used for over 20 years [30], the versatility of the methodology is still being demonstrated. For example, chromium(III) azido complexes containing a variety of multidentate ligands have been photolyzed to their corresponding nitrido complexes Table 1 [31,32]. With the cyclam derivatives, trans-$[Cr^V(N)cyclam(L)]^{1+\text{ or }2+}$ where L is N_3 or CH_3CN, the d–d transitions in their electronic spectra have finally been assigned [31a]. The reactivity of these complexes was not reported.

Synthetic methods generally used to form chromium(V) nitrido complexes involve formation of the CrN triple bond, such as the above-mentioned photolysis of azido complexes. Although photolysis of azido complexes has been successfully demonstrated with a variety of complexes, this method can be somewhat limiting. Homborg and Grunewald have employed an alternative synthetic route for generating the Cr≡N

Table 1
Nitrido complexes of chromium(V) and (VI)

Synthesis	Complex	Comments	Reference
Chromium(V) complexes			
$[Cr^{III}(N_3)_2(cyclam)]+h\nu$	*trans*-$[Cr(N)(N_3)(cylam)]^+$		[31a]
$[\{trans\text{-}[Cr^{V}(N)(cyclam)]_2\}\text{-}(\mu\text{-}N_3)]^{3+}+ClO_4^-+CH_3CN$	*trans*-$[Cr(N)(NCCH_3)(cyclam)]^{2+}$		[31a]
$[Cr^{III}(N_3)(acac)(tacn)]^+ + h\nu$	$[Cr(N)(acac)(tacn)]^+$		[31b]
$[Cr^{III}(N_3)(tacac)(tacn)]^+ + h\nu$	$[Cr(N)(tacac)tacn]^+$		[31b]
$[Cr^{III}(N_3)(pic)(tacn)]^+ + h\nu$	$[Cr(N)(pic)(tacn)]^+$		[31b]
$[Cr^{III}(N_3)(phen)(tacn)]^+ + h\nu$	$[Cr(N)(phen)(tacn)]^+$		[31b]
$[Cr^{III}(N_3)_2(mebpb)]+h\nu$	[Cr(N)(mebpb)]		[32a]
$[Cr^{III}(N_3)_2(dmbpb)]+h\nu$	[Cr(N)(dmbpb)]		[32a]
$[Cr^{III}(N_3)_2(salophen)]+h\nu$	[Cr(N)(salophen)]		[32a]
$[Cr^{III}(OH)_2(Pc2-)]^- + NH_3 + Cl_2$	[Cr(N)(Pc2−)]		[33]
$[Cr^{V}(N)(salen)]+CN^-$	$[Cr(N)(CN)_5]^{3-}$		[34a]
$[Cr^{V}(N)(salen)]+CN^-$	$[Cr(N)(CN)_4]^{2-}$		[34a]
Chromium(VI) complexes			
$[Cr(NO)(N^iPr_2)_3]+2[V^{III}(Mes)_3(THF)]$	$[Cr(N)(N^iPr_2)_3]$ (**1**)	No Reaction w/PEt_3	[35]
$[Cr(NO)(NRR')_3]$ [a] $+2[V^{III}(Mes)_3(THF)]$	$[Cr(N)(NRR')_3]$ (**2**)	Unstable w/H_2O	[35]
$[Cr(NO)(NRR'')_3]$ [a] $+2[V^{III}(Mes)_3(THF)]$	$[Cr(N)(NRR'')_3]$		[35]
1 $+I^-$	$[Cr(N)(I)(N^iPr_2)_2]$ (**3**)		[36a]
3 $+Mg(CH_2SiMe_2Ph)_2$	$[Cr(N)(CH_2SiMe_2Ph)(N^iPr_2)_2]$	Unstable	[36a]
1 $+HS^tBu$	$[Cr(N)(S-^tBu)_2(N^iPr_2)]$		[36b]
1 $+$HOPh	$[Cr(N)(OPh)(N^iPr_2)_2]$		[36b]
1 $+$HOPh	$[Cr(N)(OPh)_2(N^iPr_2)]$ (**4**)		[36b]
1 $+HOC(CF_3)Me$	$[Cr(N)(OC(CF_3)Me)(N^iPr_2)_2]$		[36b]
1 $+HOC(CF_3)Me$	$[Cr(N)(OC(CF_3)Me)_2(N^iPr_2)]$ (**5**)		[36b]
4 $+LiCH_2SiMe$	$Cr(N)(CH_2SiMe_3)_2(N^iPr_2)]$		[36b]
5 $+^tBuNC$	$[Cr(N)(C(=N^tBu)CH_2SiMe_3)(CH_2SiMe_3)_2(N^iPr_2)]$		[36b]
2 $+$Lidbabh	$[Cr(N)(I)(NRR')_2]$ (**6**)		[37]
6 $+$Lidbabh	$[Cr(N)(dbabh)(NRR')_2]$ (**7**)		[37]
$(NH_4)_2Cr_2O_7+HN(SiMe_3)_2+^tBuOH+Me_3SiCl+NEt_3$	$[Cr(N)(O^tBu)_3]$ (**8**)		[38]
$\{CrO_2[N(SiMe_3)_2]_2\}+^tBuOH$	**8**		[38]

[a] $R = C(CD_3)_2CH_3$, $R' = 2,5\text{-}C_6H_3FMe$, $R'' = 3,5\text{-}C_6H_3Me_2$.

bond [33]. They have oxidized a simple chromium(III) complex in the presence of ammonia to generate a phthalocyaninato complex, $[Cr^{V}(N)(Pc2-)]$, Table 1. However, a more simplified alternative to generating the Cr≡N bond is to create new complexes from existing nitrido complexes where the Cr≡N moiety is conserved. For example, the simple nitridocyanometalates of chromium(V) of the forms $[Cr^{V}(N)(CN)_5]^{3-}$ and $[Cr^{V}(N)(CN)_4]^{2-}$ have recently been formed by ligand substitution on (nitrido)chromium(V) salen, Table 1 [34].

Similar to the oxidative cleavage of (azido)chromium(III) used to generate the corresponding chromium(V) nitrido complexes, oxidative cleavage has been achieved on nitrosyl chromium(II) compounds to generate Cr^{VI}≡N complexes. Deoxygenation of chromium(II) nitrosyl complexes by $[V^{III}(Mes)_3(THF)]$ formed the four-coordinate chromium(VI) nitrido complexes in high yields, Table 1 [35]. Although these complexes did not react with nucleophiles, such as triethylphosphane, or a number of protic reagents, interestingly, the nitrido moiety was unstable towards water and was readily hydrolyzed [36b]. However, the Cr≡N moiety was stable enough to make these complexes useful starting materials. For example, a variety of simple chromium(VI) compounds have been synthesized by ligand substitution reactions, Table 1 [36].

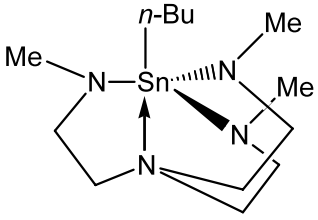
Mindiola and Cummins have utilized a clever analogue of the azide ion in their synthesis of the pseudo-tetrahedral $[Cr^{VI}(N)(I)(NRR'_2)_2]$ where $R = C(CD_3)_2CH_3$ and $R' = 2,5\text{-}C_6H_3FMe$ [37]. With the generation of anthracene as the driving force, Li(dbabh)(OEt_2) was reacted with a chromium(IV) complex to produce the (nitrido) chromium(VI) complex, **6**, Table 1. In the presence of excess Li(dbabh)(OEt_2), substitution of the iodide ligand was observed to occur to give, **7**, Table 1. The reactivity of these complexes was not reported.

7.1.1.2. Molybdenum nitrido complexes. Molybdenum nitrido complexes contain very strong Mo≡N bonds where the nitrogen atom behaves as a nucleophile. The Mo≡N moiety can also be sensitive towards protonation with protic agents and thus considered basic. However, this reactivity will depend on the ancillary ligands, which may be more reactive than the nitrido ligand. The typical bond lengths for the MoN bond in molybdenum(VI) nitrido complexes are ca. 1.6 Å. Interestingly,

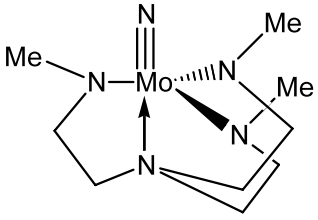
Table 2
Nitrido complexes of molybdenum(V) and (VI)

Synthesis	Complex	Comments	Reference
From the alkoxide complex, $[Mo^{VI}(N)(O^tBu)_3]$ (**9**)			
9 + $[Sn^{IV}(n\text{-Bu})(R_3N)]$[a]	$[Mo(N)(R_3N)]$[b]	H_2O sensitive	[39]
9 + $[Mo(NR'Ar)]$[c]	$[Mo(N)(NR'Ar)]$		[40]
9 + NpMgBr	$[Mo(N)(Np)_3]$	Reacts with H_2O, ROH, HX	[41a]
9 + MesMgBr	$[Mo(N)(Mes)_3]$		[41b]
9 + LiR'''[d]	$[Mo(N)(^tBuO)(R''')_2]$		[41b]
9 + 3 $[Ti(SAd)(O^iPr)_3]$	$[Mo(N)(SAd)_3]$	Reacts w/Mo^{III}	[42]
From the metal halides			
$[Mo(N)Cl_3]$ (**10**) + 1,2-$C_6H_4(CN)_2$	[Mo(N)Pc] Where Pc = phthalocyaninato		[43]
10 + C_6H_4-1,2-$(CN)_2$-4,5-$(Pr)_2$	[Mo(N)Pc'] Where Pc' = octapropylphthalocyaninato		[43]
10 + C_6H_4-1,2-$(CN)_2$-4,5-$(Bu)_2$	[Mo(N)Pc''] Where Pc'' = octabutylphthalocyaninato		[43]
10 + C_6H_4-1,2-$(CN)_2$-4,5-$(C_5H_{11})_2$	[Mo(N)Pc'''] Where Pc''' = octapentylphthalocyaninato		[43]
$[Mo(N)Cl_4]^-$ (**11**) + 2 Li_2bdt	$[Mo(N)(bdt)_2Cl]^{2-}$	Reacts w/H_2O and air	[44a]
10 + $[NEt_4]Cl + H_2O$ + MeCN	$[Mo(N)Cl_3(OH)(MeCN)]^-$		[44b]
From azido, azides or nitrous oxide			
$[MoCp^*_2(N_3)_2]$ + heat	$[(\eta^3\text{-Cp}^*)_2Mo(N)(N_3)]$		[45a]
$[\{(\eta^4\text{-Me}_3SiNCH_2CH_2)_3N\}MoCl]$[e] + TMS-$N_3$	$[\{(\eta^4\text{-Me}_3SiNCH_2CH_2)_3N\}Mo(N)]$ Reacts w/MeOTf, or (TMS)OTf		[45b]
$[\{(\eta^4\text{-C}_6F_5NCH_2CH_2)_3N\}MoCl] + NaN_3$	$[\{(\eta^4\text{-C}_6F_5NCH_2CH_2)_3N\}Mo(N)]$		[45c]
$[Mo(TTP)]_2$ + TMS-N_3	$[Mo(N)(TTP)]$		[45d]
$[Mo(TPP)]_2$ + TMS-N_3	$[Mo(N)(TPP)]$ (**12**)	Reacts w/MeI, EtI, BF_3	[45d]
		Reacts w/S_8, Bu_3P	[45e]
$[Mo(TMP)]$ + TMS-N_3	$[Mo(N)(TMP)]$ (**13**)	Reacts w/H^+, MeI	[45d]
$[Mo^{III}(N^tBuAr)_3]$[c] + N_2	$[Mo(N)(N^tBuAr)_3]$ (**14**)		[46b]
$[Mo^{III}(N^tBuAr)_3]$[c] + $MesN_3$	**14**		[46b]
$[Mo^{III}(N^tBuAr)_3]$[c] + N_2O	**14**		[46b]
$[Mo^{III}(NadAr)_3]$[c] + $MesN_3$	$[Mo(N)(NAdAr)_3]$ (**15**)		[46a]
$[Mo^{III}(NadAr)_3]$[c] + N_2O	**15**		[46a]
Other reactions			
$[Mo^{VI}(N)(OsiMe_3)_3(NH_3)]_2$ + py	$[Mo(N)(OSiMe_3)_3(py)]$		[44]
trans-$[Mo(N_2)_2(dppe)_2]$ + benzoylacetonitrile	*trans*-$[Mo(N)(dppe)_2(NCCCOPh)]$		[52]

a [a,b]



b



[c] R = $MeHNCH_2CH_3$, R' = $C(CD_3)_2Me$, R'' = Ad or ^tBu, Ar = 3,5-$C_6H_3Me_2$.
[d] R''' = 2-$Me_2NCH_2C_6H_4$, Ar = 3,5-$C_6H_3Me_2$.
[e] $(\eta^4\text{-Me}_3SiCH_2CH_2)_3N$ represents a trianion.

the well-known molybdenum(VI) alkoxide complex, $[Mo^{VI}(N)(O^tBu)_3]$ (**9**) is believed to be polymeric in the solid state due to Mo ≡ N → Mo interactions.

The alkoxide complex, **9**, has been involved in some quite interesting chemistry. For example, transmetallation was observed to occur when this complex was reacted with an organostannane compound, $[\{N(MeHNCH_2CH_2)_3\}Sn^{IV}(n\text{-Bu})]$ to give the corresponding nitrido$[\{N(MeHNCH_2CH_2)_3\}Mo^{VI}(N)]$, Table 2 [39]. In addition, intermetal nitrogen atom transfer has been observed to occur in the absence of dinitrogen between $[Mo^{VI}(N)(O^tBu)_3]$ and a molybdenum(III) complex, $[Mo^{III}(NR'Ar)_3]$ where R' = $C(CD_3)_2Me$, Ar = 3,5-$C_6H_3Me_2$, Table 2 [40]. This reaction was coupled with Mo≡Mo bond formation. Intermetal nitrogen atom transfer between these two complexes

has also been observed in the presence of dinitrogen. Furthermore, the nitrogen atom of the alkoxide complex, **9**, is not reactive towards nucleophiles such as Grignard reagents and carbanions. Thus, only ligand substitution has been observed, making **9** a useful starting material, Table 2 [41]. Additionally, ligand exchange with a titanium(IV) complex produced a molybdenum(VI) nitrido thiolate, Table 2 [42].

Other useful starting materials for (nitrido)molybdenum(VI) complexes are the (nitrido)molybdenum chlorides, $[Mo^{VI}(N)Cl_3]$ (**10**) and $[Mo^{VI}(N)Cl_4]^-$ (**11**). Recently, macrocyclic nitrido molybdenum(VI) compounds were produced from $[Mo^{VI}NCl_3]$ and substituted phthalocyanides, Table 2 [43]. Although the reactivity of the corresponding nitrido complexes was not reported, Nakamura and coworkers reported on the weakened Mo≡N bond due to thiolate coordination. When benzenethiolate ligands were substituted for the chloride ligands on the anion, $[Mo^{VI}(N)Cl_4]^-$, the anionic product would readily react with water or molecular oxygen to give the oxomolybdenum(VI) complex, Table 2 [44a]. This reactivity towards water and oxygen was reported to be greater than the reactivity of $[Mo^{VI}(N)Cl_4]^-$, which has been reported to hydrolyze to $[Mo^{VI}(O)Cl_4]^-$. Insight into the hydrolysis of $[Mo^{VI}(N)Cl_4]^-$ has been provided by the isolation of a possible hydrolysis intermediate, $[Mo^{VI}(N)Cl_3(OH)(CH_3CN)]^-$, Table 2 [44b].

Formation of the Mo≡N bond has been achieved by N–N bond cleavage. Nitrido complexes have formed from the decomposition of (azido)molybdenum complexes and from reactions involving organic azides, such as mesityl azide and trimethylsilyl azide, Table 2 [45,46]. The reaction of mesityl azide with transition metals usually results in oxidation of the metal and formation of imido moiety. Thus the production of nitrido complexes from mesityl azide is quite rare, $[Mo^{VI}(N)(NR''Ar)_3]$, where $R'' = {}^tBu$ (**14**) or Ad (**15**), and $Ar = 3,5\text{-}C_6H_3Me_2$, Table 2 [46]. Interestingly, the same nitrido products are produced from the reaction of $[Mo^{III}(NR''Ar)_3]$ with nitrous oxide (N_2O) [46]. It should be noted that this reactivity of N_2O in these reactions with molybdenum(III) is unusual. Nitrous oxide normally behaves similar to organic azides, where both release dinitrogen.

Reactivity of molybdenum(V) nitrido porphyrins have been reported. Although the MoN moiety is nucleophilic in complexes **12** and **13** and reacts with alkyl halides, **12** was reported to react with elemental sulfur and tri-*n*-butylphosphane [45e]. This reactivity represents a good example of how nitrido ligands can behave as both an electrophile and nucleophile.

7.1.1.3. Tungsten nitrido complexes. Nitrido complexes of tungsten are usually stable and contain a nucleophilic W≡N moiety. Formation of new nitrido complexes of tungsten(VI) has been achieved by decomposition of (azido)tungsten(IV) and by ligand substitution on a common tungsten(VI) starting material, $[W^{VI}(N)Cl_3]$, Table 3 [7a,43]. Using sodium azide and $[W^{IV}Cl\{(Me_3SiNCH_2CH_2)_3N\}]$, the nucleophilic (nitrido)tungsten(VI) complex, $[W^{VI}N\{(Me_3SiNCH_2CH_2)_3N\}]$ was formed [7a]. This complex would readily form the methylimido product upon addition of methyl triflate, demonstrating the nucleophilicity of the W≡N moiety. Interestingly, the macrocyclic compound, nitrido-(phthalocyaninato)tungsten(VI) complex would produce the corresponding oxo complex, $[W(O)Pc]^+$ in the presence of triphenylphosphane [43]. The mechanism of this reaction is not fully understood.

An unstable tungsten(IV) nitrido complex, $[Tp^*(CO)_2W{\equiv}N]$ (**16**) was prepared by either oxidation of a tungsten(II) complex with N_3^- or by deprotonation of $[Tp^*(CO)_2WNH]^+$ [47]. The complex, **16**, reacts readily with MeOTf, $[Ph_3C][BF_4]$, TsCl, $CH_3(O)CCl$, and acetic anhydride to give the corresponding alkyl,

Table 3
Nitrido complexes of tungsten(IV) and (VI)

Synthesis	Complex	Comments	Reference
From azides			
$[W^{IV}(Cl)(N_3N)]+NaN_3$	$[W^{VI}(N)(N_3N)]$ Where $N_3N = (\eta^4\text{-}Me_3SiNCH_2CH_2)_3N$ (trianion)	Reacts with MeOTf	[7a]
$[Tp^*(CO)_2WI]+N_3^-$	$[Tp^*W(N)(CO)_2]$ (**16**)	Reacts w/MeOTf, TsCl, AA, and $ClC(O)CH_3$	[47]
From metal halides			
$[W(N)Cl_3]+1,2\text{-}C_6H_4(CN)_2$	[W(N)Pc] Where Pc = phthalocyaninato		[43]
$[WNCl_3]+C_6H_4\text{-}1,2\text{-}(CN)_2\text{-}5\text{-}(C_5H_{11})_2$	[W(N)Pc′] Where Pc′ = octapentylphthalocyaninato		[43]
$[WNCl_3]+C_6H_4\text{-}1,2\text{-}(CN)_2\text{-}5\text{-}({}^tBu)_2$	$[W(N)Pc^{t\text{-}Bu}]$ Where $Pc^{t\text{-}Bu}$ = octa-*tert*-butylphthalocyaninato		[43]
Other reactions			
$[Tp^*W(NH)(CO)_2]^+ + Et_3N$	**16**	Reacts with H^+, Ph_3C^+	[47]

Table 4
Imido complexes of chromium(III), (IV), and (V)

Synthesis	Complex	Comments	Reference
From azides			
$[Cr^{II}(TPP)]+Tol\text{-}N_3$	$[Cr^{IV}(NTol)TPP]$	Reacts w/PPh_3, MeI, CS_2, styrene, and $C_6H_5C(O)H$	[18]
$[Cr^{II}(TPP)]+p\text{-}Cl\text{-}Ph\text{-}N_3$	$[Cr^{IV}(N\text{-}4\text{-}ClPh)TPP]$	Reacts w/CS_2	[18]
$[Cr^{II}(TPP)]+p\text{-}I\text{-}Ph\text{-}N_3$	$[Cr^{IV}(N\text{-}4\text{-}IPh)TPP]$		[18]
$[Cr^{II}(TPP)]+p\text{-}Ome\text{-}Ph\text{-}N_3$	$[Cr^{IV}(N\text{-}4\text{-}OMePh)TPP]$	Reacts w/styrene	[18]
$[Cr^{II}(TTP)]+Tol\text{-}N_3$	$[Cr^{IV}(NTol)TTP]$		[18]
From lithium amide reagents			
$[Cr^{III}Cp^*Br_2]_2+2Li[N(^tBu)SPh]$	$[Cr^{V}Cp^*(N^tBu)(SPh)_2]$ (**17**)	No reaction w/CO or isocyanides	[48]
$[Cr^{III}Cp^*Br_2]_2+2Li(N(2\text{-}^iPrPh)SPh)$	$[Cr^{V}Cp^*(N\text{-}2\text{-}^iPrPh)(SPh)_2]$ (**18**)		[49]
$[Cr^{III}Cp^*Br_2]_2+2Li(N(4\text{-}MePh)SPh)$	$[Cr^{V}Cp^*(N\text{-}4\text{-}MePh)(SPh)_2]$		[49]
$[Cr^{III}Cp^*Br_2]_2+2Li(N(2\text{-}^tBuPh)SPh)$	$[Cr^{V}Cp^*(N\text{-}2\text{-}^tBuPh)(SPh)_2]$ (**19**)		[49]
$[Cr^{III}Cp^*Br_2]_2+PhC_2Ph+2Li(HN\text{-}2,6\text{-}^iPr_2Ph)$	$[Cr^{III}Cp^*(N\text{-}2,6\text{-}^iPr_2Ph)(Ph_2C_2)]$		[50]
Ligand substitution and metathesis			
17$+BCl_3$	$[Cr^{V}Cp^*(N^tBu)Cl_2]$		[49]
18$+BCl_3$	$[Cr^{V}Cp^*(N\text{-}2\text{-}^iPrPh)Cl_2]$		[49]
19$+BCl_3$	$[Cr^{V}Cp^*(N\text{-}2\text{-}^tBuPh)Cl_2]$		[49]
$[Cr(N^tBu)Cl_3(dme)]+[9]aneS_3$	$[Cr(N^tBu)Cl_2([9]aneS_3)]^+$	No reaction w/styrene	[51]
$[Cr(N^tBu)Cl_3(dme)]+Cp^-$	$[Cr(N^tBu)Cl_2(Cp)]$ (**20**)		[19]
$[Cr(N^tBu)Cl_3(dme)]+L_{OEt}$	$[Cr(N^tBu)Cl_2(L_{OEt})]$ Where $L_{OEt}=\eta\text{-}C_5H_5Co[PO(OEt_2)]_3^-$		[19]
$[Cr(N^tBu)Cl_4]^-+Cp^-$	**20**		[19]
$[Cr(N^tBu)Cl_3(dme)]+tb_2salen$	$[Cr(N^tBu)Cl(tb_2salen)]$ (**21**)		[19]
$[Cr(N^tBu)Cl(salen)]+AgBF_4$	$[Cr(N^tBu)(salen)]^+$	Reacts w/PPh_3	[19]
21$+AgBF_4$	$[Cr(N^tBu)(tb_2salen)]^+$	Reacts w/PPh_3	[19]

aryl and acyl imido products again demonstrating the significant nucleophilicity of the nitrido ligand on tungsten.

7.1.2. Imido complexes of Group 6

7.1.2.1. Chromium imido complexes. Terminal imido complexes of chromium(IV), (V) and (VI) have been reported. Although, the number of such complexes is small compared to the other metals of Group 6. The (imido)chromium(VI) complexes often contain other multiply bonded ligands, such as terminal oxo. Thus, only chromium complexes in the oxidation states (IV) and (V) will be considered herein.

Paramagnetic (arylimido)chromium(IV) porphyrin complexes have been prepared from the oxidation of chromium(II) porphyrins with aryl azides, Table 4 [18]. Interestingly, the complexes were moisture sensitive and gave the corresponding oxo compounds. In addition, the Cr≡NR moiety was reported to be electrophilic and susceptible to NR group transfer with triphenylphosphane and styrene. However, the Cr≡NR moiety also reacted with the following electrophiles: benzaldehyde, carbon disulfide and methyl iodide. Thus, the imido ligand in these chromium(IV) complexes behaves as both an electrophile and nucleophile.

Formation of the Cr≡NR bond from lithium amide reagents has afforded a convenient entry to organometallic chromium(V) complexes. Employing the lithium amide reagent, Li(NRSPh), where R = alkyl [48] or aryl [49] as the source of nitrene, a series of cyclopentadienyl complexes have been prepared, Table 4. It is worth noting that the arylimido complexes of chromium(V) are rare. The arylimido complexes reported by Danaopoulos, Hursthouse, and coworkers [49] react with Lewis acids but do so with retention of the Cr≡NR moiety to give only ancillary ligand substitution products, Table 4. Interestingly, with the same chromium(III) starting material, $[Cr(\eta^5\text{-}C_5Me_5)Br_2]_2$, and an alternative lithium amide reagent, Li(NHR) where R = 2,6-diisopropylphenyl, a chromium(III) imido complex, $[Cr(NR)(\eta^5\text{-}C_5Me_5)(PhCCPh)]$, was reported to be produced in the presence of diphenylacetylene [50].

Leung and coworkers have produced a variety of chromium(V) imido complexes containing macrocyclic ligands by simple ligand substitution on $[Cr(NBu^t)Cl_3(dme)]$, a common staring material [19,51]. They have also reported the synthesis of the first cationic chromium(V) complexes, $[Cr(NBu^t)(salen)]^+$ and $[Cr(NBu^t)(tb_2salen)]^+$ and their reactivity with nucleophiles [19]. Both complexes will transfer the NBu^t group to triphenylphosphane to give $Bu^tN{=}PPh_3$ and chromium(III).

Table 5
Imido complexes of molybdenum(IV), (V), and (VI)

Synthesis	Complex	Comments	Reference
From the nitrido			
$[\{(\eta^4\text{-}Me_3SiNCH_2CH_2)_3N\}]Mo(N)]$ (**21**) + (TMS)Otf	$[Mo^{VI}(NSiMe_3)-\{(\eta^4\text{-}Me_3SiNCH_2CH_2)_3N\}]^+$ (**22**)	Stable	[7a]
21 + MeOTf	$[Mo^{VI}(NMe)\{(\eta^4\text{-}Me_3SiNCH_2CH_2)_3N\}]^+$ (**23**)	Stable	[7a]
[Mo(N)(TMP)] + HCl	$[Mo(=NH)TMP]^+$	Unstable	[45d]
[Mo(N)(TPP)] + HCl	$[Mo(=NH)TPP]^+$	Stable	[45d]
[Mo(N)(TPP)] + MeI	$[Mo(=NMe)TPP(H_2O)][I_3]$	Stable	[53]
$[Mo(N)(N_3)(syn\text{-}Me_8[16]aneS_4)]$ + HOTf	$[Mo^{IV}(NH)(Otf)(syn\text{-}Me_8[16]aneS_4)]^+$ (**24**)	Stable; reacts w/MeC(O)Me,PhC(O)H to give organo-imido products	[54]
24 + MeC(O)Me	$[Mo=(NCMe_2OH)-(OTf)(syn\text{-}Me_8[16]aneS_4)]^+$		[54]
24 + PhC(O)H	$[Mo=(NCHPhOH)-(OTf)(syn\text{-}Me_8[16]aneS_4)]^+$		[54]
From bis-imido			
$[Mo^{VI}(N^tBu)_2Cl_2] + py + O(Ph_2SiOH)_2$	$[Mo^{IV}(N^tBu)(py)(O(Ph_2SiO)_2)_2]$		[55a]
$[Mo^{VI}(NTos)_2Cl_2]_n + PMe_3$	$[Mo(NTos)Cl_2(PMe_3)_3]$		[55b]
$[Mo^{VI}(NTos)_2Cl_2(dme)] + Pme_3$	$[Mo(NTos)Cl_2(PMe_3)_3]$		[55b]
$[Tp^*Mo^{VI}(N^tBu)_2Cl] + H^+$	$[Tp^*Mo^{VI}(N^tBu)(N^tHBu)Cl]^+$		[55c]
$[Mo^{VI}(N^tBu)_2(NH^tBu)_2] + LH_4$	$[Mo(N^tBu)L]$ Where $LH_4 = p\text{-}tert\text{-}$butyl-calix[4]areneH$_4$	Stable	[56d]
$[Mo^{VI}(NMes)_2Cl_2(dme)] + LH_4$	[Mo(NMes)L] Where $LH_4 = p\text{-}tert\text{-}$butyl-calix[4]areneH$_4$	Stable	[56d]
$[Mo^{VI}(NR)_2(O^tBu)_2(CH_2CH_2)] + LH_4$	[MoL(NR)(NCMe)] Where R = 2,6-C_6H_3-^{i}Pr$_2$ and LH_4 = calix[4]areneH$_4$		[57c]
$[Mo^{VI}(NR)_2(O^tBu)_2(CH_2CH_2)] + LH_6$	$[Mo(LH_2)(2\text{-}NC_6H_4CH_2CH_2C_6H_4NHC(Me)NH\text{-}2)]$ Where R = 2,2′-(*N*)-C_6H_4 and $LH_6 = p\text{-}tert\text{-}$butyl-calix[6]areneH$_6$		[57b]
$[Mo^{VI}(NMes)_2Cl_2(dme)] + [MoCl_4(THF)_2]$	$[Mo^{V}(NMes)Cl_3(dme)]$		[58a]
$[Mo^{VI}(NPh)_2Cl_2(dme)] + Li_2[TMS_2pda]$	$[Mo(NPh)Cl_2(TMS_2pda)(NH_2Ph)]$		[59b]
$[Mo^{VI}(N^tBu)_2(OSiMe_3)_2] + CatH_2 + py$	$[Mo(N^tBu)(Cat)(OsiMe_3)_2(py)]$ Where $CatH_2 = 1,2\text{-}(OH)_2C_6H_4$		[57d]
From isonitrile complexes			
trans-$[Mo(dppe)_2(N_2)(NCPh)]$ + HCl	*trans*-$[Mo^{IV}Cl(NCH_2Ph)(dppe)_2]^+$		[58b]
trans-$[Mo(dppe)_2(N_2)(NCMe)]$ + HCl	*trans*-$[MoCl(NCH_2Me)(dppe)_2]^+$		[58b]
trans-$[Mo(dppe)_2(N_2)(NC\text{-}p\text{-}OMePh)]$ + HCl	*trans*-$[MoCl(NCH_2\text{-}p\text{-}OMePh)(dppe)_2]^+$		[58b]
trans-$[Mo(dppe)_2(N_2)(NCTol)]$ + HX	*trans*-$[MoX(NCH_2Tol)(dppe)_2]^+$ Where X = Cl or Br		[58b]
trans-$[Mo(dppe)_2(N_2)(NCMe)] + HBF_4$	*trans*-$[MoF(NCH_2Me)(dppe)_2]^+$		[58b]
trans-$[Mo(dppe)_2(N_2)(NCPh)] + HBF_4$	*trans*-$[MoF(NCH_2Ph)(dppe)_2]^+$		[58b]
trans-$[Mo(dppe)_2(N_2)(NCTol)] + HBF_4$	*trans*-$[MoF(NCH_2Tol)(dppe)_2]^+$		[58b]
trans-$[Mo(dppe)_2(N_2)(NC\text{-}p\text{-}OMePh)] + HBF_4$	*trans*-$[MoF(NCH_2\text{-}p\text{-}OMePh)(dppe)_2]^+$		[58b]
Using primary amines			
$[CpMoCl_4]$ (**25**) + 2,6-Me_2PhNH_2	$[CpCl_2Mo(N\text{-}2,6\text{-}Me_2Ph)]$		[61a]
$[Cp^{Me}MoCl_4]$ (**26**) + 2,6-Me_2PhNH_2	$[Cp^{Me}Cl_2Mo(N\text{-}2,6\text{-}Me_2Ph)]$		[61a]
$[Cp^{i\,Pr}MoCl_4]$ (**27**) + 2,6-Me_2PhNH_2	$[Cp^{i\,Pr}Cl_2Mo(N\text{-}2,6\text{-}Me_2Ph)]$		[61a]
$[Cp^{Cl}MoCl_4] + 2,6\text{-}Me_2PhNH_2 + Net_3$	$[Cp^{Cl}Cl_2Mo(N\text{-}2,6\text{-}Me_2Ph)]$	Could not be oxidized	[62b]
25 + ^{t}BuNH$_2$	$[CpCl_2Mo(N^tBu)]$ (**29**)		[63b]
[Cp*MoCl$_4$] (**28**) + ^{t}BuNH$_2$	$[Cp^*Cl_2Mo(N^tBu)]$ (**30**)		[62a,63b]
26 + ^{t}BuNH$_2$	$[Cp^{Me}Cl_2Mo(N^tBu)]$ (**31**)		[62c]
27 + ^{t}BuNH$_2$	$[Cp^{i\text{-}Pr}Cl_2Mo(N^tBu)]$ (**32**)		[62c]
25 + ^{i}PrNH$_2$	$[CpCl_2Mo(N^iPr)]$		[62c]
28 + ^{i}PrNH$_2$ + Net$_3$	$[Cp^*Cl_2Mo(N^iPr)]$		[62a]
26 + ^{i}PrNH$_2$	$[CpCl_2Mo(N^iPr)]$		[61a]
25 + ^{n}PrNH$_2$	$[CpCl_2Mo(N^nPr)]$		[62c]
25 + PhNH$_2$	$[CpCl_2Mo(NPh)]$ (**33**)		[62c]
26 + PhNH$_2$	$[Cp^{Me}Cl_2Mo(NPh)]$		[62c]
28 + $C_6F_5NH_2$ + NEt$_3$	$[Cp^*Cl_2Mo(NC_6F_5)]$		[62a]
28 + 2,6-^{i}Pr$_2$PhNH$_2$ + NEt$_3$	$[Cp^*Cl_2Mo(N\text{-}2,6\text{-}^iPr_2Ph)]$		[62a]
$[Cp^{Me}MoBr_4] + {}^tBuNH_2$	$[Cp^{Me}Br_2Mo(N^tBu)]$		[62c]

Table 5 (*Continued*)

Synthesis	Complex	Comments	Reference
$Na[MoO_4]$ (**34**) + NEt_3 + $SiMe_3Cl$ + 2-$(H_2N)C_6H_4CO_2H$	$[MoCl_3\{N\text{-}2\text{-}Me_3SiO_2CC_6H_4\}\{2\text{-}(HN)C_6H_4CO_2\}]^-$		[64]
34 + NEt_3 + $SiMe_3Cl$ + 2-$(H_2N)C_6H_4SO_3H$	$[MoCl_3\{N\text{-}2\text{-}SO_3C_6H_4\}\{2\text{-}(HN)C_6H_4SO_3\}]^{2-}$		[64]
34 + NEt_3 + $SiMe_3Cl$ + 2,6-$^i Pr_2C_6H_4NH_2$ + 2-$(H_2N)C_6H_4CO_2H$	$[MoCl_3\{N\text{-}2,6\text{-}^iPr_2C_6H_4\}\{2\text{-}(HN)C_6H_4CO_2\}]^-$		[64]
34 + NEt_3 + $SiMe_3Cl$ + 2,2-diphenylglycine	$[MoCl_3\{2\text{-}(HN)C_6H_4CO_2(CO_2H)\}-(NCHPh_2)]^-$		[64]
34 + NEt_3 + $SiMe_3Cl$ + 2-aminoterephthalic acid	$[MoCl_3\{2\text{-}(HN)C_6H_4CO_2(CO_2H)\text{-}1,4\}\{2\text{-}(CO_2H)_2C_6H_4N\}]^-$		[64]
$[Mo(O)(S_2CNEt_2)_2Cl_2]$ (**35**) + *p*-$XC_6H_4NH_2$	$[Mo(N\text{-}4\text{-}XC_6H_4)(S_2CNEt_2)_2Cl_2]$ Where X = I, X = NO_2, X = NH_2, or X = NMe_2		[65]
35 + 2-MeC_6H_3-1,4-$(NH_2)_2$	$[Mo(N\text{-}2\text{-}MeC_6H_3\text{-}4\text{-}NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + 2,3-$Me_2C_6H_3$-1,4-$(NH_2)_2$	$[Mo(N\text{-}2,3\text{-}Me_2C_6H_3\text{-}4\text{-}NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + 2,5-$Me_2C_6H_3$-1,4-$(NH_2)_2$	$[Mo(N\text{-}2,5\text{-}Me_2C_6H_3\text{-}4\text{-}NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + 2,3,5,6-$Me_4C_6H_3$-1,4-$(NH_2)_2$	$[Mo(N\text{-}2,3,5,6\text{-}Me_4C_6H_3\text{-}4\text{-}NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + 3-$NO_2C_6H_3$-1,4-$(NH_2)_2$	$[Mo(N\text{-}3\text{-}NO_2C_6H_3\text{-}4\text{-}NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + 2,6-$Cl_2C_6H_3$-1,4-$(NH_2)_2$	$[Mo(N\text{-}2,5\text{-}Cl_2C_6H_3\text{-}4\text{-}NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + H_2NRNH_2[a]	$[Mo(NRNH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + $H_2NR'NH_2$[b]	$[Mo(NR'NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
35 + $H_2NC_{10}H_6NH_2$	$[Mo(N\text{-}1,5\text{-}C_{10}H_6NH_2)(S_2CNEt_2)_2Cl_2]$		[65]
Oxidation/reduction			
22 + $Li_2C_8H_8$	$[\{(\eta^4\text{-}Me_3SiNC_2H_3)_3N\}Mo^V(NSiMe_3)]$	No reaction w/MeOTf, (TMS)OTf, Py^+Cl, TMS-Cl, MeI, acetyl chloride. Only oxidation to nitrido: $[\{(\eta^4\text{-}Me_3SiNC_2H_3)_3N\}Mo^V(N)]$	[7a]
29 + Na/Hg + CO	$[CpClMo^{IV}(N^tBu)(CO)]$	Stable	[62c]
29 + Na/Hg + C_2Me_2	$[CpClMo^{IV}(N^tBu)(C_2Me_2)]$	Stable	[62c]
29 + KC_8 + C_2H_4	$[CpClMo^{IV}(N^tBu)(C_2H_4)]$	Air sensitive	[62c]
29 + Na/Hg + styrene	$[CpClMo^{IV}(N^tBu)(CH_2CHPh)]$	Isomeric mixture	[62c]
31 + KC_8 + C_2H_4	$[Cp^{Me}ClMo^{IV}(N^tBu)(C_2H_4)]$	Air sensitive	[62c]
31 + Na/Hg + Pme_3	$[Cl_2Mo^{IV}(N^tBu)(PMe_3)_3]$	Stable	[62c]
32 + KC_8 + C_2H_4	$[Cp^{i\text{-}Pr}ClMo^{IV}(N^tBu)(C_2H_4)]$	Air sensitive	[62c]
33 + Na/Hg + C_2Me_2	$[CpClMo^{IV}(NPh)(C_2Me_2)]$		[62c]
29 + Na[Cp]	$[(Cp)_2Mo^{IV}(N^tBu)]$		[61a]
31 + Na[Cp]	$[(Cp^{Me})_2Mo^{IV}(N^tBu)]$		[61a]
32 + Na[Cp]	$[(Cp^{iPr})_2Mo^{IV}(N^tBu)]$		[61a]
$[CpMo^V(N^iPr)Cl_2]$ + Na[Cp]	$[(Cp)_2Mo^{IV}(N^iPr)]$		[61a]
$[Cp^{Me}Mo^V(N^iPr)Cl_2]$ + Na[Cp]	$[(Cp^{Me})_2Mo^{IV}(N^iPr)]$		[61a]
33 + Na[Cp]	$[(Cp)_2Mo^{IV}(NPh)]$		[61a]
$[Cp^{Me}Mo^V(NPh)Cl_2]$ + Na[Cp]	$[(Cp^{Me})_2Mo^{IV}(NPh)]$		[61a]
$[CpMo^V(N\text{-}2,6\text{-}Me_2Ph)Cl_2]$ + Na[Cp]	$[(Cp)_2Mo^{IV}(N\text{-}2,6\text{-}Me_2Ph)]$		[61a]
$[Cp^{Me}Mo^V(N\text{-}2,6\text{-}Me_2Ph)Cl_2]$ + Na[Cp]	$[(Cp^{Me})_2Mo^{IV}(N\text{-}2,6\text{-}Me_2Ph)]$		[61a]
$[Cp^{iPr}Mo^V(N\text{-}2,6\text{-}Me_2Ph)Cl_2]$ + Na[Cp]	$[(Cp^{iPr})_2Mo^{IV}(N\text{-}2,6\text{-}Me_2Ph)]$		[61a]
$[Mo^V(NMes)Cl_3(dme)]$ + Na/Hg + PMe_3	$[Mo^{IV}(NMes)(PMe_3)_2Cl_2]$		[58b]
$[Mo^V(NMes)Cl_3(dme)]$ + Na/Hg + $P(OMe)_3$	$[Mo^{IV}(NMes)(P(OMe)_3)_3Cl_2]$		[66b]
30 + PCl_5	$[CpCl_3Mo^{VI}(N^tBu)]$ (**36**)		[63b]
29 + Cl_2	$[(Cp)Mo^{VI}(N^tBu)Cl_3]$		[61b]
31 + Cl_2	$[(Cp^{Me})Mo^{VI}(N^tBu)Cl_3]$		[61b]
32 + Cl_2	$[(Cp^{iPr})Mo^{VI}(N^tBu)Cl_3]$		[61b]
$[(Cp^{Me})_2Mo^{IV}(N^tBu)]$ + MeI	$[(Cp^{Me})_2Mo^{VI}(N^tBu)(Me)]^+$	Stable	[61a]
$[(Cp)_2Mo^{IV}(N^iPr)]$ + MeI	$[(Cp)_2Mo^{VI}(N^iPr)(Me)]^+$	Stable	[61a]
$[(Cp)_2Mo^{IV}(N\text{-}2,6\text{-}Me_2Ph)]$ + MeI	$[(Cp)_2Mo^{VI}(N\text{-}2,6\text{-}Me_2Ph)(Me)]^+$	Stable	[61a]
$[(Cp^{Me})_2Mo^{IV}(N^tBu)]$ + (allyl)I	$[(Cp^{Me})Mo^V(N^tBu)(I)_2]$	Air sensitive	[61a]
From isocyanates			
$[Mo(O)_2(S_2CNEt_2)_2]$ (**36**) + RNCO	$[Mo(NR)(\eta^2\text{-}S_2)(S_2CNEt_2)_2]$ Where R = Ph, R = Tol, R = *o*-MePh, R = 2,6-Me_2Ph, R = 2,6-Cl_2Ph, R = 2,6-$^iPr_2$Ph, R = Ad, R = ^{t}Bu		[66a]
$[Mo(O)Cl_4]$ + 2,6-$^iPr_2C_6H_3NCO$ + *p*-xylene	$[Mo(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_3L_2]$ Where L = *N*-2′,6′-diisopropylphenyl-2,5-dimethylbenamide		[66b]
$[Mo(O)Cl_4]$ + 2,6-$^iPr_2C_6H_3NCO$ + dme	$[Mo(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_3(dme)]$		[66b]

Table 5 (*Continued*)

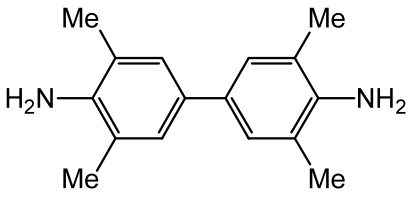
Synthesis	Complex	Comments	Reference
Ligand substitution			
23 + MeMgCl	[{(R)$_3$N}Mo^{VI}(NMe)(Me)] Where R = η^4-Me$_3$-SiNCH$_2$CH$_2$	Unstable	[7a]
22 + MeMgCl	[{(R)$_3$N}Mo^{VI}(NSiMe$_3$)(Me)] Where R = η^4-Me$_3$-SiNCH$_2$CH$_2$	Thermally stable	[7a]
[Mo^{VI}Cp*(N^{t}Bu)Cl$_3$] + 2LiMe	[Cp*ClMe$_2$Mo^{VI}(N^{t}Bu)]	Stable	[63b]
[Mo^{VI}Cp*(N^{t}Bu)Cl$_3$] + 3LiMe	[Cp*Me$_3$Mo^{VI}(N^{t}Bu)]	Stable	[63b]
[Mo(NMes)Cl$_3$(dme)] + NaL$_{OEt}$	[Mo^V(NMes)Cl$_2$(L$_{OEt}$)] Where L$_{OEt}$ = η-C$_5$H$_5$Co{P(O)(OEt)$_2$}$_3$	Air/H$_2$O sensitive in sol.	[58a]
[Mo(NMes)Cl$_3$(dme)] + Tl(acac)	[Mo^V(NMes)Cl(acac)$_2$]	Air/H$_2$O sensitive in sol.	[58a]
[Mo(NMes)Cl$_3$(dme)] + depe	[Mo^V(NMes)Cl$_3$(depe)]	Air/H$_2$O sensitive in sol.	[58a]
[Mo^{IV}(NMes)(PMe$_3$)$_3$Cl$_2$] (**37**) + HBr	[Mo^{IV}(NMes)(PMe$_3$)$_3$Br$_2$]		[58b]
37 + HNCS	[Mo^{IV}(NMes)(PMe$_3$)$_3$(NCS)$_2$]		[58b]
37 + KS$_2$COPr^i	[Mo^{IV}(NMes)(PMe$_3$)(S$_2$COPr^i)$_2$]		[58b]
37 + depe	[Mo^{IV}(NMes)(PMe$_3$)Cl$_2$(depe)]		[58b]
37 + L	[Mo^{IV}(NMes)Cl$_2$(PMe$_3$)$_2$L] Where L = P(OMe)$_3$, L = P(OCH$_2$)$_3$CH$_2$CH$_3$, L = CO, L = CN^{t}Bu, L = MeCN, L = C$_2$H$_4$, L = CH$_2$CHCO$_2$Me, L = PhC$_2$H, L = Ph$_2$C$_2$		[58b]
37 + KS$_2$COMe	[Mo^{IV}(NMes)(PMe$_3$)$_2$(S$_2$COMe)Cl] (**38**)		[58c]
37 + 2KS$_2$COMe	[Mo^{IV}(NMes)(PMe$_3$)(S$_2$COMe)$_2$]		[58c]
37 + 2KS$_2$C(NC$_4$H$_4$)	[Mo^{IV}(NMes)(PMe$_3$)(S$_2$C(NC$_4$H$_4$)$_2$]		[58c]
37 + CS$_2$	[Mo^{IV}(NMes)Cl$_2$(S$_2$CPMe$_3$)]		[58c]
38 + CO	[Mo^{IV}(NMes)(PMe$_3$)(CO)(S$_2$COMe)Cl]		[58c]
[Mo^{VI}(NMes)(O)(dme)Cl$_2$] (**39**) + MgMeCl	[Mo^{VI}(NMes)ClMe$_3$]		[58d]
39 + Mg(CH$_2$C(Me)$_2$Ph)Cl	[Mo^{VI}(NMes)Cl(CH$_2$C(Me)$_2$Ph)$_3$]		[58d]
39 + Mg(CH$_2$SiMe$_3$)Cl	[Mo^{VI}(NMes)Cl(CH$_2$SiMe$_3$)$_3$]		[58d]
[Mo^{VI}(NPh)Cl$_2$(TMS$_2$pda)(NH$_2$Ph)] (**40**) + L	[Mo(NPh)Cl$_2$(TMS$_2$pda)L] Where L = THF or PMe$_3$		[59b]
[Mo^{VI}(NPh)Cl$_2$(L)THF] (**41**) + MeMgCl	[Mo(NPh)Me$_2$(L)] Where L = TMS$_2$pda		[59b]
41 + NpMgCl	[Mo(NPh)Np$_2$(TMS$_2$pda)]		[59b]
40 + NpMgBr	[Mo(NPh)Np$_2$(TMS$_2$pda)]		[59b]
41 + PhCH$_2$MgCl	[Mo(NPh)(PhCH$_2$)$_2$(TMS$_2$pda)]		[59b]
41 + Me$_3$SiCH$_2$MgCl	[Mo(NPh)(Me$_3$SiCH$_2$)$_2$(TMS$_2$pda)]		[59b]
40 + Me$_3$SiCH$_2$MgBr	[Mo(NPh)(Me$_3$SiCH$_2$)$_2$(TMS$_2$pda)]		[59b]
41 + PhMgBr	[Mo(NPh)(Ph)$_2$(TMS$_2$pda)]		[59b]
[Cp$^{i\,Pr}$Mo(N^{t}Bu)Cl(η^2-C$_2$H$_4$)] + Na[Cp]	[(Cp$^{i\,Pr}$)(Cp)Mo^{IV}(N^{t}Bu)]	Air sensitive	[61a]
[Cp$^{i\,Pr}$Mo(N^{t}Bu)Cl(η^2-C$_2$H$_4$)] + Na[In]	[(Cp$^{i\,Pr}$)(In)Mo^{IV}(N^{t}Bu)]	Air sensitive	[61a]
[(Cp^{Me})$_2$Mo^{IV}(N^{t}Bu)] + PMe$_3$	[(Cp^{Me})Mo^{IV}(N^{t}Bu)(PMe$_3$)$_2$]$^+$	Air sensitive	[61a]
[Cp^{Me}Mo(N^{t}Bu)Cl(η^2-C$_2$H$_4$)] + LiMe	[(Cp^{Me})(Me)Mo-(N^{t}Bu)(η^2-C$_2$H$_4$)]	Air sensitive	[61b]
[Cp^{Me}Mo(N^{t}Bu)Cl(η^2-C$_2$H$_4$)] + LiBHEt$_3$	[(Cp^{Me})(Me)Mo-(N^{t}Bu)(η^2-C$_2$H$_4$)]	Air sensitive	[61b]
[CpMo(N^{t}Bu)Cl(η^2-C$_2$H$_4$)] + PhI	[(Cp)(Ph)Mo(N^{t}Bu)(η^2-C$_2$H$_4$)]	Air sensitive	[61b]
[Cp^{Me}Mo(N^{t}Bu)Cl(η^2-C$_2$H$_4$)] + PMe$_3$ + *hv*	[(Cp^{Me})(PMe$_3$)ClMo(N^{t}Bu)]	Air sensitive	[61b]
[Cp^{Me}Mo(N^{t}Bu)Cl(η^2-C$_2$H$_4$)] + PMe$_3$ + *hv*	[(Cp^{Me})(PMe$_3$)$_2$Mo(N^{t}Bu)]$^+$		[61b]
[(Cp^{Me})(Me)Mo(N^{t}Bu)(η^2-C$_2$H$_4$)] + PMe$_3$ + *hv*	[(Cp^{Me})(PMe$_3$)MeMo(N^{t}Bu)]	Air sensitive	[61b]
[(Cp^{Me})ClMo(N^{t}Bu)(η^2-C$_2$H$_4$)] + PMe$_2$Ph + *hv*	[(Cp^{Me})(PPhMe$_2$)ClMo(N^{t}Bu)]	Air sensitive	[61b]
Other reactions			
[Mo(NPh)(TMS$_2$pda)(η^2-(propene)] + butadiene	[Mo(NPh)(TMS$_2$pda){η^4-H$_2$CCHCHCH$_2$}]	Unstable	[59a]
[Mo(NPh)(TMS$_2$pda)(η^2-(propene)] + pyridine	[Mo(NPh)(TMS$_2$pda)(py)$_2$]	Thermally unstable	[59c]
[Mo(NPh)(TMS$_2$pda)(η^2-(isobutene)] + butadiene	[Mo(NPh)(TMS$_2$pda){η^4-H$_2$CCHCHCH$_2$}]	Unstable	[59a]
[Mo(NPh)(TMS$_2$pda){η^4-H$_2$CCHCHCH$_2$}] + 2-butyne	[Mo(NPh)(TMS$_2$pda){η^4-CH$_2$CHC(Me)C(Me)CHCH$_2$}]		[59a]
Mo(NPh)(TMS$_2$pda)(η^2-(isobutene)] + 2,3-dimethyl-1,3-cyclohexadiene	[Mo(NPh)(TMS$_2$pda){η^4-CH$_2$CHC(Me)C(Me)CHCH$_2$}]		[59a]

Table 5 (*Continued*)

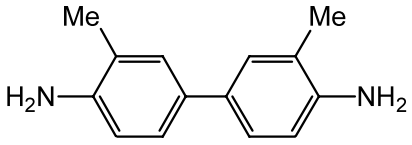
Synthesis	Complex	Comments	Reference
$Mo(NPh)(TMS_2pda)(\eta^2\text{-(isobutene)}]+$ 2-butyne	$[Mo(NPh)(TMS_2pda)\{\eta^2\text{-2-butyne}\}]$	Unstable	[59a]
$Mo(NPh)(TMS_2pda)(\eta^4\text{-}(CH_2CHCHCH_2)]+$2-butyne	$[Mo(NPh)(TMS_2pda)\{\eta^2\text{-2-butyne}\}]$	Unstable	[59a]
$Mo(NPh)(TMS_2pda)(\eta^2\text{-(isobutene)}]+$ pyridine	$[Mo(NPh)(TMS_2pda)(py)_2]$	Thermally unstable	[59c]
$[(Cp^{i\,Pr})ClMo(N^tBu)(\eta^2\text{-}C_2H_4)]+$ (allyl)MgCl+*hv*	$[(Cp^{i\,Pr})(\eta^3\text{-}C_3H_5)Mo(N^tBu)]$	Air sensitive	[61b]
$[(Cp^{Me})ClMo(N^tBu)(\eta^2\text{-}C_2H_4)]^+$ (allyl)MgCl+*hv*	$[(Cp^{Me})(\eta^3\text{-}C_3H_5)Mo(N^tBu)]$	Air sensitive	[61b]
$[Mo(N^tBu)L]+HCl$	$[Mo(N^tBu)Cl(cax(OH)O_3]$ Where LH_4 = *p-tert*-butyl-calix[4]arene = cax-O_4H_4	Reversible formation	57a
$[Mo(N^tBu)L]+PhICl_2$	$[Mo(N^tBu)Cl(cax^{Cl}O_4)]$ Where L = *p-tert*-butyl-calix[4]arene = cax-O_4^{4-}		[57a]

[a,b]

H_2NRNH_2 =



$H_2NR'NH_2$ =



7.1.2.2. Molybdenum imido complexes. Molybdenum imido complexes are very common. The reactivity of the imido moiety in molybdenum compounds will depend on the ancillary ligands, which may be more reactive than the Mo≡NR moiety. In addition, substrates may react with the metal rather than reacting with the imido ligand. Terminal imido complexes are known for molybdenum(IV), (V) and (VI). Unlike chromium(VI), where imido complexes are usually found with more than one multiply bonded ligands, molybdenum(VI) complexes containing only one imido ligand are known. The stability and the sensitivity towards air and moisture of the imido complexes of molybdenum depend on both the oxidation state and the ancillary ligands. Typical bond lengths for the Mo≡NR moiety are ca. 1.7 Å with linear bond angles (170–177°). As mentioned before, the number of molybdenum imido complexes is significant. Table 5 contains a list of complexes made since 1994 and is organized by synthetic route. Stability and reactivity are highlighted where appropriate.

Syntheses that have been employed to make molybdenum imido complexes include alkylation [7a,53,54] or protonation [45d,54] of the nitrido bond, removal of an imido ligand from bis-imido species with reduction of the metal [55,56d,57b–57d,58a,59b], and by the protic reduction of the isonitrile ligand [58b]. Formation of the imido bond has also been achieved utilizing primary amines [61a,62,64,65] and isocyanates [66]. Additionally, oxidation/reduction and ligand exchange type reactions have also been applied.

Molybdenum(IV), (V) and (VI) imido complexes have been prepared from the corresponding nitrido derivatives. Interestingly, the imido ligand in the molybdenum(IV) complex, **23**, underwent reversible C–N bond formation with acetone and benzaldehyde to give imido products, $[Mo(NCRR'OH)(OTf)(L)]^+$ where R = Me or Ph, R′ = Me or H and L = *syn*-Me_8[16]aneS_4, Table 5 [54]. Alternatively, formation of the imido moiety in molybdenum(IV) complexes has also arose from the protic reduction of the nitrile ligand [58]. In these cases, the nitrile carbon atom was protonated twice, Table 5.

The η^5-cyclopentadienyl complexes of molybdenum(V) and (VI) are quite common [60]. The molybdenum(V) complexes can be made from the η^5-cyclopentadienyl metal chloride complexes of the form, $[Cp^RMoCl_4]$ and primary amines, Table 5 (where Cp^R represents a monosubstituted Cp ring) [61,62]. One electron oxidation of the (imido)molybdenum(V) η^5-cyclopentadienyl complexes provides access to the molybdenum(VI) derivatives. Furthermore, bis-η^5-cyclopentadienyl complexes of molybdenum(IV) have also been prepared and are easily oxidized to molybdenum(VI) upon addition of alkyl halides.

7.1.2.3. Tungsten imido complexes. Terminal imido complexes of tungsten in general are also quite common. For the η^5-cyclopentadienyl derivatives, both tung-

Table 6
Imido complexes of tungsten(II), (IV), (V), and (VI)

Synthesis	Complex	Comments	Reference
Use of primary amines			
[Cp*WCl_4] (**42**) + 3^tBuNH_2	[Cp*$Cl_2W^V(N^tBu)$] (**43**)	Sensitive to air/H_2O	[62a,63b]
42 + 3^iPrNH_2 + NEt_3	[Cp*$Cl_2W(N^iPr)$]	Sensitive to air/H_2O	[62a]
42 + $3C_6F_5NH_2$ + NEt_3	[Cp*$Cl_2W(NC_6F_5)$]	Sensitive to air/H_2O	[62a]
42 + NEt_3 + $3(2,6\text{-}^iPr_2C_6H_3)NH_2$	[Cp*$Cl_2W(N\text{-}2,6\text{-}^iPr_2C_6H_3)$] (**44**)	Sensitive to air/H_2O	[62a]
[$Cp^{Cl}WCl_4$] (**45**) + 3^tBuNH_2 + NEt_3	[$Cp^{Cl}Cl_2W(N^tBu)$] (**46**)	Sensitive to air/H_2O	[62b]
[$CpWCl_4$] (**47**) + $^tBuNH_2$	[$CpCl_2W(N^tBu)$] (**48**)		[62c,63b]
[$Cp^{Me}WCl_4$] (**49**) + $^tBuNH_2$	[$Cp^{Me}Cl_2W(N^tBu)$] (**50**)		[62c]
42 + NEt_3 + NH_2-2,6-$Me_2C_6H_3$	[Cp*WCl_2(N-2,6-$Me_2C_6H_3$)] (**51**) Sensitive to air/H_2O		[63d]
[Cp*WCl(HNNNH)]$^+$ + H_2NCHMe_2	[Cp*W($NCHMe_2$)(HNNNH)] Where HNNNH= $HNC_6H_4NC_6H_4NH$ (trianion)		[67]
[WCl_4(O)] + NH_2-2,6-$^iPr_2C_6H_3$	[WCl_4(N-2,6-$^iPr_2C_6H_3$)(NH-2,6-$^iPr_2C_6H_3$)]$^-$		[56a]
Oxidation/reduction reactions			
43 + PCl_5	[Cp*$Cl_3W^{VI}(N^tBu)$] (**52**)		[63b]
44 + air	[Cp*Cl_3W^{VI}(N-2,6-$^iPr_2C_6H_3$)]	Sensitive to air	[62a]
46 + 1/2PCl_5	[$Cp^{Cl}Cl_3W^{VI}(N^tBu)$]		[62b]
48 + PCl_5	[$CpCl_3W^{VI}(N^tBu)$] (**53**)		[63b,63d]
50 + Cl_2	[$Cp^{Me}Cl_3W^{VI}(N^tBu)$] (**54**)		[63a]
51 + PCl_5	[Cp*Cl_3W^{VI}(N-2,6-$^iPr_2C_6H_3$)] (**55**)	Sensitive to air/H_2O	[63d]
[Cl_3W^V(N-2,4,-$^iPr_2C_6H_3$)(PMe_3)$_2$] + air	[Cl_3W^{VI}(N-2,4,-$^iPr_2C_6H_3$)(PMe_3)($OPMe_3$)]		[72c]
54 + KC_8 + CH_2CH_2	[$Cp^{Me}ClW^{IV}(N^tBu)(\eta\text{-}C_2H_4)$]		[63a]
54 + Na/Hg + MeC_2Me	[$Cp^{Me}ClW^{IV}(N^tBu)(\eta\text{-}C_2Me_2)$]		[63a]
From amido complexes			
[Tp*W^{II}(NHTs)(CO)$_2$] (**56**) + AgOTf or I_2	[Tp*$W^{IV}(CO)_2$(NTs)]$^+$ (**57**)	Reduces to **56** w/ $LiBH_4$ Reacts w/Pme_3 No reaction w/olefins	[20]
[Tp*W^{II}(NHPh)(CO)$_2$] + LDA	[Tp*$W^{II}(CO)_2$(NPh)]$^-$	Basic; will reform amido	[23]
[Tp*W^{II}($NHCH_2Ph$)(CO)$_2$] + LDA	[Tp*$W^{II}(CO)_2(NCH_2Ph)]^-$	Basic; will reform amido	[23]
[Tp*W^{II}(NH_2)(CO)$_2$] + LDA	[Tp*$W^{II}(CO)_2$(NH)]$^-$	Basic; will reform amido	[23]
[Tp*W^{II}(NHPh)(CO)$_2$] + CPh_3^+	[Tp*$W^{IV}(CO)_2$(NPh)]$^+$	Basic; will reform amido	[23]
[Tp*W^{II}($NHCH_2Ph$)(CO)$_2$] + CPh_3^+	[Tp*$W^{IV}(CO)_2(NCH_2Ph)]^+$	Deprotonated at β-C w/NEt_3	[23]
[Tp*W^{II}(NH^tBu)(CO)$_2$] + CPh_3^+	[Tp*$W^{IV}(CO)_2(N^tBu)]^+$	Basic; will reform amido	[23]
[Tp*W^{II}(NH^nBu)(CO)$_2$] + CPh_3^+	[Tp*$W^{IV}(CO)_2(N^nBu)]^+$	Deprotonated at β-C w/NEt_3	[23]
[Tp*W^{II}(NH_2)(CO)$_2$] + CPh_3^+	[Tp*W^{IV}(CO)$_2$(NH)]$^+$		[23]
[Tp*W^{II}(NH_2)(CO)$_2$] + CPh_3^+	[Tp*W^{IV}(CO)$_2$($NCPh_3$)]$^+$		[23]
From bis-imido complexes			
[$W^{VI}(N^tBu)_2(NH^tBu)_2$] + $O(Ph_2SiOH)_2$	[$W(N^tBu)(NH^t_2Bu)(O(Ph_2SiO)_2)_2$]	Basic	[55a]
[W($NTs)_2Cl_2$(dmbpy)] + PMe_3	[W(NTs)Cl_2(dmbpy)(PMe_3)$_2$]	Stable	[55b]
[Tp*W($N^tBu)_2$Cl] + H^+	[Tp*W(N^tBu)(N^tHBu)Cl]$^+$		[55c]
[$W^{VI}(N^tBu)_2(NH^tBu)_2$] + *nido*-7,8-$C_2B_9H_{13}$	[$W(N^tBu)(NH^tBu)_2(C_2B_9H_{11})$]	Air/H_2O sensitive	[56b]
[$W^{VI}(N^tBu)_2(NH^tBu)_2$] + LH_4	[W(N^tBu)L] Where LH_4 = *p-tert*-butyl-calix[4]arene	Stable	[56d]
[W(NMes)$_2Cl_2$(dme)] + LH_4	[W(NMes)L] Where LH_4 = *p-tert*-butyl-calix[4]arene	Stable	[56d]
From isonitrile complexes			
[Tp*WI(MeCN)(CO) + py-*N*-oxide	[Tp*WI{(NC(O)Me)}(CO)]	No reaction w/PPh_3, or PMe_2Ph	[69a,69d]
[Tp*WI(EtCN)(CO)] + py-*N*-oxide	[Tp*WI{(NC(O)Et)}(CO)]	No reaction w/PPh_3, or PMe_2Ph	[69a]
[Tp*WI(PhCN)(CO)] + py-*N*-oxide	[Tp*WI{(NC(O)Ph)}(CO)]	No reaction w/PPh_3, or PMe_2Ph	[69a]
trans-[W(dppe)$_2$(N_2)(NCPh)] + HCl	*trans*-[WCl(NCH_2Ph)(dppe)$_2$]$^+$		[69b]
trans-[W(dppe)$_2$(N_2)(NCMe) + HCl	*trans*-[WCl(NCH_2Me)(dppe)$_2$]$^+$		[69b]
trans-[W(dppe)$_2$(N_2)(NC-*p*-OMePh)] + HCl	*trans*-[WCl(NCH_2-*p*-OMePh)(dppe)$_2$]$^+$		[69b]

Table 6 (*Continued*)

Synthesis	Complex	Comments	Reference
trans-[W(dppe)$_2$(N$_2$)(NCMe)]+HBF$_4$	*trans*-[WF(NCH$_2$Me)(dppe)$_2$]$^+$		[69c]
Using hydrazine or organic azides			
[W$_2$(H)(O^{i}Pr)$_7$]+PhHNNHPh/py	[W(NPh)(py)(O^{i}Pr)$_4$]		[70]
[W$_2$(H)(OC$_5$H$_9$)$_7$(HNMe$_2$)]+PhHNNHPh/py	[W(NPh)(py)(OC$_5$H$_9$)$_4$]		[70]
[W$_2$(O^{i}Pr)$_6$]+PhHNNHPh/py	[W(NPh)(py)(O^{i}Pr)$_4$]		[70]
[W$_2$(OCH$_2$CMe$_3$)$_6$]+PhHNNHPh/py	[W(NPh)(py)(OCH$_2$CMe$_3$)$_4$]		[70]
[W$_4$(OCH$_2$C$_4$H$_7$)$_{12}$]+2PhHNNHPh/py	[W(NPh)(py)(OCH$_2$C$_4$H$_7$)$_4$]		[70]
[Tp*(CO)$_2$WI]+TsN$_3$	[Tp*W(NTs)(CO)I]		[20]
[{calyx[4]-(O)$_4$}W^{IV}(η^2-C$_6$H$_{10}$)]+TMS-N$_3$	[{calyx[4]-(O)$_4$}W^{IV}(NTMS)]		[71]
[{calyx[4]-(O)$_4$}W^{IV}(η^2-C$_6$H$_{10}$)]+Ph$_3$C-N$_3$	[{calyx[4]-(O)$_4$}W^{IV}(NCPh$_3$)]		[71]
Ligand substitution			
52+2MgClMe	[Cp*ClMe$_2$W(N^{t}Bu)] (**58**)		[63b]
52+2LiMe	**58**		[63b]
52+3MgClMe	[Cp*Me$_3$W(N^{t}Bu)] (**59**)		[63b]
52+3LiMe	**59**		[63b]
52+ZnMe$_2$	**59**		[63d]
53+2MgClMe	[CpClMe$_2$W(N^{t}Bu)] (**60**)		[63b]
60+MgClMe	[CpMe$_3$W(N^{t}Bu)]		[63b]
59+2MgClMe	[Cp*Me$_2$W(N^{t}Bu){C(Me)N(2,6-Me$_2$C$_6$H$_3$)}]	Very air sensitive	[63b]
52+MgClEt	[Cp*Cl$_2$EtW(N^{t}Bu)]		[63c]
52+MgClEt	[Cp*Et$_3$W(N^{t}Bu)]	Forms alkylidene w/ Δ	[63c]
52+MgClPr	[Cp*Pr$_3$W(N^{t}Bu)]	Forms alkylidene w/ Δ	[63c]
53+3MgClEt	[CpEt$_3$W(N^{t}Bu)]	Unstable	[63c]
53+3MgClPr	[CpPr$_3$W(N^{t}Bu)]	Unstable	[63c]
55+ZnMe$_2$	[Cp*W(N-2,6-^{i}Pr$_2$C$_6$H$_3$)Me$_3$]	Sensitive to air/H$_2$O, Forms alkylidene w/ Δ	[63d]
[(CO)$_2$W^{VI}(NPh)I$_2$]$_2$ (**61**)+S	[(CO)$_2$W(NPh)(S)I$_2$]		
	Where S = THF (**62**)	Not isolated	[68a]
	or py (**63**)	Stable	[68a]
	or MeCN, or Et$_3$N,	Stable	[68b]
	or 2,4,6-Me$_3$C$_6$H$_2$NH$_2$	Stable	[68b]
62 or **63**+PMe$_3$	[(CO)$_2$W(NPh)(PMe$_3$)$_2$I$_2$]		[68a]
62 or **63**+P(OMe)$_3$	[(CO)$_2$W(NPh)(P(OMe)$_3$)$_2$I$_2$]		[68a]
[(CO)$_5$WNPhNPhC(OMe)Ph]^a+2I$_2$	[I$_3$(PhN)W^{VI}(NphCPhO)]		[68b]
[(CO)$_2$W^{VI}(NPh)Br$_2$]$_2$+MeCN	[(CO)$_2$W(NPh)(MeCN)Br$_2$] (**64**)	Stable	[68c]
[(CO)$_2$W^{VI}(NPh)Cl$_2$]$_2$+MeCN	[(CO)$_2$W(NPh)(MeCN)Cl$_2$] (**65**)	Stable	[68c]
64+L	[W(NPh)(CO)$_2$Cl$_2$(L)] Where L = 2,4,6-Me$_3$C$_6$H$_3$NH$_2$ or *i*-C$_4$H$_9$NH$_2$		[68c]
64+PMe$_3$	[W(NPh)(CO)$_2$Cl$_2$(PMe$_3$)$_2$]		[68c]
65+L	[W(NPh)(CO)$_2$Cl$_2$(L)] Where L = 2,4,6-Me$_3$C$_6$H$_3$NH$_2$ or *i*-C$_4$H$_9$NH$_2$		[68c]
[(CO)$_2$W^{VI}(NPh)BrI]$_2$+MeCN	[(CO)$_2$W(NPh)(MeCN)BrI]	Stable	[68c]
57+PMe$_3$	[Tp*W^{IV}(NTs)(CO)(PMe$_3$)]$^+$ (**66**)		[20]
66+I$_2$	[Tp*W^{IV}(NTs)(CO)I]		[20]
[Tp*WI{(NC(O)Me)}(CO)]+SPh$^-$	[Tp*W(SPh){(NC(O)Me)}(CO)]	Stable	[69a]
[WCl$_4$(NR)]+Me$_3$SiNHR+S	[WCl$_3$(NR)(NHR)(S)] Where R = 2,6-^{i}Pr$_2$C$_6$H$_3$ and S = THF or py	Stable	[56a]
[WCl$_4$(NR)]+NH$_2$R	[WCl$_4$(NR)(H$_2$NR)] Where R = 2,6-^{i}Pr$_2$C$_6$H$_3$	Stable	[56a]
[WCl$_2$(NR)(H$_2$NR)]+Me$_3$SiNHR	[WCl$_3$(NR)(NHR)(NH$_2$R)] Where R = 2,6-^{i}Pr$_2$C$_6$H$_3$	Stable	[56a]
[WCl$_5$(NR)]$^+$+Me$_3$SiNHR	[WCl$_4$(NR)(NHR)]$^+$ Where R = 2,6-^{i}Pr$_2$C$_6$H$_3$	Stable	[56a]
[WCl$_5$(NR)]$^+$+Me$_3$SiNHR	[WCl$_4$(NR)(NHR)]$^+$ Where R = 2,6-Me$_2$C$_6$H$_3$	Stable	[56a]
[W^{VI} (NTol)Cl$_4$]+LiL	[W(NTol)L$_4$] Where L = 1,2:5,6-di-*o*-isopropylidene-α-D-gluco-furanose		[56c]
[W(NR)Cl$_4$]+LH$_4$	[W(NR)L] Where LH$_4$ = *p*-*tert*-butyl-calix[4]arene and R = Ph, Tol, *o*-MePh, or *m*-MePh	Stable	[56e]
[W(N^{t}Bu)(NH^{t}Bu)$_2$(C$_2$B$_9$H$_{11}$)]+2,6-Me$_2$-C$_6$H$_3$OH	[W(N^{t}Bu)(NH^{t}Bu)(2,6-Me$_2$C$_6$H$_3$O)(C$_2$B$_9$H$_{11}$)]		[56b]
[W(N^{t}Bu)(NH^{t}Bu)$_2$(C$_2$B$_9$H$_{11}$)]+Me$_3$SiCl	[W(N^{t}Bu)(NH^{t}Bu)(Cl)(C$_2$B$_9$H$_{11}$)]		[56b]
Other reactions			

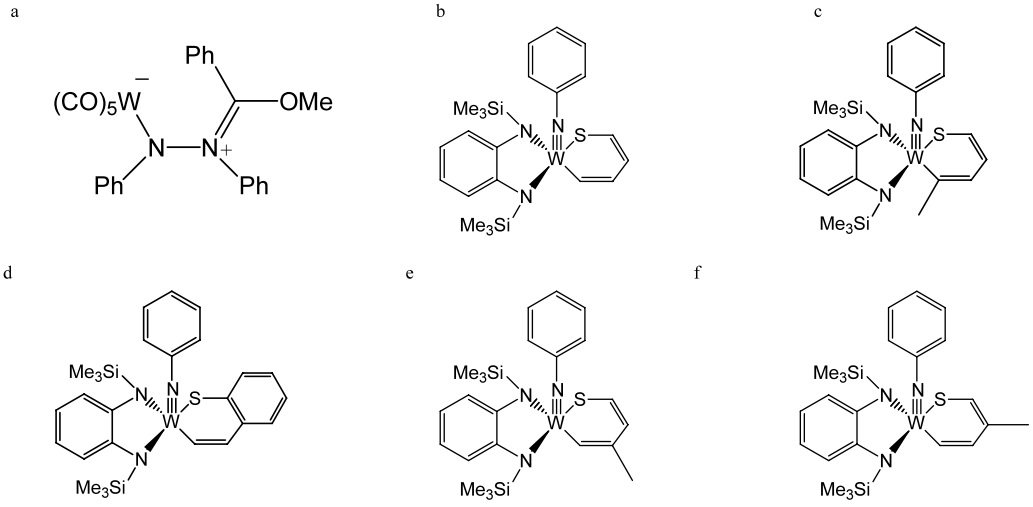
Table 6 (*Continued*)

Synthesis	Complex	Comments	Reference
$[WCl_2(NR)(Pme_3)_2]+TolCN$	$[WCl_2(NR)(\eta^2\text{-TolCN})(PMe_3)_2]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72a]
$[\{WCl_4(PhC_2Ph)\}_2]+[NEt_4]Cl+Me_3SiNH^tBu$	$[W(N^tBu)Cl_3(PhC_2Ph)(NH_2^tBu)]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+bpy+Me_3SiNH^tBu$	$[W(N^tBu)Cl_2(PhC_2Ph)(bpy)]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+dmbpy+Me_3SiNH^tBu$	$[W(N^tBu)Cl_2(PhC_2Ph)(dmbpy)]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+py+Me_3SiNH^tBu$	$[W(N^tBu)Cl_2(PhC_2Ph)(py)]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+PMe_3+Me_3SiNH^tBu$	$[W(N^tBu)Cl_2(PhC_2Ph)(PMe_3)_2]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+PMe_2Ph+Me_3SiNH^tBu$	$[W(N^tBu)Cl_2(PhC_2Ph)(PMe_2Ph)_2]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+dmbpy+Me_3SiNH^iPr$	$[W(N^iPr)Cl_2(PhC_2Ph)(dmbpy)]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+dmbpy+Me_3SiNHEt$	*cis*/*trans*-$[W(NEt)Cl_2(PhC_2Ph)(dmbpy)]$		[72b]
$[\{WCl_4(PhC_2Ph)\}_2]+4PMe_3+2Na/Hg$	$[W^VCl_3(NR)(PMe_3)_2]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$	Air sensitive	[72c]
$[\{WCl_4(PhC_2Ph)\}_2]+6PMe_3+4Na/Hg$	$[W^{IV}Cl_2(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_3]$		[72c]
$[\{WCl_4(PhC_2Ph)\}_2]+4PMe_2Ph+2Na/Hg$	$[W^VCl_3(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_2]$		[72c]
$[\{WCl_4(PhC_2Ph)\}_2]+6PMe_2Ph+4Na/Hg$	$[W^{IV}Cl_2(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_3]$		[72c]
$[Cl_2W^{IV}(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_3]+R'C_2R''$	$[WCl_2(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_2(R'C_2R'')]$ Where R′ = R″ = Ph or Me		[72c]
$[Cl_2W^{IV}(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_3]+R'C_2R''$	$[WCl_2(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_2(R'C_2R'')]$ Where R′ = Ph, R″ = H		[72c]
$[Cl_2W^{IV}(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_2Ph)_3]+R'C_2R'$	$[WCl_2(N\text{-}2,4,\text{-}^iPr_2C_6H_3)(PMe_3)_2(R'C_2R'')]$ Where R′ = R″ = Ph		[72c]
$[Cl_3W^V(NR)(PMe_3)_2]+C_2H_2+Na/Hg$	$[WCl_2(NR)(PMe_3)_2(C_2H_2)]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72c]
$[Cl_3W^V(NR)(PMe_3)_2]+Na/Hg+CHMeCH_2$	$[WCl_2(NR)(PMe_3)_2(CH_2CHMe)]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72c]
$[\{WCl_4(NR)\}_2]+Na/Hg+dmbpy$	$[W^V(NR)Cl_3(dmbpy)]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72d]
$[\{WCl_4(NR)\}_2]+Na/Hg+dppe$	$[W^V(NR)Cl_3(dppe)]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72d]
$[W^V(NR)Cl_3(dmbpy)]+Na/Hg+PhC_2Ph$	$[W^{IV}(NR)Cl_2(dmbpy)(PhC_2Ph)]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72d]
$[W^V(NR)Cl_3(dmbpy)]+Na/Hg+H_2C_2$	$[W^{IV}(NR)Cl_2(dmbpy)(H_2C_2]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72d]
$[W^V(NR)Cl_3(dmbpy)]+Na/Hg+CO$	$[W^{IV}(NR)Cl_2(dmbpy)(CO)]$ Where R = 2,4,-^{i}Pr$_2$C$_6$H$_3$		[72d]
$[W(NPh)Cl_4]+(TMS_2pda)$	$[(TMS_2pda)W(NPh)Cl_2]$	Air/H_2O sensitive	[73e]
$[(TMS_2pda)W(NPh)Cl_2]+Pme_3$	$[(TMS_2pda)W(NPh)Cl_2(PMe_3)]$		[73e]
$[(TMS_2pda)W(NPh)Cl_2]+THF$	$[(TMS_2pda)W(NPh)Cl_2(THF)]$		[73e]
$[(TMS_2pda)W(NPh)Cl_2]+MeCN$	$[(TMS_2pda)W(NPh)Cl_2(NCMe)]$		[73e]
$[(TMS_2pda)W(NPh)Cl_2]+{}^tBuCN$	$[(TMS_2pda)W(NPh)Cl_2(NC^tBu)]$		[73e]
$[(TMS_2pda)W(NPh)Cl_2]+L$	$[(TMS_2pda)W(NPh)Cl_2(L)]$ Where L = 3-picoline		
$[(TMS_2pda)W(NPh)Cl_2]+MgIMe$	$[(TMS_2pda)W(NPh)Me_2]$	Air/H_2O sensitive	[73e]
$[(TMS_2pda)W(NPh)Cl_2]+MgClEt$	$[(TMS_2pda)W(NPh)Et_2]$	Air/H_2O sensitive	[73e]
$[(TMS_2pda)W(NPh)Cl_2]+MgClCH_2Ph$	$[(TMS_2pda)W(NPh)(CH_2Ph)_2]$	Air/H_2O sensitive	[73e]
$[(TMS_2pda)W(NPh)Cl_2]+MgClNp$	$[(TMS_2pda)W(NPh)Np_2]$	Air/H_2O sensitive	[73e]
$[(TMS_2pda)W(NPh)Cl_2]+MgClCH_2CmePh$	$[(TMS_2pda)W(NPh)(CH_2CMePh)_2]$	Air/H_2O sensitive	[73e]
$[(TMS_2pda)W(NPh)Me_2]+PMe_3$	$[(TMS_2pda)W(NPh)Me_2(PMe_3)]$		[73e]
$[(TMS_2pda)W(NPh)(Np)_2]+H_2+PMe_3$	$[(TMS_2pda)W(NPh)(H)_2(PMe_3)_2]$		[73f]
$[(TMS_2pda)W(NPh)(Et)_2]+H_2+PMe_3$	$[(TMS_2pda)W(NPh)(H)_2(PMe_3)_2]$		[73f]
$[(TMS_2pda)W(NPh)(PMe_3)(CHCMe_3)]+H_2+PMe_2Ph$	$[(TMS_2pda)W(NPh)(H)_2(PMe_2Ph)_2]$		[73f]
$[(TMS_2pda)W(NPh)(Np)_2]+H_2+PMe_2Ph$	$[(TMS_2pda)W(NPh)(H)_2(PMe_2Ph)_2]$		[73f]
$[(TMS_2pda)W(NPh)(Et)_2]+H_2+PMe_2Ph$	$[(TMS_2pda)W(NPh)(H)_2(PMe_2Ph)_2]$		[73f]
$[(TMS_2pda)W(NPh)(Np)_2]+H_2+dppe$	$[(TMS_2pda)W(NPh)(H)_2(dppe)]$		[73f]
$[(TMS_2pda)W(NPh)(Np)_2]+H_2+Pcy_3$	$[(TMS_2pda)W(NPh)(H)_2(PCy_3)]$		[73f]
$[(TMS_2pda)W(NPh)(H)_2(PMe_3)]+CH_2CH_2$	$[(TMS_2pda)W(NPh)(H)_2(PMe_3)(CH_2CH_2)]$		[73f]
$[(TMS_2pda)W(NPh)(H)_2(PphMe_2)]+CH_2CH_2$	$[(TMS_2pda)W(NPh)(H)_2(PPhMe_2)(CH_2CH_2CH_2CH_2)]$		[73f]
$[(TMS_2pda)W(NPh)(Np)_2+\Delta$	$[(TMS_2pda)W(NPh)(CH_2C(Me)_2CH_2)]$	Unstable	[73a]
$[(TMS_2pda)W^{VI}(NPh)L_2+H_2+$toluene	$[W^{IV}(NPh)(TMS_2pda)(\eta^6\text{-arene})]$ Where L = CH_2CH_2Ph and η^6-arene = η^6-EtC_6H_5		[73b]
$[(TMS_2pda)W^{VI}(NPh)L_2+H_2+$toluene	$[W^{IV}$ $(NPh)(TMS_2pda)(\eta^6\text{-arene})]$ Where L = $CH_2CH_2CH_2Ph$ and η^6-arene = η^6-PrC_6H_5		[73b]
$[W(NPh)(TMS_2pda)(\eta^6\text{-arene})]+PhC_2Ph$	$[W(NPh)(TMS_2pda)(CH_2C(Ph)C(Ph)CHPh)]$		[73b]
$[(TMS_2pda)W^{VI}(NPh)Me_2+{}^tBuNC$	$[W(NPh)(TMS_2pda)(^tBuNC)Me_2]$	Unstable	[73c]
$[(TMS_2pda)W^{VI}(NPh)Np+{}^tBuNC$	$[W(NPh)(TMS_2pda)(^tBu)NC)(Np)]$	Air/H_2O sensitive	[73c]
$[W(NPh)(TMS_2pda)(^tBuNC)Me_2]+{}^tBuNC$	$[W(NPh)(TMS_2pda)(\eta^2\text{-}(^tBu)NCMe)_2]$	Thermally unstable	[73c]
$[W(NPh)(TMS_2pda)(^tBu)NC)(Np)]+{}^tBuNC$	$[W(NPh)(TMS_2pda)(\eta^2\text{-}(^tBu)NCH_2CMe)_2]$	Stable	[73c]
$[W(NPh)(TMS_2pda)(\eta^2\text{-}(^tBu)NCMe)_2]+\Delta$	$[W(NPh)(TMS_2pda)\{(^tBu)NC\text{-}(Me)=C(Me)N(^tBu)\}]$	Stable	[73c]
$[W^{IV}(NPh)(TMS_2pda)(py)_2]+$thiophene	$[W^{VI}(NPh)(TMS_2pda)(SC_4H_4)]$[b]	Stable	[73d]
$[W(NPh)(TMS_2pda)(py)_2]+$2-methylthiophene	$[W(NPh)(TMS_2pda)(SC_5H_6)]$[c]	Stable	[73d]
$[W(NPh)(TMS_2pda)(py)_2]+$benzothiophene	$[W(NPh)(TMS_2pda)(SC_8H_6)]$[d]	Unstable	[73d]

Table 6 (*Continued*)

Synthesis	Complex	Comments	Reference
$[W(NPh)(TMS_2pda)(py)_2]$+3-methylthiophene	$[W(NPh)(TMS_2pda)(L)]$ Where L = $SCH_2CH_2C(Me)CH$[e] or $SCH_2C(Me)CH_2CH$[f]	Stable	[73d]

a,b,c,d,e,f



sten(V) and (VI) oxidation states are accessible. However, of the two oxidation states for these organometallic complexes, tungsten(VI) is more common. The tungsten(V) imido η^5-cyclopentadienyl complexes are air and moisture sensitive. Typical W≡NR bond lengths for tungsten(V) an (VI) η^5-cyclopentadienyl complexes are around 1.7 Å and bond angles show linear bonding of the imido moiety. However, there are examples where deviations from linearity occur; for example $[Cp^*W(NC_6F_5)Cl_3]$ was reported with a C–N–W bond angle of 169.2° [62a]. A common synthetic route to these compounds is aminolysis of the tetrachloride η^5-cyclopentadienyl complexes of the form, $[W^VCl_4Cp]$ (where $Cp = \eta^5$-C_5H_5, $Cp^* = \eta^5$-C_5Me_5, $Cp^{Cl} = \eta^5$-$C_5H_4SiMe_2Cl$, or $Cp^{Me} = \eta^5$-C_5H_4Me), with primary amines, Table 6 [62,63,67]. These paramagnetic imido complexes were easily oxidized to tungsten(VI), the more stable oxidation state, $[CpW^{VI}(NR)Cl_3]$, Table 6 [62a,62b,63]. The tungsten(VI) complexes, $[CpW^{VI}(NR)Cl_3]$ (where $Cp = \eta^5$-C_5H_5, $Cp^* = \eta^5$-C_5Me_5, $Cp^{Cl} = \eta^5$-$C_5H_4SiMe_2Cl$, or $Cp^{Me} = \eta^5$-C_5H_4Me), were easily alkylated with carbocations to give the ligand substituted products, Table 6 [63b,63c,63d]. However, some of these alkylated products were thermally unstable resulting in α-hydrogen elimination and the alkylidene complexes formed, [W(=NR)(=CRH)XCp], Table 6 [63c,63d].

An alternative route to simple carbonyl imido complexes of tungsten(VI) has been developed by McElwee-White and coworkers who have used a transient zerovalent complex, $[(CO)_5W{=}NPh]$ in the form of a zwitterionic complex, $[(CO)_5WNPhNPhC(OMe)R]$, where R = Me or Ph [68]. Interestingly, oxidation of the zwitterionic complex with two equivalents of iodide resulted in a metallocyclic tungsten(VI) complex, $[I_3(PhN)W^{VI}NPhCPhO]$, Table 6 [68b]. These zwitterionic complexes were also easily oxidized with one equivalent of iodide to the dimeric imido species, which could then be converted to the monomeric terminal imido forms upon addition of coordinating solvents, Table 6 [68]. The resulting tungsten(VI) imido complexes have proved to be useful starting materials for further ligand exchange reactions, Table 6 [68].

As mentioned before, the terminal imido functionality is found in quite a number of tungsten complexes. Thus, it should not be too surprising that there is a variety of ways to create new tungsten imido complexes. The imido bond can be also formed from amido [20,23], bis-imido [55], and isonitrile [69] complexes and from the use of hydrazines [70], or azides [20,71], Table 6. Examples of the use of ligand substitution as a means to forming new terminal imido complexes of tungsten while preserving the imido moiety are listed in Table 6 [20,56]. Furthermore, oxidation or reduction of imido tungsten complexes, as demonstrated with the η^5-cyclopentadienyl complexes, provides synthetic alternatives.

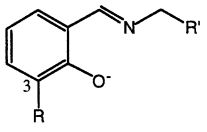
Table 7
Nitrido complexes of manganese(V)

Synthesis	Complex	Comments	Reference
From azido or azides			
$[Mn^{III}(N_3)_2salen]+h\nu$	[Mn(N)(salen)] (**67**)	Reacts w/TFAA	[9]
$[\{trans\text{-}[Mn^{V}(N)(cyclam)]_2\}\text{-}(\mu\text{-}N_3]^+ + h\nu$	*trans*-$[Mn(N)(NCCH_3)(cyclam)]^{2+}$ (**68**)		[75]
$[Mn^{III}(N_3)(Me_3tacn)]+h\nu$ (350 nm)	$[Mn(N)(N_3)_2(Me_3tacn)]$		[75]
$[Mn^{III}(acac)(N_3)(Me_3tacn)]+h\nu$	$[Mn(N)(acac)(Me_3tacn)]^+$		[75]
$[Mn^{III}(tpfc)]+NaN_3$	$[Mn(N)(tpfc)]^-$		[105a]
$[Mn^{III}(tpfc)]+TMSN_3$	$[Mn(N)(tpfc)]^-$		[105b]
Oxidation in presence of ammonia			
$[Mn(OAc)_2{\cdot}4H_2O]+NH_4OH+NaOCl+H_2$salen	**67**		[9a]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_4OH+NaOCl+H_2$saltmen	[Mn(N)(saltmen)]	Reacts w/TFAA	[9a]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_4OH+NaOCl+H_2$salchxn	[Mn(N)(salchxn)]	Reacts w/Ts_2O	[8b,12]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_4OH+NaOCl+H_2(tb_2$salchxn)	[Mn(N)(tb_2salchxn)]	Reacts w/TFAA	[9b]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_4OH+NaOCl+$ H_2(Brtbsalchxn)	[Mn(N)(Brtbsalchxn)]	Reacts w/Ts_2O	[8b,9b,12]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_4OH+NaOCl+H_2(tb_2$salphen)	[MnNtb_2salphen]	Reacts w/BF_3, TFA	[12]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_4OH+NaOCl+H_2$(Metbsal-phen)	[Mn(N)(Metbsalphen)]	Reacts w/TFAA	[9b,74]
$[Mn(X)(3\text{-Ph-sal-Me})_2]^a+NH_3+NBS$	[Mn(N)(OAc)(3-Ph-sal-Me)$_2$] Where X = OAc or Cl		[9e]
$[Mn(X)(Ph\text{-sal-}^iPr)_2]^a+NH_3+NBS$	[Mn(N)(OAc)(3-Ph-sal-^{i}Pr)$_2$] Where X = OAc or Cl		[9e]
$[Mn(X)(3\text{-Ph-sal-Ph})_2]^a+NH_3+NBS$	[Mn(N)(OAc)(3-Ph-sal-Ph)$_2$] Where X = OAc or Cl	Reacts w/TFAA	[9e]
$[Mn(X)(3OMe\text{-sal-Me})_2]^a+NH_3+NBS$	[Mn(N)(OAc)(3-OMe-sal-Me)$_2$] Where X = OAc or Cl		[9e]
$[Mn(X)(3\text{-OMe-sal-Ph})_2]^a+NH_3+NBS$	[Mn(N)(OAc)(3-OMe-sal-Ph)$_2$] Where X = OAc or Cl		[9e]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_3+NBS+H_2(Hoz\text{-}^iPr)^b$	[Mn(N)(Hoz-^{i}Pr)$_2$]		[9a]
$[Mn(OAc)_2{\cdot}4H_2O]+NH_3+NBS+H_2(Hoz\text{-Ph})^b$	[Mn(N)(Hoz-Ph)$_2$]		[9a]
$[Mn^{III}Cl_2cyclam]^+ + NH_3 + NaOCl$	*trans*-$[Mn(N)(Cl)(cylam)]^+$		[75]
Ligand substitution			
67 $+CN^-$	$[Mn(N)(CN)_5]^{3-}$		[34a]
67 $+CN^-$	$[Mn(N)(CN)_4]^{2-}$	Can be reduced to Mn^{IV}	[34a]
67 $+AgClO_4$	$[Mn(N)(cyclam)(ClO_4)]^+$		[75]
67 +TFAA	$[Mn(N)(cyclam)(CF_3CO_2)]^+$		[75]
$[\{trans\text{-}[Mn^{V}(N)cyclam]_2\}\text{-}(\mu\text{-}N_3]^+ + CN^-$	*cis*-$[Mn(N)(CN)(cyclam)]^+$		[75]

[a,b]

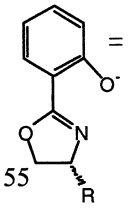
a

3-R-sal-R' =



b

Hoz-R =



Formation of imido complexes from amido complexes is a result of deprotonation. Most often the deprotonation is facilitated by addition of a base. However, amido ligands on tungsten(II) complexes display ambiphilic behavior. Deprotonation was observed with the addition of strong bases as well as addition of a carbocation [23].

Complex **57** displayed interesting reactivity with trimethylphosphane [20]. The electrophilic imido moiety reacted with PMe_3 to give the expected NR-group transfer products, TsN=PMe_3 and $[Tp^*W^{II}(CO)_2(PMe_3)_2]^+$. However, ligand substitution was also observed and complex **66** was produced as well. In addition, the imido moiety in **66** was not reactive enough to react with olefins.

The acylimido complexes of the general form, $[W^{IV}Tp^*I(CO)\{NC(O)R\}]$ where R = Me, Et or Ph were formed from the corresponding nitriles and pyridine-*N*-oxide [69]. Although typically acylimido complexes are more reactive than other imido complexes, no reaction was observed with organic phosphanes. These acylimido complexes were formed by oxygen

Table 8
Nitrido complexes of technetium(V)

Synthesis	Complex	Comments	Reference
Ligand substitution on $[Tc^{V}(N)Cl_2(PPh_3)_2]$ and analogs			
$[Tc(N)Cl_2(PPh_3)_2]$ (**69**) + POP [a]	$[Tc(N)Cl_2(POP)]$		[78]
69 + PNP [b]	$[Tc(N)Cl_2(PNP)]$		[78]
69 + $Ph_2P(CH_2)_2SH$	$[Tc(N)(Ph_2P(CH_2)_2S)_2]$		[79]
69 + $MeO_2P(CH_2)_2SH$	$[Tc(N)(MeO_2P(CH_2)_2S)_2]$		[79]
69 + $Ph_2P(CH_2)_3SH$	$[Tc(N)(Ph_2P(CH_2)_3S)_2]$		[79]
69 + $Tol_2P(CH_2)_3SH$	$[Tc(N)(Tol_2P(CH_2)_3S)_2]$		[79]
69 + Ph_2P-*o*-C_6H_4SH	$[Tc(N)(Ph_2P$-*o*-$C_6H_4S)_2]$		[79]
69 + $N(SPPh_2)_2^-$	$[Tc(N)\{N(SPPh_2)_2\}_2]$	Reacts w/BCl_3	[80]
$[Tc(N)Cl_2(PPhMe_2)_3]$ (**70**) + $N(SPPh_2)_2^-$	$[Tc(N)(PPhMe_2)_2\{N(SPPh_2)_2\}]$	Reacts w/S_2Cl_2	[80]
69 + ($FeCS_2$)	$[Tc(N)(FeCS_2)_2]$ Where $FeCS_2 = [Fe^{II}(C_5H_4CS_2)(C_5H_5)]^-$		[81]
69 + Hpnao [c]	$[TcN(H_2O)(pnao)]^+$		[82a,82b]
69 + Hbnao [d]	$[TcN(H_2O)(bnao)]^+$		[82a]
69 + Hpentao [e]	$[TcN(H_2O)(pentao)]^+$		[82a]
69 + HL	$[TcN(H_2O)(HL)_2]^{2+}$ Where HL = 1,1-dimethylbiguanide		[83a]
69 + HL	$[Tc(N)(H_2O)(HL)_2]^{2+}$ Where HL = 1-phenethylbiguanide		[83a]
69 + HL	$[Tc(N)(H_2O)(HL)_2]^{2+}$ Where HL = 1-phenylbiguanide		[83a]
69 + $H_2NNMeC(S)Sme$	$[Tc(N)(HNNMeC(S)SMe)_2]$		[83b]
69 + Ph_2P-*o*-C_6H_4-H_2N	$[Tc(N)Cl(Ph_2P$-*o*-C_6H_4-$H_2N)_2]^+$		[109]
69 + HL	$[Tc(N)Cl(L)(PPh_3)]$ Where HL = 2-(dicyclohexylphosphino)ethanethiol		[84]
69 + HL	$[Tc(N)(L)_2]$ Where HL = 2-(dicyclohexylphosphino)ethanethiol		[84]
70 + mnt^{2-}	$[Tc(N)(mnt)(PPhMe_2)_2]$		[86a]
70 + mnt^{2-}	$[Tc(N)(mnt)_2]^{2-}$		[86a]
70 + Et_2dtc^-	$[TcN(Et_2dtc)Cl(PPhMe_2)_2]$		[86b]
70 + Et_2dtc^-	$[Tc(N)(Et_2dtc)_2(PPhMe_2)]$		[86b]
70 + Et_2dtc^-	$[Tc(N)(Et_2dtc)_2]$		[86b]
Ligand substitution on $[Tc^{VI}(N)Cl_4]^-$			
$[Tc(N)Cl_4]^-$ (**71**) + dppf	$[Tc(N)Cl_2(dppf)]$		[77b]
71 + $Ph_2P(CH_2)_2SH + H^+$	$[Tc(N)(Ph_2P(CH_2)_2S)_2]$		[79]
71 + $MeO_2P(CH_2)_2SH + H^+$	$[Tc(N)(MeO_2P(CH_2)_2S)_2]$		[79]
71 + $Ph_2P(CH_2)_3SH + H^+$	$[Tc(N)(Ph_2P(CH_2)_3S)_2]$		[79]
71 + $Tol_2P(CH_2)_3SH + H^+$	$[Tc(N)(Tol_2P(CH_2)_3S)_2]$		[79]
71 + Ph_2P-*o*-$C_6H_4SH + H^+$	$[Tc(N)(Ph_2P$-*o*-$C_6H_4S)_2]$		[79]
71 + $N(SPPh_2)_2^-$	$[Tc(N)\{N(SPPh_2)_2\}_2]$	Reacts w/BCl_3	[80]
71 + Ph_2P-*o*-C_6H_4-H_2N	$[Tc(N)Cl(Ph_2P$-*o*-C_6H_4-$H_2N)_2]^+$		[109]
71 + HL	$[Tc(N)(L)_2]$ Where HL = 2-(dicyclohexylphosphino)ethanethiol		[84]
71 + $dmit^{2-}$	$[Tc(N)(dmit)_2]^{2-}$		[86c]
Other ligand substitutions			
cis-$[Tc(N)Cl_2(POP)] + OSH_2$ [f]	$[Tc(N)(SO)(POP)]$		[78]
cis-$[Tc(N)Cl_2(PNP)] + OSH_2$ [f]	$[Tc(N)(SO)(PNP)]$		[78]
$[Tc(N)(H_2O)(HL)_2]^{2+} + OH^-$	$[Tc(N)(H_2O)(L)_2]$ Where HL = 1,1-dimethylbiguanide		[83]
$[Tc(N)(H_2O)(HL)_2]^{2+} + OH^-$	$[Tc(N)(H_2O)(L)_2]$ Where HL = 1-phenethylbiguanide		[83]
$[Tc(N)(H_2O)(HL)_2]^{2+} + OH^-$	$[Tc(N)(H_2O)(L)_2]$ Where HL = 1-phenylbiguanide		[83]
$[TcCl_2\{NPr(CH_2CH_2PPh_2)_2\}] + H_2L + NEt_3$	$[Tc(N)(HL)_2\{NPr(CH_2CH_2PPh_2)_2\}]^+$ Where $H_2L = H_2NNMeC(S)SMe$		[83b]
$[TcNCl(tu)_2]^+ + dmpe$	$[TcN(dmpe)Cl]^+$		[85]
$[Tc(N)Cl(tu)_2]^+ + dppe$	$[Tc(N)(dppe)Cl]^+$		[85]
Other reactions			
$[TcCl_4(PPh_3)_2] + H_2L + NEt_3$	$[Tc(N)(HNNMeC(S)SMe)_2]$ Where $H_2L = H_2NNMeC(S)SMe$		[83b]

[a] POP = $Ph_2P(CH_2)_2O(CH_2)_2PPh_2$.
[b] PNP = $Ph_2P(CH_2)_2N(CH_2CH_2OMe)(CH_2)_2PPh_2$.
[c] Hpnao = $HONCMeCMe_2NH(CH_2)_3NHCMe_2CMeNOH$.
[d] Hbnao = $HONCMeCMe_2NH(CH_2)_4NHCMe_2CMeNOH$.
[e] Hpentao = $HONCMeCMe_2NH(CH_2)_5NHCMe_2CMeNOH$.
[f] OSH_2 = 2-mercaptoethanol, 2-mercaptoacetic acid and 2-mercaptobenzoic acid.

atom transfer to the nitrile carbon. Alternatively, protic reduction of the isonitrile ligand can result in the imido moiety [69b,69c]. In these cases, the isonitrile carbon atom is doubly protonated with the loss of dinitrogen and change in oxidation state.

Table 9
Nitrido complexes of rhenium(V)

Synthesis	Complex	Comments	Reference
Ligand substitution on $[Re^{V}(N)Cl_2(PR_3)_2]$ and analogues			
$[ReNCl_2(PPh_3)_2]$ (**72**) + L^-	$[Re(N)L_2]$ Where $L = N(SPPh_2)_2^-$	Reacts w/BCl_3, TFAA, CCl_2HCOCl, $CClH_2COCl$, and CH_3COCl	[80,91h] [10b]
72 + ($FeCS_2$)	$[Re(N)(PPh_3)(FeCS_2)_2]$ Where $FeCS_2 = [Fe^{II}(C_5H_4CS_2(C_5H_5))]^-$		[81]
72 + Ph_2P-*o*-C_6H_4-H_2N	$[Re(N)Cl(Ph_2P\text{-}o\text{-}C_6H_4\text{-}H_2N)_2]^+$	Stable	[84]
72 + HPO	mer-$[Re(N)(PPh_3)(PO)_2]$ Where HPO = bis(*o*-hydroxyphenyl)phenylphosphine		[90a]
72 + POH	$[Re(N)(PPh_3)(PO)_2]$ Where POH = 1-phenyl-2-(diphenylphosphino)ethanone		[90b]
72 + py′	$[Re(N)(PPh_3)(py')Cl]^+$ Where py′ = quaterpyridine	Stable 7-coord.	[91a]
72 + py	$[Re(N)(PPh_3)_2(py)_2Cl]^+$	Stable	[91b]
72 + LiMe	$[Re(N)(PPh_3)_2(Me)_2]$	Stable	[91c]
72 + $LiCCBu^t$	$[Re(N)(PPh_3)_2(CCBu^t)_2]$	Stable	[91c,91f]
72 + LiPh	$[Re(N)(PPh_3)_2(Ph)_2]$	Stable	[91c]
72 + LiTol	$[Re(N)(PPh_3)_2(Tol)_2]$	Stable	[91c,91f]
72 + dppe	$[Re(N)(dppe)_2Cl]^+$	Stable	[91d]
72 + dppbz	$[Re(N)(dppbz)_2Cl]^+$	Stable	[91d]
72 + dpae	$[Re(N)(dpae)_2Cl]^+$	Stable	[91d]
72 + dadpe	$[Re(N)(dadpe)_2Cl]^+$	Stable	[91d]
72 + R-1,2-dppp	$[Re(N)(R\text{-}1,2\text{-}dppp)_2Cl]^+$	Stable	[91d]
72 + dmeppe	$[Re(N)(dmeppe)_2Cl]^+$	Stable	[91g]
72 + dmppe	$[Re(N)(dmppe)_2Cl]^+$	Stable	[91g]
72 + dfppe	$[Re(N)(dfppe)_2Cl]^+$	Stable	[91g]
72 + $NH(PPh_2)_2$	$[Re(N)Cl\{NH(PPh_2)_2\}_2]^+$		[91h]
72 + $NH(SPPh_2)_2$	$[Re(N)Cl\{N(SPPh_2)_2\}PPh_3]$		[91h]
72 + $NH(SePPh_2)_2$	$[Re(N)\{N(SePPh_2)_2\}_2]$		[91h]
72 + NP_3	$[Re(N)(\eta^2\text{-}P,P\text{-}NP_3)Cl_2]$ Where $NP_3 = N(CH_2CH_2PPh_3)_3$		[92]
72 + 1dppm	$[Re(N)(dppm)(PPh_3)Cl_2]$		[100a]
72 + 2dppm	$[Re(N)(dppm)_2Cl]^+$		[100a]
72 + $2PCy_3$	$[Re(N)(PCy_3)_2Cl_2]$		[100c]
72 + atp^-	$[Re(NPPh_3)(atp)_2]$	Neutral, diamagnetic complex believed to result from nucleophilic attack on $[Re(N)(atp)_2(PPh_3)]$	[101]
72 + L_{OEt^-}	$[Re(N)(PPh_3)(L_{OEt})Cl]$ Where $L_{OEt} = Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3$	Reacts w/MeOTf, $PhCH_2Br$, CPh_3^+	[102]
72 + SCN^-	$[ReN(PPh_3)_2(SCN)_2]$	Stable	[95d]
72 + L	$[ReN(L)Cl_2]$ Where L = bis(diphenylphosphinoethyl)propylamine		[100b]
72 + L	$[ReN(L)Cl_2]$ Where L = 1,1,1-tris(diphenylphosphinomethyl)ethane		[100b]
72 + L	$[ReN(L)Cl_2]$ Where L = 1,8-bis(diphenylphosphino)3,6-dioxaoctane		[100b]
$[Re(N)Br_2(PPh_3)_2] + 2PCy_3$	$[Re(N)(PCy_3)_2Br_2]$		[100c]
$[Re(N)Cl_2(PPhMe_2)_3]$ (**73**) + L^-	$[Re(N)L_2]$ Where $L = N(SPPh_2)_2^-$	Reacts w/BCl_3, S_2Cl_2	[80]
73 + Me_2dtc^-	$[Re(N)Cl(Me_2dtc)(PPhMe_2)_2]$		[93a]
		Reacts w/$B(C_6F_5)_3$	[93f]
73 + Me_2dtc^-	$[Re(N)(Me_2dtc)_2(PPhMe_2)]$		[93a]
73 + Et_2dtc^-	$[Re(N)Cl(Et_2dtc)(PPhMe_2)_2]$	Reacts w/BCl_2Ph	[93a] [93e,94a]
73 + morphdtc$^-$	$[Re(N)Cl(morphdtc)(PPhMe_2)_2]$		[93a]
73 + morphdtc$^-$	$[Re(N)(morphdtc)_2(PPhMe_2)]$		[93a]
73 + pipdtc$^-$	$[Re(N)Cl(pipdtc)(PPhMe_2)_2]$		[93a]
73 + pipdtc$^-$	$[Re(N)(pipdtc)_2(PPhMe_2)]$		[93a]
73 + Et_2dtc^-	$[Re(N)(Et_2dtc)_2(PPhMe_2)]$	Reacts w/CPh_3^+, BCl_3, $GaCl_3$, S_2Cl_2, BPh_3, BCl_2Ph, and $B(C_6F_5)_3$	[93a,93b,93c,93d,93e,93f]

Table 9 (*Continued*)

Synthesis	Complex	Comments	Reference
73 + $S_2PPh_2^-$	$[Re(N)Cl(S_2PPh_2)(PPhMe_2)_2]$		[94a]
73 + Et_2tcb^-	$[Re(N)Cl(Et_2tcb)(PPhMe_2)_2]$	Reacts w/S_2Cl_2, BBr_3, $B(C_6F_5)_3$, $GaCl_3$	[94a,94c,94h,94e]
73 + morphtcb$^-$	$[Re(N)Cl(morphtcb)(PPhMe_2)_2]$	Reacts w/S_2Cl_2	[94a,94c]
73 + piptcb$^-$	$[Re(N)Cl(piptcb)(PPhMe_2)_2]$	Reacts w/S_2Cl_2	[94a,94c]
73 + Me_3SiBr	$[Re(N)Br_2(PPhMe_2)_3]$	Reacts w/BBr_3	[95a]
73 + KSCN	$[Re(N)(NCS)_2(PPhMe_2)_3]$	Stable	[95c]
Ligand substitution on $[Re^{VI}(N)Cl_4]^-$			
$[Re(N)Cl_4]^-$ (**74**) + dppf	$[Re(N)Cl_2(dppf)]$		[77b]
74 + Et_2dtc^-	$[Re(N)(Et_2dtc)_2]$	Stable	[97]
74 + mnt^{2-}	$[Re(N)(mnt)_2]^{2-}$		[97]
Other ligand substitutions and metathesis			
$[Re(N)(PPh_3)(PO)_2]$ [a] + py	$[Re(N)(py)(PO)_2]$		[90b]
$[Re(N)(PPh_3)(PO)_2]$ [a] + $PTol_3$	$[Re(N)(PTol_3)(PO)_2]$		[90b]
$[Re(N)(PPh_3)(PO)_2]$ [a] + L	$[Re(N)(L)(PO)_2]$ Where L = methylimidazole		[90b]
$[Re(N)(dppe)_2Cl]^+$ + AgOTf + MeCN	$[Re(N)(dppe)_2MeCN]^{2+}$		[91e,91f]
$[Re(N)(dppe)_2MeCN]^{2+}$ + [*n*-Bu_4N]F	$[Re(N)(dppe)_2F]^+$		[91f]
$[Re(N)(dppe)_2MeCN]^{2+}$ + [*n*-Bu_4N]Br	$[Re(N)(dppe)_2Br]^+$		[91f]
$[Re(N)(dppe)_2MeCN]^{2+}$ + [*n*-Bu_4N]I	$[Re(N)(dppe)_2I]^+$		[91f]
$[Re(N)(dppe)_2MeCN]^{2+}$ + SCN^-	$[Re(N)(dppe)_2SCN]^+$		[91f]
$[Re(N)(dppe)_2MeCN]^{2+}$ + OCN^-	$[Re(N)(dppe)_2OCN]^+$		[91f]
$[Re(N)(dppe)_2MeCN]^{2+}$ + NaN_3	$[Re(N)(dppe)_2(N_3)]^+$		[91f]
$[Re(N)(dppbz)_2Cl]^+$ + AgOTf + MeCN	$[Re(N)(dppbz)_2MeCN]^{2+}$		[91f]
$[Re(N)(dmeppe)_2Cl]^+$ + AgOTf + MeCN	$[Re(N)(dmeppe)_2MeCN]^{2+}$		[91f]
$[Re(N)(dmppe)_2Cl]^+$ + AgOTf + MeCN	$[Re(N)(dmppe)_2MeCN]^{2+}$		[91f]
$[Re(N)(\eta^2\text{-}P,P\text{-}NP_3)Cl_2]$ + EtOH + $NaBPh_4$	$[Re(N)(\eta^4\text{-}NP_3)Cl]^+$ Where $NP_3 = N(CH_2CH_2PPh_3)_3$		[92]
$[Re(N)Cl(Et_2tcb)(PPhMe_2)_2]$ + NaN_3	$[Re(N)(N_3)(Et_2tcb)(PPhMe_2)_2]$	Stable	[94b]
$[Re(N)Cl(morphtcb)(PPhMe_2)_2]$ + KSCN	$[Re(N)(NCS)(morphtcb)(PPhMe_2)_2]$	Stable	[94b]
$[Re(N)Cl(morphtcb)(PPhMe_2)_2]$ + KCN	$[Re(N)(NC)(morphtcb)(PPhMe_2)_2]$	Stable	[94b]
$[Re(N)Cl(morphtcb)(PPhMe_2)_2]$ + NaI	$[Re(N)(I)(morphtcb)(PPhMe_2)_2]$	Stable	[94b]
$[Re(N)Cl(morphtcb)(PPhMe_2)_2]$ + 2,6-DMTPH	[Re(N)(2,6-DMTP)(morphtcb)($PPhMe_2$)]	Stable	[94f]
$[Re(N)Cl(morphtcb)(PPhMe_2)_2]$ + mnt^{2-}	[Re(N)(mnt)($PPhMe_2$)]	Stable	[94f]
$[Re(N)(NCS)_2(PPh_3)_2]$ + MeCN	$[Re(N)(NCS)_2(MeCN)(PPh_3)_2]$	Stable	[95d]
Other reactions			
$[Re(O)\{HNN(Me)CS_2Me\}_2]^+$ + Me_2dtc^-	$[Re(N)(Me_2dtc)_2]$		[98]
$[Re(O)\{HNN(Me)CS_2Me\}_2]^+$ + Et_2dtc^-	$[Re(N)(Et_2dtc)_2]$		[98]
$[Re(O)\{HNN(Me)CS_2Me\}_2]^+$ + Ph_2dtc^-	$[Re(N)(Ph_2dtc)_2]$		[98]
$[ReO\{HNN(Me)CS_2Me\}_2]^+$ + $\{[-CH_2-]_5NCS_2\}^-$	$[Re(N)\{[-CH_2-]_5NCS_2\}_2]$		[98]
Re_2O_7 + 1,2-$(CN)_2C_6H_4$ + NH_4I	[Re(N)(Pc2−)]	Stable	[99a]
$NH_4[ReO_4]$ + 1,2-$(CN)_2C_6H_2$-4,5-^{n}Bu	[Re(N)(Pc^{n}Bu$_8$)] Where Pc = phthalocyaninato		[99b]
$NH_4[ReO_4]$ + 1,2-$(CN)_2C_6H_2$-4,5-C_5H_{11}	$[Re(N)\{Pc(C_5H_{11})_8\}]$ Where Pc = phthalocyaninato	Reacts w/BBr_3 Reacts w/PPh_3 with loss of nitrido ligand to form oxo	[99b,43]
$NH_4[ReO_4]$ + 1,2-$(CN)_2C_6H_2$-4,5-C_6H_{13}	$[Re(N)\{Pc(C_6H_{13})_8\}]$ Where Pc = phthalocyaninato		[99b]

Table 9 (*Continued*)

Synthesis	Complex	Comments	Reference
$NH_4[ReO_4]+1,2\text{-}(CN)_2C_6H_2\text{-}4,5\text{-}C_7H_{15}$	$[Re(N)\{Pc(C_7H_{15})_8\}]$ Where Pc = phthalocyaninato		[99b]
$[Re^{V}(N)(PPh_3)(L_{OEt})Cl]+AgBF_4$	$[Re^{VI}(N)(PPh_3)(L_{OEt})Cl]^+$		[10a]

[a] Where PO^- = 1-phenyl-2-(diphenylphosphino)ethanone monoanion (from POH).

7.2. Group 7: manganese, technetium, rhenium

7.2.1. Nitrido complexes of Group 7

7.2.1.1. Manganese nitrido complexes. Manganese(V) nitrido complexes are usually quite stable, have a short Mn≡N bond lengths (1.50–1.55 Å) and are diamagnetic. The Mn≡N moiety is nucleophilic and reacts with electrophiles such as trifluoroacetic anhydride (TFAA) [8a,9] and *p*-toluenesulfonic anhydride (Ts_2O) [8b,8c]. Additionally, the Mn≡N moiety has enough basic character that it is also susceptible to attack by both Bronsted and Lewis acids [12]. The common routes to create the nucleophilic Mn≡N bond are via photolysis of an (azido)manganese(III) complex and by oxidation of manganese(III) in the presence of aqueous or gaseous ammonia. Common oxidants used for the latter route are bleach (NaOCl), NBS, PhI=O, and Cl_2. Most manganese(V) nitrido complexes are five-coordinate. Only recently have six-coordinate complexes been prepared.

The most frequently prepared and studied complexes of (nitrido)manganese(V) have contained the macrocyclic ligands derived from salen and Schiff bases, Table 7 [8b,8c,9,12,74]. Chiral complexes have been prepared and utilized for asymmetric aziridination [8b,12] and amination [9b] reactions. Once activated with TFAA or Ts_2O, the nitrogen atom is transferred to an olefin as an N-TFA or N-Ts group via an imido intermediate. This reactivity has even been applied to the synthesis of 2-amino-2-deoxy sugars [9a,9d,9g]. These complexes can be prepared from photolysis of the corresponding manganese(III) salen compound [9a]. However, yields are typically low. So an alternative method has been developed where the appropriate manganese(II) starting material is oxidized in the presence of ammonia and ligand [9a].

Two other macrocyclic ligands employed for the synthesis of new manganese(V) nitrido complexes are the four-coordinate cyclam [75] and the three-coordinate tacn [75], Table 7. Interestingly, photolysis of trans-$[Mn^{III}(N_3)_2(cyclam)]^+$ produced a dimeric nitrido manganese(V) species which could then be converted to the monomeric nitrido upon addition of sodium cyanide. Similar results were obtained with $[Mn^{III}(N_3)_3(Me_3\text{-}tacn)]$, however, the formation of the dimeric species was wavelength dependent. The reaction of $[Mn^{V}(N)(cyclam)(CH_3CN)]^{2+}$ with trifluoroacetic anhydride only resulted in ligand substitution of the acetonitrile with retention of the Mn≡N moiety. All of the complexes with either the cyclam or tacn ligands were six-coordinate; of which $[(Me_3tacn)Mn(N)(acac)]^+$ was the first to be structurally characterized [75]. The Mn≡N bond lengths were still short (1.51–1.54 Å) and the trans influence was pronounced in these complexes. Additional six-coordinate (nitrido)manganese(V) complexes have been prepared by ligand substitution of [Mn(N)(salen)] complexes, Table 7 [34a].

7.2.1.2. Technetium nitrido complexes. Technetium nitrido complexes have received a considerable amount of attention due to the potential application of these complexes as radiopharmaceuticals. The Tc≡N moiety is rather stable and not very reactive. Thus, nitrido complexes of technetium are of interest for their use in diagnostic purposes that employ the radioactive isotope, Tc-99m. Most technetium(V) and (VI) nitrido complexes are five- or six-coordinate. The review by Baldas covers technetium nitrido complexes through 1994 [76]. Thus, the focus here will be on complexes prepared from 1995 onwards.

The common synthetic strategies used to make new technetium nitrido complexes has been ligand substitution on $[Tc^{V}(N)Cl_2(PR_3)_2]$ and $[Tc^{VI}(N)Cl_4]^-$. With the anionic complex, $[Tc^{VI}(N)Cl_4]^-$, reduction of the tech-

Table 10
Imido complexes of manganese(V)

Synthesis	Complex	Comments	Reference
From organic azides			
$Mn^{III}(tpfc)+MesN_3+h\nu$	$[Mn^{V}(NMes)(tpfc)]$	Reacts w/PPh_3, PEt_3	[105b]
$Mn^{III}(tpfc)+ArN_3+h\nu$	$[Mn^{V}(NAr)(tpfc)]$ Where Ar = 2,4,6-trichlorophenyl	Reacts w/PPh_3, PEt_3	[105b]

netium occurs either with the aid of reducing ligands (such as phosphanes or thiols) or with addition of a reducing agent. A list of new technetium(V) nitrido complexes is presented in Table 8 [77–86,109]. A variety of ligands containing S, P or N donor atoms have successfully been reported to chelate to technetium(V).

Although the Tc≡N bond is known for its stability, there is a recent example where the moiety was lost and a technetium(III) complex was formed. The reaction of $[Tc^{VI}(N)Cl_4]^-$ with phosphane-thiol ligands of the type $R_2P(CH_2)_nSH$, in the absence of acid results in formation of technetium(III) and loss of the Tc≡N moiety [79]. Additionally, $[Tc^{V}(N)(N(SPPh_2)_2)]$ was reported to react with Lewis acids, such as BCl_3; and $[Tc^{V}(N)(PPhMe_2)_2(N(SPPh_2)]$ formed the thionitrosyl complex upon addition of S_2Cl_2 [80].

Technetium complexes used in nuclear medicine contain the isotope Tc-99m and are prepared from $[^{99m}TcO_4]^-$. There are three synthetic strategies that have been used to make nitrido technetium(V) complexes from Tc-99m enriched pertechnetate. Pertechnetate can be reduced with stannous chloride in the presence of propylenediaminitetraacetic acid (PDTA) and succinic dihydrazide (SDH) and the appropriate ligand to make the desired nitrido complex. Furthermore, it is known that $[^{99m}Tc^{VI}(N)Cl_4]^-$ is formed from the reaction of $[^{99m}TcO_4]^-$ with hydrochloric acid and sodium azide. Thus, an alternative synthesis where $[^{99m}TcO_4]^-$ is reacted with HCl and NaN_3 in situ, followed by addition of ligand and if necessary reducing agent has also been developed. Finally, another method used to make nitrido complexes of Tc-99m has employed $[^{99m}TcO_4]^-$ and *S*-methyl-*N*-methyldithiocarbazate ($H_2NNMeC(=S)SMe$) with an organic phosphane or stannous chloride as the reducing agent and acid (such as DTPA) followed by addition of ligand. The ligands of interest for creating new diagnostic nitrido complexes have been derivatives of peptides (L-cysteine), dithiocarbamates (RHNC(=S)SNa), thioamides, (RHNC(=S)R′), dithiolphosphinates (SPS), and diphosphines (PXP where X = O or N) [87–89]. Generating complexes with a mixture of ligands has also been of further interest [87].

7.2.1.3. Rhenium nitrido complexes. The terminal nitrido complexes of rhenium(V) and (VI) are usually stable complexes with a strong triple bond between the rhenium and nitrogen atom. Thus, the most common synthetic route to making new nitrido complexes of rhenium is simply by ligand exchange with retention of the nitrido moiety. The common starting materials are $[Re^{V}(N)Cl_2(PPh_3)_2]$ (**72**), $[Re^{V}(N)Cl_2(PPhMe_2)_3]$ (**73**), and $[Re^{VI}(N)Cl_4]^-$ (**74**), Table 9. One electron reduction of $[Re^{VI}(N)Cl_4]^-$ is often facilitated by the chelating ligands. The Re≡N bond length is short, ranging from 1.61 to 1.67Å. However, there are a few examples where the Re≡N was found to be quite long. For example, $[Re(N)(dpae)_2Cl]^+$ was reported to have a Re≡N bond length of 1.84 Å; and the Re≡N bond in $[Re(N)(dmppe)_2Cl]^+$ was found to be 1.76 Å [91d,91g].

The nitrido ligand is most often nucleophilic and Lewis basic. In fact, quite a number of rhenium nitrido complexes have been found to react with Lewis acids to form Lewis acid adducts or bridging type complexes [96]. Furthermore, there are examples where the nitrido ligand will attack electrophiles such as CPh_3^+ to form the corresponding imido product with no change in rhenium's oxidation state. Examples of both of these types of reactions of the nitrido moiety are listed within Table 9. However, there is one recent example where the nitrido moiety behaved as an electrophile. When $[Re(N)Cl_3(PPh_3)_2]$ was reacted with two equivalents of 2-aminothiophenol, the imido product resulted, $[Re^{V}(=NPPh_3)(SC_6H_4NH_2)_2]$ [101]. This imido product was believed to result from the nucleophilic attack of triphenylphosphane on the nitrido ligand in $[Re^{V}(N)(PPh_3)(SC_6H_4NH_2)_2]$ to give a rhenium(III) intermediate, $[Re^{III}(=N-PPh_3)(PPh_3)(SC_6H_4NH_2)_2]$. This intermediate was postulated to undergo subsequent oxidization with loss of triphenylphosphane to give the product, $[Re^{V}(=N=PPh_3)(SC_6H_4NH_2)_2]$ [101]. (The product was characterized by X-ray crystallography: Re=N=P bond angle = 160.3°, Re=N bond length = 1.799 Å and N=P bond length = 1.595 Å.)

As mentioned previously, the rhenium–nitrogen bond in (nitrido)rhenium(V) complexes is usually quite stable. Interestingly, there is a recent example where the nitrido group was displaced and the corresponding oxo complex was formed. The nitrido ligand was displaced from $[Re(N)Cl_2(PPh_3)_2]$ upon addition of 8-hydroxyquinoline (Hquin), or *N*-phenylsalicylideneimine (Hpsal) to give $[Re(O)Cl(quin)_2]$ and $[Re(O)Cl_2(PPh_3)(psal)]$, respectively [103].

7.2.2. Imido complexes of Group 7

7.2.2.1. Manganese imido complexes. Terminal manganese(V) imido complexes have long been postulated to be the reactive intermediates in the formation of aziridines and amines from the reaction of activated nitridomanganese(V) complexes with alkenes [8,9]. Although an acylimido manganese(V) complex has been spectroscopically identified [8a,104], only recently have manganese(V) imido complexes been prepared, isolated, and fully characterized. Utilizing the stabilizing effect of a corrole macrocyle, terminal (imido)manganese(V) complexes, [Mn(NMes)(tpfc)] and [Mn(NAr)(tpfc)], where Ar = 2,4,6-trichlorophenyl, have been prepared from the oxidation of the corresponding manganese(III) with organic azides, Table 10 [105b]. Neither complex is reactive enough to react with olefins, even electron rich alkenes such as silyl enol

ethers. However, both complexes contain an electrophilic NR moiety, which is readily transferred to organic phosphanes.

7.2.2.2. Technetium imido complexes. Compared to rhenium, the number of technetium imido complexes prepared is significantly smaller. This could be due to lack of viable starting materials. Although the rhenium(V) analogue has been known for over 30 years, only recently has $[Tc(NPh)Cl_3(PPh_3)_2]$ been prepared. The technetium complex $[Tc(NPh)Cl_3(PPh_3)_2]$ can be synthesized from pertechnetate and 1-acetyl-2-phenylhydrazine in the presence of HCl and triphenylphosphane [106]. Similarly, $[Tc(NPh)Br_3(PPh_3)_2]$ [107], $[Tc(NPh)Cl_3(PMePh_2)_2]$ [108], and $[Tc(NPh)Br_3(PMePh_2)_2]$[108] have been prepared, Table 11. The Tc≡NR moiety is typically linear with approximate bond lengths of 1.7 Å. Complexes of the form, $[Tc(NPh)X_3(PR_3)_2]$, where X = Cl or Br, and PR_3=PPh_3 or $PMePh_2$, have been used as synthetic precursors to new (imido)technetium(V) complexes. For example, ligand substitution on $[Tc(NPh)Cl_3(PPh_3)_2]$ has been reported to occur by both monodentate and bidentate phosphanes, Table 11 [77]. However, the use of arylthiols in ligand substitution reactions, can result in the loss of the NPh group and formation of the technetium(V) oxo compound [107]. The use of sterically larger arylthiols has allowed isolation of the corresponding technetium(V) imido products, Table 11 [107]. However, even those isolable complexes were unstable in solution.

7.2.2.3. Rhenium imido complexes. Imido complexes of rhenium are plentiful. The most common oxidation states one finds terminal imido ligands on rhenium is (V). Although higher oxidation states usually contain more than one multiply bonded ligand, (imido)rhenium(VI) complexes containing one imido ligand have recently been prepared by oxidation of the corresponding (imido)rhenium(V) compounds, Table 12 [111g]. Typical bond lengths for Re≡NR of rhenium(V) complexes are 1.71 Å. However, deviations from this ideal length have been observed. Although most Re≡NR moieties of rhenium(V) are linear, a recent example of a bent imido ligand was reported [109]. The complex, $[Re(=NC_6H_4-o\text{-}PPh_2)(NHC_6H_5-o\text{-}PPh_2)Cl_2]$ contains an Re–N–C bond angle of 137° [109]. It should be also noted that in this case the imido ligand is bidentate; both the imido nitrogen and the phosphane are coordinated to the metal center. Although (imido)rhenium(V) complexes are expected to be electrophilic, there are only few examples of this type of reactivity. Even a recently prepared acylimido complex, $[Re^{V}(NC(O)CF_3)(OCOCF_3)\{N(SPPh_2)_2\}_2]$ was found to be unreactive towards olefins even electron rich types, such as silyl enol ethers [10b]. Thus, most imido complexes of rhenium(V) are, with a few exceptions, quite stable, Table 12 [115].

A common synthetic approach to forming new (imido)rhenium(V) complexes has been to utilize the corresponding nitrido and oxo analogues. From the nitrido, alkylation or acylation has been achieved with carbanions, and anhydrides, Table 12 [10a,10b,93b,110].

Table 11
Imido complexes of technetium(V)

Synthesis	Complex	Comments	Reference
From pertechnetate			
$[TcO_4]^- + HBr + PhNHNHCOCH_3 + PPh_3$	$[Tc(NPh)Br_3(PPh_3)_2]$		[107]
$[TcO_4]^- + HBr + PhNHNHCOCH_3 + PMePh_2$	$[Tc(NPh)Br_3(PMePh_2)_2]$		[108]
$[TcO_4]^- + HCl + PhNHNHCOCH_3 + PMePh_2$	$[Tc(NPh)Cl_3(PMePh_2)_2]$		[108]
From $[Tc(NPh)Cl_3(PPh_3)_2]$			
$[Tc(NPh)Cl_3(PPh_3)_2]$ (**75**) + PMe_2Ph	$[Tc(NPh)Cl_2(PMe_2Ph)_3]^+$		[77a]
75 + dppf	$[Tc(NPh)Cl_3dppf]$		[77b]
75 + TMBTH	$[Tc(NPh)(TMBT)_3PPh_3]$	Unstable (reverts to oxo)	[107]
75 + DMBTH	$[Tc(NPh)(DMBT)_4]^-$	Unstable	[107]
Other reactions			
$[Tc(O)Cl_4]^- + H_2L$	$[Tc\{PPh_2(C_6H_4\text{-}N\text{-}2)\}Cl_2\{PPh_2C_6H_4NH\}]$[a] Where H_2L = (*o*-aminophenyl)diphenylphosphine		[109]

[a]

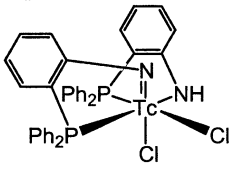


Table 12
Imido complexes of rhenium(V) and (VI)

Synthesis	Complex	Comments	Reference
From the nitrido			
$[Re(N)(Et_2dtc)_2(Me_2PhP)]+CPh_3^+$	$[Re(NCPh_3)(Et_2dtc)_2(Me_2PhP)]^+$	Stable	[93b]
$[Re(N)(L_{OEt})(PPh_3)Cl]$ [a] $+MeOTf$	$[Re(NMe)(L_{OEt})(PPh_3)Cl]^+$	Stable	[10a]
$[Re(N)(L_{OEt})(PPh_3)Cl]+PhCH_2Br$	$[Re(NCH_2Ph)(L_{OEt})(PPh_3)Cl]^+$	Stable	[10a]
$[Re(N)(L_{OEt})(PPh_3)Cl]+CPh_3^+$	$[Re(NCPh_3)(L_{OEt})(PPh_3)Cl]^+$	Stable	[10a]
$[Re(N)Cl_2(PMe_2Ph)_3]$ **73** $+DMSMe_2$	$[Re\{NC(Me)_2(Me_2PhP)\}(DMSMe_2)_2]$		[110]
73 $+SbCl_5+HCl$	$[Re(NH)Cl_2(Pme_2Ph)_3]^+$		116b
73 $+TaCl_5+CH_2Cl_2$	$[Re(NH)Cl_2(Pme_2Ph)_3]^+$	Stable	[116c]
$[Re(N)\{N(SPPh_2)_2\}_2]+TFAA$	*trans*-$[Re(NC(O)CF_3)(OCOCF_3)\{N(SPPh_2)_2\}_2]$	No reaction w/olefins	[10b]
$[Re(N)\{N(SPPh_2)_2\}_2]+TFAA+air$	$[Re(NH)(OCOCF_3)L_2]$ Where $L=N(SPPh_2)_2^-$	Deprotonate to give nitrido	[10b]
$[Re(N)\{N(SPPh_2)_2\}_2]+(CCl_3CO)_2O$	$[Re(NH)(OCOCCl_3)L_2]$ Where $L=N(SPPh_2)_2^-$	Deprotonate to give nitrido	[10b]
$[Re(N)\{N(SPPh_2)_2\}_2]+Ts_2O$	$[Re(NH)(OTs)\{N(SPPh_2)_2\}_2]$	Moisture sensitive	[10b]
$[Re(N)\{N(SPPh_2)_2\}_2]+MeCOCl$	$[Re(NC(O)Me)(Cl)\{N(SPPh_2)_2\}_2]$	Moisture sensitive	[10b]
$[Re(N)\{N(SPPh_2)_2\}_2]+CClH_2COCl$	$[Re(NC(O)CClH_2)ClL_2]$ Where $L=N(SPPh_2)_2^-$	Moisture sensitive	[10b]
$[Re(N)\{N(SPPh_2)_2\}_2]+CCl_2HCOCl$	$[Re(NC(O)CCl_2H)ClL_2]$ Where $L=N(SPPh_2)_2^-$	Gives oxo w/air	[10b]
$[Re(N)\{N(SPPh_2)_2\}_2]+[CPh_3][BF_4]$	$[Re(NCPh_3)(F)\{N(SPPh_2)_2\}_2]$		[10b]
$[Re(N)Cl_4]^-+CPh_3^+$	$[Re(NCPh_3)Cl_4]$		[116a]
$[Re(N)Br_4]^-+CPh_3^+$	$[Re(NCPh_3)Br_4]$		[116a]
Ligand substitution on $[Re^V(NR)Cl_3(PR_3)_2]$ and analogues			
$[Re(NPh)Cl_3(PPh_3)_2]$ (**76**)	fac-*cis*/*trans*-$[Re(NPh)Cl(PPh_3)(PO_2)]$		[90a]
$+H_2PO\cdot HCl$	Where H_2PO = bis(*o*-hydroxyphenyl)phenylphosphine		
76 $+HPO\cdot HCl$	*trans*-$[Re(NPh)(PO)(PO_2)]$ Where HPO = (*o*-hydroxyphenyl)diphenylphosphine		[90a]
76 $+POH$	$[Re(NPh)Cl(PO)_2]$ Where $POH=Ph_2PCH_2C_6H_3(CH_3)OH$		[90c]
76 $+6$-mebpy $+EtOH$	$[Re(NPh)(6\text{-mebpy})(PPh_3)Cl(OEt)]^+$		[112a]
76 $+dmp$	$[Re(NPh)(dmp)(PPh_3)Cl(OEt)]^+$		[112a]
76 $+o$-bpy $+EtOH$	$[Re(NPh)(o\text{-bpy})(OEt)]^+$		[112b]
76 $+dppe+EtOH$	$[Re(NPh)Cl(dppe)_2]^{2+}$	Amido also produced	[112c,112d]
76 $+dppee+EtOH$	$[Re(NPh)Cl(dppee)_2]^{2+}$		[112d]
76 $+dppbz+EtOH$	$[Re(NPh)OH(dppbz)_2]^{2+}$		[112d]
76 $+tacn$	$[Re(NPh)(OH)(PPh_3)tacn]^+$	Catalyzes alkene oxidation w/PhIO where the imido complex behaves as a Lewis acid	114b
76 $+dppf$	$[Re(NPh)Cl_3(dppf)]$		[77b,114c]
76 $+terpy$	$[Re(NPh)Cl_2(terpy)]^+$		[112e]
76 $+H_2dpa$ [b]	$[Re(NPh)Cl(Hdpa)_2]$	Stable in solid state	[118a]
76 $+H_2dpa$	$[Re(NPh)Cl_3(H_2dpa)]$	Stable in solid state	[118a]
76 $+H_2dpa+NEt_3/MeOH$	$[Re(NPh)(Ome)(Hdpa)_2]$	Stable in solid state	[118a]
76 $+H_2dpa+MeOH+NaClO_4$	$[Re(NPh)(Cl)(Hdpa)(H_2dpa)]^+$	Stable in solid state	[118a]
76 $+H_2dppd$ [c]	$[Re(NPh)(Cl)(Hdppd)]^+$	Stable in solid state	[118a]
76 $+H_2dppd+NEt_3/MeOH$	$[Re(NPh)(Ome)(Hdppd)]$	Stable in solid state	[118a]
76 $+P_1\sim OH$ [d] $+NEt_3$	*cis*-$[Re(NPh)(Cl)(P_1\sim O)_2]$		[118b]
76 $+P_1\sim OH$	*trans*-$[Re(NPh)(Cl)_2(P_1\sim O)(PPh_3)]$		[118b]
76 $+P_1\sim OH+NEt_3+EtOH$	*trans*-$[Re(NPh)(OEt)(P_1\sim O)_2]$		[118b]
76 $+P_2\sim OH$ [e] $+NEt_3$	*cis*/*trans*-$[Re(NPh)(Cl)(P_2\sim O)_2]$		[118b]
76 $+P_2\sim OH$	*trans*-$[Re(NPh)(Cl)_2(P_2\sim O)(PPh_3)]$		[118b]
76 $+P_3\sim OH$ [f]	*trans*-$[Re(NPh)(Cl)_2(P_3\sim O)(PPh_3)]$		[118b]
76 $+H_2L$	$[Re(NPh)L(HL)]$ Where H_2L = 2-hydroxybenzaldehyde-((1*R*,2*S*)-1-amino-2-indanol)imine		[112f]
$[Re(NC_6H_4\text{-}p\text{-}Cl)Cl_3(PPh_3)_2]+dppe+EtOH$	$[Re(NC_6H_4\text{-}p\text{-}Cl)Cl(dppe)_2]^{+2}$	Amido also produced	[112c]
$[Re(NC_6H_4\text{-}p\text{-}Ome)Cl_3(PPh_3)_2]+dppe+EtOH$	$[Re(NC_6H_4\text{-}p\text{-}OMe)Cl(dppe)_2]^{+2}$	Amido also produced	[112c]
$[Re(NC_6H_4\text{-}p\text{-}Ome)Cl_3(PPh_3)_2]+H_2L$	$[Re(NC_6H_4\text{-}p\text{-}OMe)L(HL)]$ Where H_2L = 2-hydroxybenzaldehyde-((1*R*,2*S*)-1-amino-2-indanol)imine		[112f]
$[Re(NMe)Cl_3(PPh_3)_2]$ (**77**) $+dppm$	fac-$[Re(NMe)Cl_3(dppm)]$		[100]
77 $+py+EtOH$	*cis*/*trans*-$[Re(NMe)Cl(py)_2(PPh_3)(OEt)]^+$		[91b]
77 $+py+EtOH$	$[Re(NMe)Cl(py)_3(OEt)]^+$	Stable	[91b]
77 $+4$-Mepy $+EtOH$	$[Re(NMe)Cl(4\text{-Mepy})_2(PPh_3)(OEt)]^+$		[91b]
77 $+HL$	$[Re(NMe)Cl(HL)(PPh_3)]^{2+}$		[83a]

Table 12 (*Continued*)

Synthesis	Complex	Comments	Reference
	Where HL = 1,1-dimethylbiguanide		
77 + HL	$[Re(NMe)(HL)_2]^+$		[83a]
+ NEt_3	Where HL = 1,1-dimethylbiguanide		
77 + HL	$[Re(NMe)Cl(HL)(PPh_3)]^{2+}$		[83a]
	Where HL = 1-phenethylbiguanide		
77 + HL + NEt_3	$[Re(NMe)(HL)_2]^+$		[83a]
	Where HL = 1-phenylbiguanide		
77 + $NH(PPh_2)_2$	$[Re(NMe)Cl_3\{NH(PPh_2)_2\}]$		[91h]
77 + $NH(OPPh_2)_2$	$[Re(NMe)Cl_2\{N(OPPh_2)_2\}PPh_3]$		[91h]
77 + $NH(SPPh_2)_2$	$[Re(NMe)Cl_2\{N(SPPh_2)_2\}PPh_3]$		[91h]
77 + $NH(SePPh_2)_2$	$[Re(NMe)Cl_2\{N(SePPh_2)_2\}PPh_3]$		[91h]
77 + $NH(SPPh_2)_2$	$[Re(NMe)Cl\{N(SPPh_2)_2\}_2]$		[91h]
77 + $NH(SePPh_2)_2$	$[Re(NMe)Cl\{N(SePPh_2)_2\}_2]$		[91h]
From the oxo			
$[Re(O)Cl_2(OEt)(PPh_3)_2] + H_2L$	$[Re(L)Cl_2(HL)]$ [g]	Bent imido	[109]
	Where H_2L = (*o*-aminophenyl)diphenylphosphane		
$[TpRe(O)Cl_2]$ + *p*-NH_2-Tol	[ReTp(NTol)Cl_2] (**82**)		[111a]
$[TpRe(O)I_2]$ + *p*-NH_2-Tol	[ReTp(NTol)I_2] (**83**)		[111a]
$[Re(O)Cl_3(ClL)]$ [h] + NH_2Ph	$[Re(NPh)Cl_3(ClL)]$		[111c]
$[Re(O)Cl_3(ClL)]$ + *p*-NH_2Tol	$[Re(NTol)Cl_3(ClL)]$		[111c]
$[Re(O)Cl_3(ClL)]$ + *p*-ClC_6H_4-NH_2	$[Re(NC_6H_4Cl)Cl_3(ClL)]$		[111c]
$[Re(O)Cl_3(pbo)]$ [i] + NH_2Ph	$[Re(NPh)Cl_3(pbo)]$		[111d]
$[Re(O)Cl_3(pbt)]$ [j] + NH_2Ph	$[Re(NPh)Cl_3(pbt)]$		[111d]
$[Re(O)Cl_3(bpy)] + NH_2Ph$	$[Re(NPh)Cl_3(bpy)]$		[112e]
$[Re(O)Cl_3(dmbpy)] + NH_2Ph$	$[Re(NPh)Cl_3(dmbpy)]$		[112e]
$[Re(O)Cl_3(PPh_3)_2]$ (**78**) + PPh_3 + $C(O)HNNHC_6H_4R$	$[Re(NC_6H_4R)Cl_3(PPh_3)_2]$	Stable	[113a]
	Where R = $C(O)NHCH_2C(O)OH$, R = $C(O)NHCH_2C(O)OEt$ R = $(CH_2)_3C(O)OH$ R = $(CH_2)_3C(O)Oet$		
78 + PPh + $N_3C_6H_4R$	$[Re(NC_6H_4R)Cl_3(PPh_3)_2]$	Unstable	[113b]
	Where R = $CO_2N(COCH_2)_2$		
78 + 1,2-$(NH_2)_2C_6H_4$	$[Re(NC_6H_4\text{-}2\text{-}NH_2)Cl_3(PPh_3)_2]$		[111e]
78 + 2,3-$(NH_2)_2C_6H_3$–OH	$[Re\{N(-3\text{-}NH_2)C_6H_3OH\}Cl_3(PPh_3)_2]$		[111e]
78 + 2,3-$(NH_2)_2C_6H_3$–CH_3	$[Re\{N(-3\text{-}NH_2)C_6H_3CH_3\}Cl_3(PPh_3)_2]$		[111e]
78 + 3,4-$(NH_2)_2C_6H_3$–C(O)Ph	$[Re\{N(-4\text{-}NH_2)C_6H_3C(O)Ph\}Cl_3(PPh_3)_2]$		[111e]
78 + EtOH + 1,2-$(NH_2)(CO_2H)C_6H_4$	$[Re(NC_6H_4CO_2)Cl(OEt)(PPh_3)_2]$		[117a]
78 + 4-(Cp–Fe–Cp)–C_6H_4–(NH_2)	$[Re(NR)Cl_3(PPh_3)_2]$		[117b]
	Where R = C_6H_4–4-(Cp–Fe–Cp)		
78 + 4-(Cp–Fe–Cp)–C(O)O–C_6H_4–(NH_2)	$[Re(NR)Cl_3(PPh_3)_2]$		[117b]
	Where R = C_6H_4–4-OC(O)(Cp–Fe–Cp)		
78 + 4-(Cp–Fe–Cp)–C(O)O–(C_6H_4)–(NH_2)	$[Re(NR)Cl_3(PPh_3)_2]$		[117b]
	Where R = $(C_6H_4)_2$–4–OC(O)(Cp–Fe–Cp)		
$[Re(O)Br_3(PPh_3)_2]$ + 4-(Cp–Fe–Cp)–C_6H_4–(NH_2)	$[Re(NR)Br_3(PPh_3)_2]$		[117b]
	Where R = C_6H_4–4-(Cp–Fe–Cp)		
$[Re(O)Cl_3(dppf)_2]$ + 4-(Cp–Fe–Cp)–C(O)O–C_6H_4–(NH_2)	$[Re(NR)Cl_3(dppf)_2]$		[117b]
	Where R = C_6H_4–4-OC(O)(Cp–Fe–Cp)		
$[Re(O)Cl_3(dppf)_2]$ + 4-(Cp–Fe–Cp)–C_6H_4–(NH_2)	$[Re(NR)Cl_3(dppf)_2]$		[117b]
	Where R = C_6H_4–4-(Cp–Fe–Cp)		
$[Re(O)Cl(Hpda)_2] + H_2NPh$	$[Re(NPh)Cl(Hdpa)_2]$		[118a]
$[Re(O)(H)_2(Cyttp)]^+ + NH_2Tol$	$[Re(NTol)(H)_2(Cyttp)]$ [k]	Stable	[111f]
	No reaction w/CO, SO_2, Me_3O^+ or Et_3O^+		
$[Re(O)(H)_2(Cyttp)]^+ + NH_2Ph$	$[Re(NPh)(H)_2(Cyttp)]$	Stable	[111f]
	No reaction w/CO		
$[Re(O)(H)_2(Cyttp)]^+ + NH_2Cy$	$[Re(NCy)(H)_2(Cyttp)]$	Stable	[111f]
	No reaction w/CO		
From bis-imido			
$[Re^{VII}(O)(N^tBu)_2tacn]^+ + Zn$ + oxalic acid	$[Re(N^tBu)tacn(oxalate)]^+$		[114a]

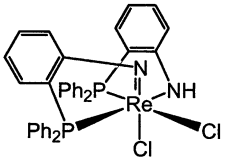
Table 12 (*Continued*)

Synthesis	Complex	Comments	Reference
$[Re^{VII}(O)(N^tBu)_2tacn]^+ + Zn + TFA$	$[Re(N^tBu)tacn(CF_3CO_2)_2]^+$		[114a]
$[Re^{VII}(NR)_2(py)Cl_3] + dppf$	$[Re(NR)Cl_3(dppf)]$ Where R = 2,6-^{i}Pr$_2$-C$_6$H$_3$		[114c]
Oxidation reactions			
$[Re^{III}OPPh_3Cl_3(HL)] + HL$	$[Re^{V}(NPh)Cl_3(HL)]$ Where HL = 2-(phenylazo)pyridine		[111c]
$[Re^{III}OPPh_3Cl_3(L)] + H_2NPh$	$[Re^{V}(NPh)Cl_3(L)]$ (**79**) Where L = py-2-C(=N)–C$_6$H$_4$–*p*-Me		[111g]
$[Re^{III}OPPh_3Cl_3(L)] + p$-$ClC_6H_4H_2N$	$[Re^{V}(NC_6H_5$-*p*-Cl$)Cl_3(L)]$ (**80**) Where L = py-2-C(=N)–C$_6$H$_4$–*p*-Me		[111g]
$[Re^{III}OPPh_3Cl_3(L)] + p$-$ClC_6H_4H_2N$	$[Re^{V}(NC_6H_5$-*p*-Cl$)Cl_3(L)]$ (**81**) Where L = py-2-C(=N)–C$_6$H$_4$-*p*-Cl		[111g]
79 + HNO_3	$[Re^{VI}(NPh)Cl_3(L')]$ Where L′ = py-2-C(O)–C$_6$H$_4$–*p*-Me monoanion		[111g]
80 + HNO_3	$[Re^{VI}(NC_6H_5$–*p*-Cl$)Cl_3(L')]$ Where L′ = py-2-C(O)–C$_6$H$_4$-*p*-Me monoanion		[111g]
81 + HNO_3	$[Re^{VI}(NC_6H_5$–*p*-Cl$)Cl_3(L')]$ Where L′ = py-2-C(O)–C$_6$H$_4$–*p*-Cl monoanion		[111g]
Other reactions			
[ReTp(NTol)Cl$_2$] (**82**) + $CDCl_3$ + *hv*	[ReTp(NTol)(I)Cl]		[111a]
82 + HSPh	[ReTp(NTol)(SPh)Cl]		[111a]
82 + $ZnEt_2$	[ReTp(NTol)(Et)Cl]		[111a]
82 + PhLi	[ReTp(NTol)(Ph)Cl]		[111b]
82 + PhMgCl	[ReTp(NTol)(Ph)$_2$]	Stable	[111b]
[ReTp(NTol)I$_2$] (**83**) + $ZnEt_2$	[ReTp(NTol)(Et)I]	Stable	[111a,111b]
83 + MeMgCl	[ReTp(NTol)(Me)I]	Stable	[111b]
83 + MeMgCl	[ReTp(NTol)(Me)$_2$]	Stable	[111b]
83 + ^{i}PrMgCl	[ReTp(NTol)(^{i}Pr)I]	Stable	[111b]
83 + ^{n}BuLi	[ReTp(NTol)(^{n}Bu)I]	Stable	[111b]
83 + AgOTf	[ReTp(NTol)(OTf)$_2$]		[111b]
[ReTp(NTol)(Ph)$_2$] + I_2	[ReTp(NTol)(Ph)I]	Stable	[111b]
[ReTp(NTol)(Ph)I] + MeMgCl	[ReTp(NTol)(Me)Ph]	Stable	[111b]
[ReTp(NTol)(Et)Cl] + LiOEt	[ReTp(NTol)(Et)(OEt)]		[111b]
[ReTp(NTol)(Ph)I] + AgOTf	[ReTp(NTol)(Ph)OTf]		[111b]
[ReTp(NTol)(Ph)I] + AgOTs	[ReTp(NTol)(Ph)OTs]		[111b]
[ReTp(NTol)(Cl)I] + AgOTf	[ReTp(NTol)(Cl)OTf]		[111b]
[ReTp(NTol)(Et)I] + AgOTf	[ReTp(NTol)(Et)OTf]		[111b]
[ReTp(NTol)(Ph)OTf] + MeCN + Δ	$[ReTp(NTol)(Ph)(NCMe)]^+$		[111b]
[ReTp(NTol)(Et)I] + AgOTf + CD_2CCl_2	$[ReTp(NTol)(H)(CH_2CH_2)]^+$		[111b]
[ReTp(NTol)(Ph)OTf] + py	$[ReTp(NTol)(py)Ph]^+$		[111b]
[ReTp(NTol)(Ph)OTf] + phen	$ReTp(NTol)(phen)Ph]^+$		[111b]
[Re(NPh)Cl$_3$(dppe)] + dppe + EtOH	$[Re(NPh)Cl(dppe)_2]^{2+}$		[112d]
[Re(NPh)Cl$_3$(dppbz)] + dppbz + EtOH	$[Re(NPh)(OH)(dppbz)_2]^{2+}$		[112d]
[Re(NPh)Cl$_3$(dppee)] + dppee + EtOH	$[Re(NPh)Cl(dppee)_2]^{2+}$		[112d]
[Re(NPh)Cl$_3$(bpy)] + bpy + EtOH	$[Re(NPh)(OEt)(bpy)_2]^{2+}$		[112e]
[Re(NPh)Cl$_3$(dmbpy)] + dmbpy + EtOH	$[Re(NPh)(OEt)(dmbpy)_2]^{2+}$		[112e]
$[Re(NPh)(OEt)(bpy)_2]^{+2}$ + HCl	[Re(NPh)Cl$_3$(bpy)]		[112e]
$[Re(NC_6H_4R)Cl_3(PPh_3)_2] + (Et_2NCS_2)_2$	$[Re(NC_6H_4R)(Et_2NCS_2)_2Cl]$ Where R = $CO_2N(COCH_2)_2$		[113b]
$[Re(NC_6H_4CO_2N(COCH_2)_2)Cl_3(PPh_3)_2] + H_2N^iPr$	$[Re(NC_6H_4C(O)N^iPrH)(PPh_3)_2Cl_3]$		[113b]
$[Re(NC_6H_4CO_2N(COCH_2)_2)Cl_3(PPh_3)_2] + H_2NCH(CH_3)CH(CH_3)_2$	$[Re\{NC_6H_4C(O)NHCH(CH_3)CH(CH_3)_2\}(PPh_3)_2Cl_3]$		[113b]
$[Re(NC_6H_4CO_2N(COCH_2)_2)Cl_3(PPh_3)_2] + H_2N(CH_2)_2Ph$	$[Re\{NC_6H_4C(O)NH(CH_2)_2Ph\}PPh_3)_2Cl_3]$		[113b]
$[Re(NC_6H_4CO_2N(COCH_2)_2)Cl_3(PPh_3)_2] + H_2NCH_2Ph$	$[Re\{NC_6H_4C(O)NHCH_2Ph\}(PPh_3)_2Cl_3]$		[113b]
$[Re(NC_6H_4CO_2N(COCH_2)_2)Cl_3(PPh_3)_2] + HN(CH_2)_4$	$[Re\{NC_6H_4C(O)N(CH_2)_4\}(PPh_3)_2Cl_3]$		[113b]
$[Re(NC_6H_4CO_2N(COCH_2)_2)Cl_3(PPh_3)_2]$ + morpholine	$[Re\{NC_6H_4C(O)N(CH_2CH_2)_2O\}(PPh_3)_2Cl_3]$		[113b]

Table 12 (*Continued*)

Synthesis	Complex	Comments	Reference
$[Re(NC_6H_4CO_2N(COCH_2)_2)Cl_3(PPh_3)_2]$ + NEt_3 + alanine ethyl ester hydrochloride	$[Re\{NC_6H_4C(O)NHCH(Me)CO_2Et\}(PPh_3)_2Cl_3]$		[113b]
$[Re(NPh)Cl_3(dppf)]$ + LiOEt	$[Re(NPh)Cl_2(OEt)(dppf)]$		[114c]

[a] $L_{OEt} = Co(\eta^5\text{-}C_5H_5\{PE(OEt)_2\}_3$.
[b] H_2dpa = (*o*-aminophenyl)diphenylphosphine.
[c] H_2dppd = *N,N′*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine.
[d] $P_1 \sim OH$ = 1-phenyl-2-(diphenylphosphino)ethanone.
[e] $P_2 \sim OH$ = 1-*t*-butyl-2-(diphenylphosphino)ethanone.
[f] $P_3 \sim OH$ = 1-phenyl-2-(diphenylphosphino)propanone,
[g]



[h] ClL = 2-((*p*-chlorophenyl)azo)pyridine.
[i] pbo = 2-(2-pyridyl)benzoxazole.
[j] pbt = 2-(2-pyridyl)benzthiazole.
[k] Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$.

From the oxo complexes, the imido moiety is formed utilizing a condensation reaction with derivatives of aniline, Table 12. Quite a number of complexes have been prepared this way. This reaction has also been coupled with ligand exchange [109]. Additionally, the reduction of bis-imido complexes combined with ligand substitution has afforded a small number of new complexes, Table 12 [114a,114c].

Another common synthetic strategy for making imido complexes of rhenium(V) has been ligand substitution. Versatile starting materials for these substitution reactions are $[Re(NPh)Cl_3(PPh_3)_2]$ and $[Re(NMe)Cl_3(PPh_3)_2]$. Table 12 lists a variety of complexes that have been recently made from these starting materials as well as others.

7.3. Group 8: iron, ruthenium, osmium

7.3.1. Nitrido complexes of Group 8

7.3.1.1. Iron nitrido complexes. Although an iron(V) nitrido porphyrin species is postulated to be the reactive intermediate for cytochrome P450-LM 3,4 catalyzed nitrogen atom transfer reactions [119], only spectroscopic evidence has been provided for the existence of such species. Recently, Weighardt and coworkers have identified complexes containing the $Fe^V{\equiv}N$ moiety by EPR and Mossbauer spectroscopies [120]. Photolysis of (azido)iron(III) complexes containing redox innocent ligands in frozen acetonitrile led to the detection of $[Fe^VN(cyclam)N_3]^+$ and $[Fe^VN(cyclam\text{-}acetato)]^+$, Table 13.

7.3.1.2. Ruthenium nitrido complexes. Although ruthenium(VI) nitrido complexes should be more oxidizing and electrophilic than their osmium(VI) counterparts [121], they have received considerably less attention. Recently, Floriani and coworkers demonstrated the usefulness of an alternative synthetic route for the formation of the $Ru^{VI}{\equiv}N$ moiety. Using an analogue of porphyrin, a porphyrinogen ruthenium(II) complex was successfully oxidized to (nitrido)ruthenium(VI), $[Ru^{VI}(N)(ocpg)]^-$, with diphenyldiazomethane, Table 14 [122]. The terminal nitrido complex was postulated to form from reductive cleavage of the N–N bond in a ruthenium(IV) diphenylhydrazone intermediate. The ruthenium(VI) nitrido complex was reported to be moderately electrophilic.

The common starting materials for making new ruthenium(VI) nitrido complexes from ligand substitution reactions have been the anions, $[Ru^{VI}(N)Cl_4]^-$ and $[Ru^{VI}(N)Me_3Br]^-$. Ligand substitution on $[Ru^{VI}(N)Cl_4]^-$ has been demonstrated with a variety of multidentate ligands, Table 14 [123]. Interestingly, there was no pronounced effect of the ancillary ligands on the reported bond lengths of the nitrido complexes (1.615–1.594 Å). Furthermore, all of the ruthenium(VI) complexes produced are electrophilic and reacted spontaneously with triphenylphosphane. Bromide exchange on $[Ru^{VI}(N)Me_3Br]^-$ was accomplished with $NaSiMe_3$, Table 14 [124]. The chemistry of the resulting

Table 13
Nitrido complexes of iron(V)

Synthesis	Complex	Comments	Reference
$[Fe^{III}(N_3)_2cyclam]^+$ in frozen MeCN+*hv*	$[Fe^{V}(N)cyclam(N_3)]^+$	Unstable	[120]
$[Fe^{III}(N_3)_2cyclam\text{-}acetato]^+$ in frozen MeCN+*hv*	$[Fe^{V}(N)cyclam\text{-}acetato(N_3)]^+$	Unstable	[120]

ruthenium(VI) nitrido complex was dominated by the $SSiMe_3^-$ ligand. For example, $[Ru^{VI}(N)Me_3(SSiMe_3)]^-$ was easily converted to the first ruthenium(VI) sulfhydryl complex, $[Ru^{VI}(N)Me_3(SH)]^-$ in the presence of halides or water, where the driving force was the production of $XSSiMe_3$ and $HOSSiMe_3$.

7.3.1.3. Osmium nitrido complexes. Common synthetic strategies for making new osmium(VI) nitrido complexes employ ligand substitution reactions. Organometallic complexes have been prepared from (nitrido)osmium(VI) alkyl and aryl starting materials, Table 15 [5,125]. The Os≡N moiety of the organometallic pyrazolylborate complexes reacts reluctantly with the electrophile methyl triflate to give alkylated products [5]. By far the most commonly used starting material is the osmium(VI) anion, $[Os^{VI}(N)Cl_4]^-$. Quite a variety of complexes have been synthesized from this complex, Table 15 [10a,123,125–132]. Accordingly, the reactivity of Os≡N bond in the resulting complexes has also varied from nucleophilic to electrophilic. Thus, the nitrido complexes of osmium(VI) demonstrate the importance of the ancillary ligands on the reactivity of the nitrido ligand. Although electrophilic behavior has been more commonly observed, the thiolato-substituted complex, $[Os^{VI}(N)(bdt)_2]^-$ reacts as a nucleophile [125b].

The reactivity of pyrazolyl borate complex, $[TpOs(N)Cl_2]$, and its analogues, $[TpOs(N)Ph_2]$, [TpOs(N)ClPh] has been studied extensively. The pyrazolyl borate complex, $[TpOs(N)Cl_2]$ was readily synthesized from $[Os(N)(O)_3]^-$ and the salt of the ligand, Table 15 [5,133,135a,135b]. Interestingly, $[TpOs(N)Cl_2]$ has also been formed from the reaction of the osmium(IV) complex $[TpOs(OTf)Cl_2]$ with acetonitrile in the presence of water, Table 15 [133a]. Upon substitution of one or both of the chloride ligands on $[TpOs(N)Cl_2]$, a difference in the reactivity of the Os≡N bond is noticed [5,133b,133d,133f]. For example, while $[TpOs(N)Cl_2]$ reacts rapidly with Grignard reagents, such as PhMgBr, the organometallic analogues react quite slowly with PhMgBr. The same difference in the rate of reaction with triphenylphosphane was observed as well. Furthermore, $[TpOs(N)Cl_2]$ was not reactive towards alkylation with methyl triflate, as to be expected from this electrophilic complex. However, the organometallic analogue $[Tp^*Os(N)Ph_2]$, has been reported to react

Table 14
Nitrido complexes of ruthenium(VI)

Synthesis	Complex	Comments	Reference
From diphenyldiazomethane			
$[Ru(ocpg)]^+ + Ph_2CN_2$	$[Ru(N)(ocpg)]^-$ Where ocpg = *meso*-octamethylporphyrinogen	Moderately electrophlic	[122]
Ligand subsitution			
$[Ru(N)Cl_4]^- + {}^aH_2L^1$	$[Ru(N)Cl(L^1)]$	Reacts w/PPh_3	[123]
$[Ru(N)Cl_4]^- + {}^bH_3L^2$	$[Ru(N)Cl(L^2)]$	Reacts w/PPh_3	[123]
$[Ru(N)Cl_4]^- + {}^cH_4L^3$	$[Ru(N)Cl(L^3)]^-$	Reacts w/PPh_3	[123]
$[Ru(N)Cl_4]^- + {}^cH_4L^4$	$[Ru(N)Cl(L^4)]^-$	Reacts w/PPh_3	[123]
$[Ru(N)Cl_4]^- + {}^dH_2L^5$	$Ru(N)Cl_3(H_2L^5)$	Reacts w/PPh_3	[123]
$[Ru(N)Me_3Br]^- + NaSSiMe_3$	$[Ru(N)Me_3(SSiMe_3)]^-$		[124]
$[Ru(N)Me_3(SSiMe_3)]^- + X^-$ or H_2O	$[Ru(N)Me_3(SH)]^-$		[124]

a,b,c,d

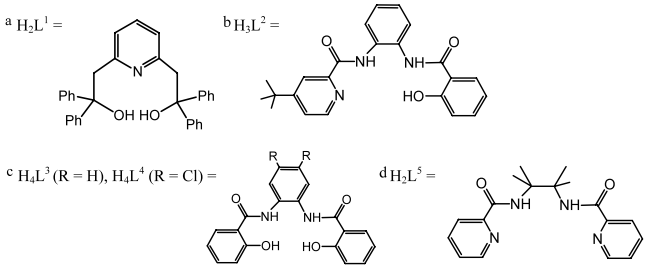


Table 15
Nitrido complexes of osmium(VI)

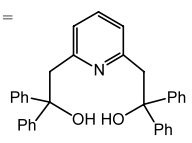
Synthesis	Complex	Comments	Reference
Organometallic compounds			
$[Os(N)Ph_2py_2]^+ + Cp^-$	$[Os(N)CpPh_2]$		[125a]
$[Os(N)Ph_2py_2]^+ + In^-$	$[Os(N)InPh_2]$		[125a]
$[Os(N)Ph_2py_2]^+ + Tp^{*-}$	$[Os(N)Tp^*Ph_2]$	Reacts w/MeOTf	[5,125a]
$[Os(N)Ph_4] + HI + Tp^-$	$[Os(N)TpPh_2]$	Reacts w/MeOTf,	[5,133b]
		$B(C_6F_5)_3$, BPh_3,	[133b]
		PhMgBr,	[133b]
		PPh_3 (very slowly)	[5,133b]
		No reaction w/NO	[133d]
$[Os(N)TpPh_2] + HCl$	[Os(N)TpPhCl]	Reacts w/PhMgBr	[5,133b]
$[Os(N)(CH_2SiMe_3)_2(py)]^+ + bdt^{2-}$	$[Os(N)(CH_2SiMe_3)_2(bdt)]^-$		[125b]
$[Os(N)(CH_2SiMe_3)_2(py)]^+ + [Zn(dmit)_2]^{2+}$	$[Os(N)(CH_2SiMe_3)_2(dmit)]^-$		[125b]
$[Os(N)(CH_2SiMe_3)_4]^- + HBF_4 + PMe_3$	$[Os(N)(CH_2SiMe_3)_3PMe_3]$		[125c]
$[Os(N)(CH_2SiMe_3)_4]^- + HBF_4 + PPh_3$	$[Os(N)(CH_2SiMe_3)_3PPh_3]$		[125c]
$[Os(N)(CH_2SiMe_3)_2Cl_2]^- + PMe_3$	$[Os(N)Cl(CH_2SiMe_3)_2(PMe_3)_2]$	Prone to ligand substitution	[125c]
$[Os(N)Cl(CH_2SiMe_3)_2(PMe_3)_2] + Ag^+$	$[Os(N)(CH_2SiMe_3)_2(PMe_3)_2]^+$		[125c]
$[Os(N)Cl(CH_2SiMe_3)_3(PMe_3)_2] + Ag^+ + MeCN$	$[Os(N)(CH_2SiMe_3)_2(PMe_3)_2(NCMe)]^+$		[125c]
$[Os(N)Cl_2(CH_2SiMe_3)_2]^- + dppe$	$[Os(N)Cl(CH_2SiMe_3)_2(dppe)]$		[125c]
$[Os(N)Cl(CH_2SiMe_3)_2]_2 + dppe$	$[Os(N)Cl(CH_2SiMe_3)_2(dppe)]$		[125c]
$[Os(N)Cl(CH_2SiMe_3)_2(dppe)] + Ag^+$	$[Os(N)(CH_2SiMe_3)_2(dppe)]^+$		[125c]
$[Os(N)Cl(CH_2SiMe_3)_2(dppe)] + Ag^+ + MeCN$	$[Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)]^+$		[125c]
$[Os(N)Cl(CH_2SiMe_3)_2]_2 + PPh_3$	$[Os(N)Cl(CH_2SiMe_3)_2(PPh_3)]$		[125c]
From $[Os(N)Cl_4]^-$ and analogues			
$[Os(N)Cl_4]^-$ (**84**) $+ bdt^{2-}$	$[Os(N)(bdt)_2]^-$	Reacts w/Ph_3C^+ Ligand reacts w/ Et_3O^+, Me_3O^+	[125b,126]
84 $+ [Zn(dmit)_2]^{2+}$	$[Os(N)(dmit)_2]^-$		[125b,126]
84 $+ mnt^{2-}$	$[Os(N)(mnt)_2]^-$		[127a]
84 $+ [N(SP^iPr_2)_2]^-$	$[Os(N)\{[N(SP^iPr_2)_2]^-\}_2]Cl$	Reacts w/$PMePh_2$	[128a]
84 $+ [N(SePPh_2)_2]^-$	$[Os(N)\{[N(SePPh_2)_2]^-\}_2]Cl$	Reacts w/PPh_3	[128a]
84 $+ [N(SPPh_2)_2]^-$	$[Os(N)\{[N(SPPh_2)_2]^-\}_2]Cl$	No reaction w/Ph_3C^+ TFAA, TFA	[128b]
84 $+ Ph_2As(CH_2)_2AsPh_2$	$[Os(N)Cl_3(L)]$ Where $L = Ph_2As(CH_2)_2AsPh_2$		[128c]
84 $+ SCH_2Ph^-$	$[Os(N)(SCH_2Ph)_4]^-$		[129a]
84 $+ OCH_2Ph^-$	$[Os(N)(OCH_2Ph)_4]^-$		[129a]
84 + glycole	$[Os(N)Cl_2(OC_2H_4)]^-$		[129b]
84 + pinacole	$[Os(N)Cl_2(O_2C_2Me_4)]^-$		[129b]
84 $+ H_2N(CMe_2)_2NH_2$	$[Os(N)Cl(L)_2]^{2+}$ Where $L = H_2N(CMe_2)_2NH_2$		[128d]
84 $+ L_{OEt^-}$	$[Os(N)Cl_2(L_{OEt})]$ propylene sulfide, PPh_3, No reaction w/MeOTf, Ph_3C^+, $PhCH_2Br$	Reacts w/N_3^-, Me_3NO	[10a]
84 $+ {}^aH_2L^1$	$[Os^{VI}(N)Cl(L^1)]$	Reacts w/PPh_3	[123]
84 $+ {}^bH_3L^2$	$[Os(N)Cl(L^2)]$	Reacts w/PPh_3	[123]
84 $+ {}^cH_4L^3$	$[Os(N)Cl(L^3)]^-$	Reacts w/PPh_3	[123]
84 $+ {}^cH_4L^4$	$[Os(N)Cl(L^4)]^-$	Reacts w/PPh_3	[123]
84 $+ {}^dH_2L^5$	$[Os(N)Cl_3(H_2L^5)]$		[123]
84 $+ salen^{2-}$	[OsNCl(salen)]		[130]
84 $+ salophen^{2-}$	[Os(N)X(salophen)] Where X = Cl or NCS	Reacts w/PPh_3	[130]
84 $+ 5,5'\text{-}Cl_2salophen^{2-}$	[Os(N)Cl(5,5′-Cl_2salophen)]	Reacts w/PPh_3 Ligand reacts w/H^- CN^-, $CF_3C(O)CH_2^-$	[130]
84 $+ 5,5'\text{-}Me_2salophen^{2-}$	[Os(N)Cl(5,5′-Me_2salophen)]	Reacts w/PPh_3	[130]
84 $+ 5,5'\text{-}(MeO)_2salophen^{2-}$	[Os(N)Cl(5,5′-$(MeO)_2$salophen)]	Reacts w/PPh_3	[130]
84 $+ NaN_3$	$[Os^{VI}(N)(N_3)_5]^{2-}$		[131]
84 + tpm	$[Os(N)(tpm)Cl_2]^+$	Reacts w/	[132a]
		cylcohexadiene,	[135a]
		N_3^-, N_3^-/CS_2,	[134c,134g]
		morpholine,	[134f,134j]
		piperidine,	[134f]

Table 15 (*Continued*)

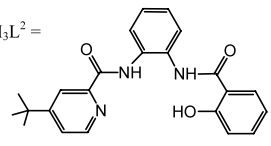
Synthesis	Complex	Comments	Reference
		$HNEt_2$	[134f]
		No reaction w/CS_2 or S_8	[134c,134g]
84 + tpy	*cis* or *trans*-$[Os(N)(tpy)Cl_2]^+$	trans-reacts w/	[132b]
		cyclohexadiene	[135a]
		$SPPh_3$,	[134b]
		N_3^-, N_3^-/CS_2,	[134c,134g]
		Me_3NO	[134i]
		CN^-,	[136b]
		PPh_3, PPh_2Me, PMe_3	[134h]
		PPh_2Me, $PPhMe_2$, PEt_3	[134h]
		cis or trans-stilbene	[135c]
		No reaction w/CS_2 or S_8	[134c,134g]
84 + dmbpy	$[Os(N)(dmbpy)Cl_3]$		[132a]
$[Os(N)Br_4]^-$ + tpy	mer-$[Os(N)(tpy)Br_2]^+$		[132c]
Other ligand subsitutions			
$[Os(N)Cl(L)_2]^{2+}$ + HOTf	$[Os(N)(L)_2]^{3+}$ Where $L = H_2N(CMe_2)_2NH_2$		[128d]
$[Os(N)Cl(5,5'\text{-}Cl_2salophen)]$ + $LiClO_4$	$[Os(N)(5,5'\text{-}Cl_2salophen)(MeOH)]^+$		[130]
$[Os(N)Cl(5,5'\text{-}Me_2salophen)]$ + $LiClO_4$	$[Os(N)(5,5'\text{-}Me_2salophen)(MeOH)]^+$		[130]
$Os(N)Cl(5,5'\text{-}(MeO)_2salophen)]$ + $LiClO_4$	$[Os(N)(5,5'\text{-}(MeO)_2salophen)(MeOH)]^+$		[130]
mer-$[Os^{VI}(N)(tpy)Cl_2]^+$ + HOTf	mer-$[Os^{VI}(N)(tpy)Cl(OTf)]^+$		[132c]
mer-$[Os^{VI}(N)(bpy)Cl_3]$ + HOTf	$[Os^{VI}(N)(bpy)Cl_2(OH_2)]^+$	Reacts w/	[132c]
	N_3^-, CN^-		[136a]
Other reactions			
$[Os^{VIII}(N)(O)_3]^-$ + Tp^- + HCl	$[Os(N)TpCl_2]$	Reacts w/	[5,133b]
		PhMgCl,	[5,133b]
		TolMgBr, PhMgBr,	[5]
		EtMgBr, MeMgBr,	[5]
		PhLi, $PhLi/ZnCl_2$,	[5]
		H_2NTol	[5]
		PPh_3, Me_3NO, S_8,	[133c]
		propylene sulfide,	[133c]
		Se,	[133c]
		NO,	[133d]
		cyclohexadiene	[135a]
		$PtCl_2(SMe_2)_2$,	[133f]
		$CpCo(\eta^4\text{-}C_5H_5\text{–}C_6F_5)$	[133f]
		$Mo(NEt_2NCS_2)_3$	[135b]
		BPh_3, $B(C_6F_5)_3$	[5,133e]
		BEt_3, $PhBCl_2$	[5,133e]
		$BEt_2(OMe)$	[5]
		Ph_2BOBPh_2	[5,133e]
		No reaction	[5,133e]
		w/BF_3, CPh^+,	[5,133e]
		MeOTf	[5,133e]
$[Os^{IV}(OTf)TpCl_2]$ [133a] + 2MeCN + H_2O	$[Os(N)TpCl_2]$		

a,b,c,d

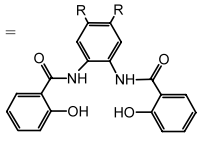
a H_2L^1 =



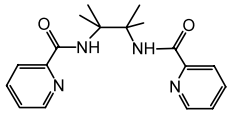
b H_3L^2 =



c H_4L^3 (R = H), H_4L^4 (R = Cl) =



d H_2L^5 =



slowly with methyl triflate [5]. These results demonstrate the importance the ancillary ligands can have on the reactivity of the metal–nitrido bond. Thus, the Os≡N moiety in $[TpOs(N)Cl_2]$ has more electrophilic character than its organometallic counterparts. However, by far the most interesting conclusion from studying the reactivity of $[TpOs(N)Cl_2]$ has been the fact that although this complex readily reacts with a variety of nucleophlies, it also reacted with Lewis acids, such as BPh_3, $B(C_6F_5)_3$, Ph_2BOBPh_2 [5,133e]. Lewis acid adducts were not observed, however. Rather insertion of the nitrogen into the boron–carbon bond occurred. Thus, the authors classify the nitrido ligand as a nucleophile rather than a Lewis base. It should be noted that $[TpOs(N)Ph_2]$ reacts with $B(C_6F_5)_3$ as a Lewis base and irreversible formation of the Lewis acid adduct occurred [5].

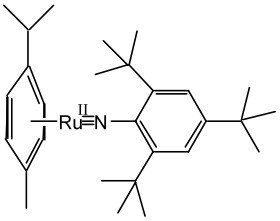
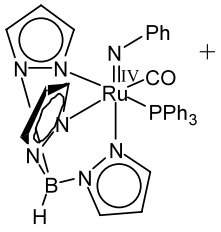
The reactivity of $[TpOs(N)Cl_2]$ is comparable to the cationic complexes, $[(Tpm)Os(N)Cl_2]^+$ and $[(Tpy)Os(N)Cl_2]^+$. All three complexes have an electrophilic Os≡N moiety, Table 15. Furthermore, all three complexes readily undergo a reversible three-electron reduction in the presence of acid to give the $Os^{III}(NH_3)$ motif [132a].

7.3.2. Imido complexes of Group 8

The imido complexes of iron are known only as reaction intermediates and have yet to be isolated and fully characterized [3a].

7.3.2.1. Ruthenium imido complexes. Although terminal imido complexes of ruthenium(V) and (VI) are known [3a], the first example of a ruthenium(II) imido complex was recently synthesized by Burrell and Steedman [137a]. Employing an amine base, LiNHAr, where Ar = 2,4,6-tri-*tert*-butylphenyl, as the source of nitrene, the imido product, $[(\eta^6\text{-}p\text{-cymene})Ru^{II}(NAr)]$ (Ar = 2,4,6-tri-*t*-butylphenyl), was formed from a ruthenium chloride dimer, $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$, Table 16 [137a]. In a similar fashion, the analogous complex, $[(\eta^6\text{-}C_6Me_6)Ru^{II}(NAr)]$, has also been prepared [137b]. The imido ligand in $[(\eta^6\text{-}p\text{-cymene})Ru^{II}(NAr)]$ is linear (Ru=N–C angle of 178°) with a Ru=N bond distance of 1.753 Å [137a]. Interestingly, when using amine bases containing a less sterically demanding substituted aryl rings for the reaction with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ or $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$, dimeric species with bridging imido ligands are formed. These results demonstrate the importance of steric congestion around the metal center

Table 16
Imido complexes of ruthenium(II) and (IV)

Synthesis	Complex	Comments	Reference
$[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ + LiNHAr		Reacts w/ N_3^- and isocyanides	[137a] [138]
$[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ + LiNHAr	$[(\eta^6\text{-}C_6Me_6)Ru^{II}(NAr)]$	Limited stability	[137b]
$[TpRu(CO)(NHPh)]^{2+} + N(SiMe_3)_2^-$	 +	Unstable Indirect Evidence	[139]

Ar = 2,4,6-tri-*tert*-butylphenyl.

and its effect on the formation of multiply bonded terminal ligands on ruthenium(II). In such cases, the use of bulky substituents has aided in the formation of terminal imido groups, but has done so at the price of their reactivity. Both complexes [(η^6-*p*-cymene)Ru^{II}(NAr)] and [(η^6-C_6Me_6)Ru^{II}(NAr)] are reported to have limited reactivity. Complex [(η^6-*p*-cymene)Ru^{II}(NAr)] does, however, produce cycloaddition products with isocyanides and organic azides [138].

Gunnoe, White and coworkers recently provided evidence for an unstable terminal imido complex of ruthenium(IV) [139]. When the ruthenium(VI) amido complex, [TpRu(CO)(NHPh)][OTf]$_2$ was reacted with Na[N(SiMe$_3$)$_2$], the amido complex was deprotonated to form the corresponding ruthenium(IV) imido, [TpRu(CO)(NPh)][OTf], Table 16. This reaction is reversible upon addition of an acid such as HBF_4. However, isolation of this d^4 imido complex was not successful due to its instability. Interestingly, a ^{1}H-NMR spectrum was not obtainable and the authors suggest that the imido complex is paramagnetic. Only terminal imido complexes of ruthenium(II), (V), and (VI) are known, and to date, no ruthenium(IV) complexes have been isolated and fully characterized.

7.3.2.2. Osmium imido complexes. Although a variety of other common synthetic routes have been successfully employed, such as using silylated amine reagents [1,3a], a frequent entry to the terminal imido complexes of osmium has been to utilize the reactivity of the osmium nitrido bond. When osmium(VI) nitrido complexes contain a nucleophilic nitrido ligand, alkylatation or acylation is possible with electrophiles such as carbocations (MeOTf, [Ph$_3$C][BF$_4$] or PhCH$_2$Br), and anhydrides (TFAA or AA). However, electrophilic osmium(VI) nitrido complexes have also been observed and alkylation via carboanions is possible. As mentioned previously, the reactivity of the nitrido ligand depends on the transition metal, the oxidation state of the transition metal and the ancillary ligands. The importance of these factors becomes readily apparent with (nitrido)osmium(VI) and its reactivity and utility as a starting material for osmium(VI) and (V) terminal imido complexes.

Compared to the variety of osmium(VI) terminal imido complexes known [3a], osmium(V) complexes are relatively few in number. Recently, the instability of a (nitrido)osmium(V) complex has been utilized in the synthesis of the corresponding terminal imido derivatives. Employing a one-electron electrochemical reduction of [Os^{VI}(N)(Tp)Cl$_2$] and [Os^{VI}(N)(bpy)Cl$_3$] in the presence of acid, Meyer and coworkers successfully prepared the imido products, Table 17 [140]. The hydrotris(pyrazolyl)borate complex, [Os^{V}(NH)(Tp)Cl$_2$] was structurally characterized. The imido ligand is considered to be long with a bond length of 1.747 Å, but is well within the range of a double bond assignment.

An imido complex of osmium(VI) has been prepared from alkylation of the corresponding nucleophilic nitrido complex, [N^{n}Bu$_4$][Os^{VI}(N)(bdt)$_2$] with [CPh$_3$][PF$_6$], Table 17 [126]. Interestingly, other electrophiles, such as Me_3O^+ and Et_3O^+ did not react with the nitrido ligand and alkylation of the ancillary ligand occurred instead. Similarly, Shapley and coworkers recently utilized the nucleophilic behavior of a (nitrido)osmium(VI) organometallic complex and isolated the corresponding alkylated product, [(η^5-C$_5$H$_5$)Os^{VI}(NCH$_3$)(CH$_2$SiMe$_3$)$_2$][OTf], Table 17 [141]. The methylimido product was thermally unstable, and readily reacted with Lewis bases, such as sodium hydride, and nucleophiles, such as organic phosphanes and alkenes. The imido complex was also susceptible to reductive elimination reactions.

Nucleophilic attack with carbanions on the nitrido ligand of osmium(VI) complexes could give the corresponding imido product. In fact, this type of reaction has been observed with [TpOs^{VI}(N)Cl$_2$] and carbanions (vide supra) [5]. However, the osmium(IV) analido complex, [TpOs^{IV}(NHPh)Cl$_2$], was isolated. Formation of this product was believed to proceed through another analido [TpOs^{IV}(NPhMgCl)Cl$_2$], which could be regarded as a very basic [TpOs^{VI}(=NR)Cl$_2$]$^-$ stabilized by $MgCl^+$ [5].

Table 17
Imido complexes of osmium(IV), (V) and (VI)

Synthesis	Complex	Comments	Reference
From the nitrido			
mer-[Os^{VI}(N)(bpy)Cl$_3$]+H$^+$+1e$^-$	[Os^{V}(NH)(bpy)Cl$_3$]		[140]
[Os^{VI}(N)(Tp)Cl$_2$]+H$^+$+1e$^-$	[Os^{V}(NH)(Tp)Cl$_2$]		[140]
mer-[Os^{VI}(N)(bpy)Cl$_3$]+N_3^-	[Os^{IV}(N-N$_3$)Cl$_3$(bpy)]$^-$		[136a]
mer-[Os^{VI}(N)(bpy)Cl$_3$]+CN$^-$	[Os^{IV}(N-CN)Cl$_3$(bpy)]$^-$	Reacts w/H$^+$ at α-N, and reacts with (MeCO)$_2$O at β-C	[136b]
[Os^{VI}(N)(tpy)Cl$_2$]$^+$+CN$^-$	[Os^{IV}(N-CN)Cl$_2$(tpy)]		[136b]
[Os^{VI}(N)Cp(CH$_2$SiMe$_3$)$_2$]+MeOTf	[(Os^{VI}(NMe)(CH$_2$SiMe$_3$)$_2$Cp]$^+$	Reacts w/Lewis bases, nucleophiles	[141]
[Os^{VI}(N)(bdt)$_2$]$^-$+CPh_3^+	[Os^{VI}(NCPh$_3$)(bdt)$_2$]		[126]

Furthermore, the electrophilic reactivity of certain (nitrido)osmium(VI) complexes can be further exploited with a variety of nucleophiles to make the corresponding imido derivatives Os=NR where R is not an alkyl or aryl substituent. For example, mer-[Os^{VI}(N)(bpy)Cl_3], reacts with CN^- and N_3^- to produce the cyanoimido and azidoimido complexes, respectively, Table 17 [136]. The imido ligand is basic and the α-N is susceptible to attack from either strong or weak acids to give mer-[Os^{IV}(N(H)CN)(bpy)Cl_3] [136b]. Interestingly, reactions with electrophiles occur only at the β-N.

8. Conclusions

In summary, the chemistry of nitrido and imido complexes of Groups 6–8 continues to attract new research activities and discoveries. A reasonably versatile library of synthetic routes is available to the practicing chemist. However, new and innovative synthetic strategies need to be sought in subduing thus far inaccessible nitrido and imido complexes that are of interest. Examples include nitrido and imido complexes of Fe(IV), (V), and (VI), as well as imido complexes of Ru(IV), Mn(IV), (V), and (VI). The reaction chemistry of nitrido and imido ligands is intriguing since these ligands behave as nucleophiles, electrophiles, or both. Harnessing this reactivity for selective functionalization of organic compounds and developing transition metal catalysts that utilize cheap and accessible sources of nitrogen (N or NR moieties) is still a promising area of research with a bright future.

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