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TRANSITION METAL COMPLEXES CONTAINING ORGANOIMIDO (NR) AND RELATED LIGANDS

WILLIAM A. NUGENT

Central Research and Development Department, E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898 (U.S.A.)

and BARRY L. HAYMORE

Corporate Research Department, Monsanto Co., St. Louis, Missouri 63166 (U.S.A.)

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CONTENTS

A. INTRODUCTION

This review is concerned with the chemistry of transition metal complexes containing organoimido ligands (formally RN^{2-}) where R is an aryl or alkyl group. We will cover both mononuclear complexes in which the ligand is multiply bonded to the metal and polynuclear derivatives in which the ligand bridges two or more metals. Also included are the related ligands XN^{2-} where X = $SiMe_3$, H, NR_2 or Cl. However, the literature concerned with transient "coordinated nitrene" intermediates in azide decomposition and related reactions will not be covered. Such reactions are the subject of two recent reviews [1,2]. Several papers dealing with formation of presumably polymeric M(NH) derivatives of Ti, Zr, V and Th in liquid ammonia [3—6] will not be covered. Coverage of the descriptive chemistry of hydrazido complexes will be restricted in detail since this area was recently reviewed [7]. The considerable literature on azoalkane complexes, M(NN=CRR'), will not be covered; a recent review briefly discusses the chemistry of these compounds [179]. We have attempted to make our coverage of the literature complete through the end of 1978.

(i) Arrangement of material

In section B we survey the general chemistry of organoimido compounds, their preparations, the nature of bonding in such species, and summarize the principal physico-chemical measurements which have been made on these compounds. In section C we consider individual complexes in more detail. Throughout the review we have followed the organization employed by Griffith in his reviews on oxo [8] and nitrido [9] complexes. It is hoped this will facilitate comparisons between these three closely related types of ligands.

(ii) Nomenclature

Compounds containing the M(NR) unit have been variously referred to in the literature as "alkylimido", "alkylimino", "alkylnitrido" and "alkylnitrene" complexes. The last name has been employed more frequently, but not exclusively, to species containing an electron deficient (electrophilic) nitrogen. We will use the "alkylimido" terminology throughout this review. The use of this name in no way implies that the nitrogen atom in the NR ligand has a full dinegative charge. The term "organoimido" will also be used when referring to alkylimido and arylimido species collectively.

The reader is however cautioned that Chemical Abstracts Service now employs yet a fifth procedure in naming the subject compounds. Although CA uses the IUPAC [10] approach in naming the parent anionic nitrogen ligands (NH_2^-, NH^{2-} and N^{3-} are amido, imido and nitrido, respectively) [11] the names for M(NR) complexes are derived from the parent amine. Thus $M(NCH_3)$ derivatives are said to contain the [methanaminato (2—)] ligand and arylimido species are named as [benzenaminato (2—)] derivatives.

(iii) Reviews

Recent reviews have covered the role of coordinated nitrene intermediates in the decomposition of metal—azide complexes [1] and in reactions of organic azides and isocyanates with metal complexes [2]. The latter review includes a brief discussion of organoimido complexes. In addition, reviews have appeared covering the related oxo [8], nitrido [9] and dialkylamido [12] ligands and their complexes.

(iv) List of abbreviations

Ar	aryl
^{n}Bu	n-butyl
^{s}Bu	sec-butyl
^{t}Bu	*t*-butyl
Cp	cyclopentadienyl
DEPE	bis(diethylphosphino)ethane
DMSO	dimethyl sulfoxide
DPPE	bis(diphenylphosphino)ethane
dtc	dialkyldithiocarbamate
Et	ethyl
IR	infrared
L	neutral ligand
Me	methyl
NMR	nuclear magnetic resonance
Np	neopentyl
pic	4-picoline
Ph	phenyl
^{i}Pr	iso-propyl
^{n}Pr	n-propyl
py	pyridine
R_f	fluoroalkyl
THF	tetrahydrofuran
X	anionic ligand
Y	anionic ligand

B. GENERAL SURVEY

(i) Occurrence

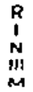
Most of the organoimido complexes prepared to date contain 2nd. and 3rd. row transition metals. Such complexes have now been prepared for all 13 naturally occurring group IVB through VIII metals of the 2nd. and 3rd. row. In contrast, the number of organoimido complexes containing first row transition metals is currently limited, and in fact no manganese derivatives have yet been reported. The rarity of first row organoimido complexes parallels a paucity of first row complexes containing multiply bonded (e.g. oxo and nitrido) ligands in general.

(ii) Stereochemistry

The majority of mononuclear organoimido complexes exhibit pseudotetrahedral or pseudooctahedral coordination geometries. The idealized geometries of the latter complexes are frequently distorted owing to the presence of the short metal—nitrogen bond. Some five-coordinate [e.g. Ir(CO)Cl(PPh$_2$Me)$_2$(NCF$_3$)] [13] and seven-coordinate [e.g. Mo(NMe)(S$_2$CNR$_2$)$_3$$^+BF_4^-$] [14] complexes are also known. Few generalizations can be made concerning the geometry of complexes containing bridging organoimido ligands. The stereochemistry of individual complexes will be discussed in section C.

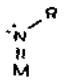
(iii) *Modes of bonding*

The four known modes of bonding are summarized below. The structure of each of the complexes cited as an example has been determined by x-ray crystallography.



1

Terminal linear
Ta(N^{t}Bu)(NMe$_2$)$_3$

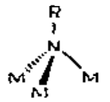


2

Terminal bent
Mo(NPh)$_2$(S$_2$CNEt$_2$)$_2$

3

Doubly bridging
[Zr(N^{t}Bu)(NMe$_2$)$_2$]$_2$



4

Triply bridging
Fe$_3$(NSiMe$_3$)(CO)$_{10}$

The terminal linear arrangement 1 is the bonding mode most commonly observed in crystal structures of organoimido complexes thus far. Linearity is generally thought to reflect triple bond character in the metal—nitrogen linkage. Several examples of non-linear geometries are known, and in the case of Mo(NPh)$_2$(S$_2$CNEt$_2$)$_2$, one M—N—C angle is 139° [15]. Moreover, other known complexes probably possess the terminal bent structure if they are correctly formulated. Compounds where the metal is in a low formal oxidation state such as Ru(NR$_f$)(CO)$_2$(PPh$_3$)$_2$ [13] are likely candidates. In general a bent M—N—R geometry can be expected when a linear, 4-electron donor NR ligand would cause the electron count (EAN rule) of the complex to exceed 18 electrons.

A number of early transition metal organoimido complexes fall in the doubly bridging category. This includes all of the group IVb derivatives; the remaining ligands in these complexes are often monodentate anions. Thus, a hypothetical neutral, monomeric complex, Ti(NMe$_2$)$_2$(NR), containing a terminal imido ligand would be severely coordinatively unsaturated. The triply bridging coordination mode is found in a number of cluster complexes of the iron triad. In such species there is a greatly diminished capacity for metal—nitrogen π-bonding, and the metal usually possesses a lower formal oxidation number than in type 1 complexes.

(iv) *Similarities with other ligands*

Because of the strong π bonding capability of the imido ligand (NH), it is best compared with the isoelectronic nitrido (N) and oxo (O) ligands which share this property. Griffith has stated that the nitrido ligand is by far the strongest π-bonding ligand known [9]. In similar coordination environments, the metal—oxo and metal—nitrido bond lengths are about the same. For example, the Mo—O distance in $MoO(S_2CN^nPr_2)_2$ [16] is 1.664(8) Å and the Re—N distance in $ReN(S_2CNEt_2)_2$ [17] is 1.656(8) Å. The Mo radius is about 0.015 Å larger than that for Re [18]. In contrast, metal—imido bond lengths are about 0.05 Å longer than corresponding metal—oxo and metal—nitrido bond lengths (see section B. (vii)). Knowing that the bonding radius of multiply bonded oxygen is about 0.03 Å smaller than that for multiply bonded nitrogen [19], we estimate the relative bond strengths (based on relative bond distance arguments) to adhere to the following order: $M{\equiv}N > M{\equiv}O > M{\equiv}NR$. This same trend also applies in a predictable manner to the relative magnitudes of the *trans* influence exerted by these three ligands. In 18-electron complexes, the magnitude of the *trans* influence decreases along the above series. For example, the lengthening of the *trans* metal—chlorine bond is 0.24 Å in K_2OsNCl_5 [20]; 0.09 Å in K_2ReOCl_5 [21], $MoOCl_2(S_2CNEt_2)_2$ [22], $MoOCl_2(PMe_2Ph)_3$ (blue isomer) [23]; and 0.00 Å in $ReCl_3(NCH_3)(PPh_2Et)_2$ [24] and $MoCl_2(NPh)(S_2CNEt_2)_2$ [25]. In light of the short metal—nitrogen distances, the total absence of a *trans* influence exerted by the organoimido ligands is quite remarkable.

The similarity of oxo and imido ligands is supported by the fact that many of the organoimido complexes and their oxo analogues are isostructural. Four such pairs are listed below.

OsO_4	$VO(OSiMe_3)_3$	$ReOCl_3(PPh_3)_2$	$[W_2F_9O_2]^-$
$Os(NR)O_3$	$V(NR)(OSiMe_3)_3$	$Re(NR)Cl_3(PPh_3)_2$	$[W_2F_9(NR)_2]^-$

Moreover, it seems that parallels can be expected in the *reaction chemistry* of oxo and organoimido compounds. The demonstration that the alkylimido compounds of Os, such as $OsO_3(N^tBu)$, will add to olefins in a manner similar to OsO_4 is a good example [26]. However, studies to date also indicate some possible differences between oxo and organoimido ligands. The latter form fewer bridging complexes, fewer anionic complexes, and fewer first row derivatives than the former.

Certain similarities between alkylimido and alkylidene ligands have been pointed out [12]. From a structural point of view, both alkylimido and *alkylidyne* ligands usually adopt linear geometries. The structural study on $CpTa(CPh)(PMe_3)_2Cl$ shows the complex to have an approximately linear [171.6(8)°] Ta—C—R angle which implies *sp* hybridization at carbon [27]. A monotonic increase in Ta—X bond length along the series $O < N < C$ is seen in comparing this complex with $TaO(N^iPr_2)_3$ [28] and $Ta(N^tBu)(NMe_2)_3$ [29]. The bond lengths are 1.725(7) Å ($X = O$), 1.77(2) Å ($X = N$) and 1.849(8) Å ($X = C$).

(v) Preparation of organoimido complexes

A number of synthetic routes to organoimido complexes have been used, and several seem to have some degree of generality.

(a) Deprotonation of primary amines.

$MCl_2 + RNH_2 \rightarrow M(NR) + 2\ HCl$

$M{-}O + RNH_2 \rightarrow M(NR) + H_2O$

$M(NR'_2)_2 + RNH_2 \rightarrow M(NR) + 2\ R'_2NH$

This is the most frequently utilized route. Sometimes these reactions are carried out with a non-coordinating base present to consume any liberated acid or with a lithium amide salt, LiNHR. The reported metallation reactions of low valent metal complexes of titanium [30] and osmium [31] with primary amines are variants on this route. In these case the metal becomes the proton acceptor.

(b) Use of silylamines.

$M{-}O + RN(SiMe_3)_2 \rightarrow M(NR) + (Me_3Si)_2O$

$Cl{-}M{-}O + 2\ RNH(SiMe_3) \rightarrow Me_3SiO{-}M(NR) + Me_3SiNH_2R^+Cl^-$

Silylated derivatives of primary amines have been used to react with metal—oxo complexes. The great strength of Si—O and Si—F bonds makes silylamines especially effective for replacing oxo or fluoro ligands. The siloxy group thus formed can either leave the coordination sphere or remain as an auxiliary ligand.

(c) Alkylation (or arylation) of nitrido complexes.

$M{\equiv}N + R{-}X \rightarrow M(NR)^+ + X^-$

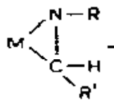
This pathway is somewhat restricted by the fact that many nitrido ligands are not sufficiently nucleophilic to promote this reaction. Consequently, electrophilic attack will often occur at other ligands or on the metal.

(d) Disproportionation of 1,2-disubstituted hydrazines.

$M{-}O + RNHNHR + PPh_3 \rightarrow M(NR) + RNH_2 + Ph_3PO$

Use of this procedure has thus far been restricted to Re complexes [32].

(e) Thermolysis of alkyliminoalkyl (C, N) metal complexes.



$\longrightarrow$ M(NR) + hydrocarbon products

Alkyliminoalkyl (C, N) complexes have thus far been reported only for tantalum [33]. However, it appears that such complexes may also form for a number of other group IV—VI metals [34,35].

(f) Oxo/imido exchange reactions using phosphinimines, isocyanates and sulfinylamines.

$$M{-}O + R'_3PNR \rightarrow M(NR) + R'_3PO$$

$$M{-}O + RNCO \rightarrow M(NR) + CO_2$$

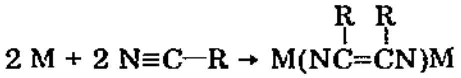
$$M{-}O + RNSO \rightarrow M(NR) + SO_2$$

The use of phosphinimines is a powerful technique owing to the high affinity of phosphorus for oxygen. Of the three reagents, R'_3PNR seems to be the most useful. Recently this procedure has allowed preparation of a tris(alkylimido) complex, $(^tBuN)_3OsO$ [36]. The use of isocyanates and sulfinylamines has been applied with varying degrees of success to the preparations of tungsten, molybdenum, rhenium and vanadium phenylimido complexes.

(g) Reaction of sulfurdiimines with metal carbonyls. Reaction of alkylsulfurdiimines, RNSNR, with metal carbonyls has afforded cluster compounds containing NR ligands. Iron, nickel and molybdenum derivatives have been prepared in this way. [37—39].

(h) Addition to nitriles.

$$MCl_2 + N{\equiv}C{-}R \rightarrow M(NCCl_2R)$$



$$2\,M + 2\,N{\equiv}C{-}R \rightarrow M(N\overset{R}{\overset{|}{C}}{=}\overset{R}{\overset{|}{C}}N)M$$

Complexes to which nitriles have been added include chloride [40], hydride [41] and alkylidene [42] derivatives. Coupling of coordinated nitriles to afford binuclear imido complexes is also known [43].

(i) Addition of chloramines.

$$M + RNHCl \xrightarrow{base} M(NR) + HCl$$

This potentially useful method has been used in only one case, namely, the preparation of a tetrakis-organoimido complex, $Os(NR)_4$, using Chloramine-T $p\text{-}CH_3C_6H_4SO_2NCl^-Na^+$ [44]. The one limitation of this method is the reduced availability of chloramines. Alkylamine dichlorides, $RNCl_2$, are also potentially useful reagents which have been used for the preparation of main group element alkylimido compounds. These reagents have not been successfully used in the synthesis of transition metal—imido complexes, but they may well afford imido complexes with low valent metals.

(j) Addition of organic azides.

$$M + RN_3 \rightarrow M(NR) + N_2$$

This is a reaction of considerable generality and the formation of the stable dinitrogen molecule supplies a large driving force. The only known alkylimido derivatives of Pd, Pt and Rh are prepared in this way utilizing the fluorinated azide $CF_3CFHCF_2N_3$ [45].

(k) Oxidation of metal carbonyls with organic nitro compounds.

$M(CO)_2 + RNO_2 \rightarrow M(NR) + 2\ CO_2$

This procedure has been used to prepare bridging iron and ruthenium alkylimido cluster compounds.

(l) Homolytic cleavage and addition of azoalkanes.

$2\ M + RN{=}NR \rightarrow 2\ M(NR)$

This type of reaction has been reported twice. In the first case $R = CF_3$ and $M = Ir$ [13] and in the other $R = SiMe_3$ and $M = Cr$ [128]. In neither instance is the mechanism of imide formation known.

(vi) Properties of organoimido complexes

The properties of organoimido complexes are dominated by the effects of strong nitrogen—metal π-bonding. Chatt et al. [46] underscored the magnitude of this donation using a series of arylimido rhenium complexes, *trans*-$ReCl_3L_2(NC_6H_4X)$, $L = PEt_2Ph$. Thus these compounds exhibit large dipole moments in the range 4.5—7.2 D. The dipole moments decrease with increasing moment of the C—X bond (X = Br, Cl, F) suggesting that the arylimido ligand lies at the positive end of the dipole with a positive charge on the nitrogen atom.

One of the consequences of the triple bond character in $M{\equiv}NR$ is the stability of the metal—nitrogen bond. The Re and Os complexes, in which especially effective π-overlap appears to occur, show a remarkable inertness to N-protonation by mineral acids [32,47]. In fact in $ReCl_3(NR)L_2$, the alkyl hydrogen α to nitrogen is sufficiently acidic to be deprotonated by amines [48]. The apparent instability of $O_3Os(NR)$ derivatives when they contain hydrogen α to nitrogen [49] may reflect a similar effect. A further consequence of π-bonding is the ability of organoimido ligands to sustain unusually high formal oxidation numbers for the metal, e.g. V^V and Cr^{VI}.

$O_3Os(NR)$ represents an interesting case where the imido nitrogen seems to exhibit electrophilic reactivity as evidenced by its ready addition to olefins. [26] (See section C(V) and especially eqn. 39). Exact mechanistic details of this reaction are not known.

Such behavior contrasts that of main group alkylimido compounds in which low-lying d-orbitals seem to be less available for π-bond formation. The phosphinimines ($R'_3P{=}NR$), for example, are potent nucleophiles [50] like the related Wittig reagents. In contrast to the Re and Os derivatives, the organoimido complexes of Ta and W exhibit somewhat greater nucleophilic reactivity. However, the alcoholysis of both W and Ta alkylimido compounds requires fairly vigorous conditions [51,52]. Thus the rate of protonolysis appears to decrease on proceeding from left to right in the periodic table along the series Ta > W > Re > Os.

In general, known organoimido complexes do not exhibit reactions attributable to free nitrene intermediates. The use of the nomenclature "alkylnitrene complex" is understandable because the notion of stabilizing reactive intermediates and using them subsequently in chemical reactions is conceptually attractive; however, there is no evidence of an NR ligand being released from a transition metal as either free NR molecules or NR^{2-} ions. This situation is not unusual though; coordinated nitric oxide (NO) and carbene (CH_2) behave much differently than the free molecules. Arguments for the existence of nitrene complexes as unstable intermediates in chemical processes have been summarized elsewhere [1,2].

(vii) Structure and bonding

A number of compounds containing imido and hydrazido ligands have been examined using x-ray diffraction techniques. Both terminal and bridging modes of ligation have been observed. In almost all cases, relatively short metal—nitrogen bond lengths are found indicating the presence of multiple bonding, and nearly linear M—N—R and M—N—N geometries are usually observed for terminal ligands.

Terminal imido ligands

Selected structural data for terminal imido ligands are summarized in Table 1. Of the 23 examples cited, 18 NR ligands possess nearly linear (>165°) M—N—R geometries. Of special note are the four Re complexes which have nearly constant Re—N distances at 1.69 Å and linear (172°—180°) Re—N—C angles.

Simple electron counting using the Effective Atomic Number Rule (EAN rule, 18-electron rule) provides a useful method of classification of organoimido complexes. If we define the maximum electron count (MEC) as the electron count which is calculated if all amphoteric ligands donate the maximum possible number of electrons to the metal, then the structures in Table 1 can be conveniently classified according to the MEC. We assume for these purposes that terminal alkoxy and siloxy ligands are 3-electron donor ligands. On this basis, the majority of the complexes in Table 1 possess the desired electron count of 18-electrons. Five complexes of the types $MX_4(NR)L$ (M = W) or $M'X_3(NR)L_2$ (M' = V, Nb, Ta) have MEC's of 16 electrons where X is a one electron donor ligand and L is a two electron donor ligand. The remaining five complexes have MEC's greater than 18 electrons.

It is not possible to have electron counts greater than 18 electrons if the EAN rule is obeyed. Indeed, symmetry restrictions alone reduce the number of π-bonds which can be formed between a metal and a group of π-bonding

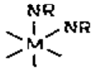
TABLE 1

Selected structural data for terminal imido ligands

Complex [f]	R	M—N(Å)	M—N—C (deg)	Maximum [a] electron count	Ref.
$[VCl_3(NR)]_n$ [e]	Cl	1.642(9)	175.2(3)	16	89
$V(NR)(OSiMe_3)_3$ [c]	1-adamantyl	1.614(2)	175.8(2)	18	126
$[LCl_4NbN\overset{Me}{\overset{\vert}{C}}=\overset{Me}{\overset{\vert}{C}}NNbCl_4L]^{2-}[(Ph_3P)_2N]_2^+$	L = CH_3CN	1.752(6)	178.1(6)	16	20
$Nb(NR)(S_2CNEt_2)_3$	p-$C_6H_4CH_3$	1.783(3)	167.4(3)	18	25
$L_2Cl_3TaN\overset{Me}{\overset{\vert}{C}}=\overset{Me}{\overset{\vert}{C}}NTaCl_3L_2$	L = C_4H_8O	1.747(7)	178.7(9)	16	99
$Ta(NR)(NMe_2)_3$ [c]	^tBu	1.77(2)	180 [b]	18	29
$Cp_2Cr_2(NR)_4$	Me_3Si	1.65(1)	161(2)	20	128
See above	Me_3Si	1.64(1)	160(2)	—	—
$Mo_2(NR)_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}S)_2$	^tBu	1.733(4)	176.3(3)	18	37
$MoCl_2(NR)(PhCONNC_6H_4CH_3)(PMe_2Ph)$	p-C_6H_4Me	1.726(9)	177(1)	18	101
$Mo(NR)_2(S_2CNEt_2)_2$	C_6H_5	1.789(4)	139.4(3)	20	15
See above	C_6H_5	1.754(4)	169.4(4)	—	—
$MoCl_2(NR)(S_2CNEt_2)_2$	C_6H_5	1.734(4)	166.8(3)	18	25
$MoCl_2O(NR)(OPPh_2Et)_2$	H	1.70(1)	157(10)	20	53
$WCl_4(NR)(NCCl_3)$ [c]	CCl_2CCl_3	1.70(3)	— [d]	16	58
$W_2Cl_6(NR)_2(\mu\text{-}Cl)_2$	CCl_2CCl_3	1.71(2)	177(2)	16	136
$ReCl_3(NR)(PEt_2Ph)_2$	CH_3	1.685(11)	173(1)	18	24
$ReCl_3(NR)(PEt_2Ph)_2$	p-C_6H_4COMe	1.690(5)	171.8(4)	18	148
$[Re(NR)(MeNH_2)_4Cl]^{2+}[ClO_4]_2^-$	CH_3	1.694(11)	180(2)	18	151
$ReCl_3(NR)(PEt_2Ph)_2$ [c]	p-C_6H_4OMe	1.709(4)	175.8(1)	18	148
$OsO_2(NR)_2$ [c]	^tBu	1.710(8)	178.9(9)	24	187
See above	^tBu	1.719(8)	155.1(8)	—	—
$OsO_3(NR)$	1-adamantyl	1.697(4)	171.4(4)	24	187

[a] Electron count if all ligands donate the maximum number to the metal. Alkoxy and siloxy ligands are assumed to be 3-electron donor ligands. [b] Required by symmetry. [c] Partially disordered. [d] angle not reported; however, authors comment that the W—N—C angle is approximately linear. [e] Monomer units are held together by chloride bridges; V atom is six-coordinate.

ligands, thus reducing the number of electrons which can be donated from the ligands to the metal. Several cases are considered below.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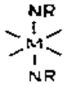
3 π-bonds
cis-octahedral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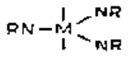
2 π-bonds
trans-octahedral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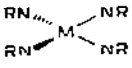
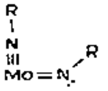
4 π-bonds
trigonal bipyramidal


8
5 π-bonds
tetrahedral

The complex Mo(NR)$_2$(dtc)$_2$ will have an MEC of 20 electrons. Because only three π-bonds are allowed between the two imido ligands (the extreme cases being **9** or **11**) a maximum of 6 electrons can be donated by both ligands and the actual electron count for the complex becomes 18 electrons with an average Mo—N bond order of 2.5 as in **10**. Similar arguments pertain to MoOCl$_2$(NR)L$_2$.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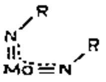
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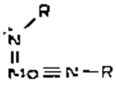
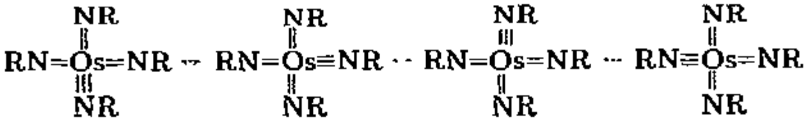

11

OsO$_3$(NR) and OsO$_2$(NR)$_2$ have MEC's of 24 electrons. However, only 5 π-bonds can be formed, and the actual electron count is again 18 electrons. Thus, one would expect an average Os—N bond order of 2.25 in Os(NR)$_4$ (resonance structures **13**—**16**).



$$\mathrm{RN{=}}\underset{\underset{\mathrm{NR}}{|||}}{\overset{\overset{\mathrm{NR}}{\|}}{\mathrm{Os}}}\mathrm{{=}NR} \leftrightarrow \mathrm{RN{=}}\underset{\underset{\mathrm{NR}}{\|}}{\overset{\overset{\mathrm{NR}}{\|}}{\mathrm{Os}}}\mathrm{{\equiv}NR} \leftrightarrow \mathrm{RN{=}}\underset{\underset{\mathrm{NR}}{\|}}{\overset{\overset{\mathrm{NR}}{|||}}{\mathrm{Os}}}\mathrm{{=}NR} \leftrightarrow \mathrm{RN{\equiv}}\underset{\underset{\mathrm{NR}}{\|}}{\overset{\overset{\mathrm{NR}}{\|}}{\mathrm{Os}}}\mathrm{{=}NR}$$

13 **14** **15** **16**

MoOCl$_2$(NH)(OPPh$_2$Et)$_2$ [53] and OsO$_2$(N^{t}Bu)$_2$ [54] allow one to study the competition between oxo and imido ligands. In the Mo complex, the equal *trans*-influence (vide infra) of the O and NH ligands suggests that the two ligands π-bond equally well with the metal. Consistent with this picture is the observation that Mo—N is 0.04 Å longer than Mo—O. In the Os complex, the distinctly shorter Os—N distances (Os—N = 1.71 Å, Os—O = 1.74 Å) indicate that the *t*-butylimido ligands form stronger π-bonds to the metal than do the oxo ligands.

There is no structurally characterized example of a 20-electron mono-imido complex with a fully bent imido ligand, although there is reason to believe that such complexes exist. A survey of Table 1 shows that only four complexes have NR ligands with appreciably bent M—N—R angles. The smallest M—N—R angle and longest M—N distance occur in Mo(NPh)$_2$(S$_2$CNEt$_2$)$_2$ [15] in which one of the imido ligands has Mo—N = 1.789(4) Å and Mo—N—C = 139.4(4)°. Even in this complex however, the expected fully bent geometry (Mo—N = 1.86 Å, Mo—N—C = 120°) is not found.

The short metal—nitrogen distances in organoimido complexes seem to vary over a large range from 1.61 Å to 1.79 Å. Despite some mediocre structural results, this variation seems to be real, and it can be conveniently rationalized on the basis of (1) the size of the metal, (2) the coordination number and (3) the MEC. All complexes with MEC's of 18 or less should have metal—nitrogen triple bonds. Using Pauling's estimates [18] of relative metallic sizes and the well established Re≡NR distance of 1.69 Å, we can estimate corresponding distances for the other six-coordinate transition metal complexes. A

Ti	V	Cr	Mn	Fe	Co	Ni
1.73	1.63	1.59	1.58	1.58	1.57	1.56
Zr	Nb	Mo	Tc	Ru	Rh	Pd
1.86	1.75	1.71	1.68	1.66	1.66	1.69
Hf	Ta	W	Re	Os	Ir	Pt
1.85	1.75	1.71	1.69	1.67	1.68	1.71

small correction for coordination number can be made by adding 0.01 Å for seven-coordinate complexes or by subtracting 0.01 Å for five- and four-coordinate complexes. These calculations give the correct M≡NR distances to within 0.02 Å. The largest discrepancy is that for Ta(N^{t}Bu)(NME$_2$)$_3$ [29] which has Ta—N = 1.77(2) Å but is expected to have Ta—N = 1.74 Å. Using the above values of metal—nitrogen triple bond lengths in imido complexes, estimates of metal—imido bond lengths for bond orders less than three can be made [25]. A Mo—N bond order of 2.5 would be near 1.78 Å, and an Os—N bond order of 2.25 would be near 1.77 Å in six-coordinate complexes.

A comparison (Table 2) of the isoelectronic oxo and organoimido ligands in similar coordination environments shows that the M—O distances are about 0.05 Å shorter than corresponding M—NR distances. Although some of the structures are of mediocre precision and some of the differences are small there is a consistent trend with M≡NR > M≡O. Indeed, the radius of multiply bonded oxygen is 0.03 Å smaller than that of nitrogen [19]. Metal—oxo distances may be shortened by an additional 0.02 Å beyond the shortening expected for the smaller oxygen, but the paucity of data and degree of structural precision disallows any firm conclusion. However, there is no doubt that metal—nitrido distances are consistently shorter (by about 0.05 Å) than corresponding metal—imido distances in isoelectronic (EAN rule) complexes [9]. This trend in the metal—oxygen and metal—nitrogen distances of oxo, nitrido and imido complexes seems to be partially obscured by the structures

TABLE 2

Structural comparison of oxo and imido complexes

Complexes	M—N (Å)	M—O (Å)	Difference (Å)	Ref.
$Nb(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$ $NbO(S_2CNEt_2)_3$,	1.783(3)	1.74(1)	0.04	25 168
$Ta(N^tBu)(NMe_3)_3$ $TaO(N^iPr_2)_3$	1.77(2)	1.725(7)	0.04	29 28
$Mo_2(N^tBu)_2Cp_2S_2$ $Mo_2O_2Cp_2S_2$	1.733(4)	1.679(4)	0.05	37 169
$Mo(NPh)_2(S_2CNEt_2)_2$ $MoO_2(S_2CN^nPr_2)_2$	1.772(avg)	1.696(avg)	0.08	15 16
$MoCl_2(NPh)(S_2CNEt_2)_2$ $MoOCl_2(S_2CNEt_2)_2$	1.734(4)	1.701(4)	0.03	25 22
$ReCl_3(p\text{-}NC_6H_4\overset{\overset{O}{\|}}{C}CH_3)(PEt_2Ph)_2$ $ReOCl_3(PEt_2Ph)_2$	1.690(5)	1.60(2)	0.09	148 170

of two complexes, $MoOCl_2(PPhEt_2)_3$ (green isomer) [55] and $ReNCl_2(PPhEt_2)_3$ [56], in which the Mo—O and Re—N distances are 1.801(9) Å and 1.788(10) Å, respectively. However, we regard these two complexes as unusual exceptions in which the Mo—O and Re—N distances are approaching double bond values.

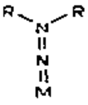
One might assume that the *trans* influence of organoimido ligands should be appreciable owing to the short metal—nitrogen distances. In fact, the situation is more complicated. If the imido complexes in Table 1 are grouped based on the MEC, obvious trends become apparent. (Throughout the discussion that follows the term "lengthening" refers to the difference between the observed bond length and the bond length for the same ligand in complexes where the *trans* influence is presumed to be unimportant.) (1) Pseudooctahedral and pentagonal bipyramidal complexes with MEC's of 18 electrons show absolutely no *trans* influence. All seven structurally characterized complexes obey this rule. (2) Pseudooctahedral complexes with MEC's of 16 electrons show a lengthening of the bond *trans* to the imido ligand by 0.20—0.25 Å. All five structurally characterized complexes obey this rule. In these complexes, nitriles, ethers (THF) and bridging chloride atoms are *trans* to the imido ligands. It is difficult to say if the nature of the *trans* ligand greatly affects the magnitude of the *trans* influence. (3) Organoimido ligands in pseudooctahedral complexes with MEC's of 20 electrons exhibit a noticeable *trans* influence. In $MoOCl_2(NH)(OPPh_2Et)_2$ [53] the two Mo—$OPPh_2Et$ distances at 2.21(1) Å and 2.22(1) Å are both lengthened by about 0.15 Å suggesting that the oxo and imido ligands π-bond equally well to the Mo. In $Mo(NPh)_2(S_2CNEt_2)_2$ [15] the two *trans* Mo—S bonds are unequally lengthened by

0.15 Å and 0.30 Å. As expected, the longer Mo—NPh bond is *trans* to the longer Mo—S bond.

In 20-electron complexes such as $Mo(NPh)_2(S_2CNEt_2)_2$, it has been suggested that the two extra electrons occupy a molecular orbital which is non-bonding with regard to the metal—nitrogen π-interactions and antibonding with regard to the metal—ligand σ-interactions where these ligands are those *trans* to the organoimido groups [15]. A similar situation exists in nitrosyl complexes with MEC's of 20 electrons [57]. The total absence of a *trans* influence in 18-electron organoimido complexes is surprising, especially in light of a noticeable *trans* influence in 16-electron complexes. Although they have the same formal oxidation number, $MoCl_2(NR)(S_2CNEt_2)_2$ [25] exhibits no *trans* influence, but $WCl_4(NR)(NCCCl_3)$ [58] shows an obvious *trans* influence. Whatever the cause, the same situation seems to be present in analogous oxo complexes. The 16-electron oxo complexes, $NbO(NCS)_5^{2-}$ [59] and $NbOF_5^{2-}$ [60], show a large *trans* influence (~0.20 Å), but the 18-electron oxo complexes (vide supra) show a noticeably reduced *trans* influence (~0.09 Å). In light of the above trends regarding the *trans* influence in organoimido complexes and the quality of available structural data, additional studies in this area would be useful.

Terminal hydrazido ligands

Table 3 contains a summary of structural data on terminal hydrazido ligands. In every case, linear ligands are found. Two extreme valence bond forms (**17**, **18**) of the linear hydrazido ligand can be imagined. The values of the nitrogen—nitrogen distances in Table 3 range from 1.26 Å to 1.37 Å suggesting N—N bond orders of 1.9 to 1.3. A N—N double bond is 1.24 Å and a N—N single bond is 1.46 Å. Similarly, the metal—nitrogen distances suggest bond orders between two and three. The N_2R_2 group is nearly planar in every case. Although some N_2R_2 ligands can be better described by formalism **17** and others by formalism **18**, the best general description is in terms of forms intermediate between **17** and **18**.



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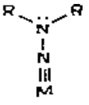

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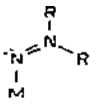

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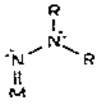


20

No bent, terminal hydrazido ligands (formalism **19**, **20**) are known. Most remarkable in this regard are the structures of $VCp_2(N_2R_2)$ [61] and $Mo(N_2R_2)_2(S_2CNMe_2)_2$ [62] which are 19- and 20-electron complexes, respectively, yet all three hydrazido ligands are essentially linear. The factors causing these ligands to remain linear must await further study.

Bridging imido and hydrazido ligands

In Table 4 are found structural data for complexes which contain bridging

TABLE 3

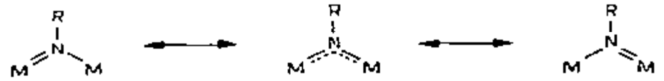
Selected structural data for mononuclear hydrazido complexes

Complex	M—N (Å)	N—N (Å)	M—N—N (deg)	Maximum [a] electron count	Ref.
$[WBr(PPhMe_2)_3(pic)(N_2H_2)]^+[Br]^-$	1.75(1)	1.34(1)	175(1)	18	171
$[WCl(dppe)_2(N_2H_2)]^+[BPh_4]^-$	1.73(1)	1.37(2)	171(1)	18	141
$[WBr(dppe)_2(N_2HMe)]^+[Br]^-$	1.77(1)	1.32(2)	174(1)	18	129
$[MoF(dppe)_2(N_2H_2)]^+[BF_4]^-$	1.76(1)	1.33(2)	176(1)	18	112
$[MoI(dppe)_2(N_2H(C_8H_{17}))]^+[I]^-$	1.801(5)	1.259(8)	174(1)	18	120
$[Mo(S_2CN(CH_2)_5)_3(N_2EtPh)]^+$-$[BPh_4]^-$	1.72(2)	1.37(2)	170(2)	18	129
$[ReCl_2(NH_3)(PMe_2Ph)_2$-$(N_2HPh)]^+[Br]^-$	1.75(1)	1.28(2)	172(1)	18	154
$VCp_2(N_2(SiMe_3)_2)$	1.666(6)	1.369(9)	180 [b]	19	61
$MoO(N_2Me_2)(S_2CNMe_2)_2$	1.80(1)	1.29(1)	168.0(7)	20	14
$Mo(N_2MePh)_2(S_2CNMe_2)_2$	1.790(9)	1.30(1)	172.6(8)	20	62

[a] Electron count if all ligands donate the maximum number of electrons to the metal. [b] Required by symmetry.

imido and hydrazido ligands. The complexes, $Fe_3(CO)_{10}(NR)$ [63] and $Fe_3(CO)_9(NR)_2$ [64], are electron precise (EAN rule) and contain triply bridging NR ligands which are more or less symmetrically bonded to the three metals. Both complexes are structurally related to $Fe_3(CO)_{12}$. $Fe_3(CO)_{10}(NR)$ has one imido ligand replacing two carbonyl ligands and in $Fe_3(CO)_9(NR)_2$ [Fig. 1] a second imido ligand replaces an additional carbonyl ligand and one of the three metal—metal bonds. $Cp_3Ni_3(NR)$ [39] is paramagnetic and contains one electron too many to obey the EAN rule.

The doubly bridging imido and hydrazido ligands are generally symmetric with metal—nitrogen distances indicating some π-bonding to metal as in **21**.



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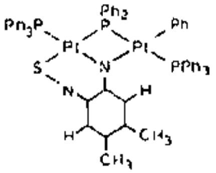
$Mo_2Cp_2(NO)_2I_2(N_2Me_2)$ [65] has an unsymmetrically bridged hydrazido ligand and no metal—metal bond. $Ti_2Cp_4(NH)_2H$ [30] has unusually long Ti—N distances (2.23 Å average); this may be the result of the bridging hydrido ligand or possibly an incorrect characterization. When metal—metal bonds are present, the M—N—M angles fall in the range 78°—84°, but with no metal—metal bonding these angles are greater than 94°. $Mn_2Cp_2(N_2R_2)_2$ [66] contains a metal—metal double bond and bridging hydrazido ligands with N—N distances (1.44 Å) close to those for N—N single bonds.

TABLE 4

Selected structural data for complexes containing bridging imido and hydrazido ligands

Complex	M—N (Å)	M—N—M (deg)	M—N—Y [a] (deg)	Ref.
$Ti_2Cp_4(NH)_2H$	2.22(2), 2.24(2), 2.26(2) 2.20(2); 2.23(avg)	98.3(7), 99.6(6) 99.0(avg)	— [b]	30
$Zr_2(NMe_2)_4(N^tBu)_2$	2.071(1), 2.060(1) 2.066(avg)	96.90(5)	126.8(1), 131.3(1) 129.1(avg)	176
$[Ti(NSiMe_3)Cl_2]_n$ [e]	1.94(3), 1.83(3) 1.99(4), 1.79(3); 1.89(avg)	93(2), 95(2); 94(avg)	127(2), 122(9), 141(2) 139(2) 132(avg)	78
$Mo_2O_3(NH)[S_2P(OEt)_2]_2$	1.936(4), 1.944(3) 1.940(avg)	83.7(1) [c]	139(4), 135(4) 137(avg)	105
$Fe_3(NSiMe_3)(CO)_{10}$	1.87(1), 1.91(1), 1.92(1) 1.90(avg)	84(1) [c], 84(1) [c], 83(1) [c] 84(avg) [c]	129(1), 129(1), 131(1) 130(avg)	63
$Fe_3(NMe)_2(CO)_9$	1.94(2), 1.92(2), 1.90(2) 1.89(2), 1.96(2), 1.95(2) 1.93(avg)	78.6(7) [c], 79.1(7) [c], 78.0(7) [c] 81.2(7) [c]; 104.7(8), 104.7(8) 79.2(avg) [c]; 104.7(avg)	126(1), 128(1), 124(1) 128(1), 128(1), 122(1) 126(avg)	64
$Mn_2Cp_2(N_2(SiMe_3)_2)_2$	1.788(7), 1.782(7) 1.785(avg) (N—N = 1.44(1) Å)	84.2(3) [c]	139(avg)	66
$Mo_2Cp_2(NO)_2I_2(N_2Me_2)$ [d]	1.92(1), 2.05(1) (N—N = 1.40(2) Å)	151(1)	135(1), 74(1)	65
$Ni_3Cp_3(N^tBu)$	1.71(avg)	— [b]	— [b]	39
$Cp_2Cr_2(NSiMe_3)_4$	1.81(2), 1.82(2), 1.92(2) 1.99(3); 1.88(avg)	85(1) [c], 87(1) [c] 86(avg) [c]	123(1), 125(2), 132(1) 140(2); 130(avg)	128
$Fe_3S(NC_6H_4CH_3)(CO)_9$ [f]	1.92(2), 1.94(2), 1.91(2) 1.95(2), 1.94(2), 1.94(2) 1.93(avg)	80.6(7) [c], 81.7(7) [c], 80.3(7) [c] 81.1(6) [c]; 112.5(9), 109.5(8) 80.9(avg) [c]; 111.0(avg)	123(2), 128(1), 119(2) 122(1), 132(2), 121(1) 124(avg)	189
$Fe_4S_2(NO)_4(N^tBu)_2$	1.912(3), 1.905(3), 1.914(3) 1.910(avg)	— [b]	— [b]	173
$Co_4(NO)_4(N^tBu)_4$	1.91(avg)	80.2(3) [c], 81.3(3) [c], 83.9(3) [c] 84.1(3) [c], 89.5(3) [c], 89.6(3) [c] 84.8(avg) [c]	— [b]	165
	2.01(3), 2.21(2)	99.1(9)	129.2(7), 130.1(7)	167

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[a] Y is the atom bonded to the imido nitrogen atom. [b] These data are not reported. [c] There is a metal—metal bond between the metal atoms. [d] The N_2Me_2 ligand is three-coordinate. [e] Ordered chain. [f] Two independent molecules.

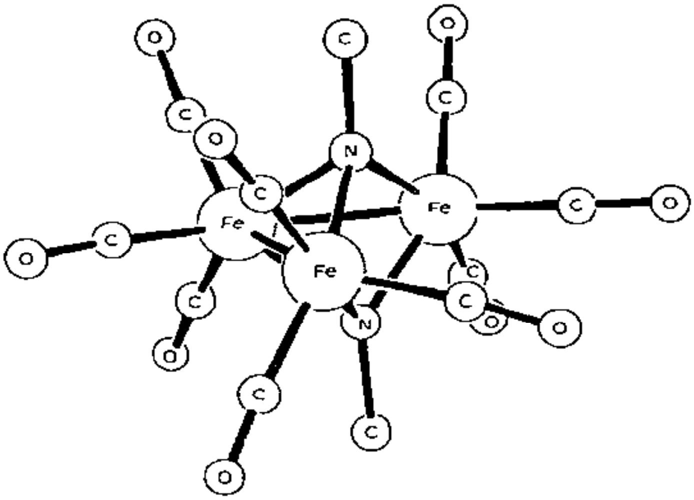
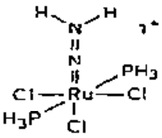


Fig. 1. The structure of $Fe_3(NMe)_2(CO)_9$ from ref. 64.

Theoretical calculations

Published calculations concerning bonding in organoimido and related complexes have been rare. Fortunately, many of the bonding models which have been developed for oxo and nitrido complexes can be used to explain bonding in imido analogues; such studies have been reviewed elsewhere [8,9]. DuBois and Hoffmann [67] have carried out some relevant calculations using the extended Hückel approach. These studies deal with the relationship between the hypothetical hydrazido derivative **22** and the protonated species **23**. Compound **23**, it was noted, is a direct analogue of known Re alkylimido derivatives of structure **24**.



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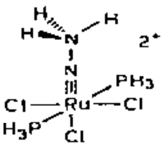

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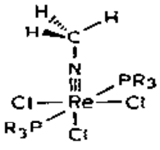

24

Figure 2 illustrates the changes in frontier orbitals on protonation of **22**. Protonation increases the local symmetry with the xz and yz planes becoming nearly equivalent. Thus the two $\pi\ a''$ orbitals drop in energy. These orbitals together with the a' orbitals of the hydrazido complex form the two e sets of **23**. The orbitals are metal xz—nitrogen x and metal yz—nitrogen y bonding and anti-bonding combinations. The b_2 orbital is a filled non-bonding orbital directed between the ligands.

(viii) Spectroscopic studies

(a) Vibrational spectroscopy

Owing to the large metal—nitrogen bond strength and the large dipole mo-

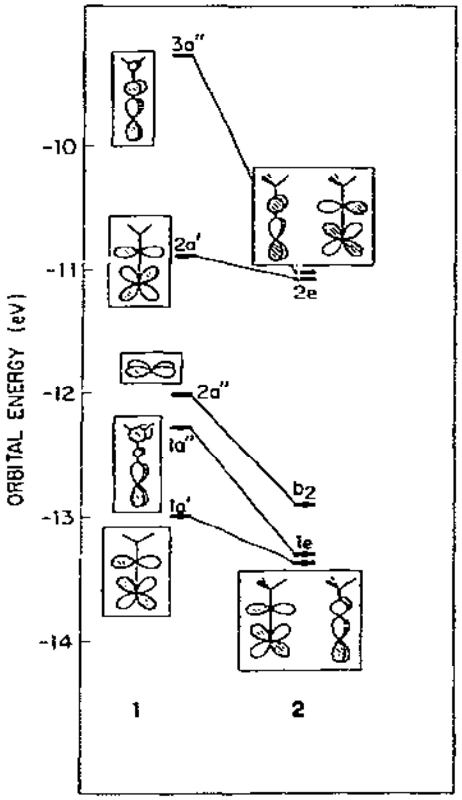

Fig. 2. Changes in frontier orbitals on protonation of compound 1, from ref. 67.

ment of the bond, it might be presumed that infrared spectroscopy would represent a useful tool for probing the structure of mononuclear organoimido complexes. However, for a variety of reasons this utility has not been fully realized. The other ligands in many organoimido complexes have bands which frequently obscure those of the imido group. Coupling of the M—N vibrational modes with other metal—ligand modes and with modes of the organic substituent on imido nitrogen atom seem to further complicate the situation. Nevertheless, common bands in several series of complexes have been assigned to ν(MN) or to related vibrations in the imido ligand. These are summarized in Table 5.

It can be seen from Table 5 that the majority of the metal—imide vibrations fall in the range 1100—1300 cm^{-1}. Some authors have stated that the indicated values represent the metal—nitrogen stretching frequencies of their complexes. Others have been more cautious in this regard and merely correlated the observed band with the presence of the organoimido ligand. It has been established that the stretching frequency for nitrido complexes (non-bridging

TABLE 5

Series of complexes displaying infrared absorbances associated with organoimido ligands

Series	Number of examples	Frequency (cm^{-1})	Ref.
$OsO_3(NR)$	3	1184—1215	36, 47
$OsO_2(NR)_2$	3	1175—1200	36
$OsO(NR)_3$	2	1160—1190	36
$WCl_4(RCN)(NCCl_2R)$	11	1262—1310	40
$X_3V(NR)$ [g]	3	1110—1123 [a]	82, 83, 88
$[WF_5(NR)]^-$	3	1286—1332 [b]	72
$ReCl_3(NMe)(QR_3)_2$ Q = P, As	2	1190—1196 [c,d]	37, 172
$Ta(NR_2)_3(NR)$	4	(1000—1200?) [e]	93
WOXY(NR) [h]	6	950—975 [f]	51

[a] Elsewhere assigned as 985—990 cm^{-1}. [b] A second band associated with W—N—C is reported at ca. 720 cm^{-1}. [c] An additional characteristic band at 1310 cm^{-1} was also noted [32]. [d] The arylimido analogues have bands associated with the NR group at 780 cm^{-1}. [e] The assigned region is obscured by ligand absorbances. [f] Four of six are insoluble polymers; the remaining two show strong absorbances at ca. 1300 cm^{-1}. [g] Compounds represented by this formulation are $Cl_3V(NCl)$, $(Me_3SiO)(R_2N)_2V(NSiMe_3)$ and $(Me_3SiO)_3V(NSiMe_3)$. [h] Compounds represented by this formulation are WOCl(NHR)(NR) and $WO(OEt)_2(NR)$ where R = methyl, ethyl and n-propyl.

N) generally falls in the range 1000—1150 cm^{-1} and for oxo complexes in the range 900—1000 cm^{-1} [8,9]. The similarity of these three ranges suggest that the values in Table 5 may indeed largely reflect metal—nitrogen stretching frequencies. However, great caution must be exercised in correlating bond strength with the apparent values of ν(MN) because (1) there is no necessary relationship between these two molecular properties and (2) few careful vibrational studies using isotopic labels have been performed on nitrido and imido complexes.

Changes in the oxo and *t*-butylimido stretching frequencies in the series $OsO_n(N^tBu)_{4-n}$ are noteworthy [36]. These are summarized in Table 6. In this series the stretching frequencies of the remaining oxo groups decrease by

TABLE 6

Oxo and t-butylimido stretching frequencies in the series $OsO_n(N^tBu)_{4-n}$ [a]

Complex	ν(OsN) (cm^{-1})	ν(OsO) (cm^{-1})
OsO_4	—	955
$OsO_3(N^tBu)$	1184	925, 912
$OsO_2(N^tBu)_2$	1200	886, 878
$OsO(N^tBu)_3$	1190	838

[a] From ref. 36.

about 40 cm^{-1} for each oxo group which is replaced by *t*-butylimido ligand. In contrast the Os—N frequency does not seem to change in any systematic way.

IR spectroscopic data have been reported for several bridging organoimido derivatives. However, in no case have frequencies been assigned to metal—nitrogen modes, and no general trends have emerged.

(b) NMR spectroscopy

Nuclear magnetic resonance spectroscopy has proven to be an effective tool for the study of organoimido derivatives which are diamagnetic and sufficiently soluble. A key feature of the ^1H NMR of alkylimido ligands is the downfield shift of hydrogen atoms located α to the imido nitrogen atom. This effect is illustrated in Table 7 for several methyl- and ethylimido derivatives. The interesting exceptions to this general trend are the rhenium complexes, $ReCl_3(NCH_3)L_2$ [32]. Here the methyl hydrogens are shifted substantially upfield from those of free trimethylamine. This anomaly is especially noteworthy since the acidity of these hydrogens (and hence electron withdrawal in Re≡NMe) is well established [48]. Similar upfield shifts in methyl proton resonances have been observed in a number of phosphine complexes containing bidentate (25) acetate ligands such as $M(CO)_2(O_2CCH_3)(PPh_3)_2$ (M = Mn, Re) [68—70]. In analogous monodentate complexes, $M(CO)_3(O_2CCH_3)(PPh_3)_2$, in which the M···C—$CH_3$ arrangement is no longer linear, the methyl resonances return to their normal chemical shift values.

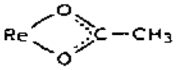

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TABLE 7

Comparison of ^1H chemical shifts of α protons in NR and NR_2 ligands and in free NR_3

Complex	Solvent	Ref.	δ (ppm) imido	δ (ppm) amido	δ (ppm) amine [a]
$Ta(NEt)(NEt_2)_3$	C_6H_6	62	4.04	3.40	2.42
$WOCl(NEt)(NHEt)$	$CDCl_3$	38	7.3	2.9	2.42
$W(NEt_2)_2(NEt)_2$	C_6D_6	64	4.22	3.63	2.42
$[WF_5(NEt)]^-$	CD_3CN	61	5.80	4.2 [b]	2.42
$[WF_5(NMe)]^-$	CD_3CN	61	5.50	3.33 [c]	2.12
$W(NMe)F_4(MeCN)$	CD_3CN	61	5.53	3.33	2.12
$[W_2F_9(NMe)_2]^-$	CD_3CN	61	4.82	3.33	2.12
$Re(NMe)Cl_3(PEtPh_2)_2$	$CDCl_3$	18	0.2	—	2.12
$Re(NMe)Cl_3(AsMe_2Ph)_2$	$CDCl_3$	18	0.7	—	2.12

[a] Free amine in CCl_4 (ref. 71, p. 257f). [b] Comparison value is for $WF_4(NEt_2)_2$ in C_6F_6 [97]. [c] Comparison value is for $W(NMe_2)_6$ in toluene-d_8. Reference is hexamethyldisiloxane [132].

Certain alkylimido complexes share with the alkyl isocyanides the unusual characteristic that coupling of the organic protons with the ^{14}N nucleus can be observed. In most nitrogen compounds, increased coupling of the electrons to the ^{14}N nucleus is caused by the nuclear quadrupole. This leads to more efficient relaxation of the ^{14}N nucleus and broadening of resonances due to nearby nuclei [71]. Winfield and co-workers first noted ^{14}N coupling with ^{1}H and ^{19}F in a series of fluorine-containing methylimido—tungsten complexes [72]. These authors point out that axially symmetric electron density at the nitrogen nucleus must be present. Hence a linear W—N—C arrangement is required. The ^{51}V NMR spectrum of $(Me_3SiO)_3V(N^tBu)$ similarly shows a 1 : 1 : 1 triplet with $J_{^{51}V-^{14}N} = 95$ Hz [54]. In contrast, the corresponding compound in which an adamantyl group replaces the *t*-butyl group shows only a broad singlet. The NMR studies noted above are an impressive demonstration of the power of multi-nuclear NMR as a probe of alkylimido compounds; data concerning the ^{1}H, ^{19}F, ^{31}P, ^{14}N and ^{183}W nucleii were employed to elucidate structures in a series of alkylimido tungsten complexes [72]. It is unfortunate that no ^{15}N NMR studies on imido ligands have been reported.

The ^{13}C chemical shifts for a series of *t*-butylimido compounds provide some insight into the nature of the metal—nitrogen bonding [73]. These are summarized in Table 8. These data suggest that increasing electron donation from nitrogen to metal causes a downfield shift for the α carbon and an upfield shift in the β carbon resonances. The difference (Δ) between these values (final column) can be considered as an approximate measure of electron density on the imido nitrogen atom. The difference values rather than absolute chemical shifts are employed in order to compensate for local solvation differences and anisotropy in the shift due to the heavy metal. The trend in Δ-values seems to parallel chemical reactivity. Thus, $OsO_3(N^tBu)$ which exhibits substantial electrophilic activity [15] has a Δ-value of 55. The nucleophilic

TABLE 8

^{13}C chemical shift data for some four coordinate *t*-butylimido complexes [a]

Metal	Complex	δ, C_α	δ, C_β	Δ
Os	$O_3Os(N^tBu)$	82.7	27.5	55
V	$(Me_3SiO)_3V(N^tBu)$	— [b]	30.7	—
Cr	$(Me_3SiO)_2Cr(N^tBu)_2$	77.8	31.3	47
Mo	$(Me_3SiO)_2Mo(N^tBu)_2$	68.8	32.2	37
Ti	$[(Me_2N)_2Ti(N^tBu)]_2$	69.7	34.6	35
Nb	$(Me_2N)_3Nb(N^tBu)$	68.6	33.5	35
Ta	$(Me_2N)_3Ta(N^tBu)$	66.7	34.6	32
Zr	$[(Me_2N)_2Zr(N^tBu)]_2$	63.2	35.7	27
Hf	$[(Me_2N)_2Hf(N^tBu)]_2$	61.4	36.6	25
P	Ph_3PN^tBu	51.9	36.0	16

[a] Tetramethylsilane used as internal reference in 0.5 M toluene-d_8 solutions. Data taken from ref. 73. [b] Not detected.

[50] main group derivative, Ph$_3$P=N^{t}Bu, which has less available d-orbitals for π-bonding, has the lowest Δ-value at 16. ^{13}C chemical shifts are heavily influenced by electron density effects [74]. However, they do not exclusively reflect simple diamagnetic circulation; excited state configurations with unshared electrons (second order paramagnetic effects) are also important. There fore, the Δ-values of Table 8 must be considered to have qualitative rather than quantitative significance.

The Δ-values are additionally influenced by the nature of the other ligands bonded to the metal. For instance, addition of an electron-donating ligand should increase the electron density on the imido nitrogen atom. This can be illustrated by comparing the Δ-value for O$_3$Os(N^{t}Bu) with that for O$_2$Os(N^{t}Bu)$_2$. Upon replacing one oxo ligand by a more electron releasing t-butylimido ligand, the Δ-value falls from 55 to 45. Consistent with this picture, (Me$_3$SiO)Re(N^{t}Bu)$_3$ exhibits and even lower Δ-value of 35 [73].

C. DESCRIPTIVE CHEMISTRY

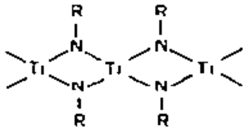
(i) Group IVB

Titanium

As noted earlier the known Group IV alkylimido derivatives are polynuclear materials containing bridging imido nitrogen ligands. One route to such derivatives has been the reaction of Ti(NMe$_2$)$_4$ or Ti(NEt$_2$)$_4$ with primary amines. [75]

$$\mathrm{Ti(NR'_2)_4} + 2\ \mathrm{RNH_2} \rightarrow [\mathrm{Ti(NR)_2}]_x + 4\ \mathrm{R'_2NH} \qquad (1)$$

The insoluble red products formed when R = ^{n}Pr, ^{i}Pr, ^{i}Bu, ^{s}Bu or cyclohexyl are readily hydrolyzed. One possible structure is the linear polymer **26**. A



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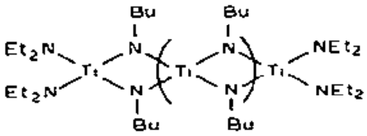
black derivative formed when R = phenyl is less hydrolytically sensitive. The reaction of Ti(NEt$_2$)$_4$ with ^{n}BuNH$_2$ affords a cyclohexane-soluble species formulated as **27** where n is estimated to be in the range 4—12. Treatment of



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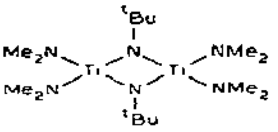
Ti(NMe$_2$)$_4$ with sterically bulky t-butylamine allows isolation of the two simple dimers **28** and **29**. It is noteworthy that t-butylamine similarly affords an unusual 4 membered ring in a group IVA imido derivative, $[R_2Sn(N^tBu)]_2$



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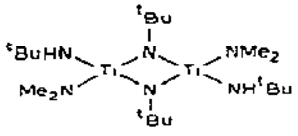

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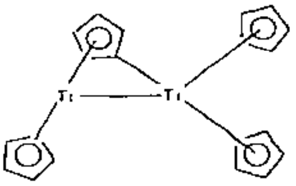
[76]. The structure of **28** is known [176].

Heating $TiCl_4$ with tris(trimethylsilyl)amine over the course of several weeks affords orange needles of $(Me_3SiNTiCl_2)_n$ [77].

$$TiCl_4 + N(SiMe_3)_3 \xrightarrow{C_6H_6} [Me_3SiNTiCl_2]_n + 2\ Me_3SiCl \tag{2}$$

The product was initially formulated as a cyclic tetramer [77] but a subsequent x-ray crystal structure [78] has shown it to be a linear polymer containing planar Ti_2N_2 rings. Chloride bridges link together the five-coordinate trigonal bipyramidal titanium atoms (Fig. 3).

Reaction of μ-(η^1 : η^5-cyclopentadienyl)-tris(η^5-cyclopentadienyl)dititanium(Ti—Ti), **30**, with excess ethylamine proceeds with evolution of 1 mol H_2 per Ti dimer [30]. The product is a red solid formulated as **31**. While the x-ray crystal structure of **31** was not determined, this formulation is supported by the structure of the analogous derivative, $Cp_4Ti_2N_2H_3$, prepared from **30** and ammonia. [30,79]. This latter complex is very reactive and treatment with CO or CO_2 yields an isocyanate and a carbamate complex respectively [79]. It is claimed that this complex can be utilized in the (non-catalytic) reduction of N_2 to NH_3 and for the catalytic hydrogenation of olefins [80].



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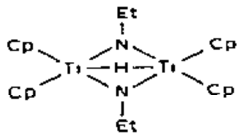


31

Reaction of Cp_2TiCl_2 with $Me_3Si—N{=}N—SiMe_3$ proceeds with formation of Me_3SiCl and dinitrogen. The diamagnetic, sublimable titanium-containing product has been tentatively formulated as a mononuclear complex $Cp_2Ti[NN(SiMe_3)_2]$ [66]. The product obtained upon treatment of $Cl_3TiN(SiMe_3)_2$ with pyridine was originally formulated as a monomeric complex, $Cl_2py_2Ti{=}NSiMe_3$ [127]. It has been subsequently suggested to be a nitrogen-bridged dimer [78] (see also ref. 190).

Zirconium

The reaction of $Zr(NEt_2)_4$ in hydrocarbon solvents with primary amines

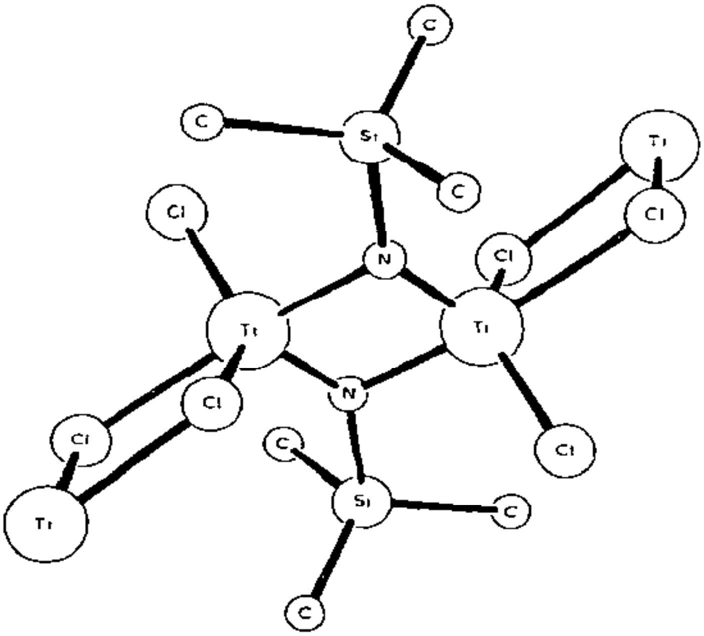
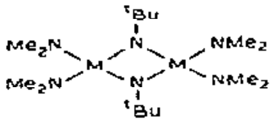


Fig. 3. The structure of $[Me_3SiNTiCl_2]_n$ (ordered chain) from ref. 78.

affords precipitates corresponding to the formula $Zr(NR)(NHR)_2$, R = Ph, Bu, Pr, Et [81]; these compounds are presumed to be polymeric. Refluxing $Zr(NMe_2)_4$ with *t*-butylamine in hexane occurs with loss of dimethylamine [176]. Sublimation of the residue from this reaction at 150°C in vacuo affords the yellow-green compound **32a**. An x-ray crystal structure confirms the symmetrically bridged dimeric structure of **32a**. The two zirconium atoms are coplanar with the two imido nitrogen atoms. Each zirconium exhibits roughly tetrahedral coordination and the dimethylamido ligands are nearly planar. The zirconium to imido nitrogen bonds (average 2.066(1) Å) are not significantly different from the zirconium to amido nitrogen bond lengths (average 2.060 (1) Å) [176].



a. M = Zr
b. M = Hf

32

Hafnium

The pale blue hafnium derivative **32b** has been prepared in a manner analogous to **32a** [176].

(ii) Group VB

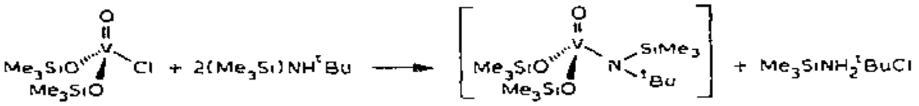
Vanadium

The reaction of vanadium oxytrichloride with sodium bis(trimethylsilyl)amide in ether or THF affords an olive green solid (m.p. 68°C) in 20% yield. The product was formulated as $(Me_3SiO)[(Me_3Si)_2N]_2V(NSiMe_3)$ rather than $[(Me_3Si)_2N]_3VO$ on the basis of its IR and NMR spectra and its ready decomposition to form hexamethyldisiloxane [82].

Reaction of $VOCl_3$ with excess hexamethyldisilazane (HMDS) in pentane affords $(Me_3SiO)_3V(NSiMe_3)$ in 18% yield [83]. It is of interest that reaction of $VOCl_3$ and HMDS in a 1 : 1 molar ratio is reported to afford a simple adduct $VOCl_3 \cdot HN(SiMe_3)_2$ [84]. Yellow needles of $(Me_3SiO)_3V(NSiMe_3)$ (m.p. 42—43°C) are obtained on sublimation in vacuo. Vibrational and mass spectra suggest that the complex is mononuclear with a nearly linear vanadium—nitrogen—silicon arrangement. The compound decomposes thermally even at —10°C. It has been reported that the same complex can be prepared by the action of HMDS on NH_4VO_3 in the presence of a deficiency of dimethylacetamide [85]. The latter report also claims the analogous reaction with n-PrHN-$(SiMe_3)$ but no yields nor experimental details are given for either reaction.

The reaction of $VOCl_3$ with $MeN(SiMe_3)_2$ affords $Cl_3V(NMe)$ as a brown crystalline solid which decomposes at 57°C [86,87]. The compound is initially soluble in benzene but even at low temperature readily decomposes to an insoluble polymeric form. The reaction could not be extended to C_6H_5N-$(SiMe_3)_2$ inasmuch as the product decomposed. It could be shown that these decomposition products were identical to those from the thermolysis of Cl_3OVL_2, L = C_6H_5NCO or C_6H_5NSO. This is cited as evidence that both reactions afford a derivative $[Cl_3V(NPh)]_x$ which then further reacts [86].

In contrast to the preceding compounds, complex 35 can be prepared in high yield and is quite thermally stable [126]. The complex is prepared by the action of *t*-butyl trimethylsilylamine on $(Me_3SiO)_2VOCl$ (33). The corresponding complex where adamantyl replaces *t*-butyl has been characterized by an x-ray crystal structure. The short V—N bond (1.61 Å) and nearly linear (176°) V—N—C unit in this tetrahedral complex confirm that even the smaller *d*-orbitals of a first row transition metal will accommodate multiple bonding to nitrogen [126]. For a possibly related species see ref. 188.



33 34 (3)

$$[34] \longrightarrow (Me_3SiO)_3V{\equiv}N^tBu \qquad (4)$$

35

Treatment of vanadium trichloride with ClN_3 gives the dark brown, explosive azido complex $Cl_2V(N_3)$. Thermal decomposition of this compound affords the unusual species $Cl_3V(NCl)$ which, in a Lewis sense, is amphoteric [88]. Reaction with antimony pentachloride affords $[Cl_3VN]^+[SbCl_6]^-$ while reaction with pyridine is reported to give $[Py_2Cl]^+[Cl_3VN]^-$. The V—N stretching frequencies of the cationic and anionic species at 1038 cm^{-1} and 1208 cm^{-1} respectively bracket that of the neutral complex at 1110 cm^{-1}. The x-ray crystal structure [89] of $Cl_3V{=}NCl$ shows the complex to be polymeric (Fig. 4) with approximate square-based pyramidal coordination of the vanadium atoms. However the dimer units are additionally linked by chloride bridges so that the vanadium atom has distorted octahedral coordination. The V—N—Cl unit is linear with V—N = 1.64 Å and N—Cl = 1.59 Å (see also ref. 181).

Treatment of vanadocene with bis(trimethylsilyl)diazene according to eqn. 5 affords the sublimable dark red brown complex **36**. Formation of **36** appears to involve rearrangement of a black-green diazene complex of the

$$Me_3Si{-}N{=}N{-}SiMe_3 + Cp_2V \xrightarrow[Et_2O]{-78°} \underset{\mathbf{36}}{Cp_2V[NN(SiMe_3)_2]} \qquad (5)$$

type $Cp_2V \cdot Me_3SiNNSiMe_3$ [90]. An x-ray crystal structure of **36** [61] reveals a linear V—N—N arrangement with a N—N bond length of 1.369(9) Å and a V—N bond length of 1.666(6) Å (see also ref. 66).

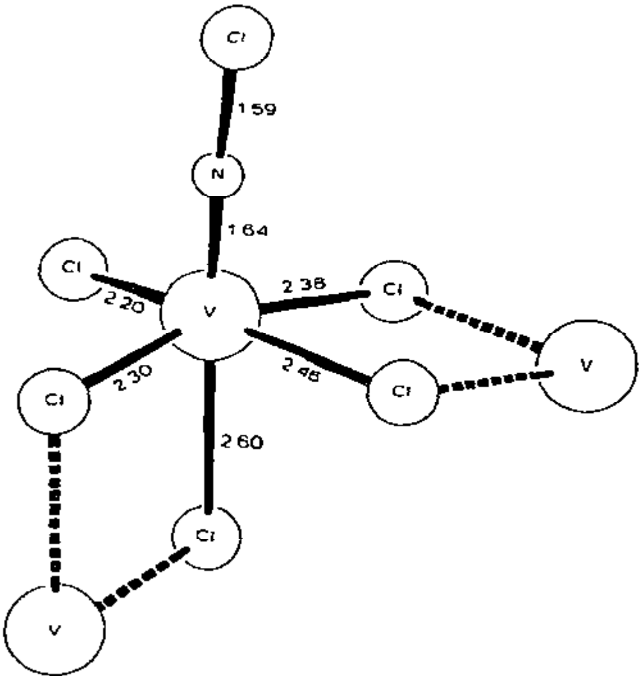


Fig. 4. The structure of $Cl_3V(NCl)$ from ref. 89.

Niobium

Bradley and Thomas demonstrated that small amounts of a butylimido niobium derivative, $(BuN)Nb(NMeBu)_3$ were generated during the thermolysis of $Nb(NMe^{n}Bu)_5$. Treatment of the butylimido product from this reaction with n-butanol affords discrete quantities of primary n-butylamine [35].

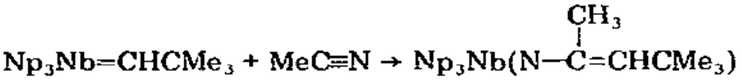
Reaction of $NbCl_5$ with lithium *t*-butylamide and lithium dimethylamide in hexane affords *N-tert*-butylimido-tris(dimethylamido)niobium (eqn. 6) [29].

$$NbCl_5 + 4\ LiNMe_2 + LiNH^tBu \rightarrow (Me_2N)_3Nb(N^tBu) + 5\ LiCl + Me_2NH \quad (6)$$

The yellow crystalline compound (m.p. 58–60°) undergoes reaction with electrophiles at the amide nitrogen. For example, the white dimethylcarbamate derivative can be prepared by insertion of CO_2 [29].

$$(Me_2N)_3Nb(N^tBu) + 3\ CO_2 \rightarrow (Me_2NCO_2)_3Nb(N^tBu) \quad (7)$$

A niobium organoimido derivative has been prepared by reaction of a neopentylidene complex with excess acetonitrile. The recrystallized product is a



$$Np_3Nb{=}CHCMe_3 + MeC{\equiv}N \rightarrow Np_3Nb(N{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CHCMe_3) \quad (8)$$

2 : 3 mixture of *E* and *Z* isomers [42].

Reaction of $NbCl_4$ with zinc in acetonitrile leads to isolation of a green powder which analyzes as $NbCl_3(CH_3CN)_3$ [20]. However, it is in fact a binuclear complex in which two niobium atoms are bridged by a $Nb(N{-}C(Me){=}C(Me){-}N)Nb$ linkage. The dianion is precipitated using $(PPh_3)_2N^+Cl^-$ and its structure is shown in Fig. 5. A crystal structure [20] confirms that the 2-butenyl bridge adopts *trans* stereochemistry and that the molecule possesses a center of symmetry. The Nb–N bond length in the linear organoimido ligands [1.752(6) Å] is remarkably similar to that [1.75(1) Å] found in a related tantalum complex (vide infra).

A series of organoimido niobium complexes have been prepared according to eqn. 9. The yellow products are typically obtained in 50% yield. The x-ray

$$NbCl_5 + RNH_2 + 3\ Me_3SiS_2CNEt_2 \xrightarrow{Et_3N} Nb(NR)(S_2CNEt_2)_3 \quad (9)$$

$R = Ph, p\text{-}C_6H_4Me, {}^tBu, {}^iPr, {}^nPr, Me$

crystal structure of the *p*-tolyl derivative has been determined. With $Ph(Me)N{-}NH_2$ the yellow-orange hydrazido complex $Nb(NNMePh)(S_2CNEt_2)_3$ is obtained [25].

Tantalum

Bradley and Thomas [91,92] have shown that reactions of $TaCl_5$ with lithium dialkylamides other than $LiNMe_2$ lead to $(RN)Ta(NR_2)_3$ species in addition to other products. Alkylimido derivatives prepared by this route have been

$$TaCl_5 + 5\ LiNEt_2 \rightarrow (Et_2N)_3Ta(NEt) + C_2H_4 + Et_2NH + 5\ LiCl \quad (10)$$

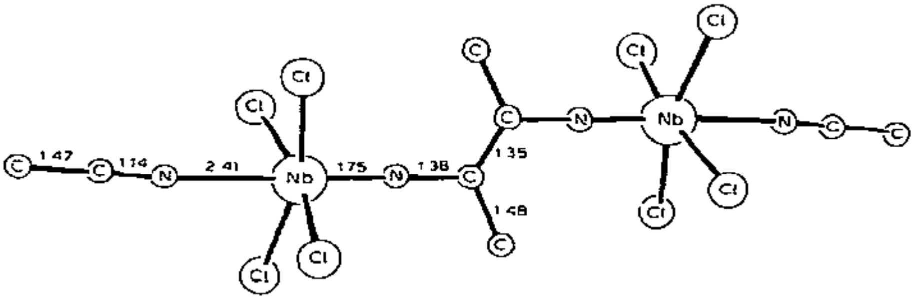
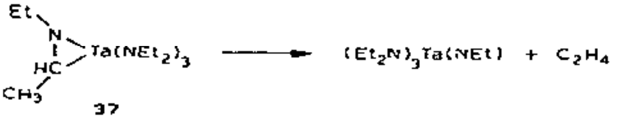


Fig. 5. The structure of the anion $[Nb_2Cl_8(CH_3CN)_2C_4H_6N_2]^{2-}$ from ref. 20.

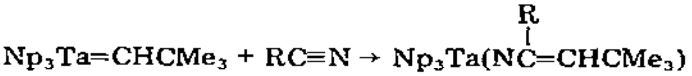
purified by fractional distillation and examined by NMR spectroscopy [93]. In this way $(RN)Ta(NR_2)_3$ species R = Et, ^nPr, ^nBu and $(BuN)Ta(NMe^nBu)_3$ have been isolated.

The mechanism of formation of alkylimido derivatives in this reaction is not clear. Simple thermolysis of $Ta(NEt_2)_5$ under the reaction conditions (room temperature or below) is ruled out since this derivative has been isolated by crystallization techniques and was found to be thermally stable [94]. Bradley and Thomas have proposed that tantalum (IV) dialkylamides are possible intermediates [91]. Subsequent work [33] has demonstrated that careful distillation of the reaction products of $LiNEt_2$ with $TaCl_5$ affords 22% of ethyliminoethyl(C,N)tris(diethylamido)tantalum, 37. When heated above 100°C 37 undergoes a first order decomposition to the ethylimido complex and ethylene (eqn. 11). That eqn. 11 does not proceed via simple loss of methylcarbene was indicated by a negative activation entropy and by trapping experiments.

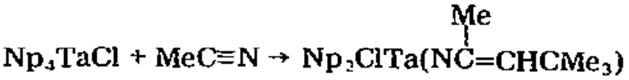


37 (11)

Tris(neopentyl)neopentylidene tantalum reacts vigorously with either acetonitrile or benzonitrile to afford organoimido compounds (eqn. 12). In each case the pure *Z* isomer can be isolated from the resultant *Z* + *E* mixtures by



$$Np_3Ta{=}CHCMe_3 + RC{\equiv}N \rightarrow Np_3Ta(N\overset{R}{C}{=}CHCMe_3) \qquad (12)$$



$$Np_4TaCl + MeC{\equiv}N \rightarrow Np_2ClTa(N\overset{Me}{C}{=}CHCMe_3) \qquad (13)$$

recrystallization and sublimation [42]. Similarly chlorotetrakis(neopentyl)tantalum reacts with acetonitrile, the *E* isomer in this case being isolated (eqn. 13) [42]. Additional examples were recently reported [180].

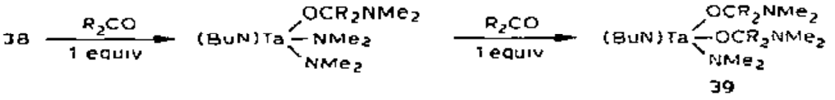
The reactions of $(Pr_2N)_3Ta{=}NPr$ with excess alcohol or triethylsilanol were studied and in each case afford the corresponding $Ta(OR)_5$ derivative in 92—98% yield [52].

The white crystalline solid $(Me_2N)_3Ta(N^tBu)$ (m.p. 68—69°C) has been prepared by two different routes [29].

$$Ta(NMe_2)_5 + {}^tBuNH_2 \rightarrow \underset{\mathbf{38}}{(Me_2N)_3Ta{\equiv}N^tBu} + 2\ Me_2NH \tag{14}$$

$$TaCl_5 + LiNH^tBu + 4\ LiNMe_2 \rightarrow \mathbf{38} + Me_2NH + 5\ LiCl \tag{15}$$

Reaction 14 has also been employed with aniline to afford a crystalline arylimido derivative [95]. Complex **38** is monomeric in solution and reacts with electrophiles at amide nitrogen [29]. Thus tris(dimethylcarbamato) and tris(dimethyldithiocarbamato) analogs of **38** can be prepared by insertion of CO_2 or CS_2 respectively. The electrophilic reactions of **38** are reversible and subject to steric constraints. Thus one or two (but not three) equivalents of benzophenone will insert into the tantalum—amide bonds (eqn. 16). Reaction of product **39** with excess CO_2 displaces benzophenone to afford the tris(dimethylcarbamate) derivative (eqn. 17b).



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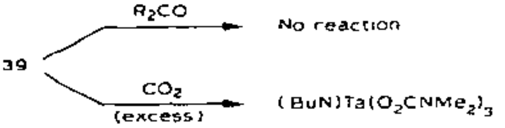


(17a)

(17b)

The x-ray crystal structure of **38** indicates a linear C—N—Ta arrangement in the *t*-butylimido ligand and planar dimethylamido ligands [29]. This structure is that expected on the basis of the EAN rule. The IR spectrum of compound **38** has been reported [96].

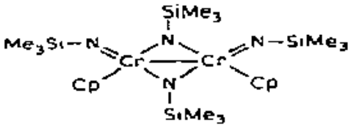
Reaction of $TaCl_4$ with acetonitrile proceeds with disproportionation to Ta^{III} and Ta^{V}. The green Ta^{V} product was originally formulated as a dimer, $Ta_2Cl_6(MeCN)_4$, with metal—metal bonding [98]. However two THF molecules will add to each tantalum with displacement of an acetonitrile ligand and the resultant dark red product, $[TaCl_3(THF)_2]_2(NCMe{=}CMeN)$ has been examined by x-ray crystallography. The complex is binuclear and contains a bridging bis(imido) ligand similar to that in Fig. 5 [99] (see also ref. 182).

(iii) Group VIB

Chromium

Reaction of CrO_2Cl_2 with an excess of ${}^tBuNH(SiMe_3)$ in hexane affords a red crystalline product [126]. This is believed to be the bis-*tert*-butylimido complex, $(Me_3SiO)_2Cr(N^tBu)_2$ rather than the alternative formulation, $O_2Cr(N^tBuSiMe_3)_2$.

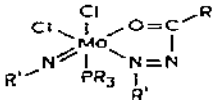
The reaction of bis(trimethylsilyl)diazene, $Me_3Si—N=N—SiMe_3$, with either chromocene or $CpCrCl_2$ affords the same dark violet crystals with a metallic luster [66,128]. An x-ray crystal structure [128] shows the product to have structure **40**. Compound **40** shows two distinct trimethylsilyl resonances in the NMR and reacts with methanol to afford a product $[CpCr(NH)(NSiMe_3)]_2$.



40

Molybdenum

$[MoOCl_2(PR_3)_3]$ reacts with substituted hydrazines, RCONHNHR', in refluxing methanol to give red, diamagnetic, crystalline arylimido complexes [100,101]. The complexes have the structure **41**. The compounds prepared to date in this series are summarized in Table 9. The crystal structure of the complex where R = phenyl, R' = *p*-tolyl and $PR_3 = PMe_2Ph$ has been determined. The Mo—N(imido) bond length is 1.726(9) Å and the Mo—N—C angle is 177°. The metal—diazene chelate system is nearly planar with considerable delocalization in the chelate ring [101] (see also ref. 191).



41

Treatment of $[CpMo(CO)_3]_2$ with *t*-butylsulfurdiimine affords yellow-orange crystals of a sulfur-bridged dimer $[CpMo(N^tBu)(\mu\text{-}S)]_2$ with the structure shown in Fig. 6 [37]. The Mo—N—C unit is nearly linear with Mo—N 1.73 Å and N—C 1.44 Å.

Chatt and co-workers [14] have prepared several organoimido complexes by treatment of the nucleophilic nitrido complexes $N{\equiv}Mo(S_2CNR_2)_3$ with electrophiles as summarized in eqns. 18a—d. It is claimed that eight-coordinate complexes (reactions 18b—d) are produced and that they can be converted to seven-coordinate pentagonal bipyramidal cations by treatment with salts of non-coordinating anions to remove Cl^-. Sulphenylimido complexes were also prepared by reaction of the thionitrosyls $[Mo(NS)(S_2CNR_2)_3]$ with electrophiles [14].

The product $C_4Cl_{11}MoN_2$ from reaction of either $MoCl_4$ or $MoCl_5$ with trichloroacetonitrile has been suggested to be a pentachloroethylimido complex. Such a $(Cl_3CCN)Cl_3Mo(NC_2Cl_5)$ derivative could arise through addition of chlorine to the C≡N bond of a coordinated nitrile. A similar product is ob-

TABLE 9

Complexes of the type $MoCl_2(NR)(RN_2COR)(PR_3)$ [a]

R'	R	PR_3	M.P.(deg) [b]	Mol. Wt. [c]
C_6H_5	C_6H_5	PMe_2Ph	179—181	672(600)
C_6H_5	p-ClC_6H_4	PMe_2Ph	295—297	638(641)
C_6H_5	p-$MeOC_6H_4$	PMe_2Ph	190—195	714(638)
C_6H_5	C_6H_5	PEt_2Ph	168—172	666(634)
p-ClC_6H_4	C_6H_5	PMe_2Ph	206—209	769(674)
p-MeC_6H_4	C_6H_5	PMe_2Ph	218—223	739(634)
p-$MeOC_6H_4$	C_6H_5	PMe_2Ph	205—208	667(666)
1-$C_{10}H_7$	C_6H_5	PMe_2Ph	213—216	714(706)
C_6H_5	1-$C_{10}H_7$	PMe_2Ph	180—183	714(656)
Et	C_6H_5	PMe_2Ph	170—172	—
^{n}Pr	C_6H_5	PMe_2Ph	178—180	518(538)
^{i}Pr	C_6H_5	PMe_2Ph	180—182	504(538)
CH_2Ph	C_6H_5	PMe_2Ph	147—149	593(634)
p-MeC_6H_4	CH_3	PMe_2Ph	—	—

[a] From ref. 101. [b] With decomposition. [c] Calculated values in parentheses.

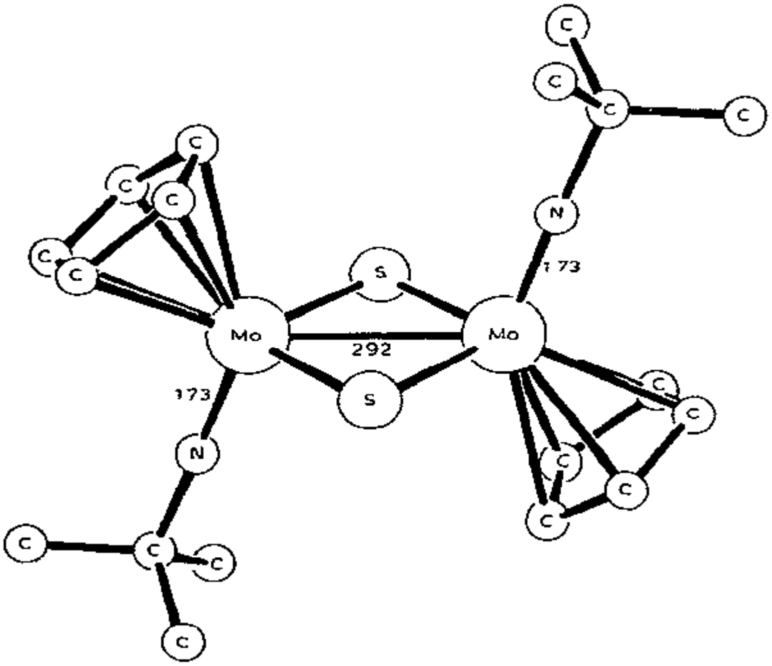
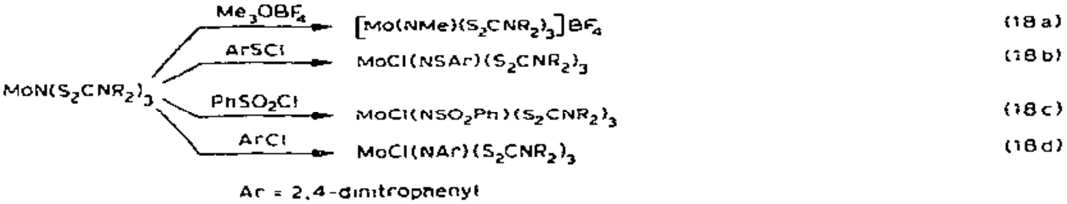


Fig. 6. The structure of $[CpMo(N^tBu)(\mu\text{-}S)]_2$ from ref. 37.

tained from the reaction of $MoCl_5$ with CH_2ClCN [102].

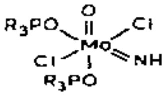


Reaction of molybdenum dioxydichloride with trimethylsilyl-*t*-butylamine (eqn. 19) in refluxing hexane is believed to proceed with rearrangement to the *t*-butylimido derivative similar to the chromium analogue [126].

$$MoO_2Cl_2 + 4\ {}^tBuNH(SiMe_3) \xrightarrow[-2\,HCl]{} (Me_3SiO)_2Mo(N^tBu)_2 \qquad (19)$$

Treatment of the nitrido complex $[MoN(N_3)(dppe)_2]$ with hydrohalic acids has afforded the first examples of simple imido complexes to be isolated, $[MoX_2(NH)(dppe)_2]$, X = Cl, Br [103,104]. Treatment of these derivatives with $NaBPh_4$ or $NaPF_6$ affords cationic complexes $[MoX(NH)(dppe)_2]^+Y^-$. All of the imido derivatives can be deprotonated with triethylamine to afford the corresponding nitrido complexes. Subsequent reprotonation with methanol can give the diamagnetic imido complexes $[Mo(NH)(OMe)(dppe)_2]^+X^-$ [103].

Reaction of $MoOCl_3$ with trimethylsilyl azide in THF followed by addition of tertiary phosphine oxides R_3PO ($R_3 = Ph_3$, Ph_2Et, Ph_2Me) and hydrolysis gives $MoOCl_2(NH)(OPR_3)_2$ [53]. An x-ray crystal structure for the case $R_3 = Ph_2Et$ shows the distorted octahedral molecule to have structure **42**. The



42

imido hydrogen has been located, and the Mo—N—H system is non-linear.

A complex with a bridging imido group $Mo_2O_3(NH)[S_2P(OEt)_2]_2$ has been prepared and its structure determined as the tetrahydrofuran solvate [105] (Fig. 7). The complex is prepared by reaction of $MoO[S_2P(OEt)_2]_2$ with aqueous HN_3. The structural results allowed the location of all the hydrogen atoms including the NH hydrogen and unequivocal confirmation that the hydrogen is bonded to a nitrogen atom. The bridging O and N atoms are not coplanar with the Mo atoms but rather are symmetrically displaced away from the terminal oxo ligands. Thus the angle between the plane defined by O, Mo_1 and Mo_2 and the one defined by Mo_1, N and Mo_2 is 159.0°. The terminal oxygens are eclipsed while the Mo_1—Mo_2 distance of 2.59 Å indicates the presence of a metal—metal single bond.

The synthesis and structure determination of the bis-phenylimido complex,

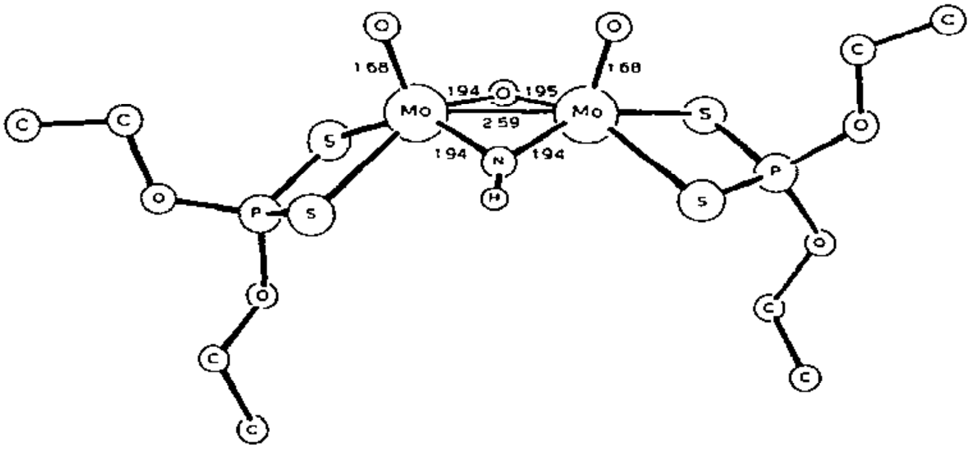


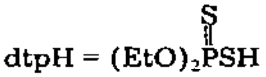
Fig. 7. The structure of $Mo_2O_3(NH)[S_2P(OEt_2)]_2$ from ref. 105.

$Mo(NPh)_2(S_2CNEt_2)_2$, has been reported [15]. The complex was prepared by reaction of $Mo(CO)_2(S_2CNEt_2)_2$ with excess phenylazide at room temperature. The phenylimido ligands are located *cis* to one another in the distorted octahedral complex. Consistent with the EAN rule, one phenylimido ligand is strongly bent (Mo—N—C = 139.4(3)°) while the other is only slightly bent (Mo—N—C = 169.4(4)°). In the bent imido ligand, the Mo—N bond is longer than that for the more linear nitrene ligand (1.789(4) Å vs. 1.754(4) Å). The more bent imido ligand also shows a significantly larger *trans* influence on the *trans* sulfur ligand than does the more linear ligand. Hydrochloric acid quantitatively displaces one imido ligand from $Mo(NPh)_2(S_2CNEt_2)_2$ forming anilinium chloride and $MoCl_2(NPh)(S_2CNEt_2)_2$ in good yields. The crystal structure of the monoimido complex shows a pentagonal-bipyramidal geometry at Mo with the NPh and Cl ligands in axial sites. The Mo—N—Ph angle is 166.8(3)° and the Mo—N bond distance is 1.734(4) Å. There is no *trans* influence exerted by the phenylimido ligand because the two Mo—Cl distances are the same. [25].

$MoCl_2(NPh)(S_2CNEt_2)_2$ has also been prepared by the action of excess PhNCO on $MoOCl_2(S_2CNEt_2)_2$ in refluxing toluene. The reaction proceeds with evolution of CO_2. A noteworthy aspect of these studies is that ^{18}O labelled starting complex yielded $^{16}OC^{18}O$ [106].

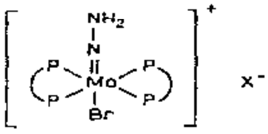
Reaction of $MoO(S_2CNEt_2)_2$ with aryl azides (CH_2Cl_2, room temperature) afford products $MoO(NAr)(S_2CNEt_2)_2$ where Ar = phenyl or *p*-nitrophenyl. The related reaction in eqn. 20 affords the novel paramagnetic imido complex 43 [107, 108].

$$MoCl_2(CO)_4 + 1.5\ PhN_3 + 2\ dtpH \rightarrow \underset{\textbf{43}}{Mo(dtp)_3(NPh)} \qquad (20)$$



$$dtpH = (EtO)_2\overset{\overset{\displaystyle S}{\|}}{P}SH$$

The protonation of some molybdenum dinitrogen complexes by hydrohalic acids has been studied [108,109]. Reaction of *trans*-[Mo(N_2)(depe)$_2$] with excess HX affords the six-coordinate hydrazide derivatives [MoX(NNH_2)(depe)$_2$]X, (X = Cl, Br). The reaction of *trans*-[Mo(N_2)$_2$(dppe)$_2$] with HBr was originally thought to afford a seven-coordinate diazene complex. However, these are now also believed to have structure 44 [7]. Treatment of the latter complex with (NEt_4)BF_4 converts it to a fluoborate salt which has been isolated as a crystalline dimethylformamide solvate (see also refs. 183, 184).



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With sulfuric acid, the complex [Mo(NNH_2)(SO_3H)(dppe)$_2$]HSO_4 is formed [110]. Either HBF_4 [111] or [Et_3O]BF_4 [112] affords the fluorohydrazido complex [MoF(NNH_2)(dppe)$_2$]BF_4. Treatment of *cis*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] with HX (X = Cl, Br, I) in methanol gives MoX_2(NNH_2)(PMe_2Ph)$_3$ [113]. One halide can be replaced in these latter complexes by substituted pyridine or tertiary phosphine ligands, L, according to eqn. 21 [114].

$$MoX_2(NNH_2)(PMe_2Ph)_3 + L \rightarrow [MoXL(NNH_2)(PMe_2Ph)_3]X \qquad (21)$$

Treatment of the methyl- or phenyldiazo complexes (R_2NCS_2)$_3MoN_2R$ with HCl, HBr or HBF_4 affords salts of [R_2NCS_2)$_3$Mo(N_2HR)]$^+$ believed to contain a linear hydrazido ligand [115,123].

Similarly, diazo complexes **45** can be protonated with hydrohalic acids to hydrazido complexes **46**. Compounds **45** in turn are prepared by acylation or alkylation of *trans*-[Mo(N_2)$_2$(dppe)$_2$] with acyl or alkyl halides. The reaction with alkyl halides is accelerated by visible light. Organohydrazido complexes **46** are also readily deprotonated by weak base to afford the starting complexes [117—122].

$$\underset{\textbf{45}}{[MoX(NNR)(dppe)_2]} \xrightarrow{HX} \underset{\textbf{46}}{[MoX(NNHR)(dppe)_2]X} \qquad (22)$$

N,N-disubstituted hydrazido(2-) complexes of molybdenum have been prepared by alkylation of phenyldiazo ligands [123] and by the reaction of MoO_2(S_2CNR_2)$_2$ complexes with disubstituted hydrazines [14]. Equation 23 has now been extended to other diazo ligands and to a variety of alkylating and acylating agents [115]. The products from eqn. 24 are air-stable pink crystalline solids with IR bands at about 850 cm^{-1} assigned to ν(Mo=O). The complexes

$$Mo(N_2Ph)(S_2CNR_2)_3 \xrightarrow[CH_2Cl_2]{R'_3OBF_4} [Mo(NNR'Ph)(S_2CNR_2)_3]BF_4 \qquad (23)$$

$$MoO_2(S_2CNR_2)_2 + R'_2NNH_2 \xrightarrow[reflux]{MeOH} MoO(NNR'_2)(S_2CNR_2)_2 \qquad (24)$$

are fluxional in CH_2Cl_2 solution at room temperature; the dithiocarbamate methyl groups appear as a singlet in the NMR spectrum which is resolved into two singlets at lower temperatures. In one case only ($R' = Ph$, $R = Me$), a yellow bis-hydrazido complex, $Mo(NNPh_2)_2(S_2CNMe_2)$ can be prepared which exhibits no Mo—O vibration in the IR spectrum [14].

Disubstituted hydrazido complexes have been prepared via eqn. 25 [7,118]. Hydrazido complexes undergo condensation reactions with organic

$$\textit{trans}\text{-}[Mo(N_2)_2(dppe)_2] + Br(CH_2)_nBr \rightarrow \{MoBr(dppe)_2(N{-}\overline{N{-}(CH_2)_n})\}Br$$

$$n = 4, 5 \tag{25}$$

carbonyl compounds to yield diazo complexes such as **47** and **48** [7,124,125].

$$\textit{trans}\text{-}[MoF(NNH_2)(dppe)_2]BF_4 + RR'CO \xrightarrow{HBF_4} \underset{\mathbf{47}}{[MoF(NNCRR')(dppe)_2]BF_4} + H_2O. \tag{26}$$

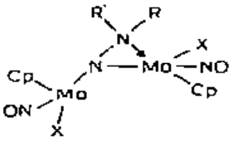
$$MoCl_2(NNH_2)(PMe_2Ph)_3 + RR'CO \rightarrow \underset{\mathbf{48}}{MoCl_2(PMe_2Ph)_3(NNCRR')} + H_2O \tag{27}$$

Recently an extensive series of molybdenum hydrazido complexes has been prepared [177]. This work includes electrochemical studies showing that the complexes can generally be oxidized by one unit but cannot be reduced.

X-ray crystal structures have been reported for several dialkylhydrazido molybdenum derivatives. The complex $[Mo(NNEtPh)(S_2CN(CH_2)_5)_3]BPh_4$ exhibits distorted pentagonal bipyramidal geometry in which the main distortional feature reflects the ligand S—Mo—S bite angle [129]. In $MoO(NNMe_2)$-$(S_2CNMe_2)_2$ the oxo and hydrazido ligands are located *cis* to one another [14]. The metal—nitrogen bond length is significantly longer (1.85 Å vs. 1.72 Å) than in the former complex suggesting less interaction between the metal and the adjacent nitrogen of the $NNMe_2$ ligand. The Mo—S bond *trans* to the oxo group (2.71 Å), but *not* that *trans* to the hydrazido ligand, is significantly longer than the remaining Mo—S bonds (2.51 Å average) indicating that the oxo group exhibits the greater *trans* influence.

The molecular structure of the benzene solvate of $[MoI(NNHC_8H_{17})$-$(dppe)_2]I$ has been determined and the unique hydrogen located [120]. The *N*-octylhydrazido and iodide ligands occupy *trans* positions in the octahedral coordination polyhedron. The Mo—N—N angle is 174°, Mo—N is 1.801(11) Å and moreover the entire six-atom Mo, N, N, C, H, I^- grouping is coplanar to within 0.02 Å. Hydrogen bonding between the hydrazido hydrogen and iodide ion is indicated by a N—H···I bond angle of 174(12)° and a 3.56(1) Å N···I^- distance. Similarly $Mo(N_2H_2)F(dppe)_2(BF_4) \cdot CH_2Cl_2$ was prepared by reaction of $Mo(N_2)_2(dppe)_2$ with excess aqueous fluoroboric acid [112]. Here the Mo—N—N angle is 176.4(13)° and Mo—N is 1.762(12) Å. Again the hydrazido ligand lies in a plane approximately perpendicular to the least-squares plane through the four phosphorus atoms and a hydrogen bond is observed to the tetrafluoroborate anion.

McCleverty and co-workers have studied the reactions of $Cp_2Mo(NO)X$ [131] and of $CpMo(NO)X_2$, X = Cl, Br, I, [65] with substituted hydrazines. The hydrazines were H_2NNHPh, H_2NNMe_2, H_2NNEt_2 and $H_2NNPhMe$. Asymmetrically bridged hydrazido complexes of type 49 were usually formed. Structure 49 has been confirmed by x-ray diffraction for the case R′=R=Me and X=I. A symmetrically bridged dimer, probably having structure 50 was formed only from phenylhydrazine when the halide was iodide. Treatment of 50 with sodium thiophenoxide gave initially $[CpMo(NO)(NNHPh)]_2I(SPh)$ and eventually $[CpMo(NO)(SPh)_2]_2$ [131].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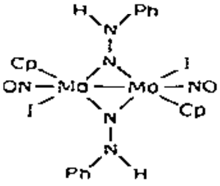

50

Tungsten

WO_2Cl_2 is claimed to react with methyl, ethyl or n-propylamine to yield amorphous products $(O_2WNR)_x$ which are insoluble in common organic solvents [51]. In contrast reaction of $WOCl_4$ with ethyl and propylamine affords crystalline derivatives $[WOCl(NHR)(NR)]_n$ which are soluble in chloroform. A large downfield shift in the nmr absorbance of the ethylimido CH_2 (7.3δ) compared to the ethylamido CH_2 (2.9δ) suggests that these derivatives indeed contain a multiply bonded W(NR) function. The monochloro species also react with ethanol to afford the corresponding diethoxy derivatives.

$$WOCl(NR)(NHR) + 2\ EtOH \xrightarrow{CHCl_3} WO(NR)(OEt)_2 + RNH_3Cl \qquad (28)$$

R = Me, Et, ^{n}Pr

A pale yellow distillable liquid, isolated from the reaction of WCl_6 with lithium diethylamide, has been formulated as $W(NEt_2)_2(NEt)_2$. The product was characterized by ^1H and ^{13}C NMR [132]. Reaction of WCl_6 in hexane with *t*-butylamine affords crystalline $(^tBuNH)_2W(N^tBu)_2$ in high yield. This complex upon treatment with *t*-butyl alcohol gives $(^tBuO)_2W(N^tBu)_2$ as a yellow oil [73].

Tungsten hexafluoride undergoes aminolysis by primary amines [72,133] to give $RNH_3^+[WF_5(NR)]^-$ derivatives, R = Me, Et, ^{n}Bu. With $^tBuNH_2$ a 3 : 1 adduct is obtained which is formulated as a 1 : 1 mixture of $^tBuNH_3^+[WF_5(N^tBu)]^-$ and $^tBuNH_3^+F^-$. WF_6 also reacts with $(Me_3Si)_2NMe$ or $Me_3SiN(Me)PF_2$ in the presence of coordinating ligands [7,134]. In this way the complexes $LWF_4(NR)$ are prepared where L = MeCN, pyridine, EtOAc, DMSO. When L = $P(OMe)_3$ other rearrangement products are obtained in addition to $WF_4(NMe)[P(OMe)_3]$. WF_6 reacts with $Me_3SiNHMe$ to give $MeNH_3^+$ salts of

WF_5NMe^- and the fluoro bridged dimer $[(MeN)F_4W—F—WF_4(NMe)]^-$. All of these tungsten fluoro complexes have been extensively investigated by NMR techniques [72].

^{19}F NMR evidence for the formation of $(MeCN)F_4W(NH)$ upon reaction of WF_6 with NH_3 or $(Me_3Si)_2NH$ in acetonitrile has been reported [135]. This report also contains a discussion in the $[F_5W(NBu)]^-$ anion.

The reaction of trichloroacetonitrile with either WCl_5 or WCl_6 affords the same pentachlorethylimido derivative [40,102]. The structure of the product, $LCl_4W{=}NCCl_2CCl_3$ ($L = N{\equiv}CCCl_3$), is a distorted octahedron with the nitrile ligand *trans* to the organoimido ligand [58]. The WCl_4 unit is not planar, the tungsten atom being 0.32 Å above the plane of the four chlorines, and the W—N—C unit is nearly linear (177°). $Cl_4W(NC_2Cl_5)$ forms a 1 : 1 complex with glyme [142]. The structure of the related chlorine bridged dimer $[WCl_4(NC_2Cl_5)]_2$ has also been determined [136]. This interesting formal insertion of a nitrile into a W—Cl bond was discovered by Fowles et al. [102] who have more recently extended the reaction to a variety of other nitriles [40]. The products along with selected IR data are tabulated in Table 10. The acetonitrile complex decomposes on warming with reduction of the metal to W(IV). It was suggested that such an insertion process may be involved in the well-known reduction of WCl_6 in acetonitrile which proceeds with loss of HCl and the formation of $WCl_4(MeCN)_2$ [137]. The similarity between the addition of nitriles to WCl_6 and the proposed intermediates in *cis*-chlorination of olefins by group VI halides has been noted [138].

N-phenylimidotetrachlorotungsten has been prepared by reaction of tungsten oxytetrachloride with phenyl isocyanate [28].

Reaction of $(R_2NCS_2)_2W(CO)_2(PPh_3)$ with two equivalents of aryl azide at room temperature allows the isolation of a stable green product, $(R_2NCS_2)_2W$-

TABLE 10

IR data for the series of compounds $[WCl_4(NCCl_2R)] \cdot RCN$ [a]

R	ν(CN) (cm⁻¹) [b]	ν(WN) (cm⁻¹) [c]
Me	2310, 2285	1280
CH_2Cl	2298	1304
$CHCl_2$	2203	1303
CCl_3	2284	1293
CCl_2CH_2Cl	2301	1284
$CH{=}CH_2$	2262	1310
CMe_3	2280	1267
Ph	2262	1282
C_6H_4Cl-4	2280, 2265	1280
C_6H_4Me-2	2259	1272
C_6H_4Me-4	2255	1262

[a] From ref. 40. [b] C—N stretching frequency for nitrile ligand. [c] W—N stretching frequency for imido ligand.

(CO)(NAr) [139]. The green $(R_2NCS_2)_2W(CO)(NAr)$ will react with additional arylazide at 80°C to form the red bis(phenylimido) complex $(R_2NCS_2)_2W(NAr)_2$ whose structure is likely to be very similar to the Mo analogue. The bis(imido) complex, $(R_2NCS_2)_2W(NAr)_2$, reacts with HCl to form the light orange complex $(R_2NCS_2)_2WCl_2(NAr)$ and $ArNH_3^+Cl^-$. The dichloro complex can also be prepared by direct reaction of $W(CO)(NAr)(S_2CNR_2)_2$ with Cl_2 [25].

Reaction of the dinitrogen complex *trans*-$[W(N_2)_2(dppe)_2]$ with organic acid chlorides (presumably containing HCl) proceeds with carbon—nitrogen bond formation [118,140]. Products **51** are deprotonated by weak base.

$$\begin{tikzcd}(dppe)_2W(N_2)_2 \arrow[r, "RCOCl", "-N_2"'] & Cl(dppe)_2WN_2COR \arrow[r, "HCl"] & \underset{\mathbf{51}}{Cl_2(dppe)_2W(NNHCOR)} \arrow[l, bend left, "Et_3N"]\end{tikzcd} \qquad (29)$$

Reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with excess HCl affords the six-coordinate $[Cl_2W(NNH_2)(PMe_2Ph)_3]$ [108,109]. Various neutral ligands will displace halide to afford salts of the type $[WX(PMe_2Ph)_3L(NNH_2)]^+X^-$. The x-ray crystal structure for the case L = 4-methylpyridine, X = bromide, has been determined and shows asymmetric hydrogen bonding from (NNH_2) to bromide. The (NNH_2) ligand is linear [7,114]. In contrast, *trans*$[W(N_2)_2(dppe)_2]$ was originally thought to react with excess HX (X = Cl, Br) to give the seven-coordinate diazene derivatives $X_2W(NHNH)(dppe)_2$. However these also appear to be monohapto six-coordinate hydrazido complexes [7]. The labile halide can be replaced affording $[XW(NNH_2)(dppe)_2]Y$, Y = BPh_4, ClO_4, PF_6, by treatment with $NaBPh_4$, $LiClO_4$ or $NaPF_6$ [108]. An x-ray crystal structure [141] of the BPh_4 complex confirms the monohapto hydrazido(2-) structure. A W—N bond length of 1.73 Å and a W—N—N bond angle of 171° are observed. For recent work in this area see refs. 183—185.

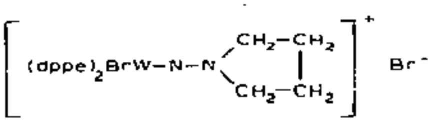
Alkyl bromides *N*-alkylate $W(N_2)_2(dppe)_2$ under the influence of visible light. Subsequent treatment with HBr provides a route to the alkylhydrazido tungsten complexes $[BrW(N_2HR)(dppe)_2]Br$, R = Me, Et, ^tBu [118,119].

$$\begin{tikzcd}{[W(N_2)_2(dppe)_2] + RBr} \arrow[r, "h\nu", "C_6H_6"'] & {[WBr(N_2R)(dppe)_2]} \arrow[r, "HBr"] & {[WBr(N_2HR)(dppe)_2]Br} \arrow[l, bend left, "Et_3N"]\end{tikzcd} \qquad (30)$$

The hydrazido structure has been confirmed for the case R = Me by an x-ray crystal structure [129]. The 1.77 Å W—N bond length and 174° W—N—N bond angle are similar to those noted above for the N_2H_2 derivative. Treatment of $W(CO)_3(PPh_3)(S_2CNMe_2)_2$ with $ArN_2^+BF_4^-$ and NaS_2CNMe_2 affords the brown complexes 52 in 40% yield (Ar = phenyl, *p*-tolyl, *p*-chlorophenyl). The complexes 52 can be either protonated or alkylated to hydrazido derivatives as shown in eqns. 31 a and b. [25].

$$\begin{tikzcd} & {[W(NNHAr)(S_2CNMe_2)_3]^+PF_6^-} & (31a) \\ \underset{52}{W(NNAr)(S_2CNMe_2)_3} \arrow[ur, "HPF_6"] \arrow[dr, "CH_3OSO_2F", "LiPF_6"'] & & \\ & {[W(NNMeAr)(S_2CNMe_2)_3]^+PF_6^-} & (31b)\end{tikzcd}$$

Coordinated dinitrogen has also been dialkylated to afford a dialkylhydrazido complex. Thus irradiation of $W(N_2)_2(dppe)_2$ with excess methyl bromide affords $[WBr(NNMe_2)(dppe)_2]Br$. Similarly with 1,4-dibromobutane there is obtained a product for which NMR spectral evidence indicates structure **53** [119].

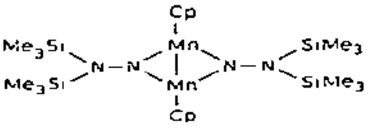

53

The reaction with 1,5-dibromopentane proceeds analogously [7].
A recent report details the preparation of an extensive series of $W(NNH_2)$ derivatives [177]. The product compounds can generally be electrochemically oxidized by one unit but cannot be reduced [177]. A notable reaction of complexes of the type $X_2W(NNH_2)(PR_3)_3$ is their addition to ketones forming azoalkane derivatives containing N—N=CRR′ ligands [143].

(iv) Group VIIB

Manganese

Reaction of bis(cyclopentadienyl)manganese with $Me_3SiNNSiMe_3$ in ether affords a dark green sublimable complex. An x-ray crystal structure showed the diamagnetic product to have the symmetrically bridged structure **54**. A


54

short Mn—Mn distance of 2.39 Å indicates Mn—Mn bonding [66].

Technetium

No technetium complexes containing organoimido or related ligands are known.

Rhenium

The first reported synthesis of organoimido rhenium derivatives was that of Chatt and Rowe [144]. This involved direct reaction of a rhenium oxo complex **55a** with substituted anilines (eqn. 32a); this reaction does not proceed analogously with alkylamines. The same green complex has been prepared by reaction of **55a** with phenyl isocyanate and complex **56b** was similarly prepared [145,146]. Compound **56b** has been prepared by reaction of **55b** with $Ph_3P{=}NPh$ [100]. The phosphinimine route also allows preparation (using

$Ph_3P{=}NCOPh$) of $ReCl_3(NCOPh)(PPh_3)_2$ which is not available through other means [100].

$$L_2Cl_3ReO \xrightarrow{\text{Reagent}} L_2Cl_3Re(NAr) \qquad (32)$$

55a, L = PEt_2Ph **56a**, L = PEt_2Ph
55b, L = PPh_3 **56b**, L = PPh_3

Reagent = $ArNH_2$ (32a); ArNCO (32b), Ph_3PNAr (32c), PPh_3 + ArNHNHCOPh (32d), ArNSO (32e).

Alternative reagents for the conversion of compounds **55** to products **56** are aryl benzoyl hydrazines (eqn. 32d) [32] and aryl sulphynilimines (eqn. 32e) [147], the latter proceeding with loss of SO_2.

The direct aminolysis route (eqn. 32a) has been used to prepare an extensive series of arylimido rhenium(V) derivatives [46] as summarized in Table 11. The dipole moments in the range 4—7 D determined for this series were taken as evidence for structures in which the phosphines were *trans* to one another and in which there is considerable electron donation from N to Re. The x-ray crystal structures of two members of this series have subsequently been determined [148]. The octahedral structures of these $Cl_3L_2Re{=}NC_6H_4X$

TABLE 11

Some arylimido complexes of rhenium(V) of the type $ReX_3L_2(NAr)$ [a]

Complex	Color	M.P. (°C) [b]	Dipole moment (±0.1 D)
$ReCl_3(NPh)(PEt_2Ph)_2$	Green	201—205	5.9
$ReCl_3(p\text{-}NC_6H_4I)(PEt_2Ph)_2$	Green	206—211	—
$ReCl_3(p\text{-}NC_6H_4Br)(PEt_2Ph)_2$	Green	216—220	5.2
$ReCl_3(p\text{-}NC_6H_4Cl)(PEt_2Ph)_2$	Green	207—210	5.0
$ReCl_3(p\text{-}NC_6H_4F)(PEt_2Ph)_2$	Green	177—181	4.6
$ReCl_3(p\text{-}NC_6H_4Me)(PEt_2Ph)_2$	Green	182—184	6.5
$ReCl_3(p\text{-}NC_6H_4OMe)(PEt_2Ph)_2$	Green	168—170	7.2
$ReCl_3(p\text{-}NC_6H_4COMe)(PEt_2Ph)_2$	Dark green	146—148	4.5
$ReCl_3(p\text{-}NC_6H_4CN)(PEt_2Ph)_2$	Dark green	203—210	—
$ReCl_3(p\text{-}NC_6H_4NH_2)(PEt_2Ph)_2$	Yellow	197—199	—
$ReCl_3(p\text{-}NC_6H_4NMe_2)(PEt_2Ph)_2$	Brown	194—197	—
$ReCl_3(pp'\text{-}NC_6H_4C_6H_4NH_2)(PEt_2Ph)_2$	Orange	195—210	—
$ReCl_3(\alpha\text{-}NC_{10}H_7)(PEt_2Ph)_2$	Brown-green	200—204	—
$ReCl_3(NPh)(PEt_3)_2$	Brown-green	132—133	—
$ReI_3(NPh)(PEt_2Ph)_2$	Golden yellow	191—193	—
$ReCl_3(NPh)(Et_2PCH_2CH_2PEt_2)$	Pale green	245—280	—
$ReCl_3(NPh)(Ph_2PCH_2CH_2PPh_2)$ [c]	Pale green	290—293	—
$ReCl_3(NPh)(PPh_3)_2$ [c]	Pale green	215—218	—

[a] From ref. 46 unless otherwise indicated. [b] (Decomposition). [c] From ref. 32.

derivatives where X = —OMe and —COMe are quite similar and contain linear Re≡N—C units. The two phosphines are located *cis* to the arylimido ligand. The Re≡N distances are similar at 1.709 Å and 1.690 Å respectively, despite the fact that methoxy is electron-releasing while acetyl is electron-withdrawing.

The direct aminolysis route has been applied to the preparation of complex **57** as shown in eqn. 33 [149]. The same complex was prepared by the action

$$Re_2O_3(S_2CNEt_2)_4 + 2\ PhNH_2 \rightarrow \underset{\mathbf{57}}{[Re(NPh)(Et_2NCS_2)_2]_2O} + 2\ H_2O \qquad (33)$$

of wet sodium diethyldithiocarbamate on $Re(NPh)Cl_3(PPh_3)_2$. A final route to **57** involved reaction of $Re(NPh)Cl(Et_2NCS_2)_2$ in acetone with sodium carbonate. The starting complex for the last reaction was prepared from $Re(NPh)Cl_3(PPh_3)_2$ and tetraethylthiuram disulphide in dry acetone [149].

Reaction of either $ReCl_3(NR)(PPh_3)_2$ or $ReCl(NR)(S_2CNEt_2)_2$ with $Me_3SiS_2CNEt_2$ affords $Re(NR)(S_2CNEt_2)_3$ where R = phenyl or *p*-tolyl. The brown-green products are obtained in ca. 80% yield. The IR spectra of these complexes suggest that one of the dithiocarbamate ligands is monodentate [25].

$ReCl_3(Ph_3P)_2(NAr)$ where R = *p*-methoxyphenyl reacts with carbon monoxide to afford a carbonyl derivative $ReCl_3(Ph_3P)(CO)(NAr)$ [147]. The weakly bound CO can be displaced by triphenylphosphine or *p*-toluidine. Reduction of several $ReCl_3(Ph_3P)_2(NAr)$ derivatives with sodium borohydride in the presence of CO or PPh_3 proceeds with production of the free aniline and $ReH(CO)_3(PPh_3)_2$ or $ReH_x(PPh_3)_3$ respectively (x probably equals five). Reduction with zinc in ethanol under CO affords $Re(Ph_3P)_2(CO)_3Cl$ and $Zn(ArNH_2)_2Cl_2$. Reaction of $ReCl_3(PPh_3)_2(NAr)$ with oxygen in boiling toluene affords a poorly characterized product thought to be $Re(OPPh_3)(ArNO)Cl_3$ [147]. Similarly Haymore has shown that reaction of $Re_2O(NPh)_2(dtc)_4$ reacts with CO (10 atm., 80°C) to afford $[Re(CO)_3(dtc)]_2$ and $Re(CO)(dtc)_3$ plus as yet uncharacterized organic products [25].

The first reported syntheses of alkylimido rhenium complexes were the salts of the $[(MeN)Re(MeNH_2)_4Cl]^{2+}$ cation. The cation is prepared using K_2ReCl_6 and methylamine as starting materials and has been isolated as the chloride, iodide, perchlorate and tetraphenylborate salts [150]. In addition hydrolysis of the chloro ligand affords the corresponding hydroxy complexes $[(MeN)Re(NH_2Me)_4OH]X_2$, X = iodide or perchlorate. The kinetics of this hydrolysis reaction have been studied [151]. The crystal structure of the $[Cl(MeNH_2)_4Re{\equiv}NMe][ClO_4]_2$ derivative has also been determined. The molecule is octahedrally coordinated with the methylimido group *trans* to Cl. A linear Re≡N—C unit (Re≡N bond length 1.694(1) Å) is observed. The amine nitrogen atoms form an almost perfect square but the metal is displaced somewhat from the plane, the average amine N—Re—Cl angle being 84.6° [151].

The reaction of $ReOCl_3(PPh_3)_2$ with 1,2-dialkylhydrazine hydrochlorides proceeds with replacement of oxo by an alkylimido ligand [32]. Once formed, the triphenylphosphines can be replaced with other ligands allowing preparation of a variety of complexes as shown in Table 12.

$$ReOCl_3L_2 + RNHNHR \cdot HCl \xrightarrow{PPh_3} Cl_3L_2Re(NR) + RNH_3Cl + OPPh_3 \qquad (34)$$

The complex $Re(NMe)Cl_3(PPh_3)_2$ is inert to HCl in benzene but reacts with elemental chlorine in CCl_4 to give $ReCl_4(PPh_3)_2$ [32]. With carbon monoxide *cis*- and *trans*-$[ReCl(CO)_3(PPh_3)_2]$ are formed [48,152]. Of importance is the demonstration that methylimido complexes 58 can be reversibly deprotonated with pyridine to yield complexes, 58, which contain NCH_2 groups. The ethyl- and propylimido complexes react similarly.

$$\underset{\textbf{58}}{ReCl_3(NMe)(PPh_2R)_2} + 2\ py \rightarrow \underset{\textbf{59}}{ReCl_2(N{=}CH_2)(py)} + py \cdot HCl \qquad (35)$$

$$\textbf{59} + 2\ HCl \rightarrow \textbf{58} + py \cdot HCl \qquad (36)$$

58 is also deprotonated by the more sterically hindered base triethylamine but stable products result only if additional ligand is available [48,152] as in eqn. 37.

$$ReCl_3(NMe)(PMe_2Ph)_2 + PMe_2Ph + NEt_3 \rightarrow [ReCl_2(N{=}CH_2)(PMe_2Ph)_3] + NEt_3 \cdot HCl \qquad (37)$$

The crystal structure of $ReCl_3(NMe)(PPh_2Et)_2$ has been determined [24]. Coordination around Re is distorted octahedral with the phosphines *trans* to one another and two Cl atoms *trans* to one another in the basal plane. The other vertices are occupied by the third Cl atom and by the methylimido group which exhibits a Re≡N bond length of 1.685(11) Å and Re—N—C angle of 173°.

The complex $Me_3SiORe(N^tBu)_3$ has been prepared by treatment of trimeth-

TABLE 12

Alkylimido complexes of rhenium (V) [a]

Complex	Appearance	Mol. wt. [b]	M.P. (°C) [c]
$Re(NMe)Cl_3(PPh_3)_2$	Light blue	—	199—202
$Re(NMe)Cl_3(PEtPh_2)_2$	Grey-blue needles	810(749)	196—197
$Re(NMe)Cl_3(PEt_2Ph)_2$	Bright blue needles	—	189—192
$Re(NEt)Cl_3(PPh_3)_2$	Blue prisms	insoluble	196—198
$Re(NEt)Cl_3(PEtPh_2)_2$	Blue needles	710(753)	193—196
$Re(NPr)Cl_3(PPh_3)_2$	Blue prisms	insoluble	188—190
$Re(NC_6H_{11})Cl_3(PPh_3)_2$	Dark blue prisms	870(913)	177—180
$Re(NMe)Cl_3(Ph_2PCH_2CH_2PPh_2)$	Violetblue	insoluble	259—263
$Re(NMe)Cl_3(AsMe_2Ph)(PPh_3)$	Light blue prisms	720(765)	198—201
$Re(NMe)Cl_3(AsMe_2Ph)_2$	Blue prisms	—	185—188

[a] From ref. 32. [b] Cryoscopic, benzene; calculated values in parentheses. [c] (Decomposition).

ylsilyl perrhenate with $^{t}\mathrm{BuNH(SiMe_3)}$. The imido ligands are hydrolytically sensitive [73].

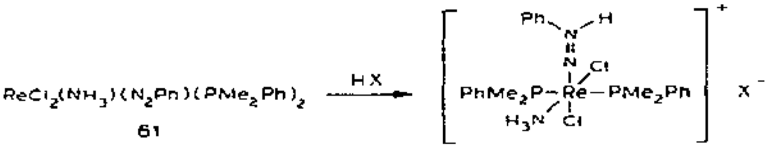
Lewis acid adducts of $\mathrm{(PEt_2Ph)_3X_2ReN}$ prepared by Chatt and Heaton [153] are relevant to imido chemistry. These complexes are asserted to have structure **60** where X = Cl or Br and Q = $\mathrm{BCl_3}$, $\mathrm{BBr_3}$, $\mathrm{BF_3}$ or $\mathrm{PtCl_2(PEt_3)}$.

$$\mathrm{(PEt_2Ph)_3X_2Re{\equiv}N \rightarrow Q}$$

60

Changes in Re—Cl frequencies upon coordination are noteworthy. In the free nitride the difference in stretching frequency between the *cis* and *trans* chlorides is ca. 70 cm^{-1} but this falls to 20 cm^{-1} upon coordination of $\mathrm{BCl_3}$ [153]. This suggests that the *trans* influence is greater for the nitride ligand than for the $\mathrm{NBCl_3}$ ligand.

The reversible protonation of the phenyldiazo complex **61** with HBr or HCl occurs on the phenyl nitrogen to afford the corresponding phenylhydrazido complex, **62** [154]. The crystal structure of **62** shows the NNHPh ligand to be planar and the Re—N—N angle to be 172°. The Re—N bond length is 1.75 Å, ca. 0.06 Å longer than in Re(V) organoimido derivatives. The reverse of eqn. 38 represents an interesting "aza analog" of eqn. 35 (see also ref. 192).



61

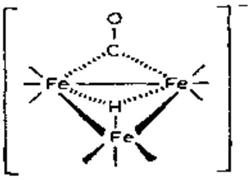
62

(38)

(v) Group VIII

Iron

The bridging alkylimido iron cluster, $\mathrm{Fe_3(CO)_9H_2(NR)}$, **64**, was prepared by Andrews and Kaesz in their demonstration of the stepwise reduction of acetonitrile on the face of a triiron nonacarbonyl cluster [41]. The reaction of the $\mathrm{HFe_3(CO)_{11}^-}$ anion, **63**, with acetonitrile followed by acidification and treatment with $\mathrm{H_2}$ gives the deep red product **64** (R = ethyl). Alternatively, reaction of **63** with nitro compounds under aprotic conditions affords the anions **65** where R is ethyl or phenyl. Protonation then converts these to the corresponding product **64**.



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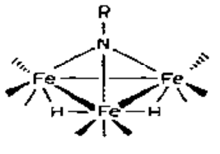
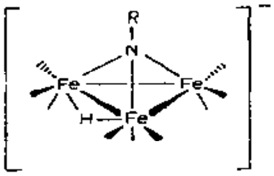


64



65

Reaction of $Fe_2(CO)_9$ with either methyl azide or nitromethane affords mixtures of products including a species $(MeN)_2Fe_3(CO)_9$ [155]. A subsequent crystal structure [64] has shown this to have the structure shown previously (sect. B(vii)) in Fig. 1. As previously noted, two of the Fe—Fe distances are indicative of Fe—Fe bonding [2.462(7) Å] while the third is a non-bonded contact of 3.044(8) Å. Treatment of $Fe_3(CO)_{12}$ with nitrobenzene apparently gives an analogous product $Fe_3(CO)_9(NPh)_2$ [155]. In contrast, room temperature reaction of $Fe_2(CO)_9$ with trimethylsilyl azide affords $(Me_3SiN)Fe_3(CO)_{10}$ [156]. The crystal structure of this derivative exhibits a CO molecule bonded to the face of the cluster opposite the imido ligand as in Fig. 8. The molecule possesses three equivalent Fe—Fe bonds and the three Fe—N bond lengths average 1.90 Å [63]. The ethylimido analog $(EtN)Fe_3(CO)_{10}$ is apparently isostructural with the trimethylsilyl derivative [178].

Another related complex is $[Fe_3(CO)_9(NR)S]$, R = *p*-tolyl which is one of the products from treatment of $Fe_2(CO)_9$ with *N*-*p*-tolylsulfurdiimine. The complex has the basic structure shown in Fig. 1 where one bridging imido ligand has been replaced by a triply bridging sulfur atom [38]. A *t*-butylimido complex with a cubane-like structure, $Fe_4(NO)_4S_2(N^tBu)_2$, has been prepared and structurally characterized [173]. A complex initially reported [174] as the imido dimer $[Fe(CO)_3NH]_2$ was subsequently shown [175] to be an amido-bridged dimer.

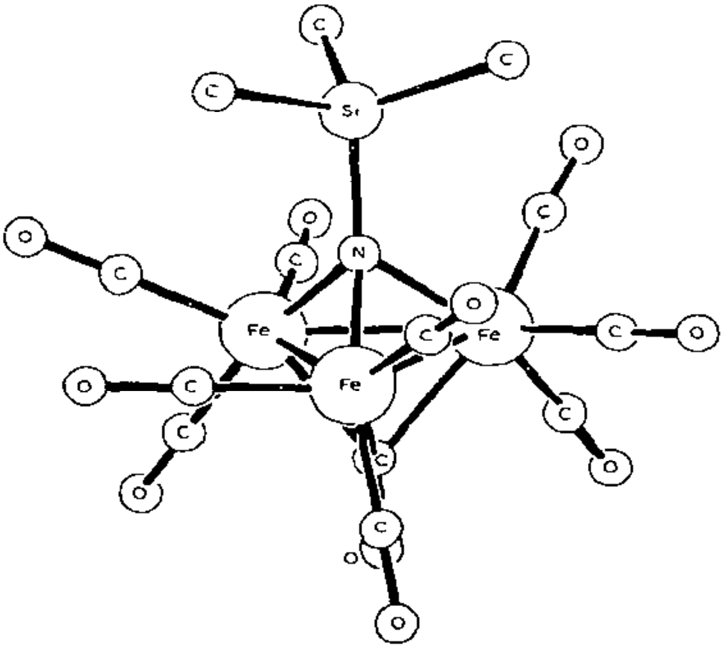


Fig. 8. The structure of $(Me_3SiN)Fe_3(CO)_{10}$ from ref. 63.

Ruthenium

The reaction of triruthenium dodecacarbonyl with nitrobenzene or phenyl isocyanate affords a mixture of two products: $Ru_3(CO)_{10}(NPh)$ and $Ru_3(CO)_9(NPh)_2$ [157]. The structure of the former compound is thought to be analogous to that in Fig. 8 while the latter is presumably similar to that in Fig. 1. The former compound can be converted to the latter with $PhNO_2$ in refluxing benzene. Treatment of $Ru_3(CO)_{10}(NPh)$ with H_2 in turn produces a hydrido complex $H_2Ru_3(CO)_9(NPh)$ which is assigned a structure analogous to **64** above [157].

$Ru_3(CO)_{12}$ reacts with 2 H-hexafluoropropyl azide to afford a product $Ru_3(CO)_9(NC_3HF_6)_2$ again thought to be analogous to the iron complex of Fig. 1. Reaction of the same azide with $(Ph_3P)_2Ru(CO)_3$ gives the mononuclear complex $(Ph_3P)_2Ru(CO)_2(NC_3HF_6)$ [45].

Osmium

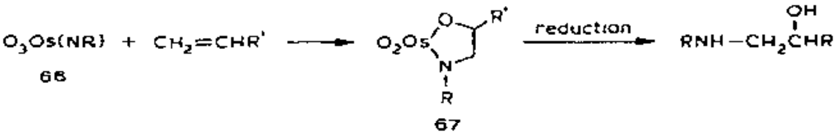
Metallation of aniline with $Os_3(CO)_{12}$ gives a $H_2Os_3(CO)_9(NPh)$ species presumed to be analogous to compound **64**. The corresponding *p*-fluoro and *p*-methyl derivatives are prepared from the substituted anilines [31]. Reaction of $(Ph_3P)_2Os(CO)_3$ with 2H-hexafluoropropyl azide yields $(Ph_3P)_2Os(CO)_2(NC_3HF_6)$ as the mononuclear product [45].

The reaction of "$OsOCl_3(PPh_3)_2$" with aroylphosphinimines, $Ph_3P{=}NCOAr$, was originally reported to yield the corresponding arylimido complexes $OsCl_3(NAr)(PPh_3)_2$. The products for the cases where Ar = phenyl, *p*-methoxyphenyl and *p*-chlorophenyl are pink crystalline air-stable solids with magnetic moments of 2.2–3.3 B.M. [100,158]. More recent work has shown that the starting osmium oxo complex is really a mixture of $OsO_2Cl_2(PPh_3)_2$ and $OsCl_4(PPh_3)_2$ [159] and that the pink products are really benzonitrile complexes, $OsCl_3(NCAr)(PPh_3)_2$ [25].

The first alkylimido transition metal complex to be prepared was *t*-butylimidotrioxo osmium ("*t*-butyl osmiamate") reported by Clifford and Kobayashi in 1956 [49]. The compound is prepared by reaction of OsO_4 with *t*-butylamine in pentane [47], ligroin [160] or water [36]. The corresponding compounds containing other tertiary alkyl groups have been prepared, i.e. *t*-amyl [36], 1-adamantyl [161] and 2,4,4-trimethyl-2-pentyl [160]. The reaction between the osmium tetroxide and the amine initially gives an amine complex, $OsO_4(RNH_2)$, which then dehydrates in the solid state or in aqueous solution to afford the imido compound [26]. Attempts to extend this reaction to amines other than these tertiary alkyl derivatives have been unsuccessful although the initial unstable amine—OsO_4 complex can be isolated in certain cases [26]. OsO_4 reacts with methyl amine at −78°C but the product decomposes violently on warming [49]. It is possible that a decomposition pathway similar to eqn. 35 is involved. Arylimido derivatives $O_3Os(NAr)$ can be isolated in low yield and purified by chromatography from the reaction of OsO_4 with anilines. However the major course of the reaction appears to involve oxidation of the aniline to organic products [25].

The complex (^{t}BuN)OsO$_3$ does not react with cold dilute nitric acid. It is decomposed by aqueous alkali and is reduced by concentrated hydrochloric acid with cleavage of the C—N bond to afford OsCl$_5$N^{2-} [47]. Milas and Iliopulos noted that (^{t}BuN)OsO$_3$ reacts with olefins but the nature of the reaction was not investigated [160]. More recently, extensive research by Sharpless and co-workers led to the discovery of conditions under which addition of imido nitrogen to olefins occurs; this reaction has been developed into a useful synthetic tool [26,161].

Addition of (^{t}BuN)OsO$_3$ to olefins proceeds with *cis* stereochemistry analogous to the reaction of olefins with OsO$_4$. The carbon nitrogen bond forms at the less substituted carbon of the olefinic double bond (eqn. 39). Cyclic intermediate **67** can then be reduced to the amino alcohol with, for instance, lithium aluminum hydride or aqueous sodium bisulfite [26]. The catalytic oxyamination of olefins based on eqn. 39 using 1% OsO$_4$ and either chloramine-T-trihydrate [162,163] or *N*-chloro-*N*-argentocarbamates [164] has been described.



(39)

Reaction of O$_3$Os(N^{t}Bu) with tertiary amines affords complexes of the type (R$_3$N)OsO$_3$(N^{t}Bu). Well characterized 1 : 1 adducts of this type have been prepared for R$_3$N = quinuclidine and 3-quinuclidone as well as 2 : 1 adducts with diazabicyclooctane and hexamethylenetetramine [44].

The bis- and tris-alkylimido osmium derivatives have been prepared by means of the corresponding phosphinimines according to eqns. 40 and 41 [36]. These compounds also react with monosubstituted and *trans*-disubstituted alkenes to afford *cis* vicinal diamines upon reductive workup [36].

$$\mathbf{66} + \mathrm{Ph_3P{=}NR'} \rightarrow \underset{\mathbf{68}}{\mathrm{O_2Os(NR)(NR')}} \tag{40}$$

$$\mathbf{68} + \mathrm{Bu_3PN^tBu} \rightarrow \mathrm{OOs(N^tBu)(NR)(NR')} \tag{41}$$

Tetraimido osmium derivatives of the type (ArSO$_2$N)Os(N^{t}Bu)$_3$, Ar = 2,4,6-trimethylphenyl, 2,4,6-triisopropylphenyl or *p*-tolyl, have now been prepared. Their synthesis involves reduction of (^{t}BuN)$_3$OsO with triphenylphosphine followed by reoxidation with ArSO$_2$NNaCl. The latter two complexes have been shown to react cleanly with dimethyl fumarate [44].

Cobalt

The only organoimido derivative of cobalt reported to date is the cluster Co$_4$(NO)$_4$(N^{t}Bu)$_4$. It is prepared by treatment of Co(NO)(CO)$_2$(PPh$_3$) with *t*-butylsulfurdiimine. The molecule has a cubane-like structure in which each organoimido ligand bridges three cobalt atoms [165].

Rhodium

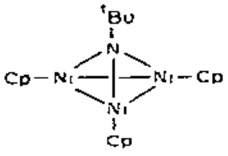
Reaction of $(Ph_3P)_3RhCl$ with 2 H-hexafluoropropyl azide affords $(Ph_3P)_2RhCl(NC_3HF_6)$. The compound reacts with hexafluoroacetone and acetyl chloride to afford $(Ph_3P)_2Rh(NC_3HF_6)[(CF_3)_2CO]Cl$ and $(Ph_3P)_2Rh(NC_3HF_6)(COCH_3)Cl_2$, respectively. Reaction of $(Ph_3P)_2RhCl(NC_3HF_6)$ with CO gives $(Ph_3P)_2Rh(NC_3HF_6)(CO)Cl$ and $(Ph_3P)_2Rh(CO)Cl$ [45].

Iridium

Hexafluoroazomethane reacts with *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I) to yield a mixture of *cis*- and *trans*-$(Ph_2PMe)_2Ir(CO)Cl(NCF_3)$. Both are obtained as white crystalline solids, the former containing a molecule of benzene of crystallization [13,166]. Similarly, treatment of $(Ph_3P)_2Ir(CO)Cl$ with 2H-hexafluoropropyl azide gives $(Ph_3P)_2Ir(CO)Cl(NC_3HF_6)$ [45]. From $(Ph_3P)_2Ir(N_2)Cl$ and the same azide, the four-coordinate complex $(Ph_3P)_2IrCl(NC_3HF_6)$ is obtained. The latter product reacts with mercuric chloride to form $(Ph_3P)_2Ir(NC_3HF_6)(HgCl)Cl_2$. Carbonylation of $(Ph_3P)_2IrCl(NC_3HF_6)$ also provides a route to $(Ph_3P)_2Ir(CO)Cl(NC_3HF_6)$ [45].

Nickel

Treatment of either Cp_2Ni or $[CpNi(CO)]_2$ with *N*-*t*-butylsulfurdiimine, $(^tBuN)_2S$, produces a black, paramagnetic complex, **69**. A preliminary x-ray crystal structure indicates considerable distortion from C_{3v} symmetry. The three Ni—Ni distances are 2.34, 2.27 and 2.21 Å [39].



69

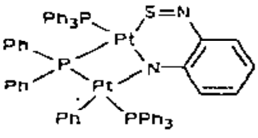
Palladium

Reaction of $(Ph_2PMe)_4Pd$ with 2H-hexafluoropropyl azide in benzene yields the deep red, air-sensitive tricoordinate complex $(Ph_2PMe)_2Pd(NC_3HF_6)$ [45].

Platinum

The air-stable $(Ph_2PMe)_2Pt(NC_3HF_6)$ can be prepared from $(Ph_2PMe)_4Pt$ and like its palladium counterpart is a microcrystalline solid [45].

Reaction of $[(Ph_3P)_2Pt(C_2H_4)]$ with 5,6-dimethyl-2,1,3-benzothiadiazole affords **70**. The crystal structure of **70** was determined and the bond distances in the six-membered metallocycle indicate extensive bond delocalization. The ^{31}P NMR spectrum shows a large upfield shift for the bridging diphenylphosphido group as expected for a four-membered ring [167].



70

D. CONCLUDING REMARKS

Organoimido transition metal compounds were unknown prior to 1956. In contrast, the preceding descriptive chemistry discussion indicates that organoimido or related complexes are now known for all of the group IV through group VIII transition metals except technetium. Moreover, a casual inspection of publication dates in the references indicates that research in this area is accelerating. This trend parallels a growing interest in multiply-bonded ligands in general; it reflects a new appreciation of the role played by such (carbene, oxo, etc.) species in important chemical transformations.

Organoimido complexes are well suited to the study of transition metal multiple bonds. The robust character of the M≡NR bond has allowed the preparation of (NR) complexes for a greater diversity of metals than is known at present for alkylidene or alkylidyne analogs. Compared with oxo complexes, organoimido compounds are often more soluble in organic solvents. The effects of multiple bonding tend to be more pronounced in M(NR) than in M(O) due to the lower electronegativity of nitrogen vs. oxygen. The organic moiety in M(NR), which is not present in oxo species, provides a convenient probe of bonding and electron distribution. This information is then accessible by ^{13}C NMR, studies on M—N—C bond angles and other techniques. In principle, changing the organic function could represent a method for "tuning" the properties of the ligand or perhaps for attaching the complex to a stationary support.

The search for new synthetic routes to organic nitrogen compounds will no doubt remain an important impetus for studying organoimido complexes. The osmium catalyzed oxyamination of olefins developed by Sharpless et al. [162] is an impressive application of organoimido chemistry to homogeneous catalysis. In the area of heterogeneous catalysis, current industrial practice includes several processes which are likely to involve intermediates related to imido complexes. The Haber ammonia process and the ammoxidation of propylene to acrylonitrile [116] are two significant examples. Imido and hydrazido complexes seem to be useful models for intermediates in enzymatic nitrogen fixation. Recently hydrazine has been identified as a product upon quenching a nitrogenase enzyme, thus implicating intermediates similar to $Mo(N-NH_2)$ [130]; this will undoubtedly further stimulate work in this area.

The considerable stability of organoimido complexes wherein nitrogen is triply bonded to metal has been noted. A loose parallel can be drawn with the well known stability of another triple-bonded nitrogen species, namely dinitrogen itself. Unfortunately. this same stability has thus far restricted the development of reaction chemistry in which the (NR) group is transferred from the complex into some other molecule. One can anticipate the synthesis of additional complexes containing bent imido ligands; these longer, weaker metal—nitrogen bonds should show enhanced reactivity. Moreover, as ancillary ligands (for instance, in organometallic complexes), organoimido ligands can be expected to stabilize high oxidation states and could impart other useful properties such as good solubility and low coordination number. Undoubtedly, research on transition metal complexes containing organoimido and related ligands will continue to afford interesting new compounds, new chemistry and new insights into the chemical transformations of tightly bound ligands.

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