Computational Studies of Transition Metal−Main Group Multiple Bonding

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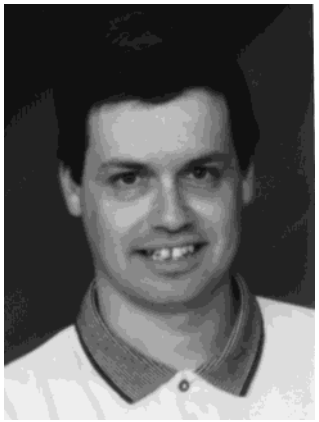
1. Preamble

Complexes with a multiple bond between a transition metal and main group element (TM=MG) have been studied intensively by inorganic and organometallic chemists. TM=MG species have been probed not only by experimental techniques (most notably NMR, infrared spectroscopy, and X-ray crystallography) but by a range of computational tools from extended Hückel to correlated, ab initio wave functions. Interest in TM=MG complexes is due in large part to the many important chemical processes, catalytic and stoichiometric, they participate in. The monograph by Nugent and Mayer, although now more than a decade old, still provides the most comprehensive overview of TM=MG chemistry in industry and biology.[1] The diversity of TM=MG chemistry has made it a fruitful area in the search for novel inorganic structure and reactivity. Similarly, it has emerged that this chemical diversity provides a rigorous challenge in the development of more efficient and reliable techniques for modeling of inorganic and organometallic chemistry.

2. Scope

This review focuses on the fundamental nature of transition metal−main group multiple bonding. Many other papers, covering the numerous reactions TM=MG species participate in, are available.[2] The present article treats coordinatively saturated complexes. Diatomics such as ZrO and $ScSe^+$ and "mass spec" entities such as $M^+{=}SiH_2$ have received considerable attention, some of these studies being the most complete theoretical treatments reported on multiply bonded complexes.[3] Of particular interest in the present contribution is comparing and contrasting multiple bonds involving light (TM=MG) elements with their less well studied, experimentally and computationally, heavy element ($TM{=}MG_{hvy}$) congeners.



Tom Cundari obtained his B.S. (1986) from Pace University (New York City) and Ph.D. (1990) in inorganic chemistry from University of Florida under the supervision of the late Russ Drago. After a postdoctoral year with Mark Gordon at North Dakota State University, he joined the faculty at The University of Memphis. This contribution is dedicated to the memory of Russ Drago—friend and mentor.

3. General Overview of Multiply Bonded Complexes

Defining a multiple bond is often problematic for TM complexes as compared to organic and main group counterparts, given the potential for up to two TM dπ−MG pπ interactions where available lone pairs exist on the MG fragment and the polarity of the bonds (σ and π) involved. The polarity issue is particularly troublesome given the predominance of TM=MG complexes where the multiple bond is formed by coordination of an electronegative, first MG row ligand to a more electropositive early-to-middle TM. Additionally, the nature of the metal−ligand π interactions can depend on the geometry of the TM=MG moiety as discussed in section 6b. Our operational definition of a multiply bonded transition

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Scheme 1

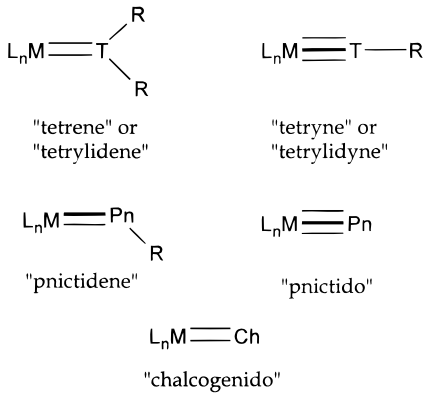


Table 1. Occurrences of TM═MG Complexes within the Main Group[a]

main group	number	%
14	1036	20
15	993	19
16	3102	60
period	**number**	**%**
2	4833	94
3	234	5
4	46	1
5	17	0
6	1	0

[a] Search done utilizing the Cambridge Structural Database[84] for the TM═MG motifs in Scheme 1. The CSD is limited to systems containing at least one carbon atom, although it is unlikely this will change the results significantly.

metal complex is structural, Scheme 1, and is based on the presence of MG fragments known to form multiple bonds in main group chemistry (e.g., $=CR_2$, =NR, and =O) and which are coordinated in a terminal fashion (i.e., R is not a TM fragment).

Nearly all complexes with a multiple bond between TM and MG elements can be divided into three subsets—those in which the metal forms a multiple bond to a tetrel (T, carbon group),[4] pnictogen (Pn, nitrogen group),[5] or chalcogen (Ch, oxygen group).[6] The results of a search of the Cambridge Structural Database (CSD) for the motifs in Scheme 1 are collected in Table 1. Not surprisingly, the overwhelming majority (94%) of structurally characterized TM═MG species in the CSD involve a second period MG element (C, N, O). Most TM═MG species involving heavier MG elements involve chalcogens (89% of $TM{=}MG_{hvy}$). Within the CSD database there are similar numbers of TM complexes with a terminal multiple bond to a tetrel (20%) or pnictogen (19%), and roughly three times as many TM═Ch (60%), Table 1.

Of course, transition metals also form multiple bonds with other transition metals. The chemistry of metal−metal multiply bonded species has emerged as a robust field[7] over the past four decades. One can also envision partial multiple bonding character between TMs with the appropriate electronic structure and the MG families that flank groups 14 and 16, the triels (boron group) and halogens. For example, several groups have discussed the formulation (albeit controversial!) of FeGa triple bonds,[8] and based on EHT calculations, Johnson et al. suggest significant Ru−X π-donation (X = univalent ligand, including Br, Cl, and I) for Cp*Ru(L)X, L = phosphine.[9] The π-donation in the latter mitigates unsaturation at Ru, making the complexes more stable than might have been supposed from their 16-electron count. It should be noted that evidence exists for partial multiple bonding in complexes with formally unidentate ligands such as alkoxides (L_nM-OR, bond angles about O that are significantly greater than 109.5°) and amides (L_nM-NR_2, coordination about N approaching trigonal planar) and their heavier congeners.[10,11]

The present contribution will focus on multiply bonded TM complexes of tetrels, pnictogens, and chalcogens. The main structural motifs observed, experimentally by techniques such as crystallography and computationally through geometry optimization, and which are the subject of this review, are shown in Scheme 1. Variations on the basic themes depicted in Scheme 1 exist, for example, linear pnictidenes ($M-Pn-R \approx 180°$)[12] are known as well as bent pnictidenes ($M-Pn-R \ll 180°$).[13] Until recently the family of silylenes ($L_nM{=}SiR_2$) was largely limited to examples in which a Lewis base is coordinated to the Si, rendering it four-coordinate and clouding the nature of the MSi multiple bonding.[14,15] Finally, the bond order designations in Scheme 1 should be viewed as artistic and not chemical. As discussed below, there is considerable contention, particularly for chalcogens and pnictogens, about this aspect of TM═MG bonding due to the presence or lack of lone pairs on the MG element. This review concentrates on the divalent Ch, PnR, TR_2 series although many of the conclusions can be extended to trivalent Pn and TR species.

It is appropriate to conclude this section with a word about metals that form TM═MG complexes, although the selection is not as narrow as for MG participants. Structurally characterized examples of multiply bonded complexes are known from the titanium through nickel triads. Reported examples of TM═MG complexes are more numerous for TMs in the middle of the series (reaching a maximum for the chromium triad) and then decrease more or less symmetrically to the left and right in the series, Figure 1.[1,16] This can be ascribed to the fact that late TMs would have occupied (TM dπ−MG pπ)* antibonding orbitals for typical TM formal oxidation states and structural motifs (square planar, tetrahedral, square pyramidal, and octahedral). Occupation of (TM dπ−MG pπ)* orbitals will obviously weaken the TM═MG linkage. As pointed out by Mayer, such a situation also leads to polarization of the multiple bond that should destabilize it kinetically and encourage oligomerization reactions.[17]

For the earliest TMs, there has been tremendous progress recently in the number of examples of TM═MG complexes for light and heavy main group elements. This is perhaps best illustrated by the structural characterization by the Parkin group of the entire series of nonradioactive chalcogenides of the form $Cp^{\dagger}{}_2M(py)(Ch)$, M = Zr, Hf; Ch = O, S, Se, Te.[18] Bona fide examples of late transition metal multiply

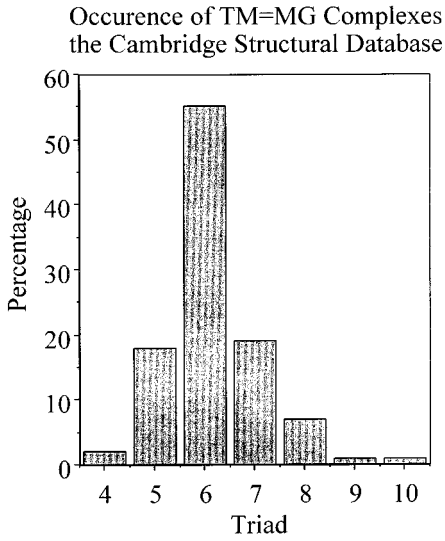


Figure 1. Histogram showing the occurrence of TM=MG complexes in the CSD as a function of triad.

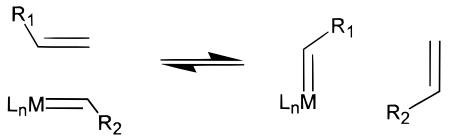
bonded complexes are also beginning to appear, for example, Cp*Ir(NR)[19] (R = ^{t}Bu, Ar, Ar*, SiMe$_2{}^t$Bu) and IrMes$_3$O,[20] although more research, particularly examples with heavy main group elements, would be welcome.

4. Multiply Bonded Complexes in Inorganic and Organometallic Chemistry

Before embarking on a review and analysis of TM=MG complexes, it is best to put their importance in chemistry into perspective.[1] Indeed, their observed chemistry has provided considerable motivation for researchers to investigate the nature of the TM=MG bond. Inarguably, the most important and well-understood families of TM=MG complexes are those in which the MG element is the lightest member of their respective main group. Of these, oxo complexes (L_nM=O) are the oldest and probably most well studied. Oxos have been implicated in biological and industrial catalytic oxidations. The active intermediate of the enzyme cytochrome P-450 is proposed to be a ferryl.[21,22] Cytochrome P-450 is responsible for oxidation of xenobiotics, engendering greater hydrophilicity in the product and assisting removal from the body. Industrial oxidations such as the conversion of butane to maleic anhydride are effected by vanadium oxides.[23] Bismuth molybdate catalysts have been used for conversion of C_4 compounds to butadiene and propylene to acrolein.[1] Wide arrays of synthetic oxidations, stoichiometric and catalytic, involve metal-oxos such as osmium-catalyzed dihydroxylation[24] and manganese-catalyzed epoxidation.[25] In a different arena, Tc-oxos of the general form TcL$_4$O (L = σ-donor ligands) are used in radiopharmaceutical imaging.[26]

Electrophilic or Fischer-type carbenes[27] have found tremendous utility in organic synthetic transformations ranging from cyclopropanation to C−H insertion to ring-forming reactions (for example, benzannulation with chromium carbenes).[28] The synthetic utility of nucleophilic (Schrock-type[29]) carbenes has largely been limited to the olefination of carbonyls.[30]

Scheme 2



A major impetus for research on Schrock-type carbenes, more commonly called alkylidenes, has come from their role in olefin metathesis, Scheme 2. Early research into olefin metathesis (e.g., the Phillips triolefin process − conversion of propylene to butene and ethylene) with metal-oxos and alkyl promoters suggested the intermediacy of alkylidenes.[31] Some of the earliest reported computations on TM=MG complexes using high-level wave functions supported alkylidene intermediates.[32] Experiments by the Schrock group with well-characterized imido-alkylidene (M(OR)$_2$(NAr)(=C(H)R′), M = Mo, W; R = hydrocarbyl or fluorinated hydrocarbyl; Ar = substituted aryl, most commonly 2,6-C$_6$H$_3{}^i$Pr$_2$; R′ = hydrocarbyl) catalysts have considerably expanded our knowledge of the stereoelectronic factors controlling olefin metathesis.[29] The Schrock catalysts have utility in their own right for the synthesis of functional polymers as they are more tolerant of functional groups than traditional olefin metathesis systems. The Schrock complexes operate as ROMP (ring-opening metathesis polymerization) or ADMET[33] (acyclic diene metathesis) catalysts and yield "living" polymers (the metal remains coordinated to the growing polymer) affording exquisite control over polymer properties. Grubbs has extended this chemistry to Ru-alkylidene catalysts of the form RuCl$_2$(PR$_3$)$_2$(=C(R)R′); (R, R′ = aryl, alkyl).[34]

Imido complexes (L_nM=NZ) are roughly the same "age" as carbenes. The first imido was reported by Clifford and Kobayashi (O$_3$Os(N^{t}Bu) from the reaction of OsO$_4$ and ^{t}BuNH$_2$) in 1956,[35] eight years before the first carbene complex of Fischer and Maasböl (CO)$_5$W(=C(OMe)Me).[27] However, until recently the computational study of imidos lagged behind that of other first main group row TM=MG complexes. Indeed, it was not until 1992 that the first comprehensive study of TM imidos using high-level wave functions was reported.[36] Wigley's authoritative review is indicative of the growing interest in imido chemistry.[5] Apart from nitrogen fixation,[37] research on TM−nitrogen multiply bonded complexes has focused on their ability, particularly for early transition metals, to effect selective C−H activation.[38] Imidos also model the isovalent, but more industrially important, oxos, but the Z substituent on the former affords control of their reactivity and forestalls oligomerization reactions that complicate the analysis of C−H activation by metal oxos.[39]

There is growing interest in multiply bonded complexes of heavier main group elements (TM=MG$_{hvy}$).[4−6,13−15] To date, scientific and technological applications of these species are limited, but given the rapid growth of interest and the myriad of new bonding regimes they display (in relation to light MG congeners) this may be just a matter of time. Multiply bonded complexes are envisaged as intermediates in chemical vapor deposition of transition

metal sulfides, silicides, etc. and silane polymerization.[40] Sulfidos ($L_nM{=}S$) are proposed intermediates in xanthine oxidase[41] and relevant to hydrodesulfurization.[42] Stephan and co-workers have exploited the chemistry of phosphinidenes ($L_nM{=}PR$) for an interesting array of group transfer reactions.[43] In many respects, $TM{=}MG_{hvy}$ complexes, despite the amount of recent research, represent a virtually untapped resource for novel chemistry. Computations suggest that weaker π-bonding, although detracting from stability, may give $TM{=}MG_{hvy}$ utility in synthetic transformations by providing a platform that is easily tunable through ligand/substituent modification.[44] One area which is virtually unexplored, experimentally and computationally, is $TM{=}MG_{hvy}$ species involving the later transition metals.

5. Multiply Bonded Complexes as Ideal Testbeds for New Theoretical Methods?

Structurally characterized examples of TM=MG species are known for each group of the transition series except the Sc-, Cu-, and Zn-triads.[1,16,17] They cover the most relevant TM coordination numbers from three (e.g., $Os(NAr)_3$ and $W(N^tBu)(OSi')_2$)[45,46] through six (e.g., $(CO)_5W{=}C(OEt)Ph$ and $ReOF_5$)[47,48] and the dominant positive formal oxidation states up to +8 (OsO_4 and RuO_4).[1,49] Thanks to recent experimental efforts, multiple bonds can now be found with the hard first row MG elements (C, N, and O) and their softer congeners from the subsequent main group periods.[4−6,13−15]

The ability to stabilize varied coordination environments, which we have in our group termed chemical diversity, is a general property of most TMs and is evident in TM=MG complexes. In our research, we have found multiply bonded complexes to be an ideal "testbed" for theoretical methods—ab initio, semiempirical quantum, and molecular mechanics—aimed at improved modeling of transition-metal-containing inorganic and organometallic compounds.[50−54] They provide a stringent test of computational methods. In the following paragraph we choose a few examples from our work to illustrate this aspect of TM=MG chemistry.

a. Re–Oxo Complexes

The first example comes from a collaboration with the Mayer group.[55] As part of this theory−experiment research, four complexes were evaluated with ECP-based ab initio techniques, Figure 2. In this case, formal rhenium oxidation states range from Re^{I} (d^6) to Re^{VII} (d^0) and coordination numbers from three to six. Hence, there is a single inorganic functionality (ReO) in four distinct chemical environments, Figure 2. As such, accurate modeling of each with a single, compact computational scheme with a flexible basis set is necessary. However, for large complexes one must balance such concerns with those of computational efficiency. Upon comparison with experimental data it was found that predicted bond lengths and bond angles involving the Re differ from experiment, on average, by only 0.02 Å and 2° using the Stevens effective core potentials and attendant valence basis

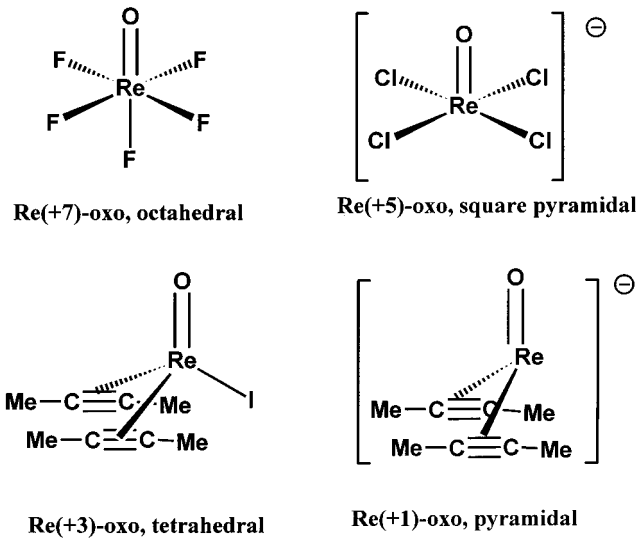
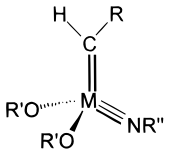


Figure 2. "Chemically diverse" assortment of Re-oxo complexes studied with ECP methods.[55]

Scheme 3



sets.[56] Fortunately, an RHF wave function is suitable as the need to go to correlated techniques would make such calculations onerous.

b. Schrock-Type ROMP Catalysts

Sometimes in the study of multiply bonded complexes, one can find chemical diversity in a single compound. A good example comes from a study of models (R, R′, R″ = H; M = Mo, W) of Schrock's ROMP catalysts, Scheme 3. In one complex there is a single, double, and triple bond (formulated as such given the near linear MNR″ coordination) with elements of differing electronegativity. Description of the bonding in these TM=MG species, and many others, is made easier by the fact that the metal is in its highest formal oxidation state (d^0). However, the agreement between theory (RHF/SBK(d)) and experiment is excellent (≈0.03 Å and ≈3° for metal-containing bond lengths and angles, respectively).[57] As in the previous example, inclusion of polarization functions to a valence double-ζ basis for MG elements is crucial for reliable description of TM=MG bonds. Folga and Ziegler also find excellent accord between theoretical and experimental geometries for ROMP catalyst models using density functional theory (DFT).[58] As with many aspects of computational chemistry of d-block metals, DFT[58] has provided a tremendous enhancement in the quantitative description of TM=MG complexes, particularly with respect to calculated energetic quantities. One can envisage DFT emerging as an almost de facto standard level of theory for TM applications requiring accurate predictions of enthalpic quantities, although post-Hartree−Fock methods will continue to find widespread application. With respect to Møller−

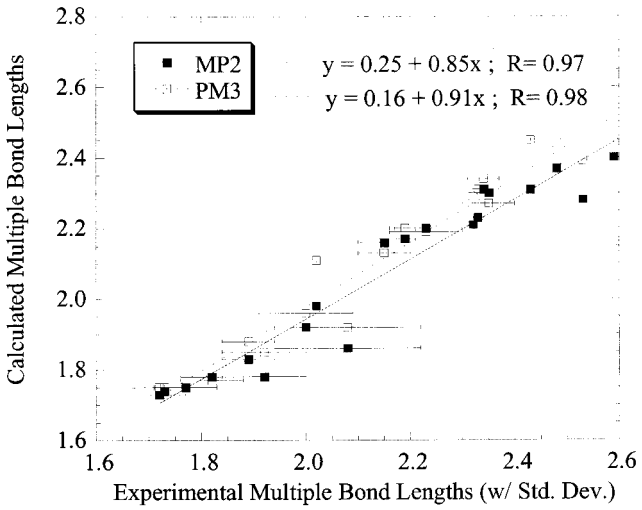


Figure 3. Comparison of predictive ability of SBK(d)/MP2[59] and PM3(tm)[53] versus experiment for multiple bond lengths. Horizontal lines represent the standard deviation of average values found in the CSD.[84] Reproduced with permission from ref 53. Copyright 1999 [American Chemical Society].

Plesset approaches, caution must be exercised given the possibility of nonuniform convergence behavior of MPn methods.[50b] In general, coupled cluster approaches yield superior results in terms of accurate energetic predictions although they represent a relatively expensive computational option.[50b]

c. Chalcogenides

A final example is from an ECP study[59] and a more recent PM3(tm) semiempirical investigation[53] of multiply bonded complexes of Zr, Ta, and W, representatives of the triads that comprise the majority of multiply bonded complexes.[53] For the ab initio based calculations, the SBK(d) ECP/valence basis set scheme was employed in conjunction with an MP2 wave function. Ancillary ligands are halides (Cl_2Zr═E, Cl_3Ta═E, Cl_4W═E; E = T, Pn, Ch) chosen for reasons of computational ease and to minimize differences arising from different coligands.

As is evident from Figure 3 agreement between SBK(d)/MP2 and experiment is excellent. Such agreement has come to be expected with ECP techniques for TM chemistry as long as a suitably flexible valence basis set is used with an appropriate wave function.[50] In our study of TM═MG complexes, we have generally found RHF wave functions suitable for metric prediction. It is plausible that this is due in part to the high formal oxidation states seen for most TM═MG species and the resulting lack of low energy excited states. Correlated wave functions can be essential for TM═MG_{hvy} complexes. Figure 3 also shows a comparison between the recently developed PM3(tm) and experiment for the same Cl_xM═E species. As can be seen, the agreement between PM3(tm) and SBK(d)/MP2 as well as experiment is commendable.[53] The many detailed and excellent works from those researching ab initio methods for computational TM chemistry have lead to an expectation of reliable structural prediction over a wide range of chemical environments, so that observing similar agreement for semiempirical schemes is encouraging.

It is worth concluding this section by making several notes. First, valence electron techniques (effective core potentials[51] and semiempirical quantum mechanical schemes) have made a tremendous impact for the modeler tackling TM═MG species given the proclivity of the heaviest TMs to form them and the rising interest in TM═MG_{hvy} chemistry. Second, in light of the recent analysis of X-ray crystallographic data for transition metal complexes by Martin and Orpen[60] it is reasonable to propose that an acceptable level of theory−experiment agreement for transition metal complexes is on the order of 0.01−0.02 Å for metal−ligand bond lengths, 1−3° for valence angles at the metal, and 5−10° for metal-dependent dihedrals. Finally, although the ability of a computational model to correctly predict the geometry of a TM═MG complex should not be the only criterion in assessing the suitability of a theoretical methodology, its value (particularly for transition metals where quantitative thermodynamic and spectroscopic information for discrete, molecular species can often be limited) cannot be underestimated. Ideally, the greatest confidence in a model vis-a-vis comparison with experimental geometries is expected from consistent agreement for a *large* and *chemically diverse* assortment of complexes. Targets should, of course, be chosen to reflect the chemical diversity of a particular d-block metal. Additionally, as computational methods and machinery continue to advance, as does the field of structural database mining,[60] it is desirable that "point by point" comparisons of theory and experiment be replaced by statistical comparisons among as large a series of target molecules as is feasible.

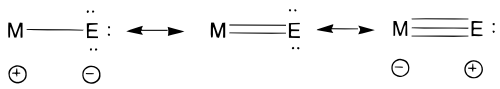
6. Computational Studies of Multiply Bonded Complexes

a. Multiply Bonded Complexes of the Chalcogens

It is not surprising that oxos are the TM═MG complexes that have garnered the greatest interest from theoretical chemists. Studies of oxos are notable not only in a scientific sense, but also historically as they represent some of the earliest computational research applied to transition metal complexes. Indeed, some of the earliest computations on inorganic complexes are those reported by Wolfsberg and Helmholz for metalates, $[M(O)_4]^{q-}$.[61] Another early computational study of oxo complexes is that of Ballhausen and Gray.[62] Müller has published calculations on metalates and their sulfur derivatives as part of his reviews of chalcogenide bonding in the 70's.[63] Much of the early research on the bonding and structure of oxos is reviewed by Nugent and Mayer,[1] and the interested viewer is referred to their monograph for further details.

A basic, but fundamental, conclusion from early studies on octahedral oxos was that perturbation from ML_6 to ML_5O splits the octahedral t_{2g} set such that, assuming the MO bond lies along the *z* axis, the d_{xy} is lower in energy than the d_{xz},d_{yz} pair. The former is nonbonding to a first approximation, and

Scheme 4

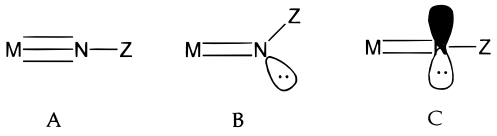


the latter participate in the metal−oxygen π^* orbitals. This simple analysis jibes with major observations regarding oxo complexes—formally d^2 oxos are diamagnetic (due to the $d_{xy}/d_{xz},d_{yz}$ energy split), oxos are almost invariably high oxidation state (d^n, $n \approx 2$), and complexes with d orbital occupancies greater than 2 such as the P-450 ferryl intermediates[21,22] and d^4-Ru^{IV}-oxos[64] tend to be highly reactive. Of course, exceptions to these generalizations such as Mayer's d^6-$[Re^{I}(O)(\eta^{2-}Me\text{-}C{\equiv}C\text{-}Me)_2]^-$ are known and have been addressed through calculation.[55] The metal formal oxidation state preferences for oxos evolve from the metal−oxygen π^* character of the d_{xz},d_{yz} pair. Calculations suggest that the nature of d^n ($n \geq 4$) oxos is complicated, requiring multiconfigurational descriptions.[22]

Interesting deviations from the picture developed by the classic works on oxos have been noted. For example, a study by Cotton and Feng employed a variety of methods (RHF/CASSCF/CI/ SCF-Xα-SW) and ECPs to investigate the complexes, *trans*-d^2-$Mo(Ch)_2(PH_3)_4$, Ch = O, S, Se, Te.[65] They conclude that the HOMO for every member of the series is a Ch pπ lone pair and not the d_{xy}. Furthermore, the calculated electronic spectra of the dioxo (which is in good agreement with experiment) is markedly different from heavier congeners for which the lowest energy transition is proposed to be Ch $\pi \rightarrow$ MCh π^*. Kaltsoyannis has studied the electronic structure of the heavier W derivatives with relativistic wave functions and demonstrates that spin−orbit coupling (SOC) can significantly shift frontier MO energies.[66] The SOC effect for Mo complexes will be less, although how much is not certain particularly for species with Te. It would be of interest to employ DV-Xα, and related approaches that explicitly include SOC, to probe the spectroscopy of *trans*-d^2-Mo-bis-(chalcogenide) species. On the basis of his DV-Xα study of d^2-W-bis(chalcogenide) complexes, Kaltsoyannis concludes that the WCh σ bond is more covalent for heavier Ch while the π bond changes little.[66] Frenking et al. used the atoms-in-molecules approach to study oxos of the form $M(O)L_n$, $n = 3-5$; L = Cl, F; M = Mo, W, Re, Os;[67] they conclude that metal−oxygen σ and π bonds are heavily polarized toward O. In a computational study of vibrational spectra, Cundari and Raby see distinctly different behavior for oxos as compared to their heavier sulfide and selenide congeners.[68]

Taken together, the preceding computations on a subset of chalcogenides are consistent with conclusions put forth by Benson et al. for a much larger assortment of chalcogenides[69] and with experiments by Parkin et al. on Ti-triad chalcogenides.[18] Metal-oxos have a dominant contribution from a singly bonded structure while the heavier congeners (Ch = S, Se, Te) are dominated by the doubly bonded structure, Scheme 4. The simplest rationalization for changes in metal−chalcogen bonding as a function of chalcogen is a difference in electronegativity.

Scheme 5



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The qualitative frontier orbital picture derived from early approximate calculations on oxos has held up very well in the face of subsequent, quantitative calculations. The qualitative MO picture derived from these seminal calculations has also been found to be transferable to other TM═MG complexes with modifications for differing strengths of (primarily) π donor ability. However, more quantitative theories have made important contributions to TM═MG chemistry, in many cases refining earlier qualitative theories as typified by the work of Cotton and Feng[65] and Kaltsoyannis.[66] Additionally, qualitative and quantitative insight into the nature of the bonding of multiply bonded complexes has been obtained from electron density partitioning of wave functions derived from higher-level theories. Examples of this analysis approach are discussed in the following two sections.

b. Multiply Bonded Complexes of the Pnictogens

Multiply bonded pnictogen complexes—pnictidenes and pnictidos—have received less theoretical attention than their chalcogen and tetrel counterparts. This is not surprising for heavier pnictogens as experimental research in this area has, until recently, been sparse. The first structurally characterized phosphido complexes were reported in 1995.[70] The first structurally characterized phosphinidene, Cp_2W═PMes*, was published little more than a dozen years ago, while the first arsinidene, $Ta(OSi')_3(AsPh)$, was reported by Wolczanski et al. in 1994.[12−13]

The main point of discussion in imido bonding has been correlations, if any, between MN bond length and metal−nitrogen−substituent (Z) angle as well as the implications of linear versus bent coordination.[1,71−81] Linear coordination is generally envisaged as M−N−Z of ≥170° and bent as M−N−Z ≤ 165°, although the dividing line is flexible. After publication of the structure of $Mo(S_2CNEt_2)_2(NPh)_2$,[71] bent and linear imidos were seen as almost tantamount to distinct ligand types. This complex has two inequivalent imidos—one bent ($M-N-C_{ipso} = 139°$) and one linear ($M-N-C_{ipso} = 169°$). Two further observations make this disparity noteworthy. First, the M−N bond length is much longer (≈0.04 Å) for the bent imido.[71] Second, using the "radical" method of electron counting (the imido is viewed a neutral ligand), $Mo(S_2CNEt_2)_2(NPh)_2$ can only attain an 18-electron count by making one imido bent (two-electron donor) and the other linear (four-electron donor). Linear imidos are thus generally depicted as triply bonded with shorter MN bonds than bent imidos and their MN double bonds. The most popular descriptions are given in Scheme 5. In addition to computation, the bonding in imidos has been probed spectroscopically (NMR and electronic spectroscopy most noticeably[1,5,81−83]) and structurally (more than

500 imidos crystal structures can be found in the Cambridge Structural Database[84]).

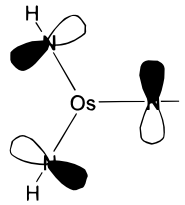
It is a signal fact that many of the bonding studies of imidos have been reported as part of experimental research. Berg and Sharp employ a frontier orbital analysis to probe the electronic structure of $W(NMe_2)_4(NPh)$.[85] This complex, unlike the vast majority of ML_4E (L = σ-donor; E = multiply bonded ligand) species, is not square pyramidal (SQP5) with E in the apical position, but trigonal bipyramidal with NPh occupying an axial coordination site.[86] Profilet et al. employed EHT to probe Ti-imido species[87] as did Rankin et al. as part of a gas-phase, electron diffraction study of tetra-imido Os complexes.[73] The latter study also included density functional calculations. Williams and co-workers[82] coupled semiempirical PM3(tm) calculations in conjunction with experiments to study the electronic spectra of Ta-imidos.

Rankin et al. also raise an interesting point in the discussion of linear/bent imido coordination, i.e., the potential energy surface for imido bending is very soft.[73] Going from the linear maximum to bent coordination for $OsO_2(NMe)_2$ and $OsO_2(N^tBu)_2$ costs 1 kcal mol^{-1} using EHT calculations. Experimental support for the softness of M−N−Z bending is provided by Bradley et al. using ^{14}N and ^{15}N NMR.[81] Crystallographic evidence highlighting the ease with which imido bending can occur comes from $Mo(S_2CNEt_2)_2(NAr)_2$,[72] which unlike its less bulky parent reported over a decade earlier[71] has two linearly coordinated imidos (M−N−C_{ipso} = 170°) and M−N bond lengths intermediate those for $Mo(S_2CNEt_2)_2(NPh)_2$.

The complex $Cp^*_2Ta(NPh)(H)$ also displays linear imido coordination, although this implies a 20-electron count.[74] However, the situation is not so straightforward as the Ta−N bond length is between double and triple bond estimates, and thus the authors interpret their data in favor of a description intermediate between canonical forms **B** and **C** (Scheme 5). This experimental study inspired extended Hückel calculations by Jorgensen on $Cp_2Ta(NPh)(H)$.[77] Linear coordination is preferred because the HOMO has π^* character between the imido nitrogen and the ipso carbon bonded to it. Calculations show that as the phenyl-imido ligand is bent, this antibonding interaction is enhanced, leading to destabilization of the HOMO.[77]

Jorgensen points out that similar thinking can be applied to $Os(NAr)_3$. This remarkable complex has three linear imidos and would appear to be a 20-electron complex.[45] SCF-Xα-SW calculations by Schofield et al. show the second HOMO (0.5 eV below the HOMO) to be an a_2' orbital that cannot interact with any Os-based valence orbitals, Scheme 6. Hence, this orbital is ligand nonbonding, and thus the required 18-electron count is found at Os. One can consider the NAr ligands in $Os(NAr)_3$ to act, on average, as $3^1/_3$-electron donors. EHT calculations are also employed in a theory−experiment study of $[CpMo(NH)(\mu\text{-}NH)]_2$ and suggest that the terminal imidos act as three-electron donors despite their linear coordination to achieve an 18-electron count

Scheme 6



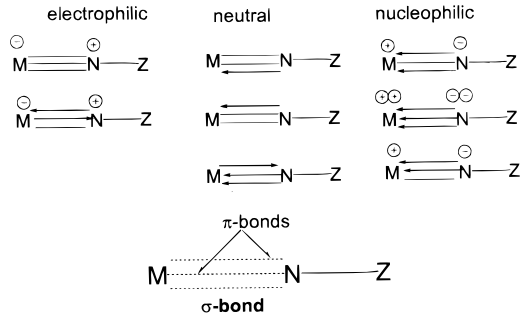
at each Mo.[76] A similar three-electron donation picture is preferred by Coffey et al. for $Mo(S_2CNEt_2)_2(NAr)_2$ with its two linear NAr ligands.[72]

The most extensive computational study of TM imidos was reported by Cundari in 1992.[36] This ECP study of numerous mono-, bis-, and tris-imido complexes focused on models from the scandium-triad (no examples yet exist except Sc^+═NH in the gas phase[88]) to cobalt-triad. Their electronic structure is probed with the MC/LMO/CI (multiconfiguration/localized molecular orbital/configuration) technique. Borrowing from earlier work,[89] the MC/LMO/CI approach seeks to combine the advantages of molecular orbital calculations with the chemically intuitive language of valence bond (VB) theory. This is desirable as the analysis of the molecular and electronic structure of imidos (and indeed most TM═MG complexes) is often couched in VB terms (see Schemes 4 and 5).[1,71,72,78−81] The MC/LMO/CI method starts with a multiconfiguration SCF (MCSCF) calculation using an active space comprised of the MN σ and π (both components) orbitals, bonding and antibonding, and the six electrons contained therein. This step improves the description of the antibonding orbitals beyond that of a Hartree−Fock calculation, although the HF determinant dominates (generally >90%) the ground-state wave function. The six active space MOs are then submitted to the Boys[89] orbital localization procedure. Localizing a subset of orbitals that includes bonding/antibonding pairs results in polarization of the LMOs to each side of the metal−nitrogen bond with a small "tail" on the opposite end. The tails (typically <2% of the orbital) maintain the orthogonality of the LMOs, and thus distinguish MC/LMO/CI from a true VB approach, but the method overcomes many difficulties arising from nonorthogonal CI. In the final step, a CI is carried out so that all 175 configuration state functions (CSFs) within the six-orbital/six-electron active space are generated, subject to spin and spatial symmetry restrictions.[36]

Eight structures dominate the description of TM imidos, Scheme 7. In Scheme 7, a straight line (M−N) denotes a covalent bond type, while an arrow signifies a dative bond (M←N) or back-bond (M→N). In our research with the MC/LMO/CI technique,[36] no attempt was made to distinguish the orthogonal TM dπ−N pπ components. Indeed, we noted their similarity in relation to the degree of polarization of the two π bonds.[36] Resonance structures were defined as nucleophilic or electrophilic depending on whether the imido nitrogen carried a formal negative or positive charge. For electron counting purposes, the N−Z bond was assumed covalent.

It is satisfying that all dominant configurations are chemically reasonable, as inferred from known imido

Scheme 7



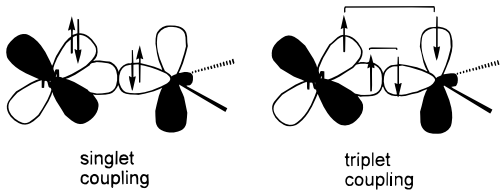
chemistry. Six structures correspond to those put forth in the literature, but the remaining two provide a new view of the metal−imido linkage. They suggest significant dative character for the MN σ bond. Although no other structures contribute for the diverse assortment of complexes studied, the composition among dominant structures varies in response to changes in bonding environment at the metal.[36] For example, electrophilic (nucleophilic) resonance structures increase (decrease) toward the left in the transition series. For the imidos studied, the MC/LMO/CI analysis suggests a metal−nitrogen bond order between two and three. As the field of imido chemistry matures, there is increasing recognition that linear/bent coordination implies neither rigid 4/2-electron donation nor triple/double bonding. To quote the original reference,[36] "the metal-imido linkage cannot be described by one 'best' structure but rather a linear combination of several is needed for an accurate description." A similar conclusion is appropriate for TM−tetrel multiply bonded complexes.[50a]

c. Multiply Bonded Complexes of the Tetrels

Theoretical studies of metal−tetrel multiple bonds have generally pursued one of two themes. The first is reminiscent of imido studies in that a dichotomy exists in carbene ($L_nM{=}C(R)R'$) chemistry, although it is not geometric, but electronic. The other point that has garnered more interest recently is the bonding in carbenes in relation to their heavier tetrel congeners. In the CSD there are more than a thousand complexes that have a double bond between a TM and a three-coordinate carbon, but only 18 (eight for Si, four for Ge, five for Sn, one for Pb) answering this description for the heavier tetrels.[84] Given the startling differences in the number of structurally characterized carbenes versus their silylene, germylene, stannylene, and plumbylene congeners, it is natural for theoreticians to investigate whether this is due to some inherent kinetic or thermodynamic factor or "synthetic neglect."

There exist two distinct classes of complexes with TM−carbon double bonds. Each is typified by its first example $(CO)_5W{=}C(OMe)Me$[27,28] and $(neopentyl)_3Ta(=C(H)^tBu)$.[29,30] The older family, generally referred to as Fischer-type carbenes, are typically characterized by electrophilic character at the carbon, are coordinated to TMs in moderate although not high positive oxidation states, and possess heteroatom substituents on the carbon (NR_2, OR, SR, etc.).

Scheme 8



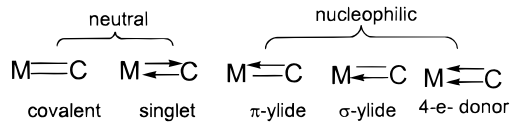
Schrock-type carbenes or alkylidenes are nucleophilic at carbon, are coordinated to high oxidation state TMs, and typically possess hydrocarbyl substituents.[1] Hence, a major point of interest in the study of TM=T species has been to understand the differences and similarities in the multiple bond linkage between Fischer- and Schrock-type carbenes.

The seminal theoretical work comparing Fischer- and Schrock-type carbenes is that of Taylor and Hall.[90] The authors take a fragment approach to understanding carbene complexes. Carbenes (CR_2) have two low energy states—one singlet and the other triplet—from partitioning the two valence electrons not involved in C−H bonds between sp^2 and a p_π orbitals. In general, hetero substituents (like those prevalent in Fischer-type carbenes) tend to stabilize the singlet, while hydrocarbyls (Schrock-type substituents) tend to stabilize the triplet. Taylor and Hall conclude that these yield singlet and triplet couplings when the carbenes are bonded to transition metal fragments, Scheme 8. Hence, one can think of the double bond in Schrock-type carbenes being more akin to what one would envisage for double bonds between carbon and the other light MG elements, although the reactivity of alkylidenes, in particular their ability to carry out Wittig-type transformations (i.e., olefination of carbonyls), suggests an ylide description may be more apropos. The Fischer-type carbene is a donor−acceptor type interaction, a two-center analogue of the bonding models used to explain the stability of metal−olefin and metal−carbonyl complexes.[91]

The Taylor−Hall model is consistent with the reactivity of the Fischer-type carbenes, i.e., the empty C p_π orbital can accept electron density from suitable donors. Insertion and cyclopropanation reactions are demonstrated by free carbenes[92] and Fischer-type carbenes. The nucleophilicity of Schrock-type complexes is rationalized from the Taylor−Hall model by the fact that both σ and π bonds will be polarized toward carbon in the typical case in which the metal is an electropositive early TM. Indeed, the name alkylidene for Schrock-type carbenes signifies their link with the well-known ylides such as those used in Wittig-type transformations.[29]

The work of Taylor and Hall inspired our group to carry out an analysis of Schrock-type carbenes using the MC/LMO/CI technique.[93,94] Unfortunately, Fischer-type carbenes could not be studied with this technique as the metal−carbon bond does not yield "bond−antibond" correlation but rather correlation of an orbital with a larger counterpart that has an extra radial node. Electron correlation is expected to be more important for Fischer-type than Schrock-type carbenes given the presence of partially occupied (albeit typically low-spin) d orbital manifolds for the

Scheme 9



former. However, the reason for the different correlation behavior of Fischer-type carbenes is unclear, although it is plausible that this may be due to the greater degree of bond polarization implied by the Taylor−Hall description, Scheme 8. The MC/LMO/CI analysis was valuable, showing five resonance structures to dominate the bonding in alkylidenes, Scheme 9. The most interesting of these is the so-called σ-ylide, as the others correspond to descriptions previously put forth in the literature. As with imidos, the MC/LMO/CI method points to a large contribution from σ-dative structures. Interestingly, neutral (the covalent and singlet representations put forth by Taylor and Hall[90]) and nucleophilic resonance structures make roughly equal contributions, 50% and 45%.

An area in which more research is needed are TM=T_{hvy} complexes. As mentioned above, examples stable enough to be characterized are extremely rare. The examples that do exist are what would be classified as Fischer-type tetrylenes. No example of a high-valent tetrylidene has been reported, although a Ti^{IV}-silylidene was proposed as an intermediate in titanium-catalyzed silane polymerization.[40] Cundari and Gordon published the optimistically titled "Strategies for Designing a High-Valent Transition metal Silylidene Complex" in 1992.[95] Substituted silylidenes of d^0 Ti- and V-triad transition metals were investigated in an attempt to isolate ligand/substituent combinations that would impart thermodynamic (as quantified by MSi force constants) and kinetic (using the GVB overlap to estimate the percent diradical character of the MSi bond) stability. One interesting computational result is that although a proper description of the MSi σ bond can be obtained at the HF level, the MSi π bond requires a multiconfiguration wave function. Electronic stabilization of the silylidene is achieved by electronegative ligands and π-donor substituents. Ostensibly, this amounts to a "push−pull" scenario in which electronegative ligands "pull" and π-donor substituents "push" electron density in the MSi π bond to make it more evenly distributed across the MSi bond.

Calculations on Fischer-type tetrylenes are more numerous than Schrock-type tetrylidenes, although still rare. Probably the earliest study is that of Nakatsuji et al. $(CO)_5Cr{=}Si(OH)H$ using all-electron SCF methods.[96] They remarked upon the greater reactivity of silylenes than Fischer-type carbenes with nucleophiles based on calculated atomic charges and frontier orbital arguments. More recent studies by the Ziegler group[97] and Marquez and Sanz[98] have focused on $(CO)_5Cr{=}TH_2$ (T = C, Si, Ge, Sn) plus substituted derivatives and examples with the heavier chromium triad metals. Jacobsen et al. conclude on the basis of density functional calculations that it is the very weak π bonding of the heavier tetrels as compared to carbon rather than any differences in the MT σ bond that is key to understanding their chemical differences.[97] In some respects, the heavier tetrylenes are essentially σ donors, and hence, this makes them prone to base coordination at the tetrel. In an interesting pair of papers, Marquez and Sanz investigate $Mo{=}TH_2$ and $(CO)_5M{=}TH_2$ using effective core potentials in conjunction with Hartree−Fock and CASSCF wave functions.[98] As in the Cundari−Gordon study,[95] they note the significant contribution made by configurations other than the HF one. There is a significant contribution to the overall wave function from the $\pi_{MSi}{}^0\pi^*_{MSi}{}^2$ configuration, leading to shortening of the MSi bond (versus HF) that the authors attribute to increased ionic character. Furthermore, they characterize the tetrylenes studied as more Fischer- than Schrock-type. This is inherently plausible as the heavier carbene analogues have singlet ground states.

7. Concluding Remarks

The chemistry, experimental and computational, of multiply bonded complexes is a vast field, and this review has just scratched the surface. For example, little mention is made of trivalent (pnictido, tetrylidyne/tetryne) species, although they can be largely understood using models developed for the TM=MG species discussed here. Likewise, there is the wide and varied reactivity of TM=MG complexes.[1,2] It is encouraging that many of these computational studies are in conjunction with or closely inspired by experiments, as a combined approach is clearly desirable. With a growing track record of success of rigorously tested methods (for which TM=MG make excellent testing sets) and constant improvements in technology, the future of computational TM=MG chemistry seems ripe to continue the transition from analysis to design. A better understanding of the TM=MG bond and its response to the chemical environment has emerged recently through calculation. These studies reveal a TM=MG bond that is, perhaps surprisingly as the residue of our greater experience with organic counterparts, more "fluid" than may have been supposed just a short time ago. This is exciting for future research, experimental and computational, in this field as it raises the exciting possibility of "engineering" TM=MG complexes by rational ligand/substituent modification.

8. Abbreviations

Ar	2,6-$C_6H_3{}^iPr_2$
Ar*	2,6-$C_6H_3Me_2$
Bz*	η^6-C_6Me_6
CASSCF	complete active space−self-consistent field
Ch	chalcogens, oxygen group elements
CI	configuration interaction
$Cp^\dagger$	η^5-C_5Me_4Et
Cp*	η^5-C_5Me_5
CSD	Cambridge Structural Database
Cym	η^6-1,4-$C_6MeH_4{}^iPr$
DFT	density functional theory
DV	discrete variational
ECP	effective core potential
EHT	extended Hückel theory
HOMO	highest occupied molecular orbital
L	σ-donor ligands

MC/LMO/CI	multiconfiguration/localized molecular orbital/configuration interaction
Mes	mesityl, i.e., 1,3,5-trimethyl-phenyl
Mes*	2,4,6-$C_6H_3{}^tBu_3$
MG_{hvy}	main group element of period 3 or higher
MP2	Møller−Plesset second order perturbation theory
PM3(tm)	parametrization method 3 for transition metals
Pn	pnictogen, nitrogen group elements
py	pyridine
RHF	restricted Hartree−Fock
ROMP	ring-opening metathesis polymerization
SBK	Stevens, Basch, Krauss, Jasien effective core potentials and valence basis sets
Si′	tris(*tert*-butyl)silyl
SOC	spin−orbital coupling
SW	scattered wave
T	tetrel, carbon group elements
TM═MG	complex with a transition metal (TM)−main group (MG) multiple bond

9. Acknowledgments

Progress in computational studies of TM═MG chemistry in our lab is due to the hard work and dedication of graduate and undergraduate students who carried out the research diligently and conscientiously: Mike Benson, Jun Deng, Tom Klinckman, Yueping Li, Soon Lim, Eddie Moody, Howard Nguyen, Karen Pierce-Beaver, Phil Raby, Leah Saunders, Laura Sisterhen, Lynn Strohecker, and Tie Zhou. We also acknowledge the many wonderful collaborators who have expanded our appreciation for experimental aspects of TM═MG chemistry. T.R.C. acknowledges the National Science Foundation (CHE-9614346) and Department of Energy (DE-FG02-97ER14811) for supporting different portions of our TM═MG research. T.R.C. also acknowledges the NSF for their support of University of Memphis computational chemistry through grants STI-9602656 and CHE-9708517 for facilities and equipment improvements.

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