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Metal–Metal Bonded Dinuclear and Organodimetallic Complexes of the Early Transition Metals (Groups 4 and 5): Synthesis, Structure, and Reactivity

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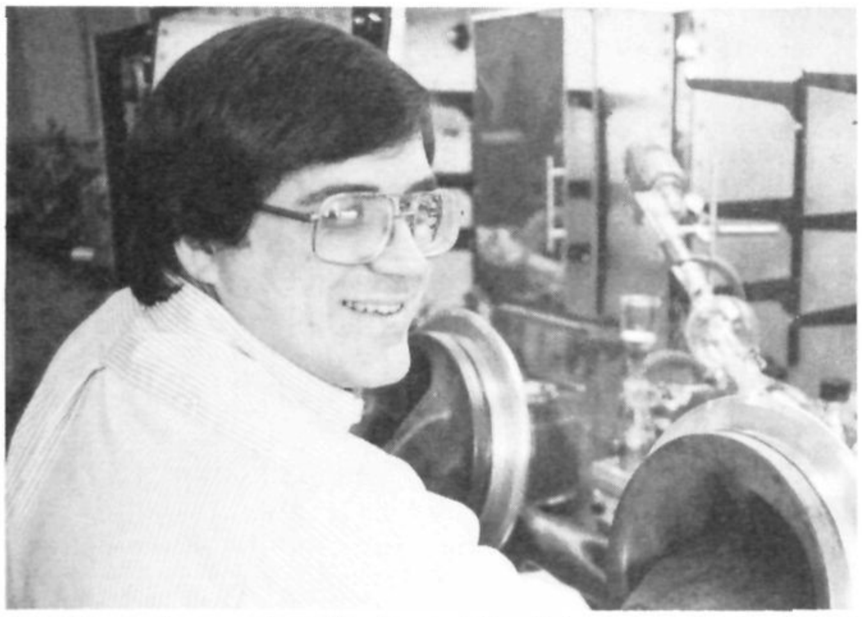
I. Introduction

Discrete single and multiple transition metal–metal bonds constitute one of the most novel structural groups in contemporary inorganic and organometallic chemistry, with metal–metal quadruple bonds having no analogue in non-transition-metal chemistry. Metal–metal bonds are found in a wide variety of dinuclear and polynuclear (cluster) molecular species with or without bridging ligands. The chemistry of multiply bonded dinuclear complexes has been reviewed extensively,[1,2] and the interest in these species extends from the synthetic to the theoretical.

A survey of the literature on the chemistry of transition metal–metal multiply bonded dinuclear complexes will lead one to the initial conclusion that synthetic and structural studies dominate the field, with less emphasis on the reactivity of these species. Unlike other inorganic and organometallic functional groups, metal–metal multiple bonds often are accompanied by bridging ligands which can lead to ambiguities in bond length/bond order assignment and which can complicate any attempt to treat such multiple bonds as a functional group. Despite these reservations, it has been shown that a functional group approach to metal–metal multiple bond reactivity can be conceptually useful[3] in developing the chemistry of these species beyond the somewhat common pattern of simple ligand substitution or metal–metal bond cleavage reactions. Unprecedented reactions such as alkyne metathesis with metal–metal triple bonds,[4] clusterification of metal–metal quadruple bonds to give tetranuclear species,[5] and coupling of metal–metal and metal–carbon triple bonds to give trinuclear μ-alkylidyne clusters[6] are among the more unusual reactions to have been observed.

One striking feature of dinuclear, metal–metal bonded transition-metal chemistry is the relative paucity of such complexes for elements of the titanium and vanadium triads. By comparison, the metal–metal bonded chemistry of the neighboring chromium triad is enormous and includes extensive synthetic, structural, theoretical, and reactivity studies for dinuclear classes such as the quadruply bonded M_2L_8 and triply bonded M_2L_6 complexes and organodimetallic complexes such



Lou Messerle was born in Jersey City, NJ, and was raised and attended public schools in Linden, NJ. He received his B.Sc. degree, magna cum laude with Honors, from Brown University in 1975 and his Ph.D. in 1979 from the Massachusetts Institute of Technology, where he worked in organotantalum and organozirconium chemistry under the direction of Professor Richard Schrock; he was a Dow Chemical Company Central Research Fellow for two of these years. From 1979 to 1981 he pursued postdoctoral studies at the University of Michigan in organodimolybdenum chemistry under the direction of Professor M. David Curtis, followed by 3 years in independent study as a Junior Fellow in the Michigan Society of Fellows at the University of Michigan. In 1984 he joined the faculty as assistant professor at The University of Iowa. He recently received a Burlington Northern Foundation Faculty Achievement Award for excellence in teaching. His research interests in synthetic and mechanistic early-transition-metal organometallic chemistry include synthesis and reactivity of metal–metal double and triple bonds, reactivity of organometallic functional groups in coordinatively unsaturated environments, intermolecular carbon–hydrogen bond activation/functionalization, and development of new techniques in organometallic synthesis.

as the triply bonded $Cp_2M_2(CO)_4$ species. The relative scarcity of dinuclear chemistry for the early transition metals is partly based on the more recent development of the inorganic[7] and organometallic[8] chemistry of these elements, on the scarcity of appropriate starting materials in lower oxidation states, and on the somewhat greater technical difficulties in the handling of the oxophilic, air- and moisture-sensitive, high-valent metal halide precursors.

There has been a great deal of progress in the area of early-transition-metal dinuclear and organodimetallic chemistry since the late 1970s, led by the pioneering synthetic and structural efforts of McCarley and co-workers, the synthetic and magnetic studies of Brown and co-workers, the structural and synthetic work of Cotton and co-workers, the specific contributions of direct, in situ reduction and ligand substitution with chelating ligands by Allen and Naito, and the synthetic/structural/reactivity research of the Sattelberger, Schrock, and Hubert-Pfalzgraf groups. This growing body of work includes some remarkable and exceptional reactivity firsts in organometallic and metal–metal multiple bond chemistry, including the first examples of direct hydrogenation of a metal–metal double bond, migratory insertion of carbon monoxide into a hydride ligand to yield a formyl species, reductive coupling of carbon monoxide to yield a μ-ethylidene group, and intermolecular C–H bond activation by a metal–metal multiple bond. Despite this decade of work, only one early (1980) review on dinuclear complexes of these metals has appeared.[9] Our developing interest in synthesis and reactivity of these dinuclear and organodimetallic systems has led to this review.

II. Scope of Review

This review is a survey of the synthesis, structure, and reactivity of discrete, metal–metal bonded dinuclear and coordinatively unsaturated organodimetallic complexes of the titanium and vanadium triads. The discussion will exclude polynuclear clusters of these metals and dinuclear species which lack metal–metal bonds. Dinuclear complexes with metals in their highest oxidation state (and thus lacking any d electrons for participation in covalent metal–metal bonding) are specifically excluded from this review. For lower valent, potentially metal–metal bonded dimetallics, the criteria for exclusion include exceptionally long metal–metal distances, which are indicative of a clear lack of direct metal–metal bonding, or paramagnetism associated with either weak metal–metal interaction or an exchange mechanism involving bridging ligands.

For the purposes of this review, metal–metal bonded *dinuclear* or *dimetallic* complexes will be defined as those species which contain bridging or terminal ligands, such as trialkylphosphine, halide, alkoxide, chalcogenide, etc., that do not involve metal–carbon bonding. Metal–metal bonded *organodimetallic* complexes will be defined as those species with metal–carbon bonding to some organic group (e.g., alkyne) or ancillary ligand (such as a cyclopentadienyl or carbonyl). The discussion of organodimetallics will be restricted to the more coordinatively unsaturated mono(cyclopentadienyl) and mono(peralkylcyclopentadienyl) complexes; lower valent organodimetallics with two cyclopentadienyl or cyclopentadienyl-like (e.g., fulvalene or $\eta^5:\eta^1$-C_5H_4) groups per metal will not be reviewed because their metal–metal interaction is often not clearly defined[10] as a result of substantial antiferromagnetic coupling between the metal centers through bridging ligands. The reader with interests in these tetrakis(cyclopentadienyl), bis(fulvalene), or mixed cyclopentadienyl/fulvalene organodimetallic complexes is directed to an extensive review of dititanium and dizirconium examples[11] and to papers on dititanium,[12] dizirconium,[13] divanadium,[14] and diniobium[15] chemistry.

The review is divided into sections on synthesis, molecular structure, and reactivity. The first two sections on synthesis and structure are subdivided into dititanium and dizirconium species, divanadium species, diniobium and ditantalum species, and organodimetallics. This somewhat arbitrary division is based on the relative scarcity of group 4 dinuclears (indeed, no dihafnium species have been reported and no dititanium species characterized structurally), the close similarities in diniobium and ditantalum chemistry, the distinctive differences between first-row elements and their second- and third-row congeners (which are readily apparent in comparisons of vanadium chemistry to niobium and tantalum chemistry), and the major structural differences between the dinuclear and organodimetallic molecules. Some brief discussion of qualitative structural details is included in the Synthesis section for unusual or noteworthy dinuclear and organodimetallic complexes since a complete separation of synthesis and approximate molecular structure is undesirable. The last section on reactivity is subdivided into reaction types and not structural or metal classes, in the expectation that some commonality of reactivity based on the dimetal center will be apparent. The reaction types include common organometallic reaction classes such as oxidative addition, ligand displacement, and migratory insertion, less common organometallic reactions such as substrate coupling, and reactions such as metal–metal bond cleavage and clusterification which are more specific to dinuclear species. These reaction classifications are strictly formal and are not meant to imply any mechanistic significance, as careful kinetic and mechanistic studies in this developing area are yet to be performed.

A simple molecular formula convention will be utilized to distinguish structurally characterized metal–metal bonded dinuclear and organodimetallic complexes, depicted by $[ML_n]_2(\mu\text{-}L)_m$, from species postulated to be dinuclear, depicted by M_2L_n, on the basis of solution molecular weight, magnetic, or mass spectrometric properties. Dinuclear reaction products with metals in their highest valency (and thus nonbonded) will be depicted by $L_nM(\mu\text{-}L)_mML_n$. The high-valent transition-metal halides, e.g., $ZrCl_4$ and $TaCl_5$, will be written in their monomeric empirical formulas for simplicity; these species are often dinuclear or polynuclear in the solid state and in solution in a number of noncoordinating solvents.[7] Equations involving syntheses will be left unbalanced in order to emphasize the synthetic principle or to point out cases where product mixture characterization is incomplete. The following abbreviations will be used in the text: M, transition metal; M′, main-group metal; L, neutral ligands (e.g., PMe_3, SMe_2), or, occasionally, anionic ligands (e.g., halide, carboxylate, alkoxide) in generalized formulas for specific structural classes; μ-L or L_μ, bridging ligand; L–L, symmetric bidentate ligand; L–L′, unsymmetric bidentate ligand; Me, CH_3; Et, CH_2CH_3; Bu, $CH_2CH_2CH_2CH_3$; Ph, C_6H_5; Cp, η-C_5H_5; Cp′, η-C_5H_4Me; Cp*, η-C_5Me_5; Cp″, η-C_5Me_4Et; X, halide; tht, tetrahydrothiophene; thf, tetrahydrofuran; OAc, acetate; py, pyridine; ax, axial; eq, equatorial; IR, infrared; NMR, nuclear magnetic resonance; EPR, electron paramagnetic resonance; NQR, nuclear quadrupole resonance; UV/vis, ultraviolet/visible.

III. Synthetic Approaches

A. General Synthetic Strategies

In principle there are three distinct methods for the preparation of metal–metal bonded dinuclear and organodimetallic complexes which can be distinguished by whether the precursors are mononuclear or dinuclear; declusterification reactions that result in dinuclear fragments are unreported with the early metals and this approach is not discussed. The first approach to the synthesis of lower valent dinuclear complexes is either coupling of low-valent mononuclear precursors through ligand loss or displacement (eq 1) or reductive coupling of high-valent monomers (eq 2), which can proceed

$$2MX_nL_m \rightarrow M_2X_{2n}L_{2m-2} + 2L \qquad (1)$$

$$2MX_nL_m + 2M' \rightarrow 2M'X + 2MX_{n-1}L_m \rightarrow M_2X_{2n-2}L_{2m} \qquad (2)$$

$$M' = \text{reducing agent}$$

through coupling of low-valent mononuclear species generated in situ. In two-electron reduction of a high-valent mononuclear precursor, the possible intermediacy of a mid-valent dinuclear species must also be considered. Common reducing agents for these synthetic-scale reductive dimerizations are alkali and alkaline earth metals or their naphthalenides or amalgams. A second approach to dinuclear synthesis is ligand substitution on a dinuclear precursor (eq 3); this

$$M_2X_nL_m + yL' \rightarrow M_2X_nL_{m-y}L'_y + yL \qquad (3)$$

method often involves substantial structural rearrangement or the formation of a dinuclear product of a different structural class (e.g., a change from a confacial bioctahedral precursor of the form $[ML_3]_2(\mu\text{-}L)_3$ to an edge-sharing bioctahedral product of the form $[ML_4]_2(\mu\text{-}L)_2$ with excess ligand). In many cases the added ligand in these ligand substitution reactions is a chelating or bridging ligand. The third approach to synthesis of dinuclear complexes is reduction of a dinuclear species to a new dinuclear product with concomitant increase in formal metal–metal bond order (eq 4).

$$M_2X_nL_m + 2M' \rightarrow M_2X_{n-2}L_m + 2M'X \qquad (4)$$

$$M' = \text{reducing agent}$$

All of these reactions have precedent in early-transition-metal dinuclear chemistry, with a greater reliance on the use of dinuclear complexes (eq 3 and 4) as synthons for the preparation of new dinuclear species. The more extensive development of diniobium and ditantalum chemistry, based on the use of several available dinuclear synthons, attests to the importance of the methods depicted in eq 3 and 4; divanadium chemistry suffers from a lack of suitable vanadium-vanadium bonded synthons, while the use of the only known dizirconium species as a synthon for other dizirconium species is unreported.

The choice of synthetic method is also predicated on solubility grounds and on the ease of isolation and purification of a desired product. In the synthesis of dinuclear products with low solubility, the direct reduction of a high-valent mononuclear precursor can be problematic for reductants which result in insoluble main-group metal halide byproducts (which is often the case since such halide insolubility will drive the reduction to completion). The popular reductant sodium amalgam can lead to additional problems with finely dispersed mercury or mercury/main-group halide suspensions which can be removed only via centrifugation or the use of a filtering agent such as Celite.

Purification methods in this area of transition-metal chemistry are unfortunately limited to fractional crystallization. Chromatographic methods are not utilized because of the oxophilicity of these species, which limits the use of oxide-based chromatographic supports. Preparative sublimation has not proven to be successful because of the generally low vapor pressures of dinuclear complexes of these metals. The lack of a range of separation techniques is most keenly felt in the study of the reactivity of these species.

Fortunately, most common spectroscopic and spectrometric methods can be employed except in cases of insolubility or involatility. Dinuclear species with ligands that contain NMR-active nuclei such as ^{31}P, ^1H, and ^{13}C can be studied by NMR spectroscopy, and homonuclear and heteronuclear decoupling methods are often invaluable, as is IR spectroscopy if carbonyl or hydride ligands are present. Mass spectrometric methods are also very useful, particularly given the isotope patterns for several of these metals and the common halides. Special air-sensitive precautions in sample handling and introduction (e.g., use of argon blanketing streams) must be employed in mass spectrometric determinations. Dinuclear complexes are often of insufficient volatility for simple electron-impact or chemical ionization methods, and common quadrupole mass spectrometers can suffer from mass range limitations for species with molecular masses in excess of 1000 amu. Modern high mass range quadrupole instruments and the increasing availability of high sensitivity and magnetic sector mass spectrometers coupled with sophisticated ionization techniques (e.g., field desorption and fast-atom bombardment or FAB) should increase the utilization of mass spectrometric methods for characterization in the area of dinuclear chemistry. In our research we have found FAB mass spectrometry to be very useful once an appropriate matrix solvent (lacking the usual hydroxyl or sulfhydryl groups which are common in FAB matrix compounds[16]) is found.

B. Dititanium and Dizirconium Complexes

There have been no studies directed toward the rational synthesis of dititanium complexes, and only limited studies[17] on lower valent titanium complexes or adducts of low-valent titanium halides which, based on magnetic moment measurements, could be either dinuclear or polynuclear. Organosulfide adducts of TiX_3

with SMe_2 or tht are postulated to be dinuclear[17a] complexes with antiferromagnetic coupling between the Ti centers. Dialkylamido Ti(III) complexes, synthesized by metathetical reactions of TiX_3 with $LiNR_2$, are dimetallic, diamagnetic complexes of general formula $Ti_2(NR_2)_6$ (R = Me, Et); in dilute solution, these species exhibit EPR spectra consistent with a Ti(III) species, presumably from dissociation of the dimetallic. In the case of R = $CHMe_2$ only incomplete substitution of the halides occurred, leading to $Ti_2Cl_2[N(CHMe_2)_2]_4$. There is no information concerning the nature of the titanium–titanium interaction in these species.

There has been a more thorough development of dizirconium(III) chemistry, including the first rational synthesis of a dinuclear group 4 complex with a metal–metal bond. A number of Zr(III) adducts of empirical formula ZrX_3L_2 were prepared[18] in 1968 by addition of L (pyridine, acetonitrile, bipyridine, or phenanthroline) to ZrX_3 and found to exhibit magnetic moments below the spin-only value; their insolubility prevented solution molecular weight determinations, but the authors postulated that several of these adducts were halogen-bridged dimetallics. In 1981, Wengrovius and Schrock reported[19a] that photolysis of a dineopentylzirconium(IV) complex resulted in a sparingly soluble, diamagnetic dizirconium species, $Zr_2Cl_6(PMe_3)_4$, in 60% yield (eq 5) rather than the expected Zr(IV) neopentylidene complex from α-elimination of neopentane.

$$\mathrm{Zr(CH_2CMe_3)_2Cl_2(PMe_3)_2 \xrightarrow{h\nu} Zr_2Cl_6(PMe_3)_4} \qquad (5)$$

In a followup study,[19b] rational syntheses were reported of the PMe_3 species and of more soluble trialkylphosphine derivatives through in situ reduction of $ZrCl_4$ with sodium amalgam in toluene (eq 6). The R = Me complex is difficult to separate from finely divided mercury and NaCl, but the higher alkyl chain length analogues are more soluble.

$$\mathrm{2ZrCl_4 + 4PR_3 + 2Na/Hg \rightarrow Zr_2Cl_6(PR_3)_4 + 2NaCl} \qquad (6)$$

$$\mathrm{R = Me, Et, CH_2CH_2CH_3, Bu}$$

The solution molecular weights are intermediate between those expected for a mononuclear and a dinuclear complex, and the authors propose that excess trialkylphosphine can exchange with both. A weak EPR signal is exhibited for solutions of the PEt_3 species with excess added PEt_3.

Cotton and co-workers have recently reported[20] the molecular structures of the isostructural PMe_2Ph, PEt_3, and $Ph_2PCH_2CH_2PPh_2$ analogues of Schrock's PBu_3 dizirconium complex which were prepared by the same synthetic route of sodium amalgam reduction of $ZrCl_4$ in the presence of the phosphine.

The preparation of the above dizirconium(III) complexes demonstrates that the only barrier to further development of metal–metal bonded dititanium and dizirconium chemistry and to the discovery of dihafnium complexes is further work. More powerful reducing agents may be needed for the synthesis of complexes with multiple bonds of these metals in their divalent or univalent state. Electrochemical studies should prove useful in defining the needed reduction potentials for single and multiple bond synthesis in this nonaqueous chemistry. In situ reduction of MX_4 or other tetravalent precursors in the presence of two-electron donor ligands (rather than adduct formation by ligand addition to lower valent metal halides) and the use of the known $Zr_2Cl_6(PR_3)_4$ complexes as dinuclear synthons will be the keys to development of metal–metal bonded, dinuclear group 4 chemistry.

C. Divanadium Complexes

Despite a great deal of work in the area of preparation of divanadium compounds, there are still few examples of nonorganometallic, metal–metal bonded divanadium complexes. The most likely reason for this is the absence of suitable metal–metal bonded divanadium precursors. A series of synthetically useful divanadium(II) species, of general formula $\{[VL_3]_2(\mu\text{-}X)_3\}^+$ (with L = thf, 3-methyltetrahydrofuran, and PMe_3), has been prepared and structurally characterized,[21] but there is controversy[21b,c] as to whether the magnetic properties and structural parameters are consistent with partial vanadium–vanadium bonding. These divanadium compounds have been used to prepare several divanadium complexes in which vanadium–vanadium bonding is more clearly present.

In 1983 the divanadium(I) species $[V(PMePh_2)_2]_2(\mu\text{-}H_2ZnH_2BH_2)_2$[22] was prepared by borohydride reduction of the cation $\{[V(thf)_3]_2(\mu\text{-}Cl)_3\}^+$ in the presence of $PMePh_2$ (eq 7). The proposed bond order of a vanadium–vanadium double bond for this vanadium(I) dimetallic is based on a model with a pair of d electrons on each vanadium which is nonbonding with respect to the dinuclear unit.

$$\mathrm{\{[V(thf)_3]_2(\mu\text{-}Cl)_3\}_2[Zn_2Cl_6] + 4PMePh_2 + 4LiBH_4 \rightarrow [V(PMePh_2)_2]_2(\mu\text{-}H_2ZnH_2BH_2)_2} \qquad (7)$$

A similar but nonreducing approach has been used by Cotton and co-workers[23,24] to prepare methylenebis(phosphine) analogues in 10 and 26% yields, respectively (eq 8 and 9), in which the diphosphine bridges, i.e., binucleates, the divanadium group and $\eta^2\text{-}H_2BH_2$ ligands are in edge-chelating locations in the edge-sharing bioctahedral structures.

$$\mathrm{\{[V(thf)_3]_2(\mu\text{-}Cl)_3\}_2[Zn_2Cl_6] + 6NaBH_4 + 4Ph_2PCH_2PPh_2 \rightarrow [V(H_2BH_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2} \qquad (8)$$

$$\mathrm{\{[V(thf)_3]_2(\mu\text{-}Cl)_3\}_2[Zn_2Cl_6] + 4LiBH_4 + {>}2Me_2PCH_2PMe_2 \rightarrow [V(H_2BH_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}Me_2PCH_2PMe_2)_2} \qquad (9)$$

The structures of both species, however, suggest that no vanadium–vanadium bond is present in these vanadium(II) dimetallics. The reason for the lack of metal–metal bonding is not clearly known.

Henkel,[25] Holm,[26] Christou[139] and co-workers simultaneously reported in 1983 the preparation of divanadium(III) 1,2-ethanedithiolate complexes by reaction of VCl_3 with either the dithiol or the disodium salt (eq 10) followed by cation (Et_4N^+ or Ph_4P^+) exchange.

$$\mathrm{2VCl_3 + HSCH_2CH_2SH \text{ or } NaSCH_2CH_2SNa \rightarrow \{[V(S_2C_2H_4)]_2(\mu,\eta^2\text{-}S_2C_2H_4)_2\}^{2-}} \qquad (10)$$

D. Diniobium and Ditantalum Complexes

The greatest number and range of examples of dinuclear, metal–metal bonded early-transition-metal complexes are found in diniobium and ditantalum chemistry. Dinuclear complexes of both elements are prepared in similar ways and are usually isostructural, so their synthesis will be discussed together.

The following discussion of synthetic approaches to metal–metal bonded diniobium and ditantalum complexes will focus on syntheses of either postulated or structurally characterized dimetallics which involve one of the approaches depicted in eq 1–4. Syntheses that involve simple ligand substitutions on dinuclear synthons and that result in dinuclear complexes of the same structural type, as confirmed by structural studies, will be discussed in section IV on molecular structures.

1. Confacial Bioctahedral Complexes

There are a number of early reports of lower valent adducts[27–29] of niobium and tantalum for which dinuclear structures were proposed[28,29] on the basis of low magnetic moments. The synthetic approach to these adducts involved direct addition of a sulfur-based ligand to the relatively insoluble tetravalent metal halide, which in one case[28] led to a small amount of byproduct with a Ta:Br ratio of approximately 1:3. A dinuclear solid-state structure for the niobium adducts of empirical formula $NbCl_4(SMe_2)$ was also proposed by these workers.[28,29]

The first clear example of a diniobium(III) species is $Nb_2Cl_9^{3-}$, which was derived via gas-phase, chemical transport reaction (650 °C) of CsCl with the lower valent triniobium species Nb_3Cl_8 (eq 11).[30] This preparation is only successful for the chloride species; the bromide and iodide complexes are paramagnetic and thus do not possess a Nb–Nb interaction. The chloride complex was shown to possess a Nb–Nb bond, presently assignable as a double bond, on the basis of structural studies.

$$12CsCl + 3Nb_3Cl_8 \rightarrow 4Cs_3Nb_2Cl_9 + Nb \quad (11)$$

In 1973 the first synthetically useful diniobium(III) species $Nb_2X_6(tht)_3$ (X = Cl, Br, I) was prepared by Maas and McCarley[31] in 60–70% yield via sodium amalgam reduction of $NbX_4(tht)_2$ (eq 12). These authors proposed a dinuclear, confacial bioctahedral structure with both bridging and terminal halide and tht ligands on the basis of IR, ^1H NMR, and halogen NQR spectroscopy, a postulate which was later shown to be correct. Two tht ligands in the chloro dimetallic can be replaced by chlorides from $Et_4N^+Cl^-$ to yield $(Et_4N)_2Nb_2Cl_8(tht)$ in which a bridging tht ligand is retained; further reaction with $Et_4N^+Cl^-$ yields the paramagnetic $(Et_4N)_3Nb_2Cl_9$ and comparison of this observation to the work of Broll et al.[30] demonstrates the cation dependence of solid-state magnetic properties.

$$2NbX_4(tht)_2 + 2Na/Hg \rightarrow Nb_2X_6(tht)_3 + 2NaX \quad (12)$$

The above report was the first use of sodium amalgam as a reductant in early-transition-metal dimetallic chemistry. The concept was extended by Allen and Naito in 1976 to give the first direct reductive dimerization starting from Nb(V) rather than the less convenient lower valent niobium precursors.[32] These workers prepared the SMe_2 analogue of the McCarley dimetallic complex in 28% yield by using Na/K alloy as the reductant (eq 13) and also showed that the SMe_2 analogue undergoes ligand substitution with chelating ligands such as $Ph_2PCH_2CH_2PPh_2$, $C_6H_4(AsMe_2)_2$ (diars), and $MeC(CH_2AsMe_2)_3$ (triars). An edge-sharing bioctahedral structure was proposed for the diars and triars complexes on the basis of NMR spectroscopy and solution molecular weight studies (with the latter containing a bidentate triars with a dangling arsine end), while the diphosphine analogue proved to be too insoluble. Hubert-Pfalzgraf and co-workers[33] later reported that a higher yield could be obtained with magnesium turnings as reductant.

$$2NbCl_5 + 2BH_3{\cdot}SMe_2 + 2Na/K\ (1:1) \rightarrow Nb_2Cl_6(SMe_2)_3 + 2NaCl + 2KCl \quad (13)$$

McCarley and co-workers in 1978 reported[34] that sodium amalgam reduction of TaX_5 in the presence of tht afforded a ditantalum analogue of the above diniobium tht and SMe_2 complexes in 75% yield (eq 14).

$$2TaX_5 + 4Na/Hg + 3.5tht \rightarrow [TaX_2(tht)]_2(\mu\text{-}X)_2(\mu\text{-}tht) + 4NaX \quad (14)$$

The new ditantalum dimetallics $[TaX_2(tht)]_2(\mu\text{-}X)_2(\mu\text{-}tht)$ with X = Cl or Br exhibited a weak temperature-independent paramagnetism which was postulated to arise from admixture of paramagnetic excited states into the diamagnetic ground state. The basic structural features, namely, a doubly bonded ditantalum center with both bridging and terminal tht and halide ligands, were confirmed by ^1H NMR, IR, and NQR spectroscopy and by a followup X-ray crystallographic study (vide infra).

Cotton and co-workers have recently extended this preparative approach to the ditantalum(II) and diniobium(II) species with formal metal–metal triple bonds,[35] the first such early metal examples and a major advance in the field. Reduction of $[MX_2(tht)]_2(\mu\text{-}X)_2(\mu\text{-}tht)$ with 2 equiv of sodium amalgam in tetrahydrofuran afforded the confacial bioctahedral, diamagnetic, triply bonded dinuclear anions $M'_2\{[MX_3]_2(\mu\text{-}tht)_3\}$ (M′ = Na, Li; M = Nb, X = Cl, Br; M = Ta, X = Cl) in 60–62% yield (eq 15); the reduction proceeds through the intermediate thf-substituted $[MX_2(thf)]_2(\mu\text{-}X)_2(\mu\text{-}tht)$ which is formed upon dissolution of the tht dimetallics in thf, as the reduction of $[MX_2(tht)]_2(\mu\text{-}X)_2(\mu\text{-}tht)$ does not proceed in toluene solution. Cation substitution with $Et_4N^+Cl^-$ is possible and yields the discrete triply bonded dianion without the normally associated alkali metal cation. The triply bonded dimetallics can be synthesized directly from MX_5 in a two-step procedure in which the doubly bonded tht dimetallic is first prepared in toluene, followed by addition of thf and further reduction. The sodium salts disproportionate in tetrahydrofuran to give the tetramers $[M_2X_5(\mu\text{-}tht)_3]_2^{2-}$.

$$[MX_2(thf)]_2(\mu\text{-}X)_2(\mu\text{-}tht) + 2Na/Hg + 2M'X \rightarrow M'_2\{[MX_3]_2(\mu\text{-}tht)_3\} \quad (15)$$

2. Edge-Sharing Bioctahedral Complexes with Monodentate Ligands

This structural class of diniobium and ditantalum species is usually prepared by reduction of NbX_5 or TaX_5 (i.e., eq 2) in the presence of two-electron donor ligands, which in many cases are trialkyl- or mixed alkyl–arylphosphines. The alternate approach of monodentate ligand addition to confacial bioctahedral synthons is rarely used, in contrast to the usual preparative approach for chelated, edge-sharing bioctahedral complexes of bidentate ligand addition to confacial bioctahedral precursors (vide infra).

Hubert-Pfalzgraf and Riess reported in 1978 the first member of this structural class by the reduction of $NbCl_5$ with excess magnesium turnings in the presence of PMe_2Ph (eq 16).[36]

$$2NbCl_5 + \text{excess } PMe_2Ph + \text{excess } Mg \rightarrow Nb_2Cl_6(PMe_2Ph)_4 + 2MgCl_2 \quad (16)$$

This is the first use of an alkaline-earth-metal reductant in dimetallic synthesis, and the high yield (87%) attests to the fact that the reduction stops at the trivalent state. Methylene chloride was used as solvent, since reduction with magnesium does not occur in toluene. A dinuclear structure was postulated on the basis of the solution diamagnetism of the compound, as determined by the Evans method, and a solution molecular weight which approximates that of a dimetallic, perhaps due to some ligand loss. The ^1H and ^{31}P NMR spectra of the isolated product suggest two inequivalent phosphine sites in the dimetallic and the presence of a second, unidentified species. One surprising feature of the compound is its lack of reactivity toward CH_3CN, from which it can be recrystallized, and CH_2Cl_2, the solvent employed in the synthesis. This stands in contrast to the case with ditantalum compounds (vide infra) and suggests that diniobium compounds are less prone toward oxidation via either reductive coupling of organic substrates or oxidative addition.

The first example of direct reduction of a tantalum(V) halide to an edge-sharing bioctahedral complex was reported by Sattelberger and co-workers in 1980;[37a,b] Schrock and co-workers reported the preparations of this dimetallic and a mononuclear precursor, $TaCl_3(PMe_3)_3$, in 1982.[37c] These workers utilized sodium amalgam and PMe_3 in toluene solvent (eq 17).

$$2TaCl_5 + 4Na/Hg + 4PMe_3 \rightarrow [TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2 + 4NaCl \quad (17)$$

Both ^1H and ^{31}P NMR spectroscopy suggested that two types of PMe_3 ligands were present in this diamagnetic complex, axial on one end of the bioctahedron and equatorial on the other end, and this stereochemistry and the Ta–Ta double bond assignment were confirmed by single-crystal X-ray diffraction. On the basis of later studies, it seems reasonable to postulate that the reduction can proceed through either $TaCl_x(PMe_3)_y$ (x = 3, 4) or through the intermediate Ta(IV) dimetallic $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_4$ (despite its lower solubility). A possibly isostructural ditantalum(III) dimethylphenylphosphine complex was subsequently reported[38] by Hubert-Pfalzgraf and co-workers via magnesium amalgam reduction of $TaCl_5$ in methylene chloride, although their NMR data show several structural isomers or other byproducts to be present.

The discovery by Sattelberger of $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$ was significant because of the reactivity of this doubly bonded species[37a,39] and because it led to a number of other reactive ditantalum species.[40] Oxidative addition of dihydrogen across the Ta=Ta in this complex (the first such hydrogenation of any transition-metal–metal multiple bond) yielded a ditantalum(IV) dihydride complex, $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2$, which can be reduced with sodium amalgam in 1,2-dimethoxyethane to a reactive dihydridoditantalum(III) compound, $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2$, with a nominal edge-sharing bioctahedral structure (eq 18).

$$[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2 + 2Na \rightarrow [TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2 + 2NaCl \quad (18)$$

Proton NMR spectroscopy indicated that the hydrides (δ 8.52) were in bridging positions and coupled to all PMe_3 ligands, and an IR absorption at 1232 cm^{-1} (shifted to 860 cm^{-1} in the deuteride analogue) was consistent with a hydrido-bridged dimetallic. This complex exhibits a rich oxidative addition chemistry (vide infra).

Several complexes of the edge-sharing bioctahedral type have been synthesized with ligands other than tertiary phosphines. Hubert-Pfalzgraf and co-workers have reported a 4-methylpyridine ditantalum complex in good yield via magnesium reduction of TaX_5 (X = Cl, Br; eq 19).[41]

$$2TaX_5 + 2Mg + 4p\text{-}MeC_5H_4N \rightarrow Ta_2X_6(NC_5H_4\text{-}p\text{-}Me)_4 \quad (19)$$

The product is diamagnetic both in the solid state and in solution, and low-temperature ^1H NMR spectra showed three methyl signals whose relative areas were a function of concentration for the X = Cl complex(es). The compound is unreactive toward MeCN and has been utilized to prepare a number of other derivatives, including alkoxide derivatives of postulated tetrameric structure (vide infra).

Dinuclear complexes of these metals with alkoxide ligands are also known, and in mixed halo/alkoxy species there seems to be a preference for μ-alkoxide ligands. Wentworth and Brubaker reported a diniobium product, $Nb_2Cl_2(OEt)_6(NC_5H_5)_2$, in 1964 from electrochemical reduction of $NbCl_5$ in EtOH, saturated with HCl, followed by pyridine addition.[42] A dinuclear formulation was proposed based on solution molecular weight studies, and it seems reasonable to postulate an edge-sharing bioctahedral structure for this Nb(IV) dimetallic. Several diniobium alkoxide complexes from alcoholysis reactions of $[NbCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht)$ were reported by Cotton and co-workers in 1985.[43] Reactions with Me_2CHOH or EtOH resulted in the elimination of 1 equiv of HCl, displacement of the tht ligands by ROH, and generation of the edge-sharing bioctahedral diniobium(III) complex $[NbCl_2(HOR)_2]_2(\mu\text{-}Cl)(\mu\text{-}OR)$ in >60% yield (eq 20), whereas MeOH yielded the bioctahedral bis(μ-methoxy)diniobium(IV) complex in 25% yield (eq 21).

$$[NbCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + ROH \rightarrow [NbCl_2(HOR)_2]_2(\mu\text{-}Cl)(\mu\text{-}OR) \quad (20)$$

$$[NbCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + MeOH \rightarrow [NbCl_2(OMe)(HOMe)]_2(\mu\text{-}OMe)_2 \quad (21)$$

The latter dimetallic can be prepared also from MeOH addition to $NbCl_4L_2$ (L = NCMe, thf). The ethoxydiniobium(III) complex reacted further with EtOH in an inert atmosphere to give a tetraniobium(IV) cluster $[Nb_2OCl_4(OR)(thf)_2]_2$, and C_2H_4. The methoxy dimetallic exists as an equilibrium mixture of at least three species of unknown nuclearity in solution, as shown by ^1H NMR spectroscopy, with the equilibrium a function of temperature and MeOH concentration and complicated by inter- and intramolecular H-bonding. Carbon-13 NMR spectroscopy, which might have provided more information about the various species, was not employed. Addition of acetonitrile to the methoxide complex resulted in displacement of the MeOH ligands (eq 22) and generation (40%

yield) of the MeCN complex, from which the liberated MeOH proved difficult to remove despite repeated MeCN washing.

$$[\mathrm{NbCl_2(OMe)(HOMe)}]_2(\mu\text{-OMe})_2 + 2\mathrm{MeCN} \rightarrow [\mathrm{NbCl_2(OMe)(NCMe)}]_2(\mu\text{-OMe})_2 + 2\mathrm{HOMe} \quad (22)$$

Recently, Canich and Cotton have shown[44] that confacial bioctahedral diniobium(III) and ditantalum(III) dimetallics of the McCarley type can exist in equilibrium with edge-sharing bioctahedral complexes in the presence of excess ligand (eq 23), with the tetrakis(dimethyl sulfide) complex being less soluble. They isolated in low (unstated) yield complexes for both metals during attempted oxidative addition reactions with the disulfide MeSSMe. This important observation shows that such equilibria must be considered in future studies of ligand addition/displacement reactions that involve these confacial bioctahedral precursors.

$$[\mathrm{MCl_2(SMe_2)}]_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2) + \mathrm{SMe_2} \rightarrow [\mathrm{MCl_2(SMe_2)_2}]_2(\mu\text{-Cl})_2 \quad (23)$$

A number of sulfide and disulfide diniobium complexes that exhibit approximate edge-sharing bioctahedral structures have been synthesized by Drew, Rice, and co-workers. Addition of excess tht to $\mathrm{NbX_3S}$ (X = Cl, Br) resulted in a reduction to niobium(III), concomitant oxidation of two sulfide ligands to an $\mathrm{S_2}^{2-}$ ligand, and the formation of a diniobium species containing both μ-S and μ,η^2-$\mathrm{S_2}$ ligands (eq 24).[45] An X-ray structure showed that the $\mathrm{S_2}^{2-}$ ligand lies perpendicular to the bioctahedral plane with its midpoint in the plane. This complex was later obtained[46] by addition of tht to $\mathrm{Nb_2X_4S_3}$, which is formed in the reaction of $\mathrm{Sb_2S_3}$ and $\mathrm{NbX_5}$ (eq 25); crystals of $\mathrm{Nb_2X_4S_3}$ could not be obtained, but these species are also believed to contain S and $\mathrm{S_2}$ ligands. A number of other diamagnetic, and thus presumably diniobium(IV), adducts were obtained with $\mathrm{SMe_2}$, NCMe, and $\mathrm{PhSCH_2CH_2SPh}$ but were not structurally characterized. Sulfur atom abstraction from the tht adduct $[\mathrm{NbCl_2(tht)_2}]_2(\mu\text{-S})(\mu\text{-S}_2)$ using $\mathrm{PPh_3}$ resulted in the diniobium(IV) species $[\mathrm{NbCl_2(tht)_2}]_2(\mu\text{-S}_2)$ which contains two sulfide bridges (eq 26).

$$3\mathrm{NbX_3S} + 6\mathrm{tht} \rightarrow [\mathrm{NbX_2(tht)_2}]_2(\mu\text{-S})(\mu\text{-S}_2) + \mathrm{NbX_5(tht)}_n \quad (24)$$

$$2\mathrm{NbX_5} + \mathrm{Sb_2S_3} \rightarrow \mathrm{Nb_2X_4S_3} \xrightarrow{\text{tht}} [\mathrm{NbX_2(tht)_2}]_2(\mu\text{-S})(\mu\text{-S}_2) \quad (25)$$

$$[\mathrm{NbCl_2(tht)_2}]_2(\mu\text{-S})(\mu\text{-S}_2) + \mathrm{PPh_3} \rightarrow [\mathrm{NbCl_2(tht)_2}]_2(\mu\text{-S})_2 + \mathrm{SPPh_3} \quad (26)$$

A related acetonitrile adduct can be prepared directly from a mononuclear niobium(IV)/nitrile adduct and $\mathrm{Sb_2S_3}$ (eq 27; n = 1 or 2).[47]

$$2\mathrm{NbCl_4(NCMe)_2} + 2\mathrm{Sb_2S_3} \rightarrow [\mathrm{NbCl_2(MeCN)_2}]_2(\mu\text{-S})_2\cdot n\mathrm{MeCN} \quad (27)$$

3. Edge-Sharing Bioctahedral Complexes with Bidentate or Binucleating Ligands

The first synthesis of members of this structural class utilized ligand substitution on confacial bioctahedral precursors, and this approach is the major synthetic route. Allen and Naito reported the preparation of the diniobium $\mathrm{Ph_2PCH_2CH_2PPh_2}$, diars, and triars adducts through ligand substitution reactions with $[\mathrm{NbCl_2(SMe_2)}]_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)$ and assigned an edge-sharing bioctahedral structure on the basis of ^{1}H NMR spectroscopy for the latter two products;[32] later work by Cotton and co-workers[48] has shown that the insoluble $\mathrm{Ph_2PCH_2CH_2PPh_2}$ species has the edge-sharing bioctahedral structure with end-chelating bidentate diphosphines.

Clay and Brown have prepared a variety of diniobium(III) and ditantalum(III) chelating diadducts by ligand addition to $[\mathrm{MCl_2(tht)}]_2(\mu\text{-Cl})_2(\mu\text{-tht})$ (eq 28).[49] Dinuclear chelates were obtained for L-L = bipyridine, $\mathrm{MeSCH_2CH_2SMe}$, $\mathrm{EtSCH_2CH_2SEt}$, and $\mathrm{Ph_2PCH_2CH_2PPh_2}$, whereas no reaction occurred at 80 °C for $\mathrm{Ph_2AsCH_2CH_2AsPh_2}$, $\mathrm{PhSCH_2CH_2SPh}$, or $\mathrm{Me_3CSCH_2CH_2SCMe_3}$. The adducts exhibited temperature-dependent paramagnetism and EPR signals (while the starting dimetallics showed no evidence of paramagnetism), which raises the possibility that M–M single bonds are present in these d^2–d^2 dimetallics.

$$[\mathrm{MCl_2(tht)}]_2(\mu\text{-Cl})_2(\mu\text{-tht}) + 2\text{L-L} \rightarrow \mathrm{M_2Cl_6(L\text{-}L)_2} + 3\mathrm{tht} \quad (28)$$

Diamagnetic β-diketonate and carboxylate ditantalum complexes which are potentially of the edge-sharing bioctahedral class have been reported by Hubert-Pfalzgraf and coworkers[50] through ligand substitution reactions involving loss of HCl (eq 29 and 30; py′ = $\mathrm{NC_5H_4}$-p-Me). In both cases the released HCl was trapped by the 4-methylpyridine and the pyridinium salt removed by sublimation or washing. The dipivaloylmethanato complex (65% yield) exhibited a single $\mathrm{CMe_3}$ resonance in the ^{1}H NMR spectrum, whereas the spectra of the pivalate complex (80% yield) showed two solution species, with one having two inequivalent pivalate environments.

$$\mathrm{Ta_2Cl_6(py')_4} + {>}4\mathrm{Me_3CCOCH_2COCMe_3} \rightarrow \mathrm{Ta_2Cl_4(Me_3CCOCHCOCMe_3)_4} + \mathrm{Hpy'^+Cl^-} \quad (29)$$

$$\mathrm{Ta_2Cl_6(py')_4} + \mathrm{Me_3CCO_2H} \rightarrow \mathrm{Ta_2Cl_4(O_2CCMe_3)_4\cdot 2Me_3CCO_2H} + \mathrm{Hpy'^+Cl^-} \quad (30)$$

Other examples of structurally characterized bidentate and binucleating ligand complexes made via ligand addition to confacial bioctahedral precursors are discussed in section IV.D.3 on molecular structures or are listed in Table V.

4. Tetragonal Face-Sharing, Double Square Antiprismatic Complexes

Dinuclear complexes in which two square antiprismatic metal coordination spheres share a common 4-fold face, and thus have four bridging ligands, make up a small but growing class of metal–metal singly bonded diniobium(IV) and ditantalum(IV) species. In a number of cases, structural studies have shown that the mononuclear compounds $\mathrm{MCl_4(PMe_3)_2}$ are, in fact, dinuclear with four chloride bridges, and it may turn out for other small cone angle ligands that the mononuclear M(IV) adducts are in fact dinuclear in the solid state. Direct syntheses of $[\mathrm{ML_4}]_2(\mu\text{-L})_4$ complexes have in most cases involved oxidative addition reactions to doubly bonded dinuclear species of the edge-sharing bioctahedral type.

Manzer reported in 1977 that addition of $\mathrm{PMe_3}$ to $\mathrm{NbCl_4(thf)_2}$ resulted in a dark green solution and a reddish precipitate of low magnetic moment.[51] It was not until later that the insoluble product was identified as a dinuclear compound (vide infra).

Sattelberger and co-workers demonstrated in 1980 that tantalum–tantalum double bonds in edge-sharing bioctahedral complexes were capable of undergoing formal oxidative addition reactions with dihydrogen, hydrogen chloride, and chlorine. The ditantalum(III) compound $[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_2$ was shown to react with dihydrogen[37,39] to give formal addition across the Ta=Ta bond (eq 31). Evidence for the bridging hydride formulation was found in both the ^{1}H NMR spectrum (δ 8.5) and the IR spectrum (Ta–D–Ta mode at 902 cm^{-1} for the deuteride analogue), and the ^{31}P NMR spectrum showed three inequivalent $\mathrm{PMe_3}$ sites in a 2:1:1 ratio consistent with both equatorial and inequivalent axial sites in the molecule. The stereochemistry from spectroscopic methods was confirmed by followup structural studies, which showed two chloride bridges and a vacancy in the bridging region consistent with the stereochemical influence of two unobserved hydrides. Hubert-Pfalzgraf and co-workers[38] also observed that a reaction of dihydrogen with their $\mathrm{PMe_2Ph}$ analogue, $\mathrm{Ta_2Cl_6(PMe_2Ph)_4}$, gave a product with ^{1}H NMR (δ −3) and IR (1730 cm^{-1}) spectral data which they ascribed to a ditantalum(IV) species, $\mathrm{Ta_2Cl_6(PMe_2Ph)_4H_2}$, with terminal hydride ligands. They rationalized the broadness of the proton signal by invoking tantalum quadrupolar broadening rather than paramagnetism or dynamical processes.

$$[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_2 + \mathrm{H_2} \rightarrow [\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_2(\mu\text{-H})_2 \quad (31)$$

Sattelberger and co-workers showed[40] that the edge-sharing bioctahedral ditantalum(III) compound $[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_2$ was also capable of oxidative addition reactions. This complex reacted readily at −20 °C with $\mathrm{Cl_2}$ to yield the known $[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_2(\mu\text{-H})_2$ in 70% yield (eq 32), with HCl at −20 °C to yield $[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})(\mu\text{-H})_3$ in 72% yield (eq 33), and with $\mathrm{H_2}$ at 25 °C to yield the tetrahydrido complex $[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_4$ (eq 34) in 85% yield. The trihydride dimetallic showed two inequivalent ^{1}H NMR resonances at δ 9.68 and 7.69 in a 1:2 ratio and a Ta–H–Ta IR mode at 1260 cm^{-1}, while the tetrahydride had a single proton resonance at δ 8.79 and IR absorption at 1225 cm^{-1}. The spectroscopic data for all three ditantalum(IV) complexes were consistent with double square-antiprismatic structures containing four bridging ligands, and the hydride ligands consistently occupied bridge sites. The tetrahydride can also be prepared by thermolysis[52] of $\mathrm{TaCl_2H_2(PMe_3)_4}$ in cyclohexane solution with loss of $\mathrm{PMe_3}$ (eq 35).

$$[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_2 + \mathrm{Cl_2} \rightarrow [\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_2(\mu\text{-H})_2 \quad (32)$$

$$[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_2 + \mathrm{HCl} \rightarrow [\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})(\mu\text{-H})_3 \quad (33)$$

$$[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_2 + \mathrm{H_2} \rightarrow [\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_4 \quad (34)$$

$$2\mathrm{TaCl_2H_2(PMe_3)_4} \xrightarrow{\Delta} [\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_4 + 4\mathrm{PMe_3} \quad (35)$$

Nielson and Boyd and their co-workers in 1984 independently prepared and characterized the single-bonded ditantalum(IV) and diniobium(IV) complexes $[\mathrm{MCl_2L_2}]_2(\mu\text{-Cl})_4$ with L = $\mathrm{PMe_3}$ and, for M = Nb, L = $\mathrm{PMe_2Ph}$.[53-55] Nielson and co-workers first observed $[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_4$ as a byproduct in unspecified yield from reactions of $\mathrm{Li_2PCMe_3}$ with $\mathrm{TaCl_5}$ in the presence of $\mathrm{PMe_3}$.[53a] The niobium analogue was obtained in 74% yield by $\mathrm{PMe_3}$ addition to $\mathrm{NbCl_4L}_x$ (L = NCMe, x = 3; L = thf, x = 2; eq 36).[53c] Cotton and co-workers found that $[\mathrm{NbCl_2(PMe_2Ph)_2}]_2(\mu\text{-Cl})_4$ could be prepared in 60% yield by direct reduction of $\mathrm{NbCl_5}$ with 1 equiv of sodium amalgam in the presence of $\mathrm{PMe_2Ph}$ (eq 37)[54] and then used the same approach to prepare $[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_4$ in 59% yield via direct reduction.[53b] The diniobium complexes were reported to be insoluble in organic solvents ($[\mathrm{NbCl_2(PMe_2Ph)_2}]_2(\mu\text{-Cl})_4$ will dissolve with added phosphine, in contrast to the $\mathrm{PMe_3}$ analogue, and may exist in solution as the monomer), to be stable as solids in air, and to be surprisingly unreactive toward EtOH.

$$2\mathrm{NbCl_4(NCMe)_3} + {>}6\mathrm{PMe_3} \rightarrow 2\mathrm{NbCl_4(PMe_3)_3} \rightarrow [\mathrm{NbCl_2(PMe_3)_2}]_2(\mu\text{-Cl})_4 \quad (36)$$

$$2\mathrm{NbCl_5} + {>}6\mathrm{PMe_2Ph} + 2\mathrm{Na/Hg} \rightarrow [\mathrm{NbCl_2(PMe_2Ph)_2}]_2(\mu\text{-Cl})_4 \quad (37)$$

5. Miscellaneous Syntheses of Nonorganometallic Dinuclear Complexes

Several new diniobium complexes of unknown structure were reported in 1981 from reactions of β-diketones with $\mathrm{Nb_2Cl_6(PMe_2Ph)_4}$ and $[\mathrm{NbCl_2(SMe_2)}]_2(\mu\text{-Cl})_2(\mu\text{-SMe_2})$.[56] In the case of acetylacetone (acacH), the species $\mathrm{Nb_2Cl_4(acac)_2(acacH)_2(PMe_2Ph)_2}$ was found, whereas dipivaloylmethane (dpmH) yielded both $\mathrm{Nb_2Cl_5(dpm)(PMe_2Ph)_2}$ and $\mathrm{Nb_2Cl_3(dpm)_3}$.

Several diniobium and ditantalum complexes of unknown structure with the bulky trialkylphosphine ligands $\mathrm{P(c\text{-}C_6H_{11})_3}$ and $\mathrm{P(CMe_3)_3}$ were reported by Morancais and Hubert-Pfalzgraf in 1984.[57] Reduction of the pentahalides with magnesium in $\mathrm{CH_2Cl_2}$ in the presence of the phosphines gave complex mixtures of products. Better results were found with a mixture of diethyl ether and $\mathrm{CH_2Cl_2}$, and the diamagnetic species $\mathrm{Nb_2Cl_8[P(CMe_3)_3]_2}$ and $\mathrm{Nb_2Cl_8[P(c\text{-}C_6H_{11})_3]_4}$ were obtained in the niobium case. Partial amalgamation of the magnesium or use of sodium naphthalenide in toluene/thf led to $\mathrm{Nb_2Cl_6[P(c\text{-}C_6H_{11})_3]_3}$ or $\mathrm{Nb_2Cl_6[P(CMe_3)_3]_2}$ with niobium and $\mathrm{Ta_2Cl_6(PR_3)_3}$ for tantalum for either phosphine. All of the new dimetallics were stable in acetonitrile, and the reductions were unsuccessful under a dinitrogen atmosphere in place of the argon atmosphere used in this chemistry.

A complex that can perhaps be viewed as the product of formal addition of an anion to a confacial bioctahedral intermediate was noted in the reaction of $[\mathrm{NbCl_2(tht)}]_2(\mu\text{-Cl})_2(\mathrm{tht})$ with $\mathrm{Me_4N^+OAc^-}$.[58] The product $\mathrm{Me_4N^+}[\mathrm{NbCl}(\eta^2\text{-OAc})]_2(\mu,\eta^2\text{-OAc})_2(\mu\text{-tht})(\mu,\eta^1\text{-OAc})^-$ possesses chelating, bridging monodentate, and bridging bidentate acetates. It seems likely that development of dinuclear carboxylate chemistry of the group 5 elements will follow an unusual and interesting course.

Two other reduction methods have been utilized in dinuclear group 5 chemistry. Electrochemical reduction of $\mathrm{Nb_2Cl_6(PMe_2Ph)_4}$ yielded a proposed diniobium(I) species on the basis of mass spectrometry, but the product has not been unequivocally characterized.[59] Pulse radiolysis in MeCN of $Ta_2Cl_6(NC_5H_4\text{-}p\text{-}Me)_4$ yielded a postulated anionic dimetallic,[60] but further data are needed.

LaPointe and Wolczanski have reported novel ditantalum(IV) and diniobium(IV) species with the first example of unbridged early metal–metal single bonds.[61] Reduction of the bulky trialkylsiloxide mononuclear compounds $[(Me_3C)_3SiO]_2MCl_3$ with excess sodium amalgam under dihydrogen gave the dimetallics $[MH_2\{OSi(CMe_3)_3\}_2]_2$ in 60% (Ta) and 40% (Nb) yields (eq 38). The diamagnetic complexes exhibited solution

$$2[(Me_3C)_3SiO]_2MCl_3 + \geq 3Na/Hg + H_2 \rightarrow [TaH_2\{OSi(CMe_3)_3\}_2]_2 \quad (38)$$

molecular weights consistent with dimetallics, IR spectral data consistent with terminal hydrides (for M = Ta, ν_{TaH} = 1791 cm^{-1}, shifted to 1270 cm^{-1} in the deuteride; for M = Nb, 1720/1230 cm^{-1}), and ^1H NMR signals for the hydrides at δ 12.13 (M = Ta) and 7.3 (M = Nb). The solid-state structure showed an unbridged Ta–Ta bond, but in solution bridging siloxide ligands cannot be ruled out if bridge/terminal exchange is rapid. The ditantalum complex reacted with 2 equiv of HCl to give H_2 and a new ditantalum(IV) species, $[\{(Me_3C)_3SiO\}_2TaCl]_2(\mu\text{-}H)_2$, with bridging hydride ligands (eq 39); the ^1H NMR resonance for the hydride was found at δ 9.35 and the IR absorption at 1595 cm^{-1} (1240 cm^{-1} for the deuteride).

$$[TaH_2\{OSi(CMe_3)_3\}_2]_2 + 2HCl \rightarrow [\{(Me_3C)_3SiO\}_2TaCl]_2(\mu\text{-}H)_2 + H_2 \quad (39)$$

E. Organodimetallic Complexes

There are fewer metal–metal bonded organodimetallic complexes of the early transition metals than metal–metal bonded dinuclear complexes, if one excludes the bis(cyclopentadienyl) and related fulvalene compounds. The known organodimetallic complexes span a wider variety of structures and thus resist any convenient classification, so this section will be organized chronologically. A majority of these organodimetallic complexes involve vanadium.

The first organodimetallic complex of these metals to be discovered was also the first example of a dinuclear compound with a niobium–niobium bond. Nesmeyanov and co-workers found[62] during their study of acetylene reactions with $CpNb(CO)_4$ that the diphenylacetylene adduct $CpNb(CO)_2(PhCCPh)$ loses 1 equiv of CO upon thermolysis (80 °C, toluene) to afford the diniobium(I) complex $[CpNb(CO)(PhCCPh)]_2$ (eq 40). The single-crystal X-ray diffraction study showed a niobium–niobium bond which was assigned as a double bond on the basis of solution diamagnetism and electron-counting considerations.

$$2CpNb(CO)_2(PhCCPh) \xrightarrow{\Delta} [CpNb(CO)(PhCCPh)]_2 + 2CO \quad (40)$$

Thermally or photochemically induced carbon monoxide loss has also been used to prepare organodivanadium complexes. The complex $Cp(OC)V(\mu,\eta^2\text{-}CO)_2V(CO)_2Cp$[63] was first reported[63a] by Fischer and Schneider in 1970 via protonation of a vanadium carbonyl dianion (83% yield, eq 41), and this unusual compound has since attracted a great deal of interest.

$$CpV(CO)_4 + 2Na \rightarrow Na_2CpV(CO)_3 \xrightarrow{HCl} Cp(OC)V(\mu,\eta^2\text{-}CO)_2V(CO)_2Cp \quad (41)$$

The complex can also be prepared in 89% yield by photolysis of $CpV(CO)_4$ using a falling film photochemical reactor[63d] to minimize competing photolytic decomposition of the organodimetallic,[63e] and the photolytic method has been extended to the preparation of the C_5Me_5 analogue.[64] Structural studies by Cotton, Caulton, and their co-workers have shown that the complex has a short vanadium–vanadium distance and two donor semibridging carbonyl groups across the asymmetric $Cp(OC)V{=}V(CO)_2Cp$ fragment. Carbon monoxide elimination via ligand diplacement was also employed in the preparation of $(C_6H_6)_2V_2(CO)_4$, which would be expected to possess a vanadium–vanadium triple bond, from thermal reaction of C_6H_6 with $V(CO)_6$; crystals of the product, obtained in 25% yield, were unfortunately twinned.[65]

The second example of an organometallic divanadium complex with vanadium–vanadium bonding, reported in 1978 by Vahrenkamp,[66] was $[V(CO)_4]_2(\mu\text{-}PMe_2)_2$. This novel species was prepared in 40% yield by addition of $PHMe_2$ to $V(CO)_6$ (eq 42). The X-ray

$$2V(CO)_6 + 2PHMe_2 \rightarrow [V(CO)_4]_2(\mu\text{-}PMe_2)_2 + H_2 + 4CO \quad (42)$$

structure showed a long vanadium–vanadium separation which was interpreted on the basis of electron counting as a double bond; Hoffmann and co-workers have examined[67] the bonding in related models, and their calculations support an approximate double-bond character. Ligand substitution reactions with tertiary phosphines and arsines afforded new organodivanadium derivatives in which either one or two carbonyl ligands had been replaced.[68] Rehder and co-workers have reported diphosphine and distibine organodivanadium analogues with bridging E_2R_4 (E = P, Sb) ligands from diphosphine reactions with $V(CO)_6^-$ and $CpV(CO)_4$.[69]

Hubert-Pfalzgraf and coworkers reported in 1981 that their ditantalum(III) complex $Ta_2Cl_6(PMe_2Ph)_4$ reacts with $CpSnMe_3$ to give, in 76% yield, a product to which they assigned the formula $Cp_2Ta_2Cl_4(PMe_2Ph)_2$ (eq 43).[38] The product is presumably undergoing rapid

$$Ta_2Cl_6(PMe_2Ph)_4 + 2CpSnMe_3 \rightarrow Cp_2Ta_2Cl_4(PMe_2Ph)_2 + 2SnMe_3Cl \quad (43)$$

rearrangement on the NMR time scale in solution, with single ^1H NMR resonances for the cyclopentadienyl groups and single ^1H and ^{31}P NMR resonances for the phosphine ligands. The solution molecular weight is between that of the calculated dinuclear and mononuclear complexes. The authors did not propose a structure for this organodimetallic, and it is difficult to conceive of a dinuclear complex with two bridging chlorides which would not result in diastereotopic phosphine Me groups; a tetrahalo bridge structure with Cp and PMe_2Ph end groups is implausible on steric grounds. An unbridged Ta=Ta with two terminal chlorides and with the phosphine on a mirror plane, though improbable, cannot be ruled out with the reported data. The complex $[Cp^*Ta]_2(\mu\text{-}X)_4$ with a Ta=Ta double bond reacts with PMe_3 to give mononuclear products via metal–metal bond cleavage (vide infra), which raises the possibility that the above Cp species is in reality a mixture of monomers.

Bunker and Green have reported two organodiniobium complexes starting from mononuclear, formally niobium(III) precursors.[70] Reduction of the diene complex $CpNbCl_2(MeCH{=}CMeCMe{=}CHMe)$ with sodium amalgam gave an organodimetallic in 34% yield (eq 44) with two bridging chlorine atoms and a planar $Nb_2(\mu\text{-}Cl)_2$ core. A dinuclear hydride complex was obtained in 11% yield by Vitride addition to the carbonyl-bis(dimethylphosphino)ethane compound $CpNbCl_2(CO)(Me_2PCH_2CH_2PMe_2)$ followed by aqueous workup (eq 45; R = CH_2CH_2OMe); the dinuclear formulation is based on IR and NMR spectroscopic data.

$$2CpNbCl_2(MeCH{=}CMeCMe{=}CHMe) + 2Na/Hg \rightarrow [CpNb(MeCH{=}CMeCMe{=}CHMe)]_2(\mu\text{-}Cl)_2 \quad (44)$$

$$2CpNbCl_2(CO)(Me_2PCH_2CH_2PMe_2) + NaAlH_2(OR)_2 \rightarrow [CpNb(Me_2PCH_2CH_2PMe_2)H]_2(\mu\text{-}H)_2 \quad (45)$$

A substantial number of metal–metal bonded organodivanadium complexes with chalcogenide bridging groups have been reported in the last 8 years, particularly from the Rauchfuss group. Petillon et al. showed in 1979[71] that a diamagnetic product, $Cp_2V_2(CO_4)(SMe)_2$, was obtained in addition to the previously reported[72] nonbonded $Cp_2V_2(SMe)_4$ from photolysis of $CpV(CO)_4$ with MeSSMe. The mass spectral and solution molecular weight data indicated a dinuclear formulation, and the authors postulated a vanadium–vanadium bond with μ-SMe groups. An organodiniobium analogue, $[CpNb(CO)_2]_2(\mu\text{-}SMe)_2$, was reported[73] by Herrmann and co-workers from the reaction of $CpNb(CO)_3(thf)$ with MeSH; H_2S gave two products, one of which was shown to be the niobium–niobium bonded $[CpNb(CO)_2]_2(\mu\text{-}S)_2$ (4% yield). Rauchfuss and co-workers have reported a variety of thermal disproportionation reactions that yield organodivanadium complexes with $\mu,\eta^2\text{-}E_2$, $\mu,\eta^1\text{-}E_2$, and μ-E (E = S, Se) groups from either mononuclear or dinuclear precursors; the complexes include $[Cp'V]_2(\mu\text{-}S)(\mu,\eta^2\text{-}S_2)(\mu,\eta^1\text{-}S_2)$,[74] $[Cp'V]_2(\mu\text{-}S)_2(\mu,\eta^1\text{-}S_2)$,[75] and $[Cp'V]_2(\mu\text{-}Se)(\mu,\eta^2\text{-}Se_2)(\mu,\eta^1\text{-}Se_2)$.[76] The ethanedithiolate-bridged compound $[CpV]_2(\mu,\sigma^2\text{-}S_2C_2H_4)_2$, from $HSCH_2CH_2SH$ addition to $CpV(CO)_4$, was reported by Dubois and co-workers in 1984.[140]

Several novel organodiniobium and organoditantalum complexes were reported[77] in 1985 by Curtis and Real, and the structural characterizations corrected an inaccurate characterization in the literature on lower valent cyclopentadienyl carbonyl complexes of these metals. Reductive, low-pressure carbonylation of $CpMCl_4$ in thf was shown to yield the nonbonded organodimetallic carbonyl complexes $[CpMCl(CO)_2]_2(\mu\text{-}Cl)_2$ in 60% yield (Nb) and 35% yield (Ta) (eq 46); a Cp′ niobium analogue was obtained in high yield, and this compound could be reduced further to the organodiniobium(II) complex $[Cp'Nb(CO)_2]_2(\mu\text{-}Cl)_2$ (eq 47; 40%) with a niobium–niobium single bond, cisoid Cp′ groups, and a $Nb_2(\mu\text{-}Cl)_2$ butterfly core. These workers also reported that the monomeric diarylacetylene complex $Cp'NbCl_2(p\text{-}MeC_6H_4CCC_6H_4\text{-}p\text{-}Me)$ can be reduced in 60% yield to a bis(diarylacetylene)organodiniobium(II) complex (eq 48) with transoid Cp′ groups and a planar $Nb_2(\mu\text{-}Cl)_2$ molecular core.

$$2CpMCl_4 + 4CO + Al + HgCl_2 \rightarrow [CpMCl(CO)_2]_2(\mu\text{-}Cl)_2 \quad (46)$$

$$Cp'_2Nb_2(CO)_4Cl_2(\mu\text{-}Cl)_2 + 2Na/Hg \rightarrow [Cp'Nb(CO)_2]_2(\mu\text{-}Cl)_2 \quad (47)$$

$$2Cp'NbCl_2(p\text{-}MeC_6H_4CCC_6H_4\text{-}p\text{-}Me) + 2Na/Hg \rightarrow [Cp'Nb(p\text{-}MeC_6H_4CCC_6H_4\text{-}p\text{-}Me)]_2(\mu\text{-}Cl)_2 \quad (48)$$

Belmonte and Schrock reported in 1980 an organoditantalum dihydride that was shown to exhibit important reactivity toward carbon monoxide and nitriles.[78] Hydrogenation of the mononuclear propylene complex $Cp''TaX_2(CH_2CHMe)$ (Cp″ = Cp*, Cp″; X = Cl, Br) gave diamagnetic μ-hydride complexes of the general formula $Cp''_2Ta_2X_4(\mu\text{-}H)_2$, which could also be prepared via hydrogenolysis of the dineopentyl compound $Cp''TaCl_2(CH_2CMe_3)_2$ (eq 49 and 50). The dihydride was found to be dinuclear in benzene and to be highly symmetric, with equivalent Cp″ groups through which pass a mirror plane. For X = Cl the hydride is found downfield in the ^1H NMR spectrum at δ 10.4 (δ 11.3 for X = Br) and at 1580 cm^{-1} in the IR spectrum (~1140 cm^{-1} for the deuteride analogue). Suitable crystals were only obtained for the monomethyl derivative $[Cp''Ta(CH_3)Cl][Cp''TaCl_2](\mu\text{-}H)_2$, and the X-ray structure determination showed a tantalum–tantalum single bond; the hydrides could not be located directly, but a bridging site seemed most reasonable. Solution ^1H NMR studies showed that these organodimetallics do not readily dissociate into mononuclear species and that halogen/hydride exchange between organodimetallics is facile.

$$2Cp''TaX_2(CH_2CHMe) + 3H_2 \rightarrow [Cp''TaX_2]_2(\mu\text{-}H)_2 + 2MeCH_2Me \quad (49)$$

$$2Cp''TaX_2(CH_2CMe_3)_2 + 3H_2 \rightarrow [Cp''TaX_2]_2(\mu\text{-}H)_2 + 2MeCMe_3 \quad (50)$$

In an attempt at the preparation of a hydrido niobium analogue of the above tantalum complex, Schrock and co-workers found[79] that hydrogenolysis of $Cp^*NbMe_2Cl_2$ gave instead a diamagnetic organodiniobium complex (eq 51) which showed no evidence for bridging or terminal hydride ligands. No hydride resonances in the ^1H NMR spectrum or ν_{NbH}/ν_{NbHNb} absorptions in the IR spectrum were observed, the IR spectra and mass spectra of the dihydrogen-derived and dideuterium-derived products were superimposable, and a dinuclear solution molecular weight was obtained. The authors postulated a niobium–niobium bonding interaction with two bridging chloride ligands, but suitable crystals for an X-ray structure determination could not be obtained.

$$2Cp^*NbMe_2Cl_2 + 2H_2 \rightarrow Cp^*_2Nb_2Cl_4 + 4MeH \quad (51)$$

After a lull of more than a decade since the discovery by Fischer and Schneider of $Cp_2V_2(CO)_5$, several organodivanadium complexes with probable or demonstrated vanadium–vanadium bonding interactions were reported. The diamagnetic organoimido species $Cp_2V_2Cl_2(NSiMe_3)_2$[80] was found in 70% yield by Wiberg and co-workers from the reaction of $Cp_2V(NSiMe_3)$ and Me_3SiCl. Moran and Gayoso reported[81] in 1981 that treatment of Cp_2V with NO yielded in 95% yield the organodimetallic $Cp_2V_2(NO)_4$ with a low effective magnetic moment; IR spectroscopy showed that the species had both bridging and terminal nitrosyl ligands. In 1983 it was found that "$VCl_2(thf)_2$" (in reality, the salt $\{[V(thf)_3]_2(\mu\text{-}Cl)_3\}_2[Zn_2Cl_6]$ reacted with NaCp and $K_2C_8H_8$ to give a diamagnetic organodivanadium complex with a bridging cyclooctatetraene (eq 52) in low

$$2\text{"}VCl_2(thf)_2\text{"} + 2NaC_5H_5 + K_2C_8H_8 \rightarrow [CpV]_2(\mu\text{-}C_8H_8) \quad (52)$$

(5%) yield.[82] An upper limit of 1.86 on the vanadium-vanadium bond order was proposed[82b] on the basis of the molecular orbital calculations, which showed a complex admixture of metal-metal and metal-ligand contributions to the overall molecular orbitals, and the authors proposed a vanadium-vanadium single bond description with an admixed low-lying triplet state.

Bridging arene ligands have also been found in organodivanadium chemistry.[83] The complex $[CpVH]_2(\mu\text{-}\eta^4,\eta^4\text{-}C_6H_6)$ was reported by Jonas and co-workers in 1983 from the reaction of vanadocene anion with 1,3-cyclohexadiene (eq 53). This diamagnetic species,

$$2KCp_2V + 1,3\text{-}C_6H_8 \rightarrow [CpVH]_2(\mu\text{-}\eta^4,\eta^4\text{-}C_6H_6) \quad (53)$$

obtained in 40% yield, was shown to have a metal-metal bond bridged by a benzene ligand which is η^4-coordinated to each vanadium. The authors did not assign a bond order, but a reasonable order of two can be postulated on the basis of metal-metal distance and electron counting arguments.

Organodivanadium complexes with an unprecedented four alkyl bridges have recently been discovered by Jonas and co-workers.[84] Displacement of naphthalene from $CpV(C_{10}H_8)$ with ethylene at 20 °C led to the binuclear bis(μ-vanadocyclopentane)$[CpV]_2(\mu\text{-}1,4\text{-}\eta^2\text{-}C_4H_8)_2$ in 33% yield (eq 54). The reaction is believed

$$2CpV(C_{10}H_8) + 4C_2H_4 \rightarrow [CpV]_2(\mu,\eta^2\text{-}CH_2CH_2CH_2CH_2)_2 \quad (54)$$

to proceed through a vanadacyclopentane intermediate which then couples to the organodivanadium(III) product. A short vanadium-vanadium distance consistent with a double bond was found by single-crystal X-ray diffraction for this novel compound, and acute V-(μ-CH_2R)-V angles were observed. The isostructural, acyclic analogue $[Cp^*V]_2(\mu\text{-}Me)_4$ with an unprecedented four simple alkyl bridges, prepared by MeLi addition to Cp*CpVMe, was also briefly described.

Cowley and co-workers reported[85] in 1987 that the vanadium carbonyl anion $CpV(CO)_3^{2-}$ reacted with an aryldichlorophosphine to give the diamagnetic, bridging phosphinidene organodivanadium complex $[CpV(CO)_2]_2(\mu\text{-}PAr)$ (Ar = 2,4,6-$(Me_3C)_3C_6H_4$) in 28% yield (eq 55). A low-field ^{31}P NMR resonance at δ 670 is

$$2Na_2CpV(CO)_3 + ArPCl_2 \rightarrow [CpV(CO)_2]_2(\mu\text{-}PAr) \quad (55)$$

consistent with a bridging phosphinidene group. A crystal structure determination showed a trigonal planar phosphorus atom and a rather long vanadium-vanadium separation, which the authors assigned as a bonding interaction on the basis of an acute V-(μ-P)-V angle.

The challenges and uncertainties in developing metal-metal bonded organodivanadium chemistry is best exemplified in a comparison of two reports from the Teuben group. The paramagnetic organodivanadium complexes $[CpV(PR_3)]_2(\mu\text{-}X)_2$ can be prepared by aluminum reduction of $CpVX_2(PR_3)_2$ (eq 56;

$$6CpVX_2(PR_3)_2 + 2Al \rightarrow 3[CpV(PEt_3)]_2(\mu\text{-}X)_2 + 2AlX_3PR_3 \quad (56)$$

X = Cl, Br; Cp = Cp, Cp′; R = Me, Et).[86] The paramagnetic $[CpV(PEt_3)]_2(\mu\text{-}Cl)_2$ was shown by X-ray crystallography to possess a long, nonbonded vanadium-vanadium distance. In contrast to this finding, a diamagnetic, centrosymmetric hydride organodimetallic with a vanadium-vanadium bond was recently prepared[87] by hydrogenolysis of an organovanadium(II) alkyl compound (eq 57). The reason for this disparity in vanadium-vanadium bonding in such similar compounds is not clear.

$$2CpV(CH_2CH_2CH_3)(Me_2PCH_2CH_2PMe_2) + 2H_2 \rightarrow [CpV(Me_2PCH_2CH_2PMe_2)]_2(\mu\text{-}H)_2 + 2C_3H_8 \quad (57)$$

A recent discovery in our laboratory has the potential for expanding the area of organoditantalum chemistry. The diamagnetic, tantalum-tantalum doubly-bonded complex $[Cp^*Ta]_2(\mu\text{-}X)_4$ can be readily prepared in 70-75% yield by reductive dimerization of Cp^*TaX_4 (X = Cl, Br; eq 58).[88] The product lacks any spectral

$$2Cp^*TaX_4 + 2Na/Hg \rightarrow [Cp^*Ta]_2(\mu\text{-}X)_4 + 2NaX \quad (58)$$

evidence for bridging or terminal hydrides, exhibits a dinuclear parent ion in the mass spectrum, and has a mirror plane passing through the peralkylcyclopentadienyl groups as shown in ^1H NMR spectra of the C_5Me_4Et analogues. A single-crystal X-ray diffraction study of $[Cp^*Ta]_2(\mu\text{-}Br)_4$ has recently established that the Ta-Ta double bond is bridged symmetrically by four bromide ligands. Its structural details will be discussed in section IV.E, while the diverse and novel reactivity of this new class of metal-metal multiply bonded organodimetallic complexes will be reviewed in section V.

IV. Molecular Structures

A. General Structural Features

A major motivation toward structural studies of metal-metal bonded dinuclear and organodimetallic complexes by single-crystal X-ray diffraction is the somewhat greater difficulty of structural characterization via spectroscopic and spectrometric methods. The presence of spectroscopically silent halide ligands in dinuclear species, with the possibility of bridge or terminal bonding, often leads to stereochemical questions which can be definitively answered only by diffraction methods (although nuclear quadrupole resonance spectroscopy has been utilized to distinguish bridging versus terminal halide bonding in some cases). Accurate bond distances and angles are also needed for electronic structure calculations which are of increasing importance in approximating the nature of the metal-metal and metal-bridging atom interactions. With one recent exception, all known early metal dinuclear complexes contain ligand-bridged metal-metal bonds, so the ever-present ambiguity of metal-metal bond order assignment in ligand-bridged dinuclear systems is a major

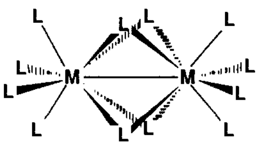


Figure 1. Face-sharing double square antiprismatic structure.

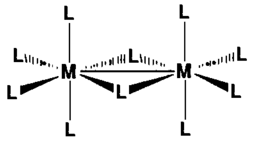


Figure 2. Edge-sharing bioctahedral structure.

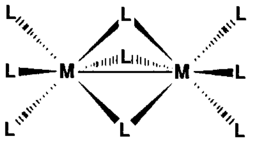


Figure 3. Confacial bioctahedral structure.

concern with low-valent early-transition-metal dimetallics. Metal–metal distances, particularly when an estimate of the covalent radius of the metal can be made from other bond distances in the dimetallic, combined with simple electron-counting considerations can serve as a useful guide for predicting formal metal–metal bond order in the absence of sophisticated molecular orbital calculations (which can occasionally be inconclusive on this point in low-symmetry species with extensive ligand orbital mixing into the metal–metal bonding orbitals).

The structural type classifications for metal–metal bonded dinuclear complexes of the early transition metals depend on the formal metal–metal bond order. In the case of metal–metal single bonds the most common structural class is quadruply bridged dimetallics of the form $[ML_4]_2(\mu\text{-}L)_4$ with two square antiprismatic metal coordination spheres sharing a 4-fold face (Figure 1). An edge-sharing bioctahedral example and a double trigonal bipyramid with an unbridged metal–metal single bond along the common equatorial site have also been observed.

Species with formal metal–metal double bonds fall predominantly into two classes, the edge-sharing bioctahedron and the confacial bioctahedron. In the edge-sharing bioctahedron, of the form $[ML_4]_2(\mu\text{-}L)_2$, two octahedral metal coordination spheres share a common edge (Figure 2); this structural type in dinuclear transition-metal chemistry has been reviewed recently.[89] The terminal ligands are in either axial or equatorial sites, and steric repulsions between axial ligands are common in these structures. The confacial bioctahedron, of the form $[ML_3]_2(\mu\text{-}L)_3$, has two octahedral metal coordinaton spheres which share a common face (Figure 3).

There are a limited number of examples of dinuclear or organodimetallic complexes with formal metal–metal triple bonds. With the exception of two divanadium examples, with unusual bridging aryl ligands leading to an eclipsed $M(\mu\text{-}LL')_4M$ structure, the diniobium and ditantalum examples belong to the confacial bioctahedral class with only neutral donor ligands in the bridging positions.

The presence of chelating ligands and their potential for bridging, i.e., binucleating, behavior lead to additional considerations which can be best answered by structural studies. Most questions arise in the analysis of edge-sharing bioctahedral complexes with chelating ligands, which can coordinate along the equatorial edge (Figure 4) or span an axial and equatorial site (Figure 5). Diastereomeric possibilities based on the actual axial and equatorial sites involved or the conformation of the chelate ring in biequatorial sites for the two dinuclear ends must also be considered. Finally, some bidentate ligands exhibit a potential for bridging or binucleating behavior and thus span the two metal centers (Figure 6). The binucleating ligand $Ph_2PCH_2PPh_2$ and, more recently, the related $Me_2PCH_2PMe_2$ are the basis for a substantial amount of binuclear late-transition-metal chemistry[90] often termed A-frame chemistry. The single methylene bridge between the two phosphorus centers leads to a greater preference for binucleating as opposed to chelating behavior because of the more unfavorable conformational factors in forming a four-membered chelate structure.

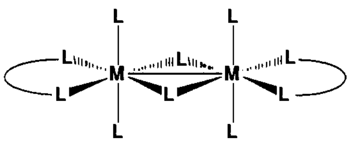


Figure 4. Edge-sharing bioctahedral structure with edge-chelating ligands.

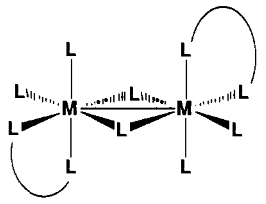


Figure 5. Edge-sharing bioctahedral structure with edge/axial chelating ligands.

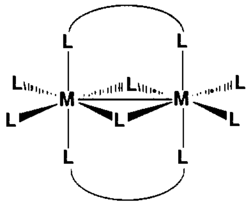


Figure 6. Edge-sharing bioctahedral structure with binucleating (i.e., bridging) ligands.

The foremost datum that is sought in structural studies is the metal–metal bond distance because an approximate bond order assessment can then be made. The presence of bridging ligands seriously complicates this analysis since dinuclear molecular orbitals that are qualitatively metal–metal in constitution can have appreciable contributions from ligand orbitals, with the resulting three-center $M(\mu\text{-}L)M$ interaction complicating the overall picture. Semiempirical molecular orbital calculations can be of tremendous help in deciding the nature of the metal–metal interaction, particularly in cases with formal metal–metal double bonds, as has been shown in a number of cases.[91] The reader with interests in theoretical approximations to multiple metal–metal bonding in transition-metal dimetallics is referred to papers on edge-sharing bioctahedral[92] and confacial bioctahedral[93] complexes.

TABLE I. Averaged Bond Distances (Å) and Bond Angles (deg) in Structurally Characterized Dizirconium Complexes[a]

compound structural class	Zr–Zr bond order	Zr–μ-Cl	Zr–Cl_{ax}	Zr–P site	Zr–μ-Cl–Zr	μ-Cl–Zr–μ-Cl	Cl_{ax}–Zr–Cl_{ax}	P_{eq}–Zr–P_{eq} (chelate)	ref
$[ZrCl_2(PBu_3)_2]_2(\mu\text{-}Cl)_2$ edge-sharing bioctahedron	3.182 single	2.544	2.431	2.835 eq	77.4	102.6	165.1		19b
$[ZrCl_2(PEt_3)_2]_2(\mu\text{-}Cl)_2$ edge-sharing bioctahedron	3.169 single	2.540	2.425	2.813 eq	77.2	102.81	163.8		20
$[ZrCl_2(PMe_2Ph)_2]_2(\mu\text{-}Cl)_2$ edge-sharing bioctahedron	3.127 single	2.547	2.417	2.765 eq	75.7	104.3	162.1		20
$[ZrCl_2(Ph_2PCH_2CH_2PPh_2)]_2(\mu\text{-}Cl)_2$ edge-sharing bioctahedron	3.104 single	2.537	2.420	2.781 eq chelate	75.4	104.6	162.8	75.9	20

[a] Abbreviations: eq, equatorial; ax, axial.

TABLE II. Averaged Bond Distances (Å) and Bond Angles (deg) in Structurally Characterized Divanadium Complexes[a]

compound	V–V bond order	V–μ-SR	V–S_{term}R	V–P site	V–μ-SR–V	ref
$[V(PMePh_2)_2]_2(\mu\text{-}H_2ZnH_2BH_2)_2$	2.400 double			2.538 ax		22
$(Et_4N)_2\{[V(S_2C_2H_4)]_2(\mu,\eta^2\text{-}S_2C_2H_4)_2\}$	2.616 single	2.459	2.375		64.2	26
$(Ph_4P)_2\{[V(S_2C_2H_4)]_2(\mu,\eta^2\text{-}S_2C_2H_4)_2\}$	2.575 single	2.434				25
	2.600 single	2.45				139

[a] Abbreviations: eq, equatorial; ax, axial; term, terminal.

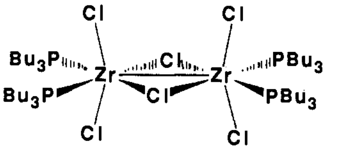


Figure 7. Molecular structure of $[ZrCl_2(PBu_3)_2]_2(\mu\text{-}Cl)_2$.

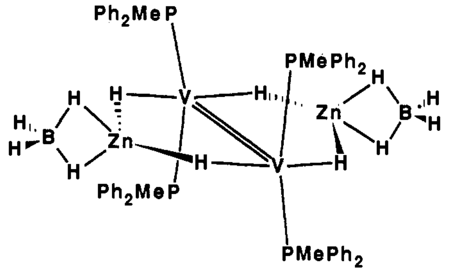


Figure 8. Molecular structure of $[V(PMePh_2)_2]_2(\mu\text{-}H_2ZnH_2BH_2)_2$.

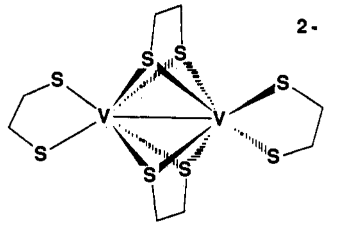


Figure 9. Molecular structure of $[V(S_2C_2H_4)_2]_2(\mu,\eta^2\text{-}S_2C_2H_4)_2^{2-}$ (cations omitted).

Additional evidence for metal–metal bonding in edge-sharing bioctahedral and confacial bioctahedral structures can be found in the M–(μ-L)–M and (μ-L)–M–(μ-L) angles. In an ideal edge-sharing bioctahedron the M–(μ-L)–M and (μ-L)–M–(μ-L) angles are both 90°, so any bioctahedral distortion which leads simultaneously to more acute M–(μ-L)–M angles of less than 90° and more obtuse (μ-L)–M–(μ-L) angles of greater than 90° is usually taken as evidence of strong metal–metal bonding interaction. The corresponding bond angles in an ideal confacial bioctahedron are 70.53° for the M–(μ-L)–M angle and 90° for the (μ-L)–M–(μ-L) angle. In this case, any distortion of the confacial bioctahedral structure which decreases the M–(μ-L)–M angle and increases the (μ-L)–M–(μ-L) angle is also described as being indicative of a bonding metal–metal interaction. The attractive and repulsive forces in a confacial bioctahedron are more complex, so care must be exercised in comparing structural parameters of different species, and bonding descriptions are complicated by the presence of the three-atom bridges.

B. Dizirconium Structures

The first structurally characterized dinuclear group 4 complex, $[ZrCl_2(PBu_3)_2]_2(\mu\text{-}Cl)_2$, has an edge-sharing bioctahedral structure (Figure 7) with a somewhat long Zr–Zr distance of 3.182 (1) Å.[19] The acute Zr–(μ-Cl)–Zr angle of 77.43 (4)° and the (μ-Cl)–Zr–(μ-Cl) angle of 102.57 (5)° are consistent with a Zr–Zr bonding interaction, which the authors estimated at 3.10 Å for a Zr(III)–Zr(III) bond. Other distances and angles for this complex and recently reported[20] analogues are given in Table I. By comparison, Corbett and co-workers have reported[94] that the inorganic compound $Cs_3Zr_2I_9$, from high-temperature reaction of CsI, Zr, and ZrI_4, has a Zr–Zr distance of 3.129 (4) Å and Zr–(μ-I)–Zr and (μ-I)–Zr–(μ-I) angles of 65.0° and 93.9°, respectively.

C. Divanadium Structures

Bond distances and angles for the limited number of metal-metal bonded divanadium complexes are listed in Table II.

In the first example, $[V(PMePh_2)_2]_2(\mu\text{-}H_2ZnH_2BH_2)_2$, the divanadium group (2.400 Å) is bridged by the perhydriodozinc borate moiety (Figure 8). Unfortunately, this unusual bridging ligand makes it difficult to utilize the divanadium distance as a benchmark for a vandium–vanadium double bond. In the case of the three determinations of the divanadium ethanedithiolate complex, all structural studies showed a vanadium–vanadium bond, reasonably assigned as a single bond,

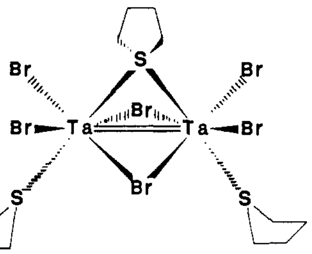


Figure 10. Molecular structure of $[TaBr_2(tht)]_2(\mu\text{-}Br)_2(\mu\text{-}tht)$.

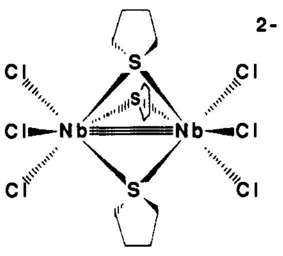


Figure 11. Molecular structure of $(Et_4N)_2[NbCl_3]_2(\mu\text{-}tht)_3$ (cations omitted).

bridged by two ethanedithiolate ligands and with a distorted trigonal prismatic sulfur atom array around each vanadium (Figure 9).

D. Diniobium and Ditantalum Structures

1. Confacial Bioctahedral Structures

Table III lists pertinent bond distances and bond angles for all structurally characterized diniobium and ditantalum complexes with a confacial bioctahedral structure.

The first detailed structural characterization of a member of this structural class was reported in 1978 by McCarley, Clardy, and co-workers.[95] The X-ray structures of the tht dimetallics of formula $[MBr_2(tht)]_2(\mu\text{-}Br)_2(\mu\text{-}tht)$ showed metal-metal separations of 2.728 (5) Å (M = Nb) and 2.710 (2) Å (M = Ta) (Figure 10). With use of a Br covalent radius of 1.14 Å,[96] an estimate of the covalent radii of Nb(III) and Ta(III) from the $M\text{-}Br_{terminal}$ distances gives values of 1.39 and 1.38 Å, respectively, so M(III)–M(III) single bond distances can be approximated with values of 2.78 (Nb) and 2.76 Å (Ta). The experimentally determined values are shorter than this, but not by substantial amounts, possibly because of repulsive ligand interactions. The Nb–(μ-Br)–Nb angle, average 62.5°, and Ta–(μ-Br)–Ta angle, average 61.9°, are rather acute and consistent with a strong metal–metal interaction that can be described approximately as a double bond. An excellent approximate molecular orbital treatment of the bonding in these species, using a descent in symmetry approach, was provided in the structural paper.[95a] Cotton and Najjar in 1981 reported structural results[97] for $[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht)$ and $[TaCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$; the tht species was found to have a Ta=Ta distance of 2.681 (1) Å, with approximately a 0.03 Å decrease in going from Br to Cl. The results of other structural studies of doubly bonded confacial bioctahedral species containing $P(NMe_2)_3$[98] and thf[99] ligands are given in Table III. All complexes show a clear distortion from idealized confacial bioctahedral geometry that is derived from strong metal–metal interaction. Metal-bridge distances are always longer than analogous terminal ligands in the same complex.

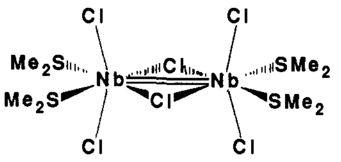


Figure 12. Molecular structure of $[NbCl_2(SMe_2)_2]_2(\mu\text{-}Cl)_2$.

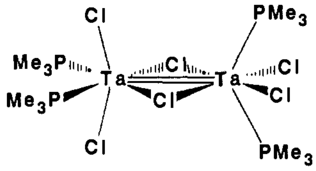


Figure 13. Molecular structure of $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$.

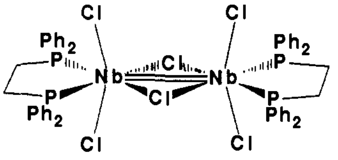


Figure 14. Molecular structure of $[NbCl_2(Ph_2PCH_2CH_2PPh_2)]_2(\mu\text{-}Cl)_2$.

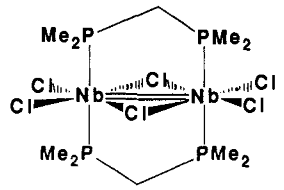


Figure 15. Molecular structure of $[NbCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}Me_2PCH_2PMe_2)_2$.

Novel confacial bioctahedral complexes with formal metal–metal triple bonds have also been structurally characterized.[35] These anionic species, of the general formula $[MCl_3]_2(\mu\text{-}tht)_3^{2-}$, have tht bridges rather than chloride bridges (Figure 11); in two of the examples, alkali-metal cations are coordinated in the solid state to the terminal chlorides. Structural evidence for these triple bonds includes short metal–metal distances (Nb≡Nb, 2.632 (1) Å; Ta≡Ta, 2.6156 (5) and 2.626 (1) Å) and acute $M\text{-}(\mu\text{-}SR_2)\text{-}M$ angles near 66°. These complexes are also listed in Table III.

2. Edge-Sharing Bioctahedral Structures with Monodentate Ligands

Table IV lists bond distances and angles for reported diniobium and ditantalum complexes with edge-sharing bioctahedral structures and monodentate ligands. The variation in metal–metal distance is greater for the double-bonded members of this class and is strongly dependent on the nature of the bridging ligands, with hydrides leading to the shortest metal–metal distances. In all cases the axial ligands are bent away from the metal–metal bond ($M\text{-}M\text{-}L_{ax} > 90°$ and $L_{ax}\text{-}M\text{-}L_{ax} < 180°$), and acute bridge angles are observed. Figures 12 and 13 show the approximate structures of two prototypical examples from Table IV, $[NbCl_2(SMe_2)_2]_2(\mu\text{-}Cl)_2$ and $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$.

3. Edge-Sharing Bioctahedral Structures with Bidentate and Binucleating Ligands

Table V lists bond distances and angles for diniobium and ditantalum complexes with bidentate ligands and

TABLE III. Averaged Bond Distances (Å) and Bond Angles (deg) in Confacial Bioctahedral Diniobium and Ditantalum Complexes[a]

compound	M–M bond order	M–μ-X	M–X_{term}	M–P	M–μ-SR_2	M–μ-X–M	μ-X–M–μ-X	M–μ-SR_2–M	ref
$[NbBr_2(tht)]_2(\mu\text{-}Br)_2(\mu\text{-}tht)$	2.728 double	Br, 2.626	Br, 2.534		2.487	Br, 62.5	Br, 78.0	66.5	95
$[NbCl_2(thf)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$	2.684 double	2.489	2.375		2.407	65.25	78.7	67.8	99
$Cs_3[NbCl_3]_2(\mu\text{-}Cl)_3$	2.70 double								30
$(NEt_4)_2[NbCl_3]_2(\mu\text{-}tht)_3$	2.632 triple		2.540		2.431			65.6	35
$[TaBr_2(tht)]_2(\mu\text{-}Br)_2(\mu\text{-}tht)$	2.710 double	Br, 2.633	Br, 2.516		2.393	Br, 61.9	Br, 77.5	69.0	95
$[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht)$	2.681 double	2.503	2.366		2.390	64.8	75.6	68.2	97
$[TaCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$	2.691 double	2.499	2.371		2.378	65.2	76.0	68.9	97
$[TaCl_2\{P(NMe_2)_3\}]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$	2.704 double	2.499	2.374	2.726	2.400	65.5	75.8	68.6	98
$[TaCl_2(thf)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$	2.669 double	2.494	2.369		2.371	64.7	78.1	68.5	99
$[Li(thf)_2]_2[TaCl_3]_2(\mu\text{-}tht)_3$	2.626 triple		2.493[b]		2.392			66.6	35
$Na_2[TaCl_3]_2(\mu\text{-}tht)_3$	2.616 triple		2.526[c]		2.399			66.1	35

[a] Abbreviations: eq, equatorial; ax, axial; X = Cl unless noted; solvate molecules in lattice not included in compound formula. [b] Only for Cl atoms not coordinated to Li cations. [c] All Cl atoms coordinated to Na cations.

TABLE IV. Averaged Bond Distances (Å) and Bond Angles (deg) in Edge-Sharing Bioctahedral Diniobium and Ditantalum Complexes with Monodentate Ligands[a]

compound	M–M bond order	M–μ-X	M–X_{ax}	M–X_{eq}	M–P	M–μ-X–M	μ-X–M–μ-X	M–M–L_{ax}	L_{ax}–M–L_{ax}[b]	ref
$[NbCl_2(SMe_2)_2]_2(\mu\text{-}Cl)_2$	2.836	2.337	2.365			74.7	105.3	103.4	153.2	44
$[NbCl_2(HO^iPr)_2]_2(\mu\text{-}Cl)(\mu\text{-}O^iPr)$	2.611 double	2.473 RO, 2.03	2.437	2.495		63.7 RO, 80.2	108.0 (μ-Cl–M–μ-OR)	Cl, 95.5 HOR, 91.1	170.0	43c
$[NbCl_2(OMe)(HOMe)]_2(\mu\text{-}OMe)_2$	2.781 single	MeO, 2.047	MeO, 1.811	2.451		MeO, 85.6	MeO, 94.4	MeO, 100.2 MeOH, 86.6	173.2	43b
$[NbCl_2(OMe)(NCMe)]_2(\mu\text{-}OMe)_2$	2.768 single	MeO, 2.033	2.413 MeO, 1.823	2.477		MeO, 85.8	MeO, 92.3	Cl, 100.4 MeO, 95.3	163.7	43b
$[NbCl_2(NCMe)_2]_2(\mu\text{-}S)_2\cdot 2MeCN$	2.862 single	S, 2.345	2.383			S, 75.2	S, 104.8	101.1	157.6	47
$[NbCl_2(NCMe)_2]_2(\mu\text{-}S)_2\cdot MeCN$ (two independent mols)	2.872	S, 2.343	2.387			S, 75.6	S, 104.4	101.3	157.3	47
	2.864 single	S, 2.341	2.393			S, 75.4	S, 104.6	100.9	158.0	
$[NbCl_2(tht)_2]_2(\mu\text{-}S)_2$	2.868	S, 2.352	2.372			S, 75.1	S, 104.9	103.8	152.3	46
$[TaCl_2(SMe_2)_2]_2(\mu\text{-}Cl)_2$	2.829	2.339	2.361			74.4	105.6	103.4	153.1	44
$[TaCl_3(SMe_2)]_2(\mu\text{-}SPh)_2$	3.165 "single"	PhS, 2.410	2.329	2.395		PhS, 82.1	PhS, 97.8	94.3	165.2	115
$[TaCl_2(thf)_2]_2(OAc')(\mu\text{-}Cl)(\mu\text{-}SMe_2)$[c] approx edge-sharing bioctahedral	2.773	2.445	2.375	2.397		69.1				137
$[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$	2.721 double	2.452	2.399	2.479	ax, 2.607 eq, 2.657	67.4	112.6	103.1	Cl:153.6	37b
$[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2$ μ-H's on diagonal plane; approx edge-sharing bioctahedral	2.545 double		2.415 (terminal)		2.595			115.7	128.8	40b

[a] Abbreviations: eq, equatorial; ax, axial; X = Cl unless noted; $^iPr = CHMe_2$; solvate molecules in lattice not included in compound formula unless necessary to differentiate similar compounds. [b] Angle of bending opposite of metal–metal bond. [c] $Ac' = O_2CCMe_3$, bridging bidentate with oxygen atoms at axial sites.

an edge-sharing bioctahedral structure. In virtually all cases (e.g., Figure 14) the ligand chelates on the equatorial ends of the edge-sharing bioctahedron. Methylenebis(phosphine) ligands tend toward binucleating behavior in which adjacent axial sites across the metal–metal bond are spanned by the ligand (Figure 15).[24,100] It was suggested recently[101] by Cotton and co-workers that the diniobium species $[NbCl_2(Ph_2PCH_2PPh_2)]_2(\mu\text{-}Cl)_2$, for which the solid-state structure showed an edge-chelating methylenebis(phosphine), could be a kinetic rather than thermodynamic product. We have recently observed both chelating and binucleating behavior for a methylenebis(phosphine) metal–metal doubly bonded complex.[102]

Dinuclear compounds with alkyl-substituted, ethylene-bridged diphosphine, diamine, and disulfide ligands have also been structurally characterized.[48,103,104,105,106,44] In all cases the ligand chelates on the equatorial sites,

TABLE V. Averaged Bond Distances (Å) and Bond Angles (deg) in Edge-Sharing Bioctahedral Diniobium and Ditantalum Complexes with Chelating or Binucleating Ligands[a]

compound chelate position[c]	M–M bond order	M–μ-X	M–X_{ax}	M–X_{eq}	M–L	M–μ-X–M	μ-X–M–μ-X	M–M–L_{ax}	L_{ax}–M–L_{ax}[b]	ref
$[NbCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}Me_2PCH_2PMe_2)_2$ binucl	2.711 double	2.438		2.444	P, 2.630	67.6	112.4	93.0	171.1	24
$[NbCl_2(Ph_2PCH_2PPh_2)]_2(\mu\text{-}Cl)_2$ eq/eq	2.696 double	2.453	2.400		P, 2.662	66.7	113.3	98.5	162.9	101
$[NbCl_2(Ph_2PCH_2CH_2PPh_2)]_2(\mu\text{-}Cl)_2$ eq/eq; two independent mols	2.729 double	2.450	2.397		P, 2.701	67.7	112.3	98.1	163.9	48
$[NbCl_2(Et_2PCH_2CH_2PEt_2)]_2(\mu\text{-}Cl)_2$ eq/eq	2.741 double	2.451	2.411		P, 2.640	68.0	112.0	98.0	164.1	106
$[NbCl_2(Et_2NCH_2CH_2NEt_2)]_2(\mu\text{-}Cl)_2$ eq/eq	2.764 double	2.435	2.410		N, 2.441	69.2	110.8	95.9	168.1	106
$[NbCl_2(EtSCH_2CH_2SEt)]_2(\mu\text{-}Cl)_2$ eq/eq	2.688 double	2.440	2.400		S, 2.635	66.8	113.2	98.6	162.8	44
$[TaCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}Me_2PCH_2PMe_2)_2$ binucl	2.692 double	2.433		2.446	P, 2.619	67.3	112.7	93.1	171.7	100
$[TaCl_2(Me_2PCH_2CH_2PMe_2)]_2(\mu\text{-}Cl)_2$ eq/eq	2.710 double	2.459	2.415		P, 2.603	66.9	113.1	98.5	163.1	103
$[TaCl_2(Et_2PCH_2CH_2PEt_2)]_2(\mu\text{-}Cl)_2$ eq/eq	2.737 double	2.441	2.411		P, 2.621	68.2	111.7	97.9	164.1	105
$[TaCl_2(Et_2PCH_2CH_2PEt_2)]_2(\mu\text{-}Cl)_2\cdot MePh$ eq/eq	2.724 double	2.443	2.403		P, 2.613	67.8	112.2	98.1	163.8	105
$[TaCl_2(dmpe)]_2(\mu\text{-}O)(\mu\text{-}SMe_2)\cdot HCl\cdot MePh$ eq/ax	2.726 double		2.407	2.447	P, 2.631			106.3		104
$[TaCl_2(Et_2NCH_2CH_2NEt_2)]_2(\mu\text{-}Cl)_2$ eq/eq	2.778 double	2.401	2.383		N, 2.471	70.7	109.3	96.9	166.3	106
$[TaCl_2(EtSCH_2CH_2SEt)]_2(\mu\text{-}Cl)_2$ eq/eq; two independent mols	2.847 double	2.356	2.368		S, 2.669	74.3	105.7	101.5	156.9	44

[a] Abbreviations: eq, equatorial; ax, axial; X = Cl unless noted; $^iPr = CHMe_2$; dmpe = $Me_2PCH_2CH_2PMe_2$; solvate molecules in lattice not included in compound formula unless necessary to differentiate similar compounds. [b] Angle of bending opposite of metal-metal bond. [c] eq/eq = chelate spanning adjacent equatorial end positions; eq/ax = chelate spanning adjacent axial and equatorial positions; binucl = binucleating, i.e., bridging metal centers by spanning adjacent axial positions across metal-metal bond.

TABLE VI. Averaged Bond Distances (Å) and Bond Angles (deg) in Diniobium and Ditantalum Complexes with Double Square Antiprismatic, Tetragonal Face-Sharing Structures[a]

compound	M–M bond order	M–μ-Cl	M–Cl_{term}	M–P	M–μ-Cl–M	μ-Cl–M–μ-Cl transoid	ref
$[NbCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_4$ all PR_3's in plane	2.836 single	2.545	2.506	2.675	67.7		53c
$[NbCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_4$ all PR_3's in plane	2.833 single	2.541	2.502	2.671	67.7	112.2	55
$[NbCl_2(PMe_2Ph)]_2(\mu\text{-}Cl)_4$ all PR_3's in plane	2.838 single	2.541	2.484	2.699	67.9	112.1	54
$[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2$	2.621 single	2.551	2.472	2.639	61.8		39
$[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$	2.511 single		2.461	2.604			40b
$[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_4$ all PR_3's in plane	2.830 single	2.544	2.497	2.677	67.6		53c
$[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_4$ all PR_3's in plane	2.830 single	2.544	2.502	2.671	67.6	112.4	53b

[a] Abbreviations: term, terminal.

and diastereomeric complexes can be obtained as a result of chelate conformation.[105] There are some surprising differences in metal–metal bond lengths for these $[MCl_2(L\text{-}L)]_2(\mu\text{-}Cl)_2$ complexes[44] which, at first sight, should be isostructural and possess metal–metal double bonds. Apparently, some subtle conformational factor in the chelate ring or other repulsive factor in the bioctahedron is responsible for the differences in metal–metal distances, which range from 2.688 (1) to a long 2.847 (1) Å. Fenske–Hall calculations have been performed with the goal of understanding the reasons for these bond length variations.[44]

4. Face-Sharing Double Square Antiprismatic Structures

Bond distances and angles for diniobium and ditantalum complexes of this structural type (e.g., Figure 16) are listed in Table VI. For the few tetrahalo-bridged species the M(IV)–M(IV) distances are approximately 2.84 Å, with successive hydride substitution at the bridge sites leading to a shortening of the metal–metal distance. Sattelberger and co-workers calculated[39] an unbridged Ta(IV)–Ta(IV) distance of 2.94 Å by estimating the Ta(IV) covalent radius from the terminal Ta–Cl distances in $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2$, but the value of 2.72 Å later found[61,107] for $[TaH_2\{OSi(CMe_3)_3\}_2]_2$ suggests that halide bridges may

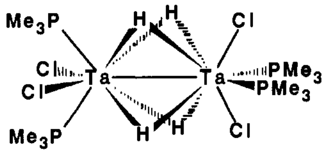


Figure 16. Molecular structure of $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$.

TABLE VII. Averaged Bond Distances (Å) and Bond Angles (deg) in Miscellaneous Diniobium and Ditantalum Complexes^a

compound	M-M bond order	M-μ-X	M-X_{term}	M-μ-X-M	ref
$[NbCl(OAc)]_2(\mu\text{-}OAc)(\mu,\eta^2\text{-}OAc)(\mu\text{-}tht)$ Me_4N^+ salt	2.764				58
$[NbCl_2(tht)_2]_2(\mu\text{-}S)(\mu,\eta^2\text{-}S_2)$ $Nb_2(S_2)$ tetrahedrane	2.844	S, 2.287	2.427	S, 76.9	45b
$[NbBr_2(tht)_2]_2(\mu\text{-}S)(\mu,\eta^2\text{-}S_2)$	2.830	S, 2.333	Br, 2.609	S, 74.7	45b
$[NbCl_2(tht)_2]_2(\mu\text{-}Se_2)_2$	2.972		2.485		138
$[TaH_2(OSi\{CMe_3\}_3)_2]_2$ unbridged	2.720 single				61

^{a}Abbreviations: ax, axial; term, terminal; X = Cl unless noted; solvate molecules in lattice not included in compound formula unless necessary to differentiate similar compounds.

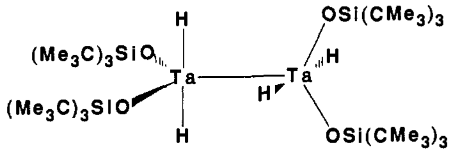


Figure 17. Molecular structure of $[TaH_2\{OSi(CMe_3)_3\}_2]_2$.

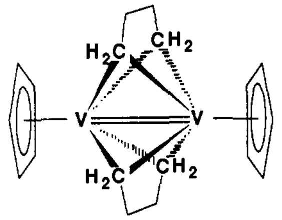


Figure 18. Molecular structure of $[CpV]_2(\mu,\sigma^2\text{-}C_4H_8)_2$.

sometimes lengthen metal-metal distances.

A structural study showed[55] that the previously reported $NbCl_4(PMe_3)_2$ was, in reality, $[NbCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_4$, a member of this structural class.

5. Nonbridged Structures

The only example of a structurally characterized early transition metal dinuclear complex with an unbridged metal-metal bond is the Ta(IV)-Ta(IV) compound $[TaH_2\{OSi(CMe_3)_3\}_2]_2$ (Table VII). This complex has a D_{2d} structure (Figure 17), consisting of two trigonal bipyramids with a common equatorial site, staggered alkoxide ends, a Ta-Ta distance of 2.720 (4) Å, and Ta-Ta-OR and RO-Ta-OR angles of 120.7° and 118.7°, respectively.[61,107]

6. Miscellaneous Structures

Miscellaneous complexes with molecular structures that do not fit any of the above structural classifications are listed in Table VII.

E. Organodimetallic Structures

Table VIII lists bond distances and angles for metal-metal bonded organodivanadium complexes, while the organodiniobium and organoditantalum complexes are given in Table IX. All of the organodimetallic complexes have bridging ligands, with unusual examples such as bridging arene and metallacycle groups (Figure 18).

The first organodivanadium complex with vanadium-carbon σ-bonds, V_2(2,6-dimethoxyphenyl)$_4$ (Figure 19), was reported by Seidel and co-workers and completely characterized by Cotton and Millar in 1977.[108] This complex and the related trimethoxyphenyl compound,[109] prepared by aryllithium addition to "$VCl_3(thf)_3$", also proved to be the first (and still only) examples of vanadium-vanadium triple bonds. The inequivalent aryl ligands were found to bridge the divanadium group via both a bidentate C,O-coordination mode and a tridentate O,C,O-bonding mode. The V≡V distances in these two isostructural complexes were 2.200 (2) and 2.223 (2) Å, respectively. A theoretical treatment has been published.[110]

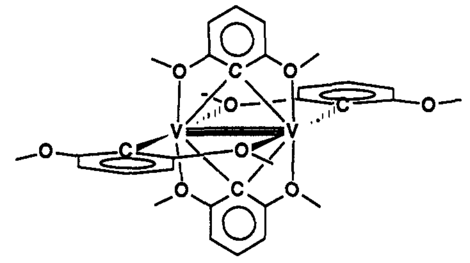


Figure 19. Molecular structure of $V_2\{2,6\text{-}(MeO)_2C_6H_3\}_4$.

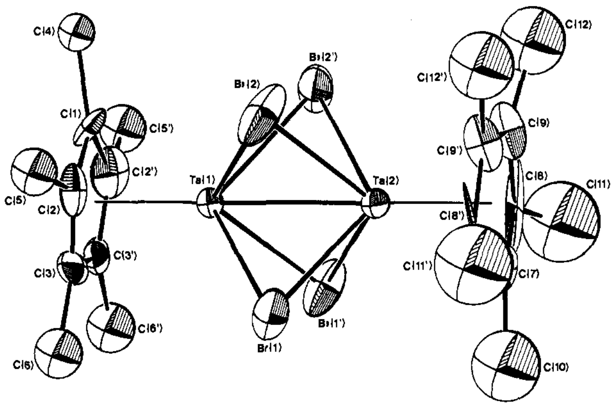


Figure 20. ORTEP diagram for $(C_5Me_5)_2Ta_2(\mu\text{-}Br)_4$. A crystallographically imposed mirror plane lies approximately in the plane of the figure, with symmetrically related atoms designated by a prime.

We have recently determined[88] the solid-state structure (Figure 20) of $[Cp^*Ta]_2(\mu\text{-}Br)_4$. The Ta-Ta double-bond, distance 2.748 (2) Å, is symmetrically bridged by four (Figure 21) instead of two bromine atoms. The acute Ta-(μ-Br)-Ta and obtuse (μ-Br)-Ta-(μ-Br) angles are indicative of strong metal-metal interaction, which we assign as a double bond on distance and electron-counting criteria.

V. Reactivity

Reactivity studies on early metal dimetallics have received a greater emphasis (as compared to synthesis and structural studies alone) than is the case with later metal complexes because of the more recent development of early metal-metal bonded dinuclear chemistry

TABLE VIII. Averaged Bond Distances (Å) and Bond Angles (deg) in Organodivanadium Complexes[a]

compound structural class	V–V bond order	V–CO_{term}	V–CO_{sb}	V–L_μ	V–L_μ–V	L_μ–V–L_μ	ref
$Cp_2V_2(CO)_5$	2.462 double	1.933	1.936				63c,f
$Cp_2V_2(CO)_4(PPh_3)$	2.466 double	1.922	1.925				63f
$[V(CO)_4]_2(\mu\text{-}PMe_2)_2$ edge-sharing bioctahedral	2.733 double	ax, 2.00 eq, 1.97		P, 2.359	P, 70.8	P, 109.3	66
$[CpV]_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)$	2.439 "single"						82
$[CpV]_2(\mu\text{-}H)_2(\mu\text{-}\eta^4,\eta^4\text{-}C_6H_6)$	2.425 "double"						83
$[CpV(CO)_2]_2(\mu\text{-}P\text{-}2,4,6\text{-}\{Me_3C\}_3C_6H_2)$	2.924 "single"			P, 2.255	P, 80.8		85
$[CpV]_2(\mu,\sigma^2\text{-}C_4H_8)_2$	2.315 "double"			C, 2.253	C, 61.7		84
$[CpV(Me_2PCH_2CH_2PMe_2)]_2(\mu\text{-}H)_2$	2.701 single				H, 107	H, 73	87
$[(C_5H_4\{CHMe_2\})V]_2(\mu\text{-}S)_2(\mu,\eta^1\text{-}S_2)$	2.610						75
$[CpV]_2(\mu,\eta^2\text{-}S_2)(\mu,\sigma^2\text{-}S_2C_2\{CF_3\}_2)$	2.574						75
$[Cp'V]_2(\mu\text{-}Se)(\mu,\eta^2\text{-}Se_2)(\mu,\eta^1\text{-}Se_2)$	2.779 single						76
$V_2(\mu,\eta^2\text{-}2,6\text{-}\{MeO\}_2C_6H_3)_4$	2.200 triple						108b
$V_2(\mu,\eta^2\text{-}2,4,6\text{-}\{MeO\}_3C_6H_2)_4$	2.223 triple						109
$[CpV]_2(\mu,\sigma^2\text{-}S_2C_2H_4)_2$	2.542						140

[a] Abbreviations: term, terminal; sb, semibridging.

TABLE IX. Averaged Bond Distances (Å) and Bond Angles (deg) in Organodiniobium and Organoditantalum Complexes[a]

compound	M–M bond order	M–CO_{term}	M–L_μ	M–L	M–L_μ–M	L_μ–M–L_μ	ref
$[CpNb(CO)(PhCCPh)]_2$	2.74 double						62
$[Cp'Nb(CO)_2]_2(\mu\text{-}Cl)_2$	3.056 single	2.077	Cl, 2.561		73.2		77
$[Cp'Nb(Ph'CCPh')]_2(\mu\text{-}Cl)_2$	3.073 single		Cl, 2.466		77.1	102.9	77
$[CpNb(CO)_2]_2(\mu\text{-}S)_2$	3.143						73
$[CpNb(CO)_2]_2(\mu\text{-}SMe)_2$	3.164						73
$[TaCl_2(thf)]_2(\mu\text{-}Cl)_2(\mu\text{-}\eta^2,\eta^2\text{-}Me_3CC_2CMe_3)$	2.677 double		Cl, 2.489	Cl, 2.345	65.0	78.2	121
$Cp''_2Ta_2Cl_3Me(\mu\text{-}H)_2$ two independent molecules	2.854 2.815 single			Cl, 2.357 Cl, 2.357			78b
$[Cp^*Ta]_2(\mu\text{-}Br)_4$	2.748 double		Br, 2.616		63.3	116.9 transoid	88

[a] Abbreviations: term, terminal; Ph′, *p*-tolyl.

and the greater interest recently in reactivity of metal–metal bonded systems. The modes of reactivity in metal–metal bonded dinuclear chemistry can be categorized conveniently into oxidative addition, migratory insertion, ligand displacement, substrate coupling, metal–metal bond cleavage, and clusterification reactions. The patterns which can be observed from this organization suggest that the metal–metal bond is playing a direct role in many of these reaction classes, but the lack of mechanistic information in this area does not allow one to determine whether a reaction occurs at one of the metal centers as opposed to the dinuclear unit. The involvement of the metal–metal bond in reactions and the possible importance of metal cooperativity in reactions of dinuclear complexes have been discussed.[111]

Caution must be exercised in any treatment of functional group reactivity of metal–metal bonds, especially in direct extrapolation from organic chemistry of carbon–carbon multiple bonds. For example, the initial expectation that reactivity should increase with

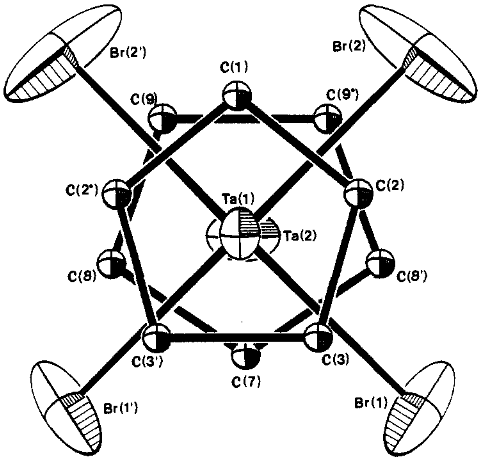


Figure 21. ORTEP diagram of $(C_5Me_5)_2Ta_2(\mu\text{-}Br)_4$ viewed approximately down the Ta(1)–Ta(2) axis. The crystallographically imposed mirror plane, perpendicular to the plane of the figure, passes through C(1), Ta(1), Ta(2), and C(7). Methyl carbons are omitted and the ring carbon thermal ellipsoids are reduced in size for clarity.

increasing bond order, as is seen in organic chemistry, is naïve: the triply bonded diniobium and ditantalum species recently found by Cotton and co-workers[35] are relatively unreactive by comparison to doubly bonded analogues (possibly because these ionic species are 18-electron complexes) and can be recrystallized from degassed water! Though formal metal–metal bond order does not necessarily correlate with reactivity, it can be a useful guide in designing reactivity probes.

A. Oxidative Addition

The oxidative addition reaction is one of the distinctive reaction classes of organotransition-metal chemistry, and formal oxidative addition to dinuclear complexes would be expected to provide perhaps the clearest support for direct metal–metal bond involvement in those cases where the dinuclear reaction product bears a close structural relationship to the dinuclear reactant.

Sattelberger and co-workers provided some of the first examples of oxidative addition to dinuclear early metal centers of the edge-sharing bioctahedral class. In an important series of papers[37,39,40] these researchers brought small-molecule reactivity to this area of transition-metal chemistry by demonstrating addition of H_2, HCl, and Cl_2 to doubly bonded ditantalum complexes (eq 59–62); this hydrogenation reaction is the first such example in metal–metal multiple-bond chemistry. Hubert-Pfalzgraf has reported hydrogenation of the related complex $Ta_2Cl_6(PMe_2Ph)_4$ to a hydrido species of unknown structure.[38]

$$[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2 + H_2 \rightarrow [TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2 \tag{59}$$

$$[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2 + Cl_2 \rightarrow [TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2 \tag{60}$$

$$[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2 + HCl \rightarrow [TaCl_2(PMe_3)_2](\mu\text{-}Cl)(\mu\text{-}H)_3 \tag{61}$$

$$[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2 + H_2 \rightarrow [TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4 \tag{62}$$

Doubly bonded dimetallics with a confacial bioctahedral structure show a more limited, though interesting, oxidative addition chemistry. Cotton and co-workers have shown that ditantalum and diniobium complexes react with azo compounds (eq 63 and 64) to

$$[TaCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + PhN{=}NPh \rightarrow Cl_2(Me_2S)(PhN)Ta(\mu\text{-}Cl)_2Ta(NPh)(SMe_2)Cl_2 \tag{63}$$

$$[NbCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + PhN{=}NPh \rightarrow Cl_2(Me_2S)(PhN)Nb(\mu\text{-}Cl)_2Nb(NPh)(SMe_2)Cl_2 \tag{64}$$

cleave the N═N bond to terminal nitrene ligands, in essence a double bond metathesis reaction involving N═N and M═M bonds.[112,113] The dinuclear products have long, nonbonded metal–metal distances consistent with M(V) centers. The diniobium product was also obtained by Hubert-Pfalzgraf and Aharonian from addition of PhN_3 to the same diniobium precursor; gas evolution was noted during the reaction (eq 65).[114]

$$[NbCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + PhN_3 \rightarrow N_2 + Nb_2Cl_6(NPh)_2(SMe_2)_2 \tag{65}$$

They also reported that the reaction with Me_3SiN_3 followed the different course of Si–N bond cleavage to give diniobium azide complexes (eq 66) of unknown

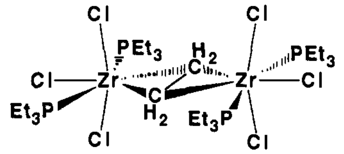


Figure 22. Molecular structure of $Zr_2Cl_6(PEt_3)_4(\mu\text{-}C_2H_4)$.

$$[NbCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + Me_3SiN_3 \rightarrow Nb_2Cl_4(N_3)_2(SMe_2)_2 + Me_3SiCl \tag{66}$$

structure. Cotton and co-workers have observed oxidative addition of disulfides to a ditantalum center (eq 67).[115] The diamagnetic product has a tantalum–tantalum single bond based on MO calculations. Cotton and Roth have shown that an acetylene can also oxidatively add to a confacial bioctahedral dimetallic to yield coordinated acetylenes (eq 68) which are best viewed as metallacyclopropenes and thus as acetylene dianions through reduction by the metal centers.[116] The niobium–niobium distance is too long for direct bonding, consistent with the view that the niobium atoms are pentavalent.

$$[TaCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + PhSSPh \rightarrow [TaCl_3(SMe_2)]_2(\mu\text{-}SPh)_2 + SMe_2 \tag{67}$$

$$[NbCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + 2PhC_2Ph \rightarrow [NbCl_2(tht)PhCCPh]_2(\mu\text{-}Cl)_2 + 3tht \tag{68}$$

Dizirconium complexes are also capable of undergoing oxidative addition reactions with olefins.[19] The complex $[ZrCl_2(PEt_3)_2]_2(\mu\text{-}Cl)_2$ was shown to react with C_2H_4 and $MeCHCH_2$ to yield "alkene"-bridged organodimetallics with aliphatic carbon atoms based on ^{13}C NMR studies (e.g., eq 69). Butadiene yielded both mononuclear and dinuclear zirconium complexes as a function of stoichiometry. Cotton and Kibala showed[117] that the μ-C_2H_4 product had a symmetric μ-η^2,η^2-C_2H_4 ligand by X-ray crystallography (Figure 22) and also demonstrated that the product can be derived from addition of 1,2-dichloroethane to the dizirconium precursor (eq 70).

$$[ZrCl_2(PEt_3)_2]_2(\mu\text{-}Cl)_2 + C_2H_4 \rightarrow [ZrCl_3(PEt_3)_2]_2(\mu\text{-}C_2H_4) \tag{69}$$

$$2Zr_2X_6(PR_3)_4 + ClCH_2CH_2Cl \rightarrow [ZrX_3(PR_3)_2]_2(\mu\text{-}CH_2CH_2) + 2ZrX_3Cl(PR_3)_2 \tag{70}$$

The organodiniobium complex $Cp^*{}_2Nb_2Cl_4$ reported by Schrock and co-workers displayed limited reactivity in potential oxidative addition chemistry, reacting only with 3-hexyne to yield the tantalacyclopropene $Cp^*NbCl_2(EtCCEt)$. The compound did not react with H_2, MeCN, or C_2H_4 under standard conditions.[79]

In contrast, we have found that the organoditantalum complexes $[Cp^*Ta]_2(\mu\text{-}X)_4$[88,118] display a diverse range of reactivity. The reactivities of diniobium and ditantalum complexes differ in small but important ways, probably because of the greater ease of oxidation of low-valent tantalum species; this pattern of greater ease of oxidation for the third-row congeners has long been apparent in comparisons of dimolybdenum and ditungsten chemistry. Oxidative addition of dihydrogen yielded the known hydride $[Cp^*TaX_2]_2(\mu\text{-}H)_2$ (vide infra), the third example of this reaction type. Reaction

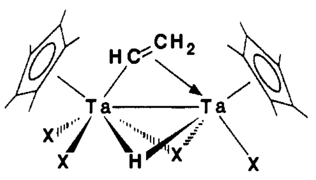


Figure 23. Proposed structure of $(C_5Me_5)_2Ta_2X_4(\mu\text{-}H)(\mu\text{-}CHCH_2)$.

with ethylene and other simple terminal olefins leads to oxidative addition of the terminal olefinic C–H bond under mild conditions and formation of a (μ-vinyl)(μ-hydride)organoditantalum complex (eq 71) in which the

$$[Cp^*Ta]_2(\mu\text{-}X)_4 + C_2H_4 \rightarrow Cp^*{}_2Ta_2X_3(\mu\text{-}X)(\mu\text{-}H)(\mu\text{-}C_2H_3) \quad (71)$$

vinyl group is strongly distorted toward a tantalum-substituted tantallacyclopropane; a preliminary X-ray analysis showed a bridging halogen atom is present (Figure 23). This result is the first observation of intermolecular C–H bond activation by *any* metal–metal multiple bond. Labeling studies have shown that the activation reaction proceeds from the dinuclear reactant and not a mononuclear intermediate from dimetallic cleavage. Kinetic studies by UV/vis spectrophotometry and ^1H NMR spectroscopy show that the reaction with ethylene is first-order in organoditantalum reactant. In contrast, the Sattelberger complex $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$ reacted with C_2H_4 to yield a mononuclear Ta(III) olefin complex (eq 72).[37]

$$[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2 + 2C_2H_4 \rightarrow 2TaCl_3(PMe_3)_2(C_2H_4) \quad (72)$$

B. Migratory Insertion

There are few examples of migratory insertion chemistry with early metal organodimetallics, in part because not many of these species contain alkyl groups. The rare examples of migratory insertions involve carbon monoxide and either bridging or terminal hydride complexes, and the results are milestones in the development of organotransiton metal chemistry.

Schrock and co-workers found that the singly bonded organoditantalum complex $[Cp''TaCl_2]_2(\mu\text{-}H)_2$ reacted readily with CO and MeCN to give products derived formally from insertion of the substrate into a Ta–H bond (eq 73 and 74).[78] The reaction with CO was the

$$[Cp''TaCl_2]_2(\mu\text{-}H)_2 + CO \rightarrow Cp''TaCl_2(\mu\text{-}H)(\mu,\eta^2\text{-}CHO)Cl_2TaCp'' \quad (73)$$

$$[Cp''TaCl_2]_2(\mu\text{-}H)_2 + MeCN \rightarrow Cp''ClTa(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}\eta^1\text{-}N,\eta^2\text{-}C,N\text{-}NCHMe)TaCl_2Cp'' \quad (74)$$

first example of migratory insertion of CO into a metal hydride to yield a formyl group, a long-sought reaction of modeling importance for Fischer–Tropsch reductive polymerization of CO. The formyl and NCHMe ligands were found in bridging positions in both cases, and the metals are best considered as Ta(V) centers.

Wolczanski and co-workers have found recently that the unbridged ditantalum(IV) compound $[TaH_2\{OSi(CMe_3)_3\}_2]_2$ reductively cleaved CO to give a (μ-methylene)(μ-oxo)ditantalum compound directly (eq 75).[119] This result is also important for modeling

$$[TaH_2\{OSi(CMe_3)_3\}_2]_2 + CO \rightarrow [\{(Me_3C)_3SiO\}_2TaH]_2(\mu\text{-}O)(\mu\text{-}CH_2) \quad (75)$$

Fischer–Tropsch syntheses which lead to hydrocarbon products. These workers have explored further reactions of the nonbonded ditantalum product, including carbonylation which resulted in carbon–carbon bond formation through a μ-formyl–μ-formaldehyde intermediate.

In contrast to these important ditantalum and organoditantalum results, the related (μ-hydrido)organodivanadium compound $[CpV(Me_2PCH_2CH_2PMe_2)]_2(\mu\text{-}H)_2$ showed no reaction with olefins.[87]

C. Ligand Displacement

Cotton and co-workers have reported a number of studies on acetylene reactions with doubly bonded McCarley-type dimetallics which resulted in ligand substitution reactions.[120-124] Diphenylacetylene reacted to yield a precipitate presumed to be a mononuclear tantalum diphenylacetylene complex, $TaCl_3(tht)_2(PhCCPh)$. Recrystallization of the precipitate from pyridine/dichloromethane yielded in 30% yield a mononuclear, anionic tantalum complex from partial hydrolysis by adventitious water and complexation of the liberated HCl (eq 76). Other substituted acetylenes yield dinuclear products (eq 77 and 78) with bridging or terminal acetylenes. Bis(diphenylphosphino)acetylene was found to react with $[TaCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$ to give two nonbonded organoditantalum(V) complexes with coupled acetylenes. In certain cases, these workers have also observed alkyne cyclotrimers and polymers[123] as a function of the metal and the alkyne substitutents (notable as the first example of a catalytic reaction by early metal dinuclear complexes).

$$[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + 2PhCCPh \rightarrow 2\text{“}TaCl_3(tht)_2(PhCCPh)\text{”} \xrightarrow{H_2O/py} pyH^+TaCl_4(py)(PhCCPh)^- \quad (76)$$

$$[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + Me_3CCCCMe_3 \rightarrow [TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}Me_3CCCCMe_3) \quad (77)$$

$$[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + MeCCCMe_3 \rightarrow (MeC_2CMe_3)Cl_2(tht)Ta(\mu\text{-}Cl)_2Ta(tht)Cl_2(MeC_2CMe_3) \quad (78)$$

D. Substrate Coupling

The most studied coupling reactions of early metal dimetallics are with nitriles and isonitriles. An early report from the McCarley laboratory[125] showed that low-valent Nb and Ta halides will couple MeCN to give a carbon–carbon bonded ligand in which the nitrogens are bound to the metals in a bridging dinuclear product. An even earlier (1972) report by Kepert and co-workers[126] suggested that $TaCl_4$ reacted with MeCN to give a diamagnetic ditantalum complex in which terminal MeCN ligands were present in an edge-sharing bioctahedral species, but the structure was not determined and coupled nitriles may be present. Cotton and co-workers proceeded to show[127] that $[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht)$ reacted with MeCN to yield the same product as that observed by McCarley, with the same dimerized nitrile bridging ligand (eq 79). Cotton later

$$[TaCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + RCN \rightarrow Cl_3(RCN)_2Ta{=}NCR{=}CRN{=}Ta(NCR)_2Cl_3 \quad (79)$$

showed that isonitriles are also coupled to bridging ligands with these confacial bioctahedral complexes (eq 80 and 81); two distinctly different types of bridging

$$[MCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + RNC \rightarrow Cl_2(RNC)_4M(\mu\text{-}RNCCNR)MCl_4 \quad (80)$$

$$[NbCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + Me_3CNC \rightarrow Nb_3Cl_8(Me_3CNC)_5 + Cl_2(Me_3CNC)_2Nb(\mu\text{-}Me_3CNCCNCMe_3)NbCl_4 \quad (81)$$

ligand were formed depending on the isonitrile substituent.[128,129] It is not clear that the dinuclear reactants, rather than mononuclear isonitrile complexes, are responsible for the dimerization of the isonitrile; a labeling experiment to distinguish the possibilities may be possible.

E. Metal–Metal Bond Cleavage

Reactions in which metal–metal bond disruption occurs are common in later transition-metal multiple bond chemistry, particularly with strong π-donor reactants such as CO. Analogous reactivity with most early metal dimetallics has not been explored in detail, but there are some examples of metal–metal bond cleavage.

The organodivanadium complex $Cp_2V_2(CO)_5$ has been shown to cleave to mononuclear products in reactions with various ligands[63] and actually slowly decomposes in solution in the absence of other ligands (with added ligands serving only to trap the mononuclear fragments after fragmentation) to give $CpV(CO)_4$ and polynuclear products[130] (vide infra). Addition of L = PBu_3, PEt_2Ph, PH_3, or CN^- has been shown by Fischer and Schneider to lead to both $CpV(CO)_3L$ and $CpV(CO)_2L_2$, while PPh_3, $AsPh_3$, and $P(CHMe_2)_3$ led to both mononuclear and dinuclear products. Nitric oxide was shown to yield $CpV(CO)(NO)_2$ in low yield.

The arene-bridged, doubly bonded organodivanadium complex $[CpVH]_2(\mu\text{-}C_6H_6)$ is reported[83] to react with CO to free hydrocarbon products, dihydrogen, and $CpV(CO)_4$ (eq 82), while treatment with iodine yielded CpVI(thf) (eq 83).

$$[CpVH]_2(\mu\text{-}C_6H_6) + \text{excess } CO \rightarrow 2CpV(CO)_4 + 0.75(1,3\text{-}C_6H_8) + 0.25(C_6H_6) + 0.25H_2 \quad (82)$$

$$[CpVH]_2(\mu\text{-}C_6H_6) + I_2 \rightarrow 2CpVI(thf) + C_6H_6 + H_2 \quad (83)$$

Clay and Brown have reported[131] that the diniobium complex $[NbCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht)$, when dissolved in neat pyridine or alkyl-substituted pyridines, dissociates to $NbCl_3L_3$; the ditantalum analogue underwent ligand substitution to yield diamagnetic $Ta_2Cl_6L_4$.

The dizirconium complex $[ZrCl_2(PEt_3)_2]_2(\mu\text{-}Cl)_2$ is reported to react with TlCp to yield the Zr(IV) complex $CpZrCl_3(PEt_3)_2$, via oxidation with Zr–Zr bond rupture, and metallic thallium.[19]

F. Clusterification

Dinuclear and organodimetallic complexes of the early metals can be used in the synthesis of trinuclear and polynuclear metal clusters, with thermolytic, atom-abstraction, reductive, and ligand-induced methods having been employed. Odd-atom clusters are presumably formed under conditions where the dimetallic or organodimetallic precursor splits into mononuclear fragments. Even-number clusters may be formed either by this mechanism or via a direct combination of the dinuclear or organodimetallic precursors, but little is known about the actual mechanisms for these clusterification reactions.

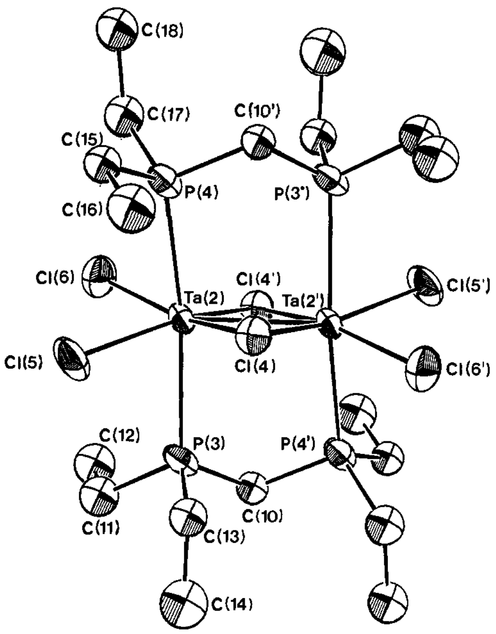


Figure 24. ORTEP diagram of $[TaCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}Et_2PCH_2PEt_2)_2$.

An early example of clusterification with an early metal organodimetallic was observed[130] in the thermolysis of $Cp_2V_2(CO)_5$. The thermal disproportionation led to a mixture of $CpV(CO)_4$, $Cp_4V_4(CO)_4$ (32%), and $Cp_3V_3(CO)_9$ Nothing is known about the mechanism of this apparently complex reaction. Thermolysis of $[ZrCl_2(PMe_2Ph)_2]_2(\mu\text{-}Cl)_2$ to the hexazirconium, octahedral cluster $Zr_6(\mu\text{-}Cl)_{12}(PMe_2Ph)_6$ (eq 84) was recently

$$3Zr_2Cl_6(PMe_2Ph)_4 \xrightarrow{\Delta} Zr_6(\mu\text{-}Cl)_{12}(PMe_2Ph)_6 \quad (84)$$

reported, but the mechanism is unknown.[132] This important result suggests that early metal dinuclear complexes may be valuable synthons in the molecular design of new classes of inorganic materials.

Abstraction of ligand atoms from organodimetallics can also lead to clusterification. A good example of this approach is the sulfur-abstraction reaction of PBu_3 with $[Cp'V]_2(\mu\text{-}S)_2(\mu,\eta^1\text{-}S_2)$ which generated organotetravanadium and organopentavanadium species (eq 85), reported by Rauchfuss and co-workers.[133]

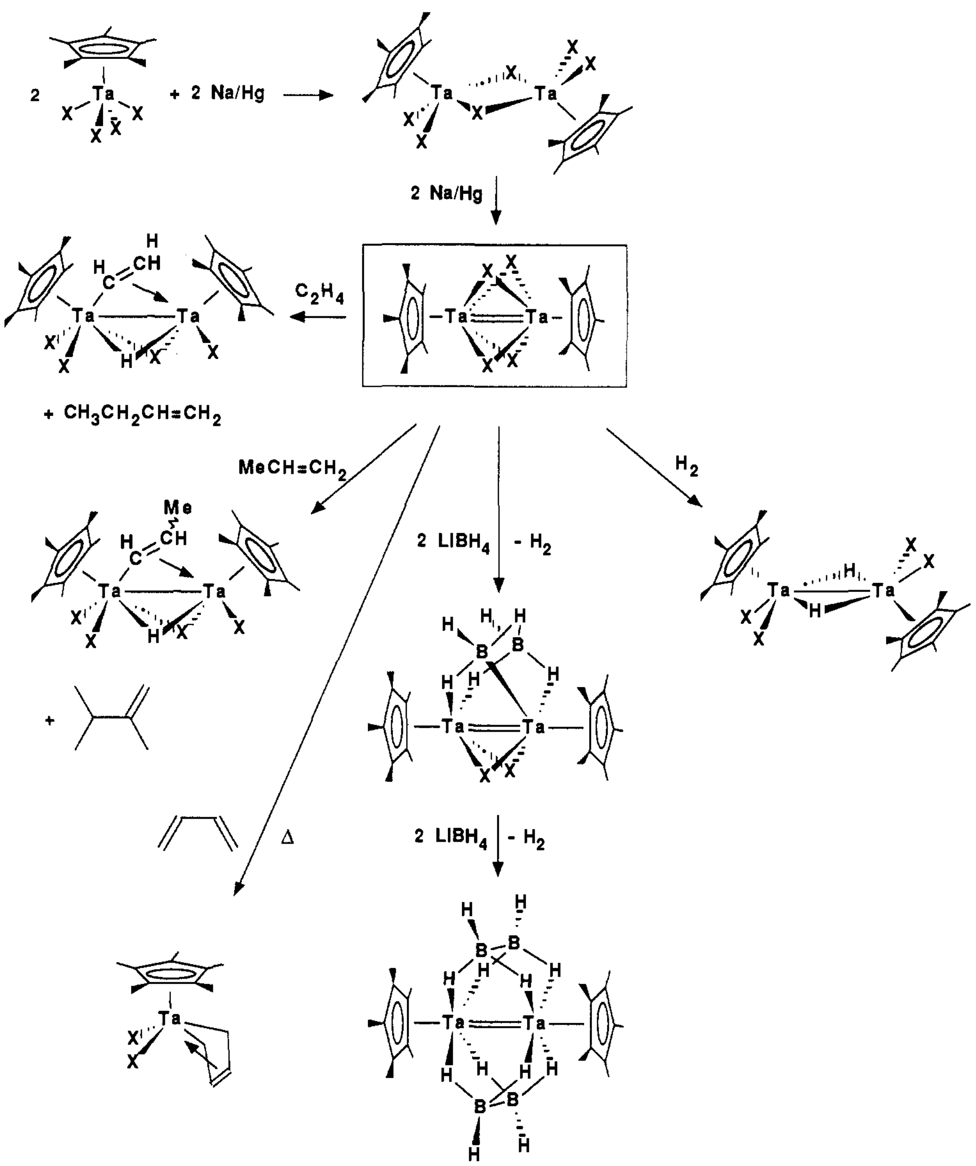
$$[Cp'V]_2(\mu\text{-}S)_2(\mu,\eta^1\text{-}S_2) + PBu_3 \rightarrow Cp'_5V_5S_6 + Cp'_4V_4S_4 + SPBu_3 \quad (85)$$

Ligand addition to dinuclear synthons can lead to clusters, as has been found in several cases. A diamagnetic alkoxide complex, believed to be tetrameric, was formed in 40% yield from the reaction of a ditantalum precursor with $LiOCMe_3$ (eq 86);[50] this work

$$Ta_2X_6(NC_5H_4\text{-}p\text{-}Me)_4 + 4LiOCMe_3 \rightarrow Ta_2Cl_2(OCMe_3)_4 + 4NC_5H_4\text{-}p\text{-}Me + 4LiCl \quad (86)$$

by the Hubert-Pfalzgraf group is one of the earliest reports of dinuclear early metal alkoxide complex synthesis via alkoxide anion metathesis rather than alcoholysis. The same group has also reported that addition

SCHEME I. Synthesis and Reactivity of $(C_5Me_5)_2Ta_2(\mu\text{-}X)_4$



of the small bite-angle ligand $MeN(PF_2)_2$ to a diniobium complex led to a mixture of tetraniobium clusters (eq 87).[137] A triniobium complex was found by Cotton and

$$Nb_2Cl_6(PMe_2Ph)_4 + MeN(PF_2)_2 \rightarrow Nb_4Cl_{12}(PMe_2Ph)_6 + Nb_4Cl_{12}(PMe_2Ph)_6[MeN(PF_2)_2] \quad (87)$$

Roth as a byproduct of isonitrile reaction with a diniobium complex, in addition to a diniobium species with reductively coupled isonitriles (eq 88; L = μ-$Me_3CNCCNCMe_3$).[129] Cotton and co-workers have also generated μ-oxo-capped triniobium species from addition of protic acids or carboxylates to $[NbCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht)$.[135]

$$[NbCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2) + Me_3CNC \rightarrow Nb_3Cl_8(CNCMe_3)_5 + Nb_2Cl_6(CNCMe_3)_2(L) \quad (88)$$

Recently, Cotton and co-workers have reported that reduction of the McCarley diniobium species with sodium amalgam in the presence of phosphines generated triniobium clusters (eq 89);[136] $Me_2PCH_2CH_2PMe_2$ and PBu_3 also gave triniobium analogues.

$$[NbCl_2(tht)]_2(\mu\text{-}Cl)_2(\mu\text{-}tht) + Na/Hg + PMe_2Ph \rightarrow Nb_3Cl_7(PMe_2Ph)_6 \quad (89)$$

VI. Conclusions and Future Directions

It is clear that the field of metal–metal bonded dinuclear and organodimetallic chemistry of the early metals has experienced rapid growth since the late 1970s. Major synthetic contributions by the McCarley, Sattelberger, and Schrock groups, structural contributions from the Cotton group, and reactivity results from the Sattelberger and Schrock groups have led this expansion.

This author believes that much remains to be done in the area of reactivity studies, particularly with small molecules. Though our knowledge of dinuclear and organodimetallic reactivity is underdeveloped, the potential for novel chemistry is clearly demonstrated by the unique reactivity that has been observed, including H_2 addition across a tantalum–tantalum double bond, migratory insertion of CO into a ditantalum hydride, and intermolecular hydrocarbon C–H bond activation by tantalum–tantalum double bonds.

Future synthetic efforts will probably focus on preparation of early metal heterobimetallics (in order to explore the role of metal cooperativity in reactivity), elaboration of group 4 chemistry and the development

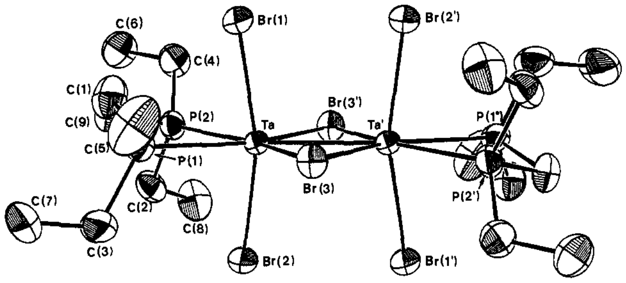


Figure 25. ORTEP diagram of $[TaBr_2(Et_2PCH_2PEt_2)]_2(\mu\text{-}Br)_2$.

of new multiply bonded synthons, synthesis of dinuclear species with presently unexplored ligand classes such as alkyls, acyls, and μ-alkylidenes, discovery of a vanadium–vanadium bonded synthon for preparation of other divanadium complexes, and attempts to employ dinuclears as templates in rational cluster synthesis.

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VII. Addendum

The author endeavored to be comprehensive in the preparation of this review and apologizes to any workers in this field whose published research was overlooked. The author would appreciate learning about these literature omissions.

The following sections list new results from our laboratory in the areas of synthesis, structure, and reactivity of ditantalum and organoditantalum complexes.

A. Ditantalum Complexes

Addition of the higher alkyl methylenebis(dialkylphosphine) ligands $R_2PCH_2PR_2$ (R = Et, $CH_2C_6H_4$-*p*-Me) to $[TaX_2(tht)]_2(\mu\text{-}X)_2(\mu\text{-}tht)$ or $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$ (X = Cl, Br) was shown by Messerle and coworkers to afford soluble complexes of the general formula $[TaX_2]_2(\mu\text{-}X)_2(R_2PCH_2PR_2)_2$ whose solid-state and solution structures are dependent on the halogen.[141] The solubility of these new complexes stands in marked contrast to that reported for the R = Me compound which has a structure with bridging (i.e., binucleating) diphosphine ligands.[100] For X = Cl, the $Et_2PCH_2PEt_2$ product exists as only one isomer in solution with equivalent phoshorus atoms and with a virtual quintet in the ^1H NMR spectrum (collapsing to a singlet upon {^{31}P}). The assignment of a binucleating structure from the NMR data was confirmed by a single-crystal X-ray diffraction study which showed a doubly bonded ditantalum group (2.698 (1), 2.711 (1) Å) with two bridging chlorine atoms and two bridging diphosphine ligands (Figure 24, one of the two independent molecules in the unit cell). In contrast, the X = Br complexes were found to exist in solution as a pair of isomers with NMR data consistent with both binucleating and edge-chelated forms. An X-ray structural study of the chelated form (Figure 25) shows that the doubly bonded ditantalum unit (2.769 (1) Å) also possesses two halogen bridges. The possibility that the isomers represent kinetic and thermodynamic products is being examined experimentally. Unlike the confacial bioctahedral precursors, $[TaCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}Et_2PCH_2PEt_2)_2$ reacts readily with dihydrogen to give a μ-hydride product as shown by ^1H NMR and IR spectroscopy.

B. Organoditantalum Complexes

Continuing studies on the doubly bonded organoditantalum(III) complexes $[(C_5Me_4R)Ta]_2(\mu\text{-}X)_4$ (R = Me, Et; X = Cl, Br) by Ting and Messerle have provided more information about the mechanism of synthesis and the diversity of reactivity of these novel compounds (summarized in Scheme I). Reduction of $(C_5Me_4R)TaX_4$ with 1 equivalent of sodium amalgam in toluene was found to yield the paramagnetic, nonbonded (Ta···Ta, 4.1230 (9) Å) organoditantalum(IV) complexes $(C_5Me_4R)_2Ta_2X_4(\mu\text{-}X)_2$ in 70% yield. These complexes could be subsequently reduced to the doubly-bonded $[(C_5Me_4R)Ta]_2(\mu\text{-}X)_4$ in essentially quantitative yield, thus establishing the organoditantalum(IV) complex as the likely intermediate, rather than a mononuclear Ta(IV) species, in the two-electron reduction of $(C_5Me_4R)TaX_4$ to $[(C_5Me_4R)Ta]_2(\mu\text{-}X)_4$.

The doubly-bonded $[(C_5Me_4R)Ta]_2(\mu\text{-}X)_4$ was found to react with $LiBH_4$ (2 equiv) in unprecedented fashion to eliminate dihydrogen and dimerize borohydride to the diamagnetic hexahydridodiborate (diborane(2–)) complexes $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_2(\mu\text{-}H_4B_2H_2)$ and $(C_5Me_4R)_2Ta_2(\mu\text{-}H_4B_2H_2)_2$. The solid-state molecular structure of $(C_5Me_5)_2Ta_2(\mu\text{-}Br)_2(\mu\text{-}H_4B_2H_2)$, as determined by single-crystal X-ray diffraction, consists of a long tantalum–tantalum double bond, 2.839 (1) Å in length, bridged by two bromine atoms and an unsymmetrical B_2H_6 group with two terminal B–H, one B–H–B bridge, three Ta–H–B, and one Ta–B bonds; the hydrogen-bridged B···B separation is 1.88 (2) Å in length. The complex $(C_5Me_4R)_2Ta_2(\mu\text{-}H_4B_2H_2)_2$, which can also be formed from addition of 2 equiv of $LiBH_4$ to $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_2(\mu\text{-}H_4B_2H_2)$, is postulated to have a highly symmetric structure with two bridging diborane(2–) groups with static $B\text{-}H_{terminal}$ and Ta–H–B groups as shown by ^1H and ^{11}B NMR spectroscopy. Kinetic studies of the formation of either diborane(2–) complex lead to rate expressions which are first-order in organoditantalum reactant and *zero-order* in $LiBH_4$; the zero-order dependence on $[LiBH_4]$ is consistent with rearrangement of the organoditantalum reactant to some intermediate in a slow step prior to reaction with borohydride. This intermediate is dinuclear, since borohydride (4 equiv) addition to a equimolar mixture of $(C_5Me_5)_2Ta_2(\mu\text{-}Br)_4$ and $(C_5Me_4Et)_2Ta_2(\mu\text{-}Br)_4$ gave the direct products $(C_5Me_5)_2Ta_2(\mu\text{-}B_2H_6)_2$ and $(C_5Me_4Et)_2Ta_2(\mu\text{-}B_2H_6)_2$ and no detectable cross product $(C_5Me_5)(C_5Me_4Et)Ta_2(\mu\text{-}B_2H_6)_2$. The ditantalatetraborane $(C_5Me_4R)_2Ta_2(\mu\text{-}H_4B_2H_2)_2$ is unreactive towards CO, PMe_3, H_2, $LiBH_4$, and C_2H_4 under mild conditions.

These ditantalatetraborane synthesis reactions represent a rare example of metal-catalyzed coupling of borohydride to a higher borane and serve as a model for coupling of methane to ethane; the molecular structure of $(C_5Me_5)_2Ta_2(\mu\text{-}Br)_2(\mu\text{-}H_4B_2H_2)$ is a prototype for ethane coordination to a heterogeneous catalyst surface. These results presage a potentially rich new area of dimetallaborane chemistry of the early transition metals and of metal–metal multiply bonded compounds.

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