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MODELS FOR SURFACE INTERMEDIATES IN CO HYDROGENATION: FINAL REPORT

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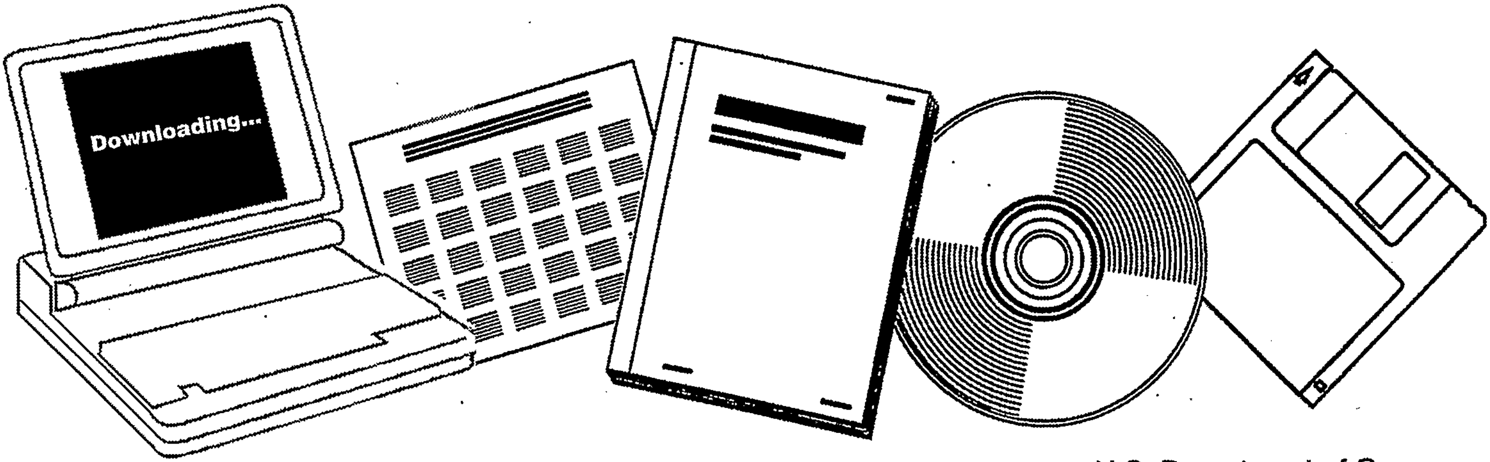

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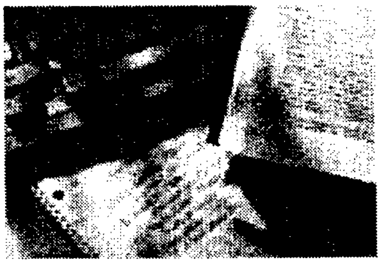

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FINAL REPORT

"MODELS FOR SURFACE INTERMEDIATES IN CO HYDROGENATION"

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Grant Number DE-FG22-85PC80513

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Introduction and Technical and Scientific Accomplishments

The author's research involves synthetic and mechanistic organotransition metal chemistry on the early metals. Three graduate students are studying mono(Cp*) ditantalum(III) (Cp* = η-C_5Me_5), Cp*Ta and Hf acyl, and ditantalum(III) $R_2PCH_2PR_2$ chemistry. Three undergraduates are studying hydrido and NR_2 Cp* ditantalum(III) and Cp* vanadium(IV) and divanadium(III) chemistry. A unifying aspect of most of these projects is the emphasis on lower-valent (η-C_5Me_4R) complexes.

One postulate in our work on lower-valent, coordinatively unsaturated Group 4/5 organometallic chemistry is that lower- and mid-valent oxidation state complexes may show less electrophilicity, which could facilitate product release in models for heterogeneous catalysis involving CO. Our results demonstrate the unusual and novel chemistry found with complexes of the early metals.

Evaluation of Reductive Carbonylation as a Route to Distorted Semi-Bridging Carbonyl Complexes

The initial studies in the project were to evaluate reductive carbonylation of early transition metal organometallics as a route to dinuclear, distorted semi-bridging carbonyl groups. We found that reduction of $(C_5Me_5)TaBr_4$ with sodium amalgam in ether gave, under mild conditions, a 40% yield of the known $(C_5Me_5)Ta(CO)_4$ instead of a dinuclear complex. However, reduction in toluene gave a dinuclear complex, $(C_5Me_5)_2Ta_2(CO)_4(\mu\text{-}Br)_2$, whose structure with terminal CO ligands is shown in Figure 1. The presence of bridging bromides rather than bridging carbonyls showed that direct reductive carbonylation of high-valent, early metal organometallics did not appear to be a viable route to semi-bridging carbonyl species. However, the question of the mechanism of formation of this product (i.e., does carbonylation occur before or after dimerization) led us to the exciting and important results described below.

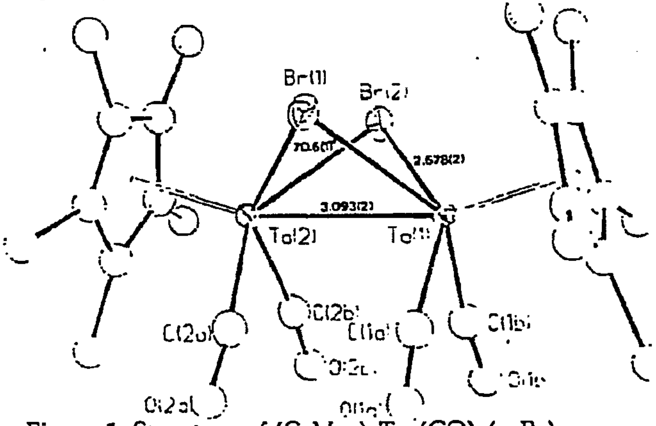


Figure 1: Structure of $(C_5Me_5)_2Ta_2(CO)_4(\mu\text{-}Br)_2$

Synthesis of Novel Organoditantalum Complexes

In research supported by this grant, we have shown that the monomeric, four-legged piano-stool $(C_5Me_4R)TaX_4$ (1, R = Me, Et; X = Cl, Br) is easily reduced with Na/Hg in toluene to afford the paramagnetic ditantalum(IV) complexes $[(C_5Me_4R)TaX_3]_2$ (2; Scheme 1). The molecular structure (Figure 2, X = Br) consists of two Ta centers (Ta···Ta, 4.1230(9) Å) bridged by two bromines, with an obtuse Ta-Br_{μ}-Ta angle of 102.68(5)° consistent with an absence of Ta-Ta bonding. Dinuclear 2 or mononuclear 1 can be reduced in high yield to the novel doubly-bonded, ditantalum(III) complex $(C_5Me_4R)_2Ta_2X_4$ (3; Scheme 1). The molecular structure of the R=Me, X=Br species (Figure 3) consists of a Ta=Ta double bond, 2.748(2) Å, bridged by four bromines. The acute Ta-Br-Ta angles, av. 63.3(1)°, and obtuse Br-Ta-Br angle, av. 116.6(2)°, are in accord with a strong Ta-Ta interaction of unusual $\sigma^2\delta^2$ electronic configuration, and the double bond formulation is consistent with the solution diamagnetism of these d^2-d^2 dinuclear complexes. The UV/VIS spectrum of this complex shows an absorption at 794 nm with extinction coefficient consistent with a metal-metal based electronic transition, possibly δ-δ^*. The distinctive UV/VIS spectrum allows the convenient following of reactions by spectrophotometry.

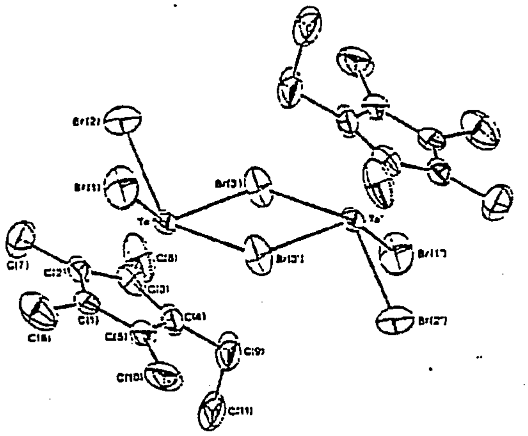


Figure 2: Structure of $(C_5Me_4Et)_2Ta_2Br_4(\mu\text{-}Br)_2$ (2)

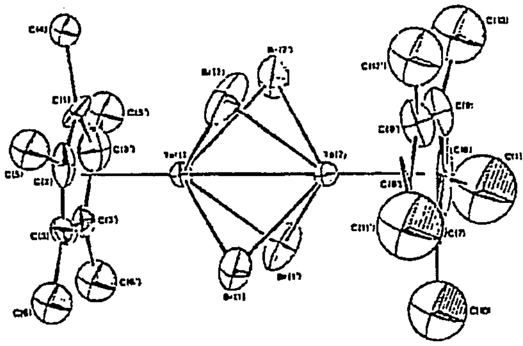


Figure 3: Structure of $Cp^*_2Ta_2(\mu\text{-}Br)_4$ (3)

Reactivity of Ditantalum Complexes

The new ditantalum species show a strikingly broad range of reactivity with small molecules, including CO, H_2, PMe_3, $LiBH_4$, diazoalkanes, and monoxygenation reagents such as Me_3NO and N_2O (Scheme 1, X = Cl and Br). Hydrogenation of $Cp^*_2Ta_2X_4$ yields $Cp^*_2Ta_2X_4(\mu\text{-}H)_2$ via oxidative addition to the Ta=Ta bond. Hydrogen oxidatively adds to the tantalum-tantalum double bond in the case of the bromide to yield a mixture of hydride complexes, of general formula $(C_5Me_5)_2Ta_2Br_{6-n}H_n$. The chloride dimer adds H_2 to give only $(C_5Me_5)_2Ta_2Cl_4(\mu\text{-}H)_2$ as the observable product. Presumably, hydride/halide exchange is fast between bromide-containing dimers but slow in the chloride analogs, enabling us to isolate the first -formed hydrogen oxidative addition product prior to exchange. Excess N_2O yields the oxo complex Cp^*TaX_2O; the presumed μ-oxo Ta(IV) intermediate has not been isolated.

We also examined methods for preparing metal hydride complexes in which the metals were multiply bonded, on the theory that hydride ligands in doubly-bonded organodimetallics would be susceptible to direct carbonylation to formyl groups, which are postulated intermediates in some mechanisms for Fischer-Tropsch reductive polymerization of carbon monoxide. Hydride addition (LiH) to $(C_5Me_5)_2Ta_2Cl_4$ yields the new hydride-bridged complex $(C_5Me_5)_2Ta_2Cl_3(\mu\text{-}H)$. We believe that this new doubly-bonded hydride complex will exhibit CO reactivity to give formyl species; exploratory reactions are in progress.

Reaction with $LiBH_4$ leads not to new hydride dimers but, rather, to unprecedented B-H activation and borohydride dehydrodimerization to ditantalum species with μ-diborane(2-) ligands such as $Cp^*{}_2Ta_2(\mu\text{-}Br)_2(B_2H_6)$ (Scheme 1, Figure 4). Addition of two equivalents of $LiBH_4$ to $Cp^*{}_2Ta_2(\mu\text{-}Br)_2(B_2H_6)$ results in substitution of all halides and formation of $Cp^*{}_2Ta_2(B_2H_6)_2$.

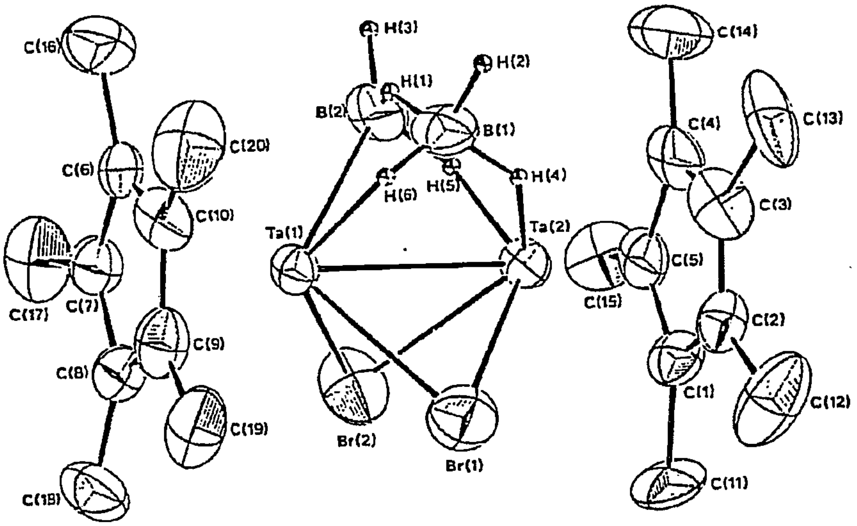
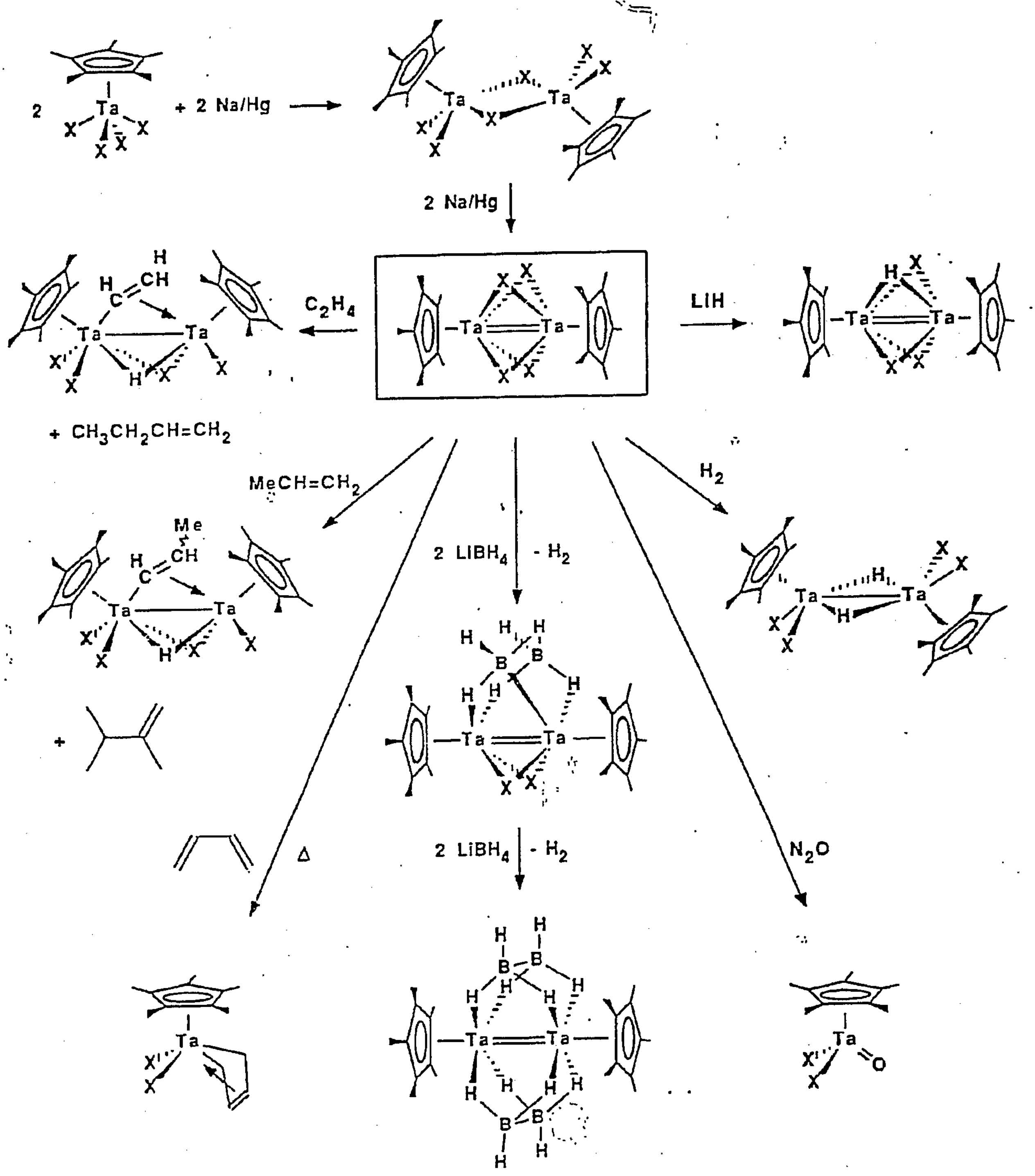


Figure 4: Structure of $Cp^*{}_2Ta_2(\mu\text{-}Br)_2(\mu\text{-}B_2H_6)$

Reaction of an equimolar mixture of $(C_5Me_4Et)_2Ta_2Br_4$ and $Cp^*{}_2Ta_2Br_4$ with $LiBH_4$ gives only the direct products $(C_5Me_4Et)_2Ta_2(B_2H_6)_2$ and $Cp^*{}_2Ta_2(B_2H_6)_2$, which demonstrates that BH_4^- activation and coupling occurs at the ditantalum moiety and not via a mononuclear complex. The rate expressions for the reaction of $LiBH_4$ with $Cp^*{}_2Ta_2Br_4$ or $Cp^*{}_2Ta_2Br_2(B_2H_6)$ are first order in ditantalum reactant and zero-order in $LiBH_4$, which suggests that the ditantalum reactants first rearrange in a slow step to a more sterically accessible structure.

This novel result with BH_4^- is significant because early metal polyborane chemistry is virtually unexplored and because $B_2H_6^{2-}$ and C_2H_6, as well as BH_4^- and CH_4, are isoelectronic. The $B_2H_6^{2-}$ complexes are models for ethane coordination to a catalyst surface in reactions such as alkane hydrogenolysis, and the BH_4^- coupling reaction is a model for dehydrodimerization of CH_4 to C_2H_6.

SCHEME 1: Synthesis and Reactivity of $(C_5Me_5)_2Ta_2(\mu\text{-}X)_4$



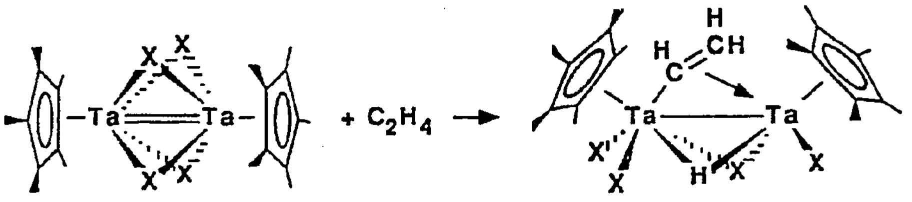
Syntheses of Organovanadium(IV) and Organodivanadium(III) Analogs

It is known from other transition metal chemistry that compounds of the first-row elements often show greater reaction rates compared to their second- and third-row congeners, so we became interested in developing organodivanadium chemistry analogous to that of our organoditantalum results with $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$. We have recently found a high yield (70%) route to Cp^*VX_3 (X = Cl, Br) via halogenation of $Cp^*V(CO)_4$; the chloride has been reported in very low yield. This high yield synthesis provides an important, new entry point for developing lower-valent mono(Cp*) vanadium chemistry. We have examined reductive dimerization reactions as a route to new divanadium complexes with the potential for V-V bonding. Reduction of the paramagnetic vanadium(IV) complexes yields divanadium complexes with mass spectra consistent with $Cp^*{}_2V_2X_4$. Well-formed crystals of $Cp^*{}_2V_2Br_4$ and $Cp^*{}_2V_2Cl_4$ unfortunately do not diffract, so efforts are focussing on C_5Me_4Et analogs. Proton NMR data indicate that the Br species is diamagnetic, whereas the Cl complex is paramagnetic (susceptibility studies are in progress); these species may thus have a thermally accessible singlet-triplet electronic transition. $Cp^*{}_2V_2X_4$ may have a doubly-bridged structure, $Cp^*{}_2V_2(\mu\text{-}X)_2X_2$, in solution rather than the quadruply-bridged structure of $Cp^*{}_2Ta_2(\mu\text{-}X)_4$ by analogy to the reported $Cp_2Cr_2(\mu\text{-}Cl)_2Cl_2$ and $(C_5H_4{}^iPr)_2Mo_2(\mu\text{-}Cl)_4$. $Cp^*{}_2V_2Br_4$ is highly reactive in test reactions; e.g., it reacts with H_2 to give a new hydride complex presently under characterization.

$$Cp^*V(CO)_4 + 1.5\,X_2 \rightarrow 4\,CO + Cp^*VX_3$$
$$2\,Cp^*VX_3 + 2\,Na \rightarrow Cp^*{}_2V_2X_4 + 2\,NaX$$

Intermolecular Vinylic C-H Bond Reactivity of Organoditantalum Complexes

The multiply-bonded ditantalum species 3 reacts with olefins under conditions which depend on the substrate (Scheme 1). Butadiene and 4-methylstyrene react at elevated temperatures to give the mononuclear complexes $Cp^*TaX_2(\eta^2,\sigma^2\text{-}CH_2CHCHCH_2)$ and $Cp^*TaX_2(\eta^2\text{-}CH_2CHPh')$. However, the reaction of 3 with C_2H_4 under mild conditions (30 psi/25°) yields the new ditantalum vinyl hydride $(C_5Me_4R)_2Ta_2X_4(\mu\text{-}CHCH_2)(\mu\text{-}H)$ (4).



(3)

This reaction is the first example of intermolecular C-H activation by a metal-metal multiple bond. The reaction of $Cp^*{}_2Ta_2Cl_4$, 3, with C_2H_4 is first order in 3, with substantially negative $\Delta S^\ddagger$ values of -39.7 (via UV/VIS) and -49.1 J K^{-1} mol^{-1} (via ^1H NMR). In situ NMR studies of the C_2H_4 reaction show the presence of 1-butene from catalytic dimerization. The vinyl hydride 4 is not a dimerization intermediate since 4 does not react with C_2H_4 under reaction conditions. One explanation involves an equilibrium between 3 and mononuclear $(C_5Me_4R)TaX_2$ (5) followed by reaction of 5 with excess C_2H_4 to form a tantallacyclopentane (a known olefin dimerization intermediate). However, the vinyl hydride 4 is derived from reaction of C_2H_4 with 3, not 5, since reaction of C_2H_4 with an equimolar mixture of 3a (R = Me) and 3b (R = Et) gives the direct products and no cross product $Cp^*(C_5Me_4Et)Ta_2X_4H(C_2H_3)$ (control experiments have shown that Cp^*/C_5Me_4Et exchange is not facile); thus, the vinyl hydride is formed by direct reaction of ethylene with the organoditantalum complex and not via initial reaction of ethylene with a monomer such as $(C_5Me_5)TaX_2$. Propylene and 1-butene lead to vinylic (not allylic) C-H activation products, with selective dimerization of propylene to $H_2C{=}CMeCHMe_2$ found. This selectivity towards vinylic C-H bonds hints at the need for precoordination of the olefin to the dinuclear center prior to C-H bond insertion.

These alkene activations are remarkable when considered in the context of known Ta(III) olefin complexes: $TaCl_3(PMe_3)_2(C_2H_4)$ and $Cp^*TaCl_2(C_2H_4)$ are stable relative to C-H insertion, while postulated olefin complex intermediates of $Cp^*{}_2Ta(III)_2X_4$ undergo C-H bond cleavage, which demonstrates the role of the Ta=Ta bond or metal cooperativity in C-H cleavage.

There is some evidence for reactivity towards a broader range of hydrocarbons, as is shown by clean first-order decomposition/rearrangement of the complex in solvents such as benzene, ether, and hexane. These rearrangements are cleanly observable via UV/VIS spectrophotometry, but the final product(s) are not definitively characterized. Solvent participation is clearly shown by the results of kinetic experiments with benzene and perdeuterobenzene, which show a kinetic isotope effect k_H/k_D of 7.2 at 25°. No halobenzenes can be detected in the volatiles from the reaction mixture, thus ruling out electrophilic aromatic substitution. The magnitude of this isotope effect (near the theoretical maximum) is consistent with substantial solvent involvement in the rate-determining step of the rearrangement.

These results demonstrate that Ta_2 species with Ta=Ta bonds exhibit a rich and diverse chemistry with modelling significance.

Synthesis of New Ditantalum Complexes; Hydrogen Addition to a Metal-Metal Double Bond

In the course of our studies on the reactivity of the tantalum-tantalum double bond in the complexes $(C_5Me_5)_2Ta_2(\mu\text{-}X)_4$, we wondered whether other doubly- or triply-bonded ditantalum systems could be synthesized and whether they would show some commonality of reactivity in reactions with small molecules. One approach which we have studied is the synthesis of early transition metal analogs of the class of late transition metal binuclear complexes known as A-frame complexes, which involve the use of methylene-bridged diphosphine ligands. These ligands are unique among diphosphine groups in that they exhibit a tendency towards bridging or binucleating behavior rather than chelating behavior. The bridging diphosphine serves as a template for holding the dimetallic center intact during metal-centered reactions.

Addition of $Et_2PCH_2PEt_2$ (two equivalents) to the confacial bioctahedral complex $Ta_2Cl_6(tht)_3$ (tht = tetrahydrothiophene) was found to yield the soluble ditantalum complex $Ta_2Cl_6(Et_2PCH_2PEt_2)_2$. This complex is sufficiently soluble for NMR spectral characterization, and the methylene-bridge signals in the proton NMR spectrum show up as a virtual quintet. The resulting prediction of bridging ligand behavior on the basis of the NMR data was confirmed by single-crystal X-ray diffraction. The molecular structure (Figure 5) consists of a tantalum-tantalum double bond, (2.700 and 2.714 Å for the two crystallographically-independent dimers in the asymmetric unit), bridged by two chlorine atoms. An acute Ta-Cl-Ta angle is consistent with a strong tantalum-tantalum bonding interaction. The diphosphine ligands binucleate (i.e., bridge) the ditantalum unit.

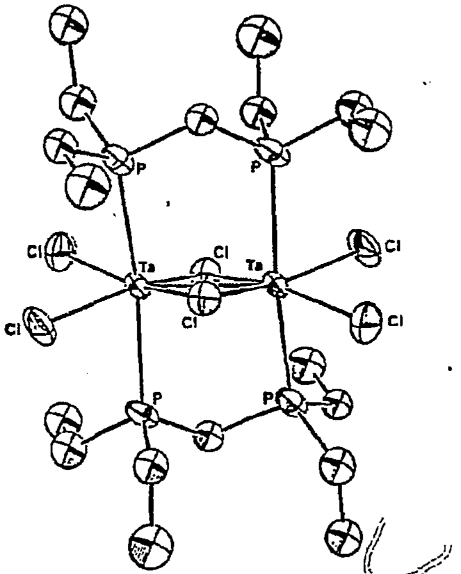


Figure 5: Structure of $Ta_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-}Et_2PCH_2PEt_2)_2$

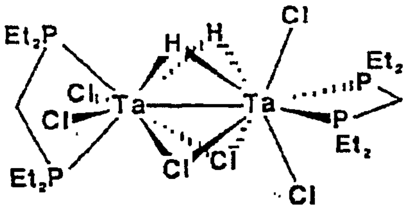


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Figure 6: Proposed Structure of H_2 Addition Product

The complex's solubility also enables us to examine its solution reactivity towards small molecules. The ditantalum compound reacts instantaneously with CO to give, after several distinct color changes, an insoluble product which does not exhibit any CO-related absorptions in the infrared spectrum; this suggests the possibility that the CO has been dissociated into carbide and oxide groups. The insolubility has precluded either NMR spectral or X-ray crystallographic characterization. The reaction of $Ta_2(\mu\text{-}Cl)_2Cl_2(Et_2PCH_2PEt_2)_2$ with dihydrogen is somewhat slower, and proton NMR spectra of the reaction mixture show a signal in a spectral region characteristic of bridging hydride groups, and the NMR data is consistent with the structure shown in Figure 6. This reactivity is highly promising; we have verified that the tht complex precursors $Ta_2X_6(tht)_3$, which are known to possess double bonds, are unreactive towards small molecules under the same reaction conditions.

The complex $Ta_2(\mu\text{-}Br)_2Br_4(Et_2PCH_2PEt_2)_2$ has been prepared from diphosphine addition to the known confacial bioctahedral complex $Ta_2Br_6(tht)_3$ (tht = tetrahydrothiophene). The resulting complex can be isolated in >95% yield as purple crystals. A single-crystal X-ray diffraction study showed that the diphosphine chelates along an edge in the resulting edge-sharing bioctahedral structure rather than bridging the two tantalum atoms (Figure 7), opposite the tendency noted in the structure of the chloride analog. The tantalum-tantalum distance, 2.769(1) Å, is consistent with a tantalum-tantalum double bond, and the acute Ta-Br-Ta angle also points to this conclusion. In the case of the bromide complex, both chelating and bridging isomers can be readily seen in the proton NMR spectrum, since the chelated isomer exhibits a triplet for the methylene bridge protons whereas the bridging diphosphine isomer exhibits a virtual quintet for the bridge methylene group This observation of both isomers in solution raises the possibilities that both isomers are in equilibrium, one isomer is a kinetic product while the other is a thermodynamic product, or that they represent two different reavction pathways depending on the approach of the diphosphine to the tht reactants. Present data rules out the first two explanations.

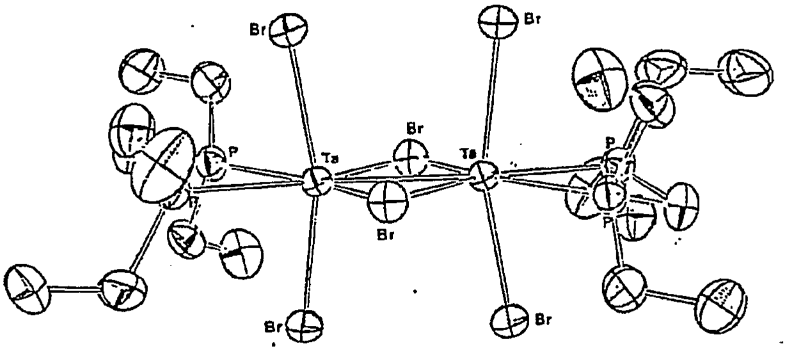
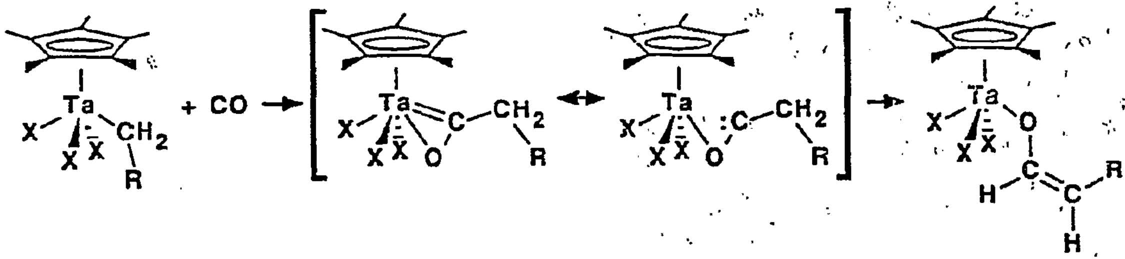


Figure 7: Structure of $Ta_2(\mu\text{-}Br)_2Br_4(Et_2PCH_2PEt_2)_2$

Migratory CO Insertion into Metal Alkyls: Generation of Enolate and Acyl Groups

In a separate project on carbon monoxide migratory insertion, we have found that carbonylation of $(C_5Me_5)TaCl_3(CH_2C_6H_4\text{-}p\text{-}Me)$ does not generate the expected η^2-acyl, $(C_5Me_5)TaCl_3[C(O)CH_2C_6H_4\text{-}p\text{-}Me)$; rather, an enolate complex, $(C_5Me_5)TaCl_3(OCH{=}CHC_6H_4\text{-}p\text{-}Me)$, is obtained. The unobserved acyl complex is a likely intermediate, from which intramolecular hydrogen migration from the methylene carbon to the carbon derived from CO occurs. We are still attempting to obtain suitable crystals of the enolate complex and to study its reduction chemistry; the latter goal is to understand the electronic structure of enolate complexes as a function of metal oxidation state. Carbonylation of the analogous neopentyl complex $(C_5Me_4R)Ta(CH_2CMe_3)Cl_3$ gives the η^2-acyl complex $(C_5Me_4R)Ta[C(O)CH_2CMe_3]Cl_3$ instead of the enolate species. A low-field ^{13}C NMR resonance for the acyl carbon at δ314 is consistent with an η^2-acyl species, which are known only in bis(cyclopentadienyl) complexes. Presumably, the electronics of the phenyl group in the benzyl case is responsible for the rearrangement to the enolate complex; we are examining other alkyls in order to gauge the relative generality of acyl/enolate formation in mono(peralkylcyclopentadienyl) systems.



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SIGNIFICANCE TO FOSSIL ENERGY PROGRAM

Single and multiple transition metal-metal bonds constitute one of the most novel structural groups in contemporary inorganic chemistry, with M-M quadruple bonds having no analog in nontransition metal chemistry. Metal-metal bonds are found in a variety of dinuclear and cluster species, often with bridging ligands. The interest in the chemistry of multiply-bonded dinuclear complexes extends from the synthetic to the theoretical.

One striking feature of dinuclear, metal-metal bonded chemistry is the relative paucity of such complexes for elements of the Ti and V triads. The relative scarcity of dinuclear chemistry for the early metals, when compared to that of the Cr triad, is based on the more recent development of their inorganic and organometallic chemistry. However, the growing body of work in this area includes some remarkable firsts in organometallic conversion modelling, including the first examples of hydrogenation of a M=M, insertion of CO into a hydride ligand to yield a formyl, reductive coupling of CO to a μ-$CHCH_3$ group, and C-H bond activation by a M-M multiple bond.

Metal-metal multiple bond chemistry is notable not only for its structural novelty and reaction diversity but also for its relevance to a wide variety of technological fields. For example, organopolymetallic chemistry has applications to research in heterogeneous catalysis; the symbiotic relationship between heterogeneous catalysis research and transition metal organometallic chemistry over the past two decades has advanced both fields considerably. The postulation of the identity, structure, and reactivity of catalytic surface intermediates is usually based on models of isolable organotransition metal species, and the information from organotransition metal model studies can lead to rational catalyst design and modification. Highly loaded catalysts presumably have surface regions with strong metal-metal interactions, possibly with multiple bonds.

Metal cooperativity in the ditantalum unit has been implicated as an important factor in the activation of vinylic C-H bonds discovered in this research, which has direct implications for heterogeneous catalysis of hydrocarbon rearrangement. The new organoditantalum complexes $(C_5Me_5)_2Ta_2(\mu\text{-}X)_4$, organodivanadium analogs, and the ditantalum complex $Ta_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-}Et_2PCH_2PEt_2)_2$ oxidatively add dihydrogen to yield hydride complexes, modeling dihydrogen dissociative chemisorption on heterogeneous catalyst surfaces. The reactions of BH_4^- with

$(C_5Me_5)_2Ta_2(\mu\text{-}X)_4$ serve as a model for heterogeneous dehydrodimerization of methane to ethane, and the structure of $(C_5Me_5)_2Ta_2(\mu\text{-}X)_2(B_2H_6)$ represents a structural model for ethane coordination to a heterogeneous catalyst surface. Finally, some theories for Fischer-Tropsch syntheses invoke acyl groups as intermediates in oxygenate formation; the observation of direct enolate generation from carbonylation of metal alkyls suggests that enolates may also have to be added to the list of possible surface intermediates in FT chemistry.

The development of fundamental organovanadium chemistry is important since vanadium complexes are often radicals, and paramagnetic organometallic chemistry is underdeveloped despite its potential for new reactivity modes. In addition, vanadium chemistry is in need of further development because of the occurrence of vanadium in fossil fuels and its deleterious effects on catalysts for petrochemical fuel processing. Organovanadium chemistry is of potential relevance to petroleum processing since crude oil contains >100 ppm of organically complexed V (vanadyl porphyrins, vanadium sulfides and diamagnetic vanadium species) which build up to the point of hydrotreating catalyst deactivation. The development of organovanadium and divanadium chemistry may lead to new methods for hydrotreating catalyst reactivation and recycling, which is desirable for environmental reasons because of the scale of oil processing. This vanadium chemistry development would also offer the possibility for enhanced hydrocarbon C-H bond reactivity towards a broader range of hydrocarbons than that shown by the organoditantalum compounds.

HIGHLIGHT ACCOMPLISHMENTS

We have discovered the first example of intermolecular C-H bond activation by a metal-metal multiply-bonded complex. Reductive dimerization of the Ta(V) organometallic $(\eta\text{-}C_5Me_4R)TaX_4$ (R = Me, Et; X = Cl, Br) yields a novel class of highly-reactive dinuclear complexes, $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$, which possess quadruply bridged Ta(III)-Ta(III) double bonds of $\sigma^2\delta^2$ electronic configuration. The non-bonded ditantalum(IV) intermediate in the reduction, $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_2X_4$, has been characterized. The Ta=Ta complexes insert into the vinylic C-H bond of 1-alkenes under mild conditions to yield the ditantalum vinyl hydride $(C_5Me_4R)_2Ta_2X_4(\mu\text{-}H)(\mu,\eta^2\text{-}CHCHR')$. The Ta=Ta complex inserts into other σ-bonds, adding H_2 to yield $(C_5Me_4R)_2Ta_2(\mu\text{-}H)_2X_4$. It inserts into B-H bonds, resulting in dehydrodimerization of BH_4^- groups to $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_2(\mu\text{-}B_2H_6)$ with a μ-diborane group. These reactions with olefins and BH_4^- are unprecedented in dinuclear M-M multiple bond and early metal chemistry. We have also found an example of direct enolate generation from CO insertion into a metal alkyl, and have made a major breakthrough for developing lower-valent organovanadium and divanadium chemistry.

ARTICLES AND PRESENTATIONS

"Intermolecular Vinylic C-H Bond Activation by a Doubly-Bonded Organoditantalum Complex."
C. Ting and L. Messerle
Journal of the American Chemical Society 1987, 109, 6506.

"A Convenient Approach to Small-Scale, High-Speed Mixing under an Inert Atmosphere."
L. Messerle
Journal of Chemical Education 1988, 65, 547.

"A New Class of Reactive, Transition Metal-Metal Doubly-Bonded Organodimetallic Complexes: Synthesis, Structure, and Reactivity of $(h\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$ (Ta=Ta; X = Cl, Br)."
C. Ting, N. C. Baenziger, and L. Messerle
Journal of the Chemical Society, Chemical Communications, 1988, 1133.

"An Inexpensive Sample Holder for Storage and Introduction of Air-Sensitive Organometallic Compounds into a Mass Spectrometer with Inert-Atmosphere Blanketing."
L. Messerle, L. M. Mallis, and P. Hatch
Journal of Chemical Education 1988, 64, in press.

"Preparation, Structure, and Reactivity of the Non-bonded Organoditantalum(IV) Complexes $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}X)_2X_4$ (R = Me, Et; X = Cl, Br), Precursors to the Doubly-Bonded Organoditantalum(III) Complexes $(h\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$."
C. Ting and L. Messerle
Inorganic Chemistry, in press.

"Chelating versus Bridging Behavior of Methylenebis(dialkylphosphine) Ligands. Synthesis, Structures, and Reactivity of the Soluble, Doubly-Bonded Ditantalum Complexes $Ta_2X_4(\mu\text{-}X)_2(R_2PCH_2PR_2)$ (R = Et, $CH_2C_6H_4$-p-Me)."
B. Ferm, S. Francis, T. Johnson, Norman C. Baenziger, and L. Messerle
Journal of the Chemical Society, Chemical Communications, submitted.

"Borohydride B-H Activation and Dimerization by a Doubly-Bonded, Early Transition Metal Organodimetallic Complex. Ditantalladiborane Syntheses as Models for Dehydrodimerization of Methane to Ethane "
C. Ting and L. Messerle
Journal of the American Chemical Society, submitted.

"Direct Synthesis of Coordinatively Unsaturated O-Enolate Complexes via Migratory CO Insertion into Metal Alkyls. Preparation, Structure, and Reductive Dimerization of $(\eta\text{-}C_5Me_4R)Ta(OCH{=}CHR')X_3$ (R = Me, Et; X = Cl, Br; R' = C_6H_4-p-Me, Me, CMe_3)."
T. Y. Meyer and L. Messerle
In preparation for either Journal of the American Chemical Society or Organometallics

"A Convenient, High-Yield Synthesis of the Organovanadium(IV) Complexes $(\eta\text{-}C_5Me_4R)VX_3$"
M. S. Hammer and L. Messerle
Manuscript in preparation for Inorganic Chemistry

Invited Publications

"Convenient Glass Pressure Reactors for Organometallic Reactivity Studies."
L. Messerle
A chapter in the ACS Monograph "New Developments in the Synthesis, Manipulation, and Characterization of Organometallic Compounds", edited by A. Wayda and M. Darensbourg
American Chemical Society Symposium Series 1987, 357, 198.

"Metal-Metal Bonded Dinuclear and Organodimetallic Complexes of the Early Transition Metals (Groups 4 and 5): Synthesis, Structure, and Reactivity"
L. Messerle
Chemical Reviews, 1988, 88, 1229.

Recent Presentations

Invited

May 30, 1986	Southwest Organometallic Chemistry Workshop, University of Oklahoma, Norman, OK "Low-Valent Early Transition Metal Chemistry"
June 2, 1986	Los Alamos National Laboratories, Los Alamos, NM "Low-Valent Early Transition Metal Chemistry"
February 6, 1987	Department of Chemistry, The University of Iowa Departmental Colloquium "Low-Valent Early Transition Metal Chemistry"
June 9, 1987	National Science Foundation Organometallic Chemistry Workshop, Monterey, CA "Low-valent Early Transition Metal Chemistry: CH Activation"
July 22, 1987	U.S. Department of Energy Pittsburgh Energy Technology Center, Pittsburgh, PA "Models for Surface Intermediates in CO Hydrogenation"
December 3, 1987	University of Northern Iowa, Cedar Falls, IA "Low-Valent Early Transition Metal Organometallic Chemistry"
February 10, 1988	Grinnell College, Grinnell, IA "Low-Valent Early Transition Metal Organometallic Chemistry"

March 11, 1988	University of Missouri, Columbia, MO "Low-Valent Early Transition Metal Organometallic Chemistry"
May 29, 1988	J.J. Zuckerman Organometallic Chemistry Workshop, University of Oklahoma, Norman, OK "Synthesis and Reactivity of Metal-Metal Doubly-Bonded Ditantalum and Organoditantalum Complexes"

Presentations (presenter underlined)

June 9, 1988	ACS National Meeting, Toronto, Ontario, Canada Session Chair, "Controlled Oxidations in Organometallics"
	"Carbon-Hydrogen Bond Activation Studies on the Doubly-Bonded Organoditantalum Complexes, $(C_5Me_4R)_2Ta_2X_4$" C. Ting and L. Messerle
	"Migratory CO Insertion into Mono(peralkylcyclopentadienyl)hafnium and -tantalum Alkyl Complexes" T. Y. Meyer and L. Messerle
	"Reactivity of Halo, Alkoxy, and Dialkylamido Derivatives of $C_5Me_4R)_2Ta_2X_4$ (Ta=Ta)" C. Ting, E. Tjaden, L. Garner, and L. Messerle
	"Low-Valent Bis(dialkylphosphino)methane Ditantalum Complexes: Structural and Reactivity Studies" B. Ferm, T. Johnson, S. Francis, and L. Messerle
	"Low-Valent Mono(peralkylcyclopentadienyl) Vanadium and Divanadium Chemistry" M. S. Hammer and L. Messerle
June 1988	American Society of Mass Spectrometry, San Francisco, CA "Analysis of Air and Moisture Sensitive Organometallic Compounds using an Argon Streaming Introduction System" L. M. Mallis, C. Ting, M. S. Hammer, and L. Messerle
April 22, 1988	Iowa Academy of Science Annual Meeting, Ames, IA "The Reactions of Doubly-Bonded Ditantalum Complexes,$(C_5Me_4R)_2Ta_2X_4$, with Oxygen and Hydride Sources" C. Ting and L. Messerle
	"Low-Valent Mono(peralkylcyclopentadienyl) Vanadium and Divanadium Chemistry" M. S. Hammer and L. Messerle

	"Structure and Reactivity of Low-valent Bis(dialkylphosphino)methane Ditantalum Complexes" B. A. Ferm, T. Johnson, S. Francis, and L. Messerle
April 24, 1987	Iowa Academy of Science, Ninety-Ninth Annual Meeting, Grinnell, IA "Synthesis, Characterization, and Reactivity of $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}Br)_4$" C. Ting and L. Messerle
	"Group 4 and 5 Coordination Chemistry of $R_2PCH_2PR_2$" B. A. Ferm and L. Messerle
	"Carbon Monoxide Migratory Insertion Studies with Mono(peralkylcyclopentadienyl Alkyl Complexes of Zirconium and Hafnium" T. Y. Meyer and L. Messerle
April 7, 1987	ACS National Meeting, Denver, CO "Intermolecular Vinylic C-H Activation by a Organoditantalum Complex" C. Ting and L. Messerle
June 2, 1986	20th Great Lakes Regional ACS Meeting, Milwaukeee, WI "Low-Valent Tantalum Mono(peralkylcyclopentadienyl) Chemistry" C. Ting and L. Messerle
April 18, 1986	ACS National Meeting, New York, NY "Low-Valent Mono(peralkylcyclopentadienyl) Chemistry of Tantalum, Zirconium, and Hafnium" C. Ting, B. Ferm, E. Davidson, L. Messerle

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