# Facile access to mid-valent Group 5 and 6 metal synthons

| | |
|---|---|
| Journal: | *Inorganic Chemistry Frontiers* |
| Manuscript ID | QI-RES-05-2023-000910.R1 |
| Article Type: | Research Article |
| Date Submitted by the Author: | 17-Jun-2023 |
| Complete List of Authors: | Shaw, Thomas; University of Central Florida, Chemistry<br>Stern, Charlotte; Northwestern University, Chemistry<br>Sattelberger, Alfred; University of Central Florida, Chemistry; Argonne National Laboratory, Chemical Sciences & Engineering Division<br>Jurca, Titel; University of Central Florida, Chemistry |
| | |

ARTICLE

# Facile access to mid-valent Group 5 and 6 metal synthons

Thomas E. Shaw,[a] Charlotte L. Stern,[b] Alfred P. Sattelberger,[*a] and Titel Jurca [*a,c]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Group 5 and 6 metal chlorides, $MCl_x$ (M = Ta, Nb, Mo, W) are easily and controllably reduced, in a stepwise fashion, by stoichiometric $PhMe_2SiH$, yielding only $PhMe_2SiCl$, a useful reagent, and $H_2$ as the byproducts. Addition of n moles of $PhMe_2SiH$ to toluene solutions of $MCl_x$ yields stepwise uncoordinated reduction products of the form $MCl_{x-n}$ (M = Nb, Ta, Mo, W; x = 5 for Nb, Ta, Mo, x = 6 for W; n = 1 for Nb and Ta, n = 1, 2 for Mo and W). The reactions proceed cleanly furnishing quantitative, analytically pure yields of the desired mid-valent binary chlorides. The obtained products are very reactive and can be further derivatized with coordinating ethers or phosphines for the on-demand preparation of desired inorganic synthons.

## Introduction

When a specific oxidation state is targeted for the synthesis of a transition metal complex, it is typically preferred to begin with a precursor of that oxidation state and follow simple ligation or metathesis type routes to install the desired ligand framework. This necessitates either the availability of stable but reactive commercial precursors of variable oxidation states, typically halide salts, or facile routes to access them synthetically. An area of particular interest are the group 5 and 6 metals which can exist in a wide range of oxidation states, e.g., Mo displays states covering 0, +1, +2, +3, +4, +5, and +6. Therein, and germane to the content of this report, Nb, Ta, Mo, and W have drawn decades worth of interest for the synthesis of coordination compounds in service of fundamental structural chemistry,[1] catalysis,[2] and biomimetics.[3] More recently with a growing interest in vapor-phase growth processes (chemical vapor deposition and atomic layer deposition)[4] for the fabrication of metal oxides and 2-D semiconductor transition metal dichalcogenides,[5] the demand for group 5[6] and 6[7] molecular precursors with diverse oxidation states and ligand topologies has increased. The synthesis of these molecular precursors, and the aforementioned coordination compounds is reliant on the availability of their $MCl_x$ (M = Nb, Ta, Mo, W) synthons. Unfortunately, for the group 5 and 6 metals, commercial availability of mid-valent halides is comparatively sparse compared to high- and low-valent analogues. Correspondingly, those which are available are often significantly more costly, and can often be less reactive due to a combination of their polymeric nature, and/or high degree of crystallinity stemming from their preparative routes.

Over the past seven decades, a variety of routes targeting mid-valent early transition metal chlorides have been reported; encompassing both high temperature and *in-situ* reduction protocols (Scheme 1).[8] The high temperature routes allow for the straightforward preparation of the desired oxidation state. However, resultant of the high temperature process, these materials are typically highly crystalline and often display lower reactivity. Conversely, as the behaviour of high-valent transition metal chlorides is generally well-understood, *in-situ* reductions to the desired oxidation become more appealing. They can be carried out *via* both heterogeneous or homogeneous reducing agents, and in the presence of a coordinating solvent or ligand to capture the desired product as a discreet molecular complex. A perfect example of this is the diethyl ether adduct of molybdenum(IV) chloride, $MoCl_4(Et_2O)_2$. Heterogenous tin metal[8c] and homogenous allyltrimethylsilane[9] are both capable of reducing $MoCl_5$ in diethyl ether, leading to the formation of $MoCl_4(Et_2O)_2$. A downside to these *in-situ* reactions is that strict control of reaction conditions is necessary to prevent unwanted side/by-products, *e.g.*, the formation of $MoOCl_3(Et_2O)_2$.[9-10]

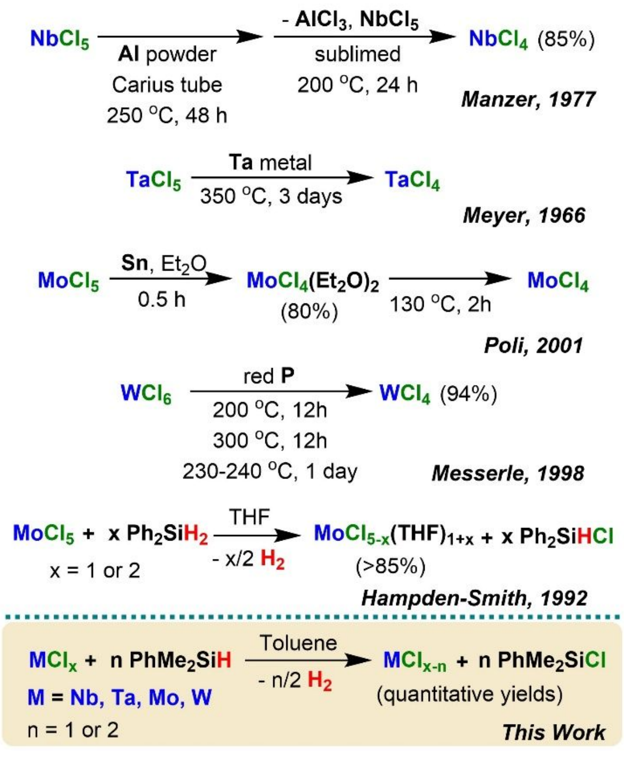
Alternatively, amorphous, uncoordinated $MCl_x$ can be prepared *via* reductions of high-valent starting materials, in non-coordinating solvents, with heterogenous reducing agents, e.g., the preparation of amorphous $WCl_4$ *via* reduction of $WCl_6$ with tin metal.[8d] Although reliable, such methods utilize tin metal as the reductant which generates chlorinated tin waste. In general, most *in-situ* reductions necessitate reagents that are either difficult to handle (pyrophoric, toxic) and/or generate unwanted by-products (metal/salt wastes). An elegant potential solution was first reported by Hampden-Smith in

[a] Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA. E-mail: al.sattelberger@knights.ucf.edu, titel.jurca@ucf.edu
[b] Department of Chemistry, Northwestern University, Evanston, IL 60208, USA
[c] Renewable Energy and Chemical Transformations (REACT) Cluster, University of Central Florida, Orlando, FL 32816, USA.

†Electronic Supplementary Information (ESI) available. CCDC 2254035-2254039. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

1992, whereby $MoCl_5$ was reacted with $Ph_2SiH_2$ under mild conditions in thf to generate $MoCl_4(thf)_2$ and $Ph_2SiHCl$.
This process utilizes a common organo-reductant that is easy to handle and yields the desired product with a readily separated chlorosilane as by-product; the latter is also synthetically useful. Unfortunately, this methodology has not been expounded on adequately in the decades since its first report. We surmise that this is likely due to the lower importance given to green chemistry at the time of publication, and looser restrictions placed on use of hazardous reagents in both industrial, academic, and national laboratory settings.

Leveraging this finding, our group recently reported the use of commercially available $PhMe_2SiH$, as a stoichiometric reducing agent for the preparation of dimeric Mo(III) synthons.[11] Herein, we report an expansion of this process as a general methodology for the reduction of high-valent Group 5 and 6 transition metal chlorides (Scheme 1). Our approach requires mild reaction conditions and generates highly reactive, uncoordinated reduced metal chlorides as a precipitate for facile separation, and only $PhMe_2SiCl$ as by-product; itself a very useful reagent for a variety of processes.[12] Critically, the degree of reduction is readily controlled by reductant stoichiometry: $1e^-$ for 1 equiv. of $PhMe_2SiH$. To the best of our knowledge there are no examples of uncoordinated transition metal halides being formed and isolated in a similar manner. Inspired by the reduction of $MoCl_4(dme)$ to '$MoCl_3(dme)$' (dme = dimethoxyethane) using $PhMe_2SiH$, we sought to explore the generality of this reduction process with other Mo, W, Nb, and Ta chlorides, and target the generation of their uncoordinated mid-valent products.




**Scheme 1.** Select examples of common group 5 and 6 $MCl_x$ reduction processes.

## Experimental

### Materials

All chemical manipulations were performed using standard glovebox and Schlenk techniques in ultra-high purity (UHP) nitrogen environments. Basic alumina (50–200 µm) was purchased from Acros Organics and activated by heating to 220 °C under vacuum ($10^{-2}$ Torr) for 12 h. Molecular sieves were purchased from Fischer Scientific and dried at 150 °C for 24 h prior to use. Diethyl ether, hexanes, and toluene were collected from an mBraun solvent purification system (SPS) and stored over basic alumina for 12 h in the glovebox prior to use. Dimethoxyethane (dme) was purchased from Sigma-Aldrich and dried over activated basic alumina for 12 h prior to use. Molybdenum pentachloride (99.6%), tungsten hexachloride (99.9%-W), niobium pentachloride (99+%-Nb), and tantalum pentachloride (99.9%-Ta) were purchased and used as received from STREM Chemicals, Inc. Dimethylphenylsilane (≥98%) was purchased from Sigma-Aldrich and stored over activated 3 Å molecular sieves for 12 h prior to use. Benzene-$d_6$ was purchased from Sigma-Aldrich and was dried over activated basic alumina for 12 h prior to use. Triethylphosphine (99%) was purchased and used as received from STREM Chemicals, Inc.

### Characterization

The purity of organic reagents was checked *via* $^1H$ NMR. Elemental analyses (C, H, Cl) were performed by Galbraith Laboratories, Inc. (Knoxville, TN). $^1H$ NMR spectra were recorded on a Bruker AvanceIII HD 600 instrument equipped with a cryoprobe and were processed using Mestrelab's MestReNova software. Spectra were referenced to residual $C_6D_5H$ ($^1H$ δ 7.16).

### General preparation of $MCl_4$

When starting from an $MCl_5$ precursor, a typical experiment proceeded as follows: Inside the glovebox, an Erlenmeyer flask was charged with 1 g of the commercial grade $MCl_5$, a stir bar, and approximately 25 ml of toluene. Whilst stirring, 1 molar equivalent of dimethylphenylsilane was introduced by syringe. The flask was then capped with a rubber septum, which was then punctured with an 18-gauge needle to function as a ventilation port for the $H_2$ gas by-product. In the case of preparing $WCl_4$ from $WCl_6$, the only experimental modification is the addition of 2 molar equivalents of dimethylphenylsilane. The reactions were then left to stir overnight. The preparation of $MoCl_4$ is an exception, where complete conversion occurs in approximately 1 h. The next day, the resulting suspensions were filtered through fine porosity sintered glass frits and washed with approximately 25 mL of fresh toluene. Then, the collected solid was washed with approximately 25 mL of hexanes and dried *in vacuo* for 0.5 hours. The resulting yields were quantitative, with slight deviations due to mechanical loss. Elemental Analyses of each $MCl_4$ product are as follows: Anal. Calcd. for $NbCl_4$: Cl, 60.42. Found: Cl, 60.38; Anal. Calcd. for $TaCl_4$: Cl, 43.94. Found: Cl, 43.48; Anal. Calcd. for $MoCl_4$: Cl, 59.64. Found: Cl, 59.69; Anal. Calcd. for $WCl_4$: Cl, 43.55. Found:

Cl, 43.45. Species-specific observations can be found in the Supplementary Information.†

**Preparation of $MoCl_3$**

Addition of two equivalents of dimethylphenylsilane to the yellow-brown suspension of $MoCl_5$ in toluene results in the immediate, visual release of $H_2$ and the precipitation of $MoCl_4$. If left to sit with no stirring, the reduction of $MoCl_4$ to $MoCl_3$ does not proceed. However, with vigorous stirring, $MoCl_4$ is fully reduced to $MoCl_3$ which is recovered as a dark, red-brown solid. This reduction is also achievable *via* the addition of one equivalent of dimethylphenylsilane to $MoCl_4$ prepared *via* the silane reduction route described above. Anal. Calcd. for $MoCl_3$: Cl, 52.57. Found: Cl, 52.66.

**Preparation of $WCl_5$**

Addition of one equivalent of dimethylphenylsilane to a stirred, royal blue suspension of $WCl_6$ in toluene results in the immediate evolution of $H_2$. This reaction is rapid, and amorphous, black $WCl_5$ settles to the bottom of the reaction vessel and a clear supernatant is observed. Anal. Calcd. for $WCl_5$: Cl, 49.09. Found: Cl, 48.73.

**Preparation of $MCl_4(PEt_3)_2$ (M = Nb, Ta)**

0.5 g of starting $MCl_4$ powder was suspended in approximately 50 mL of dry toluene inside of a Schlenk flask equipped with a stir bar. This suspension was then cycled onto the Schlenk line and kept under a UHP $N_2$ environment. While under direct nitrogen flow, 2 equivalents (0.63 mL for $NbCl_4$, 0.46 mL for $TaCl_4$) of triethylphosphine were syringed into the reaction vessel at room temperature and the reaction was allowed to stir overnight. The next day, the reaction was filtered on the Schlenk line through a freshly dried, fine porosity swivel frit to remove any insoluble materials. The obtained dark, red-yellow (Nb) and clear, yellow-green (Ta) solutions were then stripped under reduced pressure, which afforded 0.65 g of dark red $NbCl_4(PEt_3)_2$ (65%) and 0.43 g of beige $TaCl_4(PEt_3)_2$ (50%). Anal. Calcd. for $NbCl_4P_2C_{12}H_{30}$: Cl, 30.10; C, 30.60; H, 6.42. Found: Cl, 30.03; C, 30.22; H, 6.12. Anal. Calcd. for $TaCl_4P_2C_{12}H_{30}$: Cl, 25.36; C, 25.78; H, 5.41. Found: Cl, 25.64; C, 24.63; H, 4.53. C, H analyses were conducted in the presence of a combustion agent ($V_2O_5$) to obtain reliable data.

**Preparation of $MoCl_4$(dme)**

0.4 g of $MoCl_4$ powder were added to a 22 mL scintillation vial, along with a freshly dried stir bar. Then, approximately 10 mL of dry dme were added and the mixture was stirred for 1 h. At the end of the period, a homogenous solution was obtained. This solution was then treated with an equal volume of dry hexanes which resulted in the precipitation of a dull orange powder. The powder was then isolated *via* vacuum filtration and washed with fresh hexanes and dried *in vacuo*, yielding 0.52 g (95%) of $MoCl_4$(dme). Purity was assessed *via* $^1$H NMR in $d_8$-toluene: $\delta$ 16.32 (s, 6H), 1.17 (s, 4H).

**Preparation of $WCl_4$(dme)**

2 g of $WCl_4$ powder were charged to a freshly dried 125 mL Erlenmeyer flask equipped with a stir bar. Approximately 45 mL of dry dme was then added to the flask, which was then capped with a glass stopper and stirred overnight. The next day, the green reaction mixture was passed through a 30 mL fine porosity sintered glass frit charged with a quarter volume of dried Celite, *via* vacuum filtration, to remove any unreacted $WCl_4$. The Celite filter cake was then washed with 2 x 10 mL of fresh dme to recover any adduct left behind. The obtained emerald-green filtrate was then transferred to a freshly dried 100 mL Schlenk flask and cycled onto the Schlenk line. The solution is then stripped under reduced pressure with gentle heating to afford 2.17 g of a brown solid. Yield: 85%. The isolated material is then ready for employment in subsequent syntheses. Purity was assessed *via* $^1$H NMR in $d_8$-toluene: $\delta$ 9.93 (s, 6H), 0.77 (s, 4H).

**Single Crystal X-ray Diffraction**

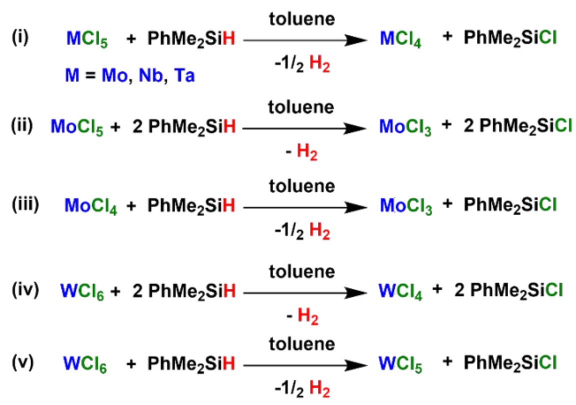
Detailed tables of crystallographic data, structural refinement information, and bond lengths and angles can be found in the Supplementary Information.† Single crystals of $NbCl_4$(dme) were obtained by creating a concentrated solution of $NbCl_4$ in dry dme and setting up a vapor diffusion crystallization with hexanes as the counter solvent. Over a period of two days, well-formed, orange needles precipitated from the solution. Single crystals of $NbCl_4(Et_2O)_2$ were obtained by saturating a solution of diethyl ether with $NbCl_4$. The resulting orange solution was then passed through a filter plug made of glass wool and Celite to remove any insoluble material. The homogenous solution was then chilled in a -35 °C freezer over a period of two days and orange, block-like crystals formed. Single crystals of $TaCl_4(Et_2O)_2$ and $Ta_2Cl_8(Et_2O)_2$ were obtained *via* the dissolution of $TaCl_4$ in minimal, dry diethyl ether. The resulting teal-green solution was then placed in the freezer and two crystalline morphologies precipitated over a period of 30 minutes. Lime green needles corresponding to $TaCl_4(Et_2O)_2$ and teal needles corresponding to $Ta_2Cl_8(Et_2O)_2$ were obtained. Single crystals of $[Ta_2Cl_6(dme)_2][TaCl_6]$ were obtained by the addition of minimal dme to amorphous $TaCl_4$. The resulting suspension was filtered through a filter plug consisting of glass wool and Celite to obtain a homogenous, dark blue solution. The solution was then placed in a -35 °C freezer and left to sit overnight, during which time yellow blocks and thin, blue plates corresponding to $[Ta_2Cl_6(dme)_2][TaCl_6]$ precipitated. X-ray diffraction studies of $NbCl_4$(dme) were conducted on a XtaLAB Synergy, single source at offset/far, HyPix diffractometer with Mo Kα (λ = 0.7103 Å) micro-focus sealed X-ray tube PhotonJet source and a mirror detector at 100(1)K. X-ray diffraction studies of $NbCl_4(Et_2O)_2$, $TaCl_4(Et_2O)_2$, $Ta_2Cl_8(Et_2O)_2$, and $[Ta_2Cl_6(dme)_2][TaCl_6]$ were conducted on a Rigaku XTA-Lab Mini II diffractometer using a Mo Kα (λ = 0.7103 Å) source and a CCD plate detector at 100(1) K. Data collection, cell parameter determinations, data reduction, and absorption corrections were performed via CrysAlis Pro.[13] Structure solution, refinement, and publication materials were generated *via* SHELXL, SHELXLT, and Olex2.[14-16]

All hydrogen atoms were attached *via* the riding model at calculated positions.

## Results and Discussion

### Synthesis

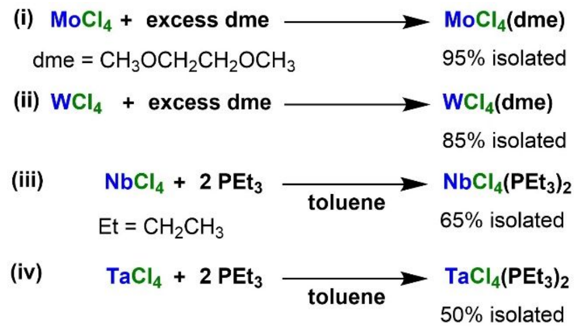
The addition of $PhMe_2SiH$ to small quantities of crystalline $MoCl_5$, partially dissolved in toluene to form a brown-yellow suspension, resulted in the vigorous evolution of gas and the precipitation of a black powder with a clear supernatant. A droplet of the supernatant was then suspended in $d_8$-toluene and analysed by $^1H$ NMR. The septet at 4.42 ppm, corresponding to the hydridosilane hydride, had disappeared and the doublet at 0.21 ppm, corresponding to the methyl groups collapsed to a singlet and shifted to 0.43 ppm, indicating the formation of the chlorinated by-product, $PhMe_2SiCl$ (Scheme 2i). The formation of the chlorinated by-product and the vigorous evolution of gas lead us to believe that this process proceeds *via* the reductive elimination of $H_2$ (*vide infra*). Elemental analysis of the isolated and dried product confirmed that we had made analytically pure $MoCl_4$. This process was then scaled to multigram quantities, with 5 grams of starting $MoCl_5$, and left to react overnight which ultimately yielded 4.14 g (95%) of $MoCl_4$. Any unreacted $MoCl_5$ can be removed by washing with anhydrous dichloromethane.



**Scheme 2.** List of demonstrated 1e⁻ and 2e⁻ $MCl_x$ (M = Mo, W, Nb, Ta) reduction processes with stoichiometric $PhMe_2SiH$**.**

Next, we sought to understand the extent of reduction, and the degree of stoichiometric control available with $PhMe_2SiH$. Reaction of $MoCl_5$ with 2 equiv. of $PhMe_2SiH$, or a suspension of isolated $MoCl_4$ (*vide supra*) with 1 equiv. of $PhMe_2SiH$ accompanied by vigorous stirring overnight yielded dark red $MoCl_3$ (Scheme 2ii, iii). Notably, the $MoCl_4 \rightarrow MoCl_3$ sequence is not accompanied by vigorous gas evolution, indicating a slower reaction process.

Both reaction sequences were conducted on the gram scale affording near quantitative yields with high purity product as confirmed by elemental analysis (see Supporting Information). The isolated $MoCl_4$ can be used to obtain solvated complexes. As an example, $MoCl_4$ was suspended in dme and stirred for one hour, furnishing $MoCl_4$(dme) in 95% yield (Scheme 3i). The silane can also be employed as a reducing agent for previously



**Scheme 3.** Derivatization reactions for amorphous $MCl_4$ (M = Nb, Ta, Mo, W) to form $MCl_4(PEt_3)_2$ (M = Nb, Ta) and $MCl_4$(dme) (M = Mo, W).

reported Mo-based systems: the syntheses of $MoCl_4(Et_2O)_2$ and $MoCl_3(thf)_3$ in lieu of $Me_3Si(C_3H_5)$ and $Ph_2SiH_2$, respectively. For $MoCl_4(Et_2O)_2$, a comparable yield of 86% is obtained in 30 min. vs. the reported 2h.[9] A 70% yield of $MoCl_3(thf)_3$ is obtained in 1 h, vs the reported 85% yield in 4 h.[8e]

Next, we targeted the synthesis of $WCl_4$. Starting with $WCl_6$ partially dissolved in toluene, stepwise reductions were performed with stoichiometric amounts of $PhMe_2SiH$ to obtain analytically pure $WCl_5$ and $WCl_4$, respectively, in essentially quantitative yields (Scheme 2iv, v). The reduction of $WCl_6$ to $WCl_5$ is complete in 2 h while $WCl_6$ to $WCl_4$ reduction was left to react overnight. We note here that $WCl_6$ is not reduced to $WCl_3$ with 3 equiv. of $PhMe_2SiH$. As with Mo, we utilized the as synthesized $WCl_4$ to obtain $WCl_4$(dme) in 86% yield (2 g scale, Scheme 3ii).

We then shifted our attention to Nb and Ta chlorides. The only commercially available chlorides are $MCl_5$ and, to the best of our knowledge, preparative routes to uncoordinated lower oxidation states are limited to high-temperature processes (Scheme 1). These are energy intensive, lengthy, and require further purification. Employing our reduction strategy, small quantities of $NbCl_5$ and $TaCl_5$ were added to toluene which resulted in dark orange-red and golden-yellow solutions, respectively. We then added excess $PhMe_2SiH$; in this instance vigorous gas evolution was not observed. We left the reactions to sit overnight and returned to brown $NbCl_4$ and olive-green $TaCl_4$, suspended in colourless supernatants, which were isolated and determined to be analytically pure. The reactions were repeated on the 5 g scale, resulting in a 96% yield of both $NbCl_4$ and $TaCl_4$. We note that our obtained olive-green $TaCl_4$ differs from the reported orange $TaCl_4$ intermediate obtained by Hayton, et al.[17] *via* the addition of triethylsilane to $TaCl_5$ but matches the reported olive-green $TaCl_4$ obtained by Manzer *via* the high-temperature reduction of $TaCl_5$ with Al powder.[8a] Efforts to reduce the Nb and Ta chlorides below the (IV) oxidation state were unsuccessful, even with mild heating or vigorous stirring.

To probe the utility of our amorphous $NbCl_4$ and $TaCl_4$ powders, we sought to form the established bis(triethyl phosphine) adducts. Both binary halides were suspended in toluene and two equivalents of triethylphosphine ($PEt_3$) were introduced at room temperature (Scheme 3iii, iv). Both *trans*-bis(triethylphosphine) complexes were formed, with 65% yield for Nb and 50% yield for Ta, comparable with reported yields of 76% and 48%, respectively.[18] Next, we examined the reactivity of amorphous $NbCl_4$ and $TaCl_4$ with ethereal solvents, with the goal of developing new synthons. While there are examples of mid-valent Nb and Ta complexes with N, S, P, and Se donor ligands, the libraries of neutral, ether-coordinated, non-oxo Nb and Ta synthons are limited.[19]

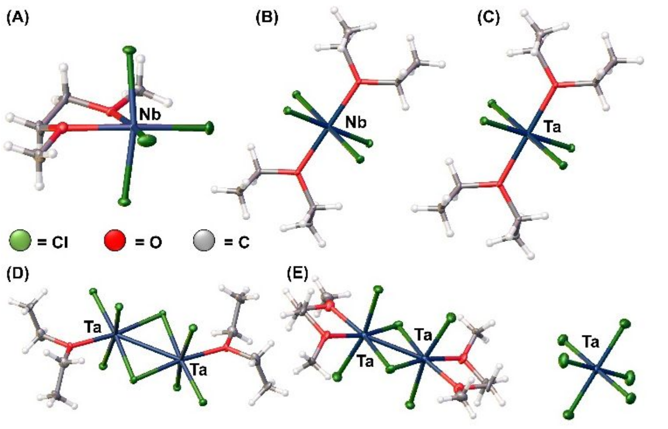



**Fig. 1.** Single crystal x-ray structures of (A) $NbCl_4$(dme), (B) $NbCl_4(Et_2O)_2$, (C) $TaCl_4(Et_2O)_2$, (D) $[TaCl_4(Et_2O)]_2$, and (E) $[TaCl_3(dme)]_2[TaCl_6]$. Thermal ellipsoids drawn at 50%; for bond lengths and angles, see Supporting Information.

The addition of $NbCl_4$ to cold (-35 °C) dme produced an orange solution, which readily precipitated bright orange $NbCl_4$(dme) in near quantitative yields upon addition of hexanes. Addition of $NbCl_4$ to thf and diethyl ether also produce the desired $NbCl_4(thf)_2$ and $NbCl_4(Et_2O)_2$ adducts, respectively. Single crystal x-ray structures were readily obtained (Figure 1A, B). These routes now provide one-step access to ethereal $NbCl_4L_2$ synthons directly from $NbCl_4$. The reaction of as prepared $TaCl_4$ with room temperature diethyl ether resulted in the immediate formation of a teal solution, from which two crystalline morphologies precipitated in ~30 min. at -35 °C. The first were lime green needles that were determined to be the monomeric *trans*-$TaCl_4(Et_2O)_2$ (Figure 1C). The second were teal needles determined to be dimeric $Ta_2Cl_8(Et_2O)_2$ (Figure 1D). The addition of $TaCl_4$ to cold dme results in the immediate formation of a blue solution. Filtration and storage of the solution at -35 °C precipitated blue crystals found to be $[Ta_2Cl_6(dme)_2][TaCl_6]$ (Figure 1E) and yellow crystals yet to be structurally characterized. The Ta-Cl distances of the $[TaCl_6]^-$ anion closely align with those of previously reported sodium hexachlorotantalate(V),[20] pointing towards the formation of a mixed valent, Ta(III)-Ta(IV) dimer stabilized by a Ta(V) counter ion. At present, we are calling this a dme-induced disproportionation; further studies will be required to fully elucidate this reaction.

The results highlighted herein provide a validation of the high reactivity of the *in-situ* reduced uncoordinated metal salts and offer a proof-of-concept for potential applicability.

## Conclusions

In summary, we have developed a benign, facile, solution-based route for the on-demand preparation of Group 5 and 6 mid-valent binary chlorides. This process employs the use of a commercially available $PhMe_2SiH$ and affords analytically pure, quantitative yields of the desired mid-valent chloride on a short time scale. The work-up procedure for each reaction is simple and requires no further separation of heterogenous by-products. These mid-valent chlorides are highly reactive and can be leveraged to reproduce classic inorganic synthons or build towards new species as exemplified by our preliminary findings on etherates. Ongoing work is focused on elucidating the latter and expanding the scope of this process beyond Groups 5 and 6.

## Author Contributions

T.E. Shaw: investigation, methodology, formal analysis, writing – original draft, writing – reviewing & editing. C. L. Stern: investigation, formal analysis. A. P. Sattelberger: supervision, methodology, conceptualization, formal analysis, project administration, funding acquisition, writing – original draft, writing – reviewing & editing. T. Jurca: supervision, methodology, conceptualization, formal analysis, project administration, funding acquisition, writing – original draft, writing – reviewing & editing.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the Department of Chemistry, College of Sciences, and the Faculty Cluster Initiative at the University of Central Florida. The use of the IMSERC Crystallography facility at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-2025633), and Northwestern University, is gratefully acknowledged. The authors acknowledge helpful conversations with Dr. Brian L. Scott at Los Alamos National Laboratory.

## References

1 D. Singh, W. R. Buratto, J. F. Torres, L. J. Murray, Activation of Dinitrogen by Polynuclear Metal Complexes, *Chem. Rev.*, 2020, **120**, 5517-5581.

2 C. Coperet, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Nunez-Zarur, P. A. Zhizhko, Surface Organometallic and Coordination Chemistry toward Single-Site Heterogeneous Catalysts: Strategies, Methods, Structures, and Activities, *Chem. Rev.*, 2016, **116**, 323-421.

3 S. Groysman, R. H. Holm, Biomimetic Chemistry of Iron, Nickel, Molybdenum, and Tungsten in Sulfur-Ligated Protein Sites, *Biochemistry*, 2009, **48**, 2310-2320.

4 a) J. Lu, J. W. Elam, P. C. Stair, Atomic layer deposition-Sequential self-limiting surface reactions for advanced catalyst “bottom-up” synthesis, *Surface Science Reports*, 2016, 410-472; b) T. J. Kunene, L. K. Tartibu, K. Ukoba, T.-C. Jen, Review of atomic layer deposition process, application and modelling tools, *Materials Today: Proceedings*, 2022, **62**, S95-S109.

5 J. Cai, X. Han, X. Wang, X. Meng, Atomic Layer Deposition of Two-Dimensional Layered Materials: Processes, Growth Mechanisms, and Characteristics, *Matter*, 2020, **2**, 587-630.

6 a) K. Khumaini, H. Roh, H. Han, H.-L. Kim, H-S. Kim, J.-H. Seok, J. W. Park, W.-J. Lee, Surface reaction mechanism of atomic layer deposition of niobium oxide: In situ characterization and first-principle study, *Applied Surface Science*, 2023, **615**, 156340; b) S. J. Song, T. Park, K. J. Yoon, J. H. Yoon, D. E. Kwon, W. Noh, C. Lansalot-Matras, S. Gatineau, H.-K. Lee, S. Gautam, D.-Y. Cho, S. W. Lee, C. S. Hwang, Comparison of the Atomic Layer Deposition of Tantalum Oxide Thin Films Using $Ta(N^tBu)(NEt_2)_3$, $Ta(N^tBu)(NEt_2)_2Cp$, and $H_2O$, *ACS Appl. Mater. Interfaces*, 2017, **9**, 537-547.

7 a) T. Jurca, M. J. Moody, A. Henning, J. D. Emery, B. Wang, J. M. Tan, T. L. Lohr, L. J. Lauhon, T. J. Marks, Low-Temperature Atomic Layer Deposition of $MoS_2$ Films, *Angew. Chem. Int. Ed.*, 2017, **56**, 4991-4995; b) M. Mattinen, J.-L. Wree, N. Stegmann, E. Ciftyurek, M. El Achhab, P. J. King, K. Mizohata, J. Raisanen, K. D. Schierbaum, A. Devi, M. Ritala, M. Leskela, Atomic Layer Deposition of Molybdenum and Tungsten Oxide Thin Films Using Heteroleptic Imido-Amidinato Precursors: Process Development, Film Characterization, and Gas Sensing Properties, *Chem. Mater.*, 2018, **30**, 8690-8701.

8 a) L. E. Manzer, Preparation of the paramagnetic alkyls bis)cyclopentadienyl)dimethylniobium and bis(methylcyclopentadienyl)dimethyltantalum and some six- and eight-coordinate phosphine derivatives of niobium(IV), *Inorg. Chem.*, 1977, **16**, 525-528; b) B. Bajan, H. -J. Meyer, Crystal structure of tantalum tetrachloride, $TaCl_4$, *Z. Kristallogr. Cryst. Mater.*, 1966, **211**, 818; c) F. Stoffelbach, D. Saurenz, R. Poli, Improved Preparations of Molybdenum Coordination Compounds from Tetrachlorobis(diethyl ether)molybdenum(IV), *Eur. J. Inorg. Chem.*, 2001, 2699-2703; d) V. Kolesnichenko, D. C. Swenson, L. Messerle, Facile Reduction of Tungsten Halides with Nonconventional, Mild Reductants. I. Tungsten Tetrachloride: Several Convenient Solid-State Syntheses, a Solution Synthesis of Highly Reactive $(WCl_4)_x$, and the Molecular Structure of Polymeric Tungsten Tetrachloride, *Inorg. Chem.*, 1998, **37**, 3257-3262; e) D. Zeng, M. J. Hampden-Smith, High yield routes to molybdenum(III) compounds by diphenylsilane and tin(II) chloride reduction of molybdenum(V) and molybdenum(IV) chlorides, *Polyhedron*, 1992, **11**, 2585-2589.

9 C. Persson, C. Andersson, Reduction of tungsten(VI) and molybdenum(V) by allyltrimethylsilane and cyclopentene. Simple high yield syntheses of $MoCl_4(OEt_2)_2$, $MoCl_4$(dme), $WCl_4(thf)_2$, $WCl_4$(dme), and $WOCl_3(thf)_2$, *Inorg. Chim. Acta.*, 1993, **203**, 235-238.

10 a) L. Castellani, M. C. Gallazzi, Facile preparation of diethyl ether complexes of molybdenum and tungsten tetrachloride, *Transition Met. Chem.*,1985, **10**, 194-195; b) T. E. Shaw, T. J. Diethrich, C. L. Stern, B. L. Scott, T. Jurca, T. M. Gilbert, A. P. Sattelberger, Synthesis, characterization, X-ray and electronic structures of diethyl ether and 1,2-dimethoxyethane adducts of molybdenum(IV) chloride and tungsten(IV) chloride, *Dalton Trans.*, 2022, **51**, 7856-7863; c) T. E. Shaw, P. LeMagueres, A. P. Sattelberger, T. Jurca, Crystal structure and Hirshfeld surface analysis of the elusive trichlorobis(diethyl ether)oxomolybdenum(V), *Acta. Cryst.*, 2020, **C76**, 947-951.

11 T. E. Shaw, T. J. Diethrich, B. L. Scott, T. M. Gilbert, A. P. Sattelberger, T. Jurca, “$MoCl_3$(dme)” Revisited: Improved Synthesis, Characterization, and X-ray and Electronic Structures, *Inorg. Chem.*, 2021, **60**, 12218-12225.

12 P. Deglmann, E. Ember, P. Hofmann, S. Pitter, O. Walter, Experimental and Theoretical Investigations on the Catalytic Hydrosilylation of Carbon Dioxide with Ruthenium Nitrile Complexes, *Chem. Eur. J.*, 2007, **13**, 2864 2879; b) K. Izod, C. Wills, W. Clegg, and R. W. Harrington, Acyclic Dialkylstannylene and -Plumbylene Compounds That Are Monomeric in the Solid State, *Organometallics*, 2009, **28**, 5661-5668; c) X. Zhang, Z. Cheng, Performance of combined use of chlorosilanes and $AlCl_3$ in the carboxylation of toluene with $CO_2$, *AIChE J.*, 2016, **63**, 185-191.

13 Rigaku Oxford Diffraction, *CrysAlis PRO.*, Rigaku Oxford Diffraction, Yarnton, Oxforshire, England. 2020.

14 *SHELXTL*, ver. 6.12; Bruker AXS, Inc.: Madison, WI, 2005.

15 Olex 2 1.2 (compiled 2014-06-27 svn.r2953 for OlexSys, GUI svn. r4855).

16 O. Dolomanov, L. Bourhis, R. Gildea, J. Howard. H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

17 P. L. Damon, C. J. Liss, R. A. Lewis, S. Morochnik, D. E. Szpunar, J. Telser, T. W. Hayton, Quantifying the Electron Donor and Acceptor Abilities of the Ketimide Ligands in $M(N{=}C^tBu_2)_4$ (M = V, Nb, Ta), *Inorg. Chem.*, 2015, **54**, 10081-10095.

18 a) F. A. Cotton, S. A. Duraj, W. J. Roth, Further studies of the phosphine complexes of niobium(IV) chloride, *Inorg Chem.*, 1984, **23**, 3592-3596; b) F. A. Cotton, S. A. Duraj, W. J. Roth, Preparation and Structural Characterization of Phosphine Adducts of Tantalum(IV) Chloride, *Inorg. Chem.*, 1984, **23**, 4046-4050.

19 a) E. J. Roskamp, S. F. Pedersen, The first practical niobium(III) reagent in organic synthesis. A convenient route to 2-amino alcohols *via* the coupling of imines with aldehydes or ketones promoted by $NbCl_3$(DME), *J. Am. Chem. Soc.*, 1987, **109**, 6551-6553; b) L. G. Hubert-Pfalzgraf, M. Tsunoda, J. G. Riess, Synthesis and characterization of niobium(III) trichloride ether and sulfide derivatives, *Inorg. Chim. Acta*, 1980, **41**, 283-286; c) G. Bresciani, S. Zacchini, F. Marchetti, G. Pampaloni, Non-precious metal carbamates as catalysts for the aziridine/$CO_2$ coupling reaction under mild conditions, *Dalton Trans.*, 2021, **50**, 5351-5359; d) R. Bini, F. Marchetti, G. Pampaloni, S. Zacchini, Further insights into the chemistry of niobium and tantalum pentahalides with 1,2-dialkoxyalkanes: Synthesis of bromo-and iodoalkoxides, spectroscopic and computational studies, *Polyhedron*, 2011, **30**, 1412-1419; e) R. Bini, C. Chiappe, F. Marchetti, G. Pampaloni, S. Zacchini, Structures and Unusual Rearrangements of Coordination Adducts of $MX_5$ (M = Nb, Ta; X = F, Cl) with Simple Diethers. A Crystallographic, Spectroscopic, and Computational Study, *Inorg. Chem.*, 2010, **49**, 339-351.

20 H. Henke, Zur kristallchemischen Einordnung von $NaSbCl_6$, $NaNbCl_6$, und $NaTaCl_6$, *Z. Kristallog.*, 1992, **198**, 1-16.