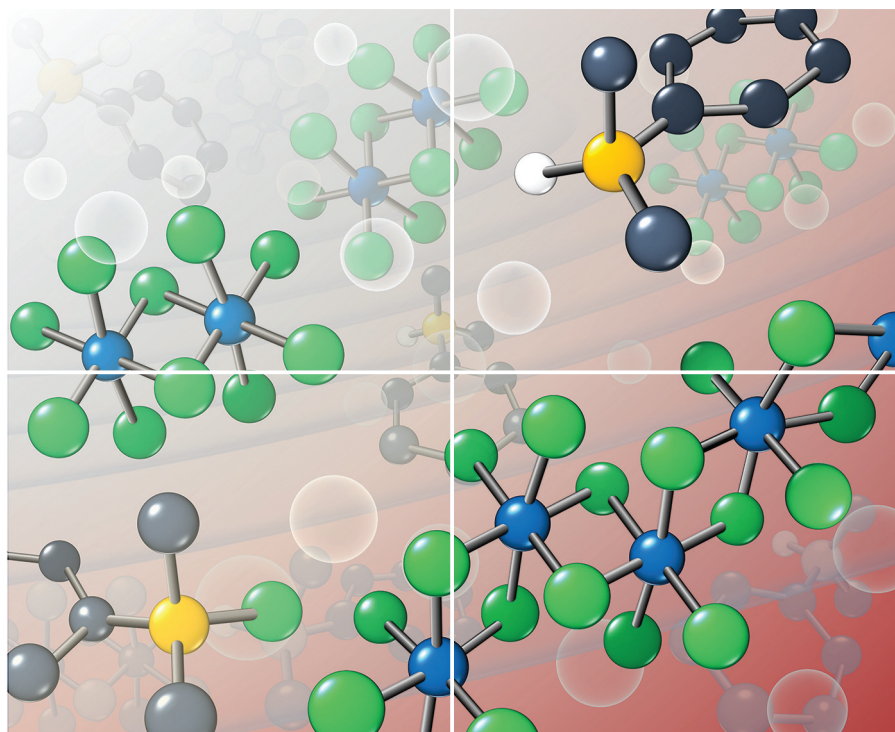


Volume 10 | Number 19 | 7 October 2023

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Cite this: *Inorg. Chem. Front.*, 2023, 10, 5584

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

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Group 5 and 6 metal chlorides, MCl_x ($M = Nb, Ta, Mo, W$) 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.

Received 17th May 2023,
Accepted 18th June 2023

DOI: 10.1039/d3qi00910f

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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 5⁶ and 6⁷ molecular precursors with diverse oxidation states and ligand topologies has increased. The synthesis of these molecular precursors, and the aforementioned coordi-

nation 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 state 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 allyltrimethylsilane⁹ 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}

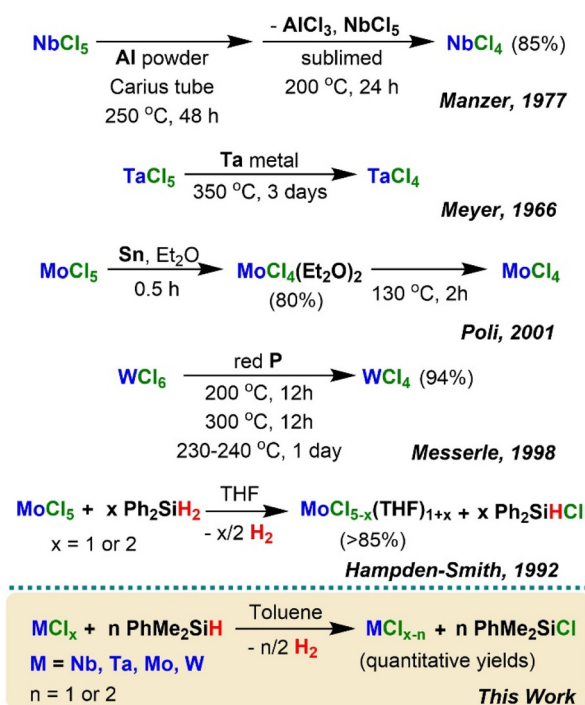
Alternatively, amorphous, uncoordinated MCl_x can be prepared *via* reductions of high-valent starting materials, in non-coordinating solvents, with heterogenous reducing agents, *e.g.*,

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† Electronic supplementary information (ESI) available. CCDC 2254035–2254039. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3qi00910f>



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

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 1992, whereby MoCl_5 was reacted with Ph_2SiH_2 under mild conditions in thf to generate $\text{MoCl}_4(\text{thf})_2$ 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 $\text{MoCl}_4(\text{dme})$ to ' $\text{MoCl}_3(\text{dme})$ ' (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.

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 $^\circ\text{C}$ under vacuum (10^{-2} Torr) for 12 h. Molecular sieves were purchased from Fisher Scientific and dried at 150 $^\circ\text{C}$ 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 ($\geq 98\%$) was purchased from Sigma-Aldrich and stored over activated 3 \AA 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 Avance III HD 600 instrument equipped with a cryoprobe and were processed using Mestrelab's MestReNova software. Spectra were referenced to residual $\text{C}_6\text{D}_5\text{H}$ (^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 ESI.†

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* 1H NMR in d_8 -toluene: δ 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 2×10 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* 1H NMR in d_8 -toluene: δ 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 ESI.† 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 $TaCl_4$. 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 $Mo K\alpha$

($\lambda = 0.7103 \text{ \AA}$) micro-focus sealed X-ray tube PhotonJet source and a mirror detector at 100(1) K. X-ray diffraction studies of $\text{NbCl}_4(\text{Et}_2\text{O})_2$, $\text{TaCl}_4(\text{Et}_2\text{O})_2$, $\text{Ta}_2\text{Cl}_8(\text{Et}_2\text{O})_2$, and $[\text{Ta}_2\text{Cl}_6(\text{dme})_2][\text{TaCl}_6]$ were conducted on a Rigaku XTA-Lab Mini II diffractometer using a Mo $K\alpha$ ($\lambda = 0.7103 \text{ \AA}$) 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, SHELXL, 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 or anhydrous toluene.

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

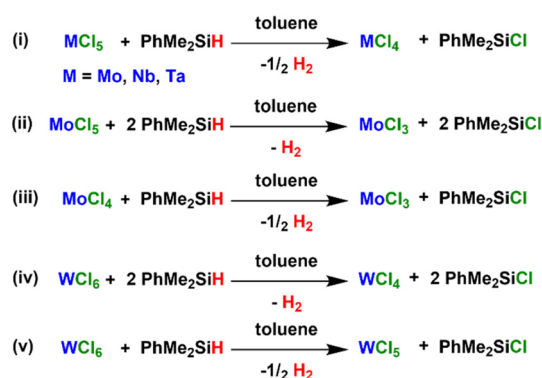
accompanied by vigorous stirring overnight yielded dark red MoCl_3 (Scheme 2ii and iii). Notably, the $\text{MoCl}_4 \rightarrow \text{MoCl}_3$ sequence is not accompanied by vigorous gas evolution, indicating a slower reaction rate.

Both reaction sequences were conducted on the gram scale affording near quantitative yields with high purity product as confirmed by elemental analysis (see Experimental section and ESI†).

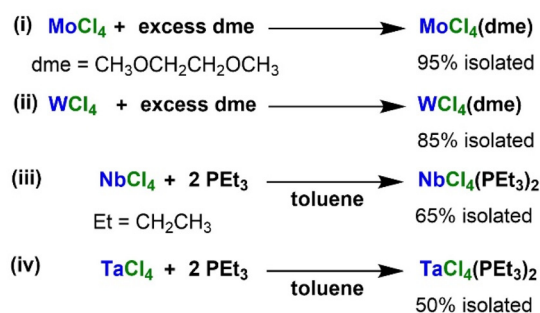
The isolated MoCl_4 can be used to obtain solvated complexes. As an example, MoCl_4 was suspended in dme and stirred for one hour, furnishing $\text{MoCl}_4(\text{dme})$ in 95% yield (Scheme 3i). The silane can also be employed as a reducing agent for previously reported Mo-based systems: the syntheses of $\text{MoCl}_4(\text{Et}_2\text{O})_2$ and $\text{MoCl}_3(\text{thf})_3$ in lieu of $\text{Me}_3\text{Si}(\text{C}_3\text{H}_5)$ and Ph_2SiH_2 , respectively. For $\text{MoCl}_4(\text{Et}_2\text{O})_2$, a comparable yield of 86% is obtained in 30 min *vs.* the reported 2 h.⁹ A 70% yield of $\text{MoCl}_3(\text{thf})_3$ 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 and 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 $\text{WCl}_4(\text{dme})$ 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



Scheme 2 List of demonstrated $1e^-$ and $2e^-$ MCl_x ($\text{M} = \text{Mo, W, Nb, Ta}$) reduction processes with stoichiometric PhMe_2SiH .



Scheme 3 Derivatization reactions for amorphous MCl_4 ($\text{M} = \text{Nb, Ta, Mo, W}$) to form $\text{MCl}_4(\text{PEt}_3)_2$ ($\text{M} = \text{Nb, Ta}$) and $\text{MCl}_4(\text{dme})$ ($\text{M} = \text{Mo, W}$).

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 and 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 our 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

The addition of NbCl_4 to cold ($-35\text{ }^\circ\text{C}$) dme produced an orange solution, which readily precipitated bright orange $\text{NbCl}_4(\text{dme})$ in near quantitative yields upon addition of hexanes. Addition of NbCl_4 to thf and diethyl ether also produce the desired $\text{NbCl}_4(\text{thf})_2$ and $\text{NbCl}_4(\text{Et}_2\text{O})_2$ adducts, respectively. Single crystal X-ray structures were readily obtained (Fig. 1A and 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 $-35\text{ }^\circ\text{C}$. The first were lime green needles that were determined to be the monomeric *trans*- $\text{TaCl}_4(\text{Et}_2\text{O})_2$ (Fig. 1C). The second were teal needles determined to be dimeric $\text{Ta}_2\text{Cl}_8(\text{Et}_2\text{O})_2$ (Fig. 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 $-35\text{ }^\circ\text{C}$ precipitated blue crystals found to be $[\text{Ta}_2\text{Cl}_6(\text{dme})_2][\text{TaCl}_6]$ (Fig. 1E) and yellow crystals yet to be structurally characterized. The Ta–Cl distances of the $[\text{TaCl}_6]^-$ 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 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 heterogeneous 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

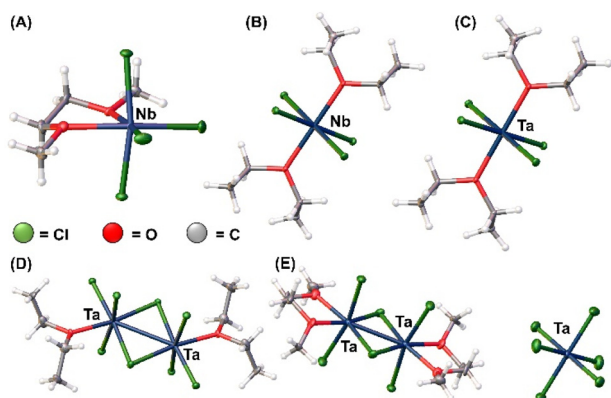


Fig. 1 Single crystal X-ray structures of (A) $\text{NbCl}_4(\text{dme})$, (B) $\text{NbCl}_4(\text{Et}_2\text{O})_2$, (C) $\text{TaCl}_4(\text{Et}_2\text{O})_2$, (D) $[\text{TaCl}_4(\text{Et}_2\text{O})_2]_2$, and (E) $[\text{TaCl}_3(\text{dme})]_2[\text{TaCl}_6]$. Thermal ellipsoids drawn at 50%; for bond lengths and angles, see ESI.†

Experimental (SHyNE) Resource (NSF ECCS-2025633), and Northwestern University, is gratefully acknowledged. The authors acknowledge insightful input from Drs. Brian L. Scott and Samuel M. Greer (Los Alamos National Lab) and Professor Thomas M. Gilbert (Northern Illinois University).

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