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PAPER

Oxygen extrusion from amidate ligands to generate terminal Ta═O units under reducing conditions. How to successfully use amidate ligands in dinitrogen coordination chemistry†

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A series of mixed Cp* amidate tantalum complexes Cp*Ta(RNC(O)R′)X_3 (where R = $Me_2C_6H_3$, ^{i}Pr, R′ = ^{t}Bu, Ph, X = Cl, Me) have been prepared *via* salt metathesis and their fundamental reactivities under reducing conditions have been explored. Reaction of the tantalum chloro precursors with potassium graphite under N_2 or Ar leads to the stereoselective formation of the terminal tantalum oxo species, Cp*Ta═O(η^2-RN═CR′)Cl. This represents the formal extrusion of oxygen from the amidate ligand to the reduced tantalum center and is accompanied by the formation of the iminoacyl fragment bound to Ta(v). Amidate dinitrogen complexes, [Cp*TaCl(RNC(O)^{t}Bu)]$_2$(μ-N_2) (where R = $Me_2C_6H_3$, ^{i}Pr) were synthesized *via* salt metathesis from the known [Cp*$TaCl_2$]$_2$(μ-N_2) precursor, establishing that amidate ligands can support dinitrogen complexes, but not the reduction process often necessary for their synthesis.

Introduction

Our interest in the preparation of dinitrogen complexes of the early metal complexes has focused mainly on reduction of high oxidation state metal complexes in the presence of N_2.[1–8] While this method is very common, it uses quite harsh reagents that can lead to side reactions such as ancillary ligand rearrangements,[9,10] metal-metal bond formation,[11] and solvent activation.[12] In order to avoid these kinds of harsh conditions, efforts have made to examine the use of dihydrogen to generate reduced hydride derivatives that can activate dinitrogen mildly and directly. However, so far this latter approach is still in its infancy and has been difficult to apply broadly to generate activated dinitrogen complexes.[13,14]

A number of recent reports[15–17] have described the isolation of a series of dinitrogen complexes with a common ligand set, that of pentamethylcyclopentadienyl (Cp*) and substituted-amidinates (amidinates = $(RN)_2CR'$, where R = ^{i}Pr, R′ = Me). Under reducing conditions, the Cp*M(amidinate) fragment has been shown to stabilize dinuclear derivatives that incorporate N_2 in both the side-on and end-on modes for M = Zr, Hf, Ta, Mo and W. Such a range of metal complexes with coordinated dinitrogen is unique and has allowed some interesting conclusions to be made about the importance of formal d-electron count on the extent of dinitrogen activation.[17]

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The amidate ligand (RNC(O)R′) is isoelectronic to the amidinate donor set and differs only by replacement of the oxygen atom of the former with a monosubstituted nitrogen donor. Given the aforementioned success of the combination of Cp* and amidinate ligands to stabilize dinitrogen complexes, we were interested in examining the effect of modifying the Cp*M(amidinate) system to the Cp*M(amidate) fragment (Chart 1). The amidate N,O chelating monoanionic ligands are easily accessible from commercially available acid chlorides and primary amines to give a wide range of white crystalline amide proligands.

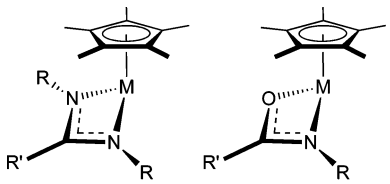


Chart 1

While amidate ligands have been successfully utilized for the synthesis of group 4[18,19] and, more recently, group 5[20] complexes for applications in catalysis, to our knowledge, early transition metal amidate derivatives have not been subjected to reducing conditions to examine their ability to support dinitrogen coordination. Herein we wish to report the reduction of amidate-containing tantalum complexes, which results in the extrusion of oxygen from the amidate moiety. While this unanticipated process did not allow the synthesis of dinitrogen complexes directly *via* reduction under N_2, we were able to prepare dinitrogen complexes of tantalum *via*

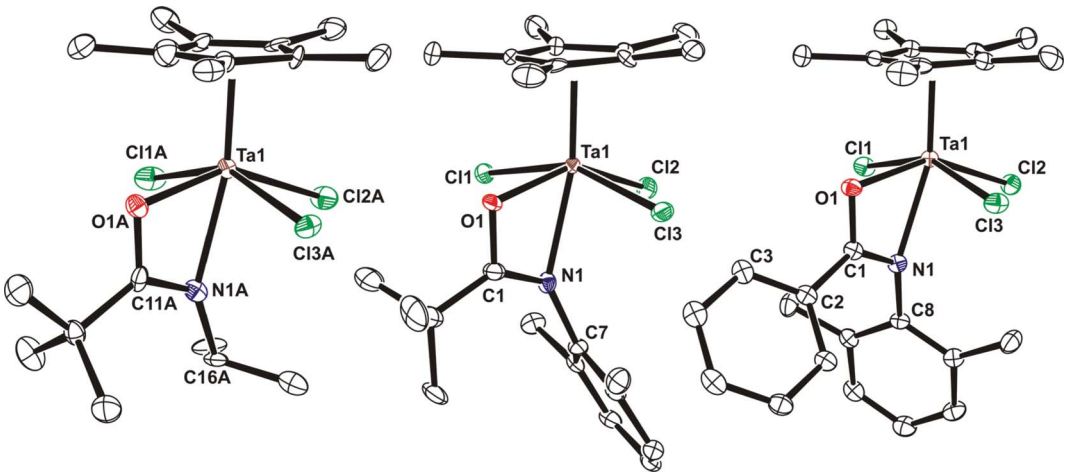


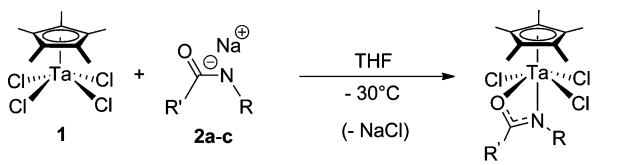
Fig. 1 ORTEP representation of the solid-state molecular structure of **3a–c** (ellipsoids at 50% probability, hydrogens omitted for clarity) with selected bond lengths (Å), and angles (°): **3a**: Ta1–Cl1A, 2.449(19); Ta1–Cl2A, 2.418(2); Ta1–Cl3A, 2.394(2); Ta1–N1A, 2.274(7); Ta1–O1A, 2.025(6); N1A–C11A, 1.296(10); O1A–C11A, 1.318(10); N1A–C16A, 1.462(9); O1A–Ta–N1A, 60.1(2); O1A–C11A–N1A, 111.7(7); **3b**: Ta1–Cl1, 2.399(2); Ta1–Cl2, 2.365(2); Ta1–Cl3, 2.445(2); Ta1–N1, 2.308(7); Ta1–O1, 2.061(6); N1–C1, 1.305(11); O1–C1, 1.320(10); N1–C7, 1.434(11); O1–Ta1–N1, 59.6(3); O1–C1–N1, 112.5(8); **3c**: Ta1–Cl1, 2.415(1); Ta1–Cl2, 2.369(1); Ta1–Cl3, 2.410(1); Ta1–N1, 2.315(3); Ta1–O1, 2.053(2); N1–C1, 1.295(5); O1–C1, 1.324(4); N1–C8, 1.444(4); O1–Ta1–N1, 59.47(10); O1–C1–N1, 112.5(3); O1–C1–C2–C3, 33.9.

an indirect method to show that amidate ligands can support N_2 coordination.

Results and discussion

Synthesis and characterization of Cp* tantalum amidate precursors

In analogy to the Cp* amidinate chemistry, we prepared Cp*Ta(amidate)Cl_3 from Cp*$TaCl_4$ *via* salt metathesis as shown in Scheme 1. Complexes **3a–c** are yellow crystalline solids that can be purified (up to 56% yield) and structurally characterized. According to ^{1}H and ^{13}C NMR spectra, the structures of **3a–c** show the NCO plane to be a symmetry plane perpendicular to the cyclopentadienyl ring, making the *N*-isopropyl methyl groups and those on the *N*-phenyl ring equivalent. Indeed, a single doublet corresponding to *N*-isopropyl methyl groups of **3a** is observed at 1.82 ppm by ^{1}H NMR spectroscopy. The ^{13}C NMR spectra display the characteristic peak near 180 ppm for k^2-amidate binding mode.[20] At room temperature, **3a–c** are stable in the solid state; however, solutions of these complexes are very moisture sensitive as evidenced by the formation of the free amide proligand and insoluble ill-defined 'Ta' species, even with attempted rigorous exclusion of water.



	R	R'
3a	^{i}Pr	^{t}Bu
3b	2,6-$Me_2C_6H_3$	^{t}Bu
3c	2,6-$Me_2C_6H_3$	Ph

Scheme 1

The solid state structures of complexes **3a–c** (Fig. 1) have been determined by single-crystal X-ray diffraction and they closely resemble the previously characterized Ta-amidinate complex Cp*Ta[MeC(N^{i}Pr)$_2$]Cl_3.[21] In all of these derivatives, the amidate NCO face lies in a molecular plane that bisects the molecule. The structures can be viewed as distorted octahedral with the N of the amidate oriented *trans* to the Cp*. The amidates are bound unsymmetrically with Ta–N distances substantially longer than Ta–O distances (av. 2.299 Å *vs.* av. 2.046 Å). The N–C distances in the amidate core are shorter than the N–R (R = alkyl, aryl) distances (av. 1.299 Å *vs.* av. 1.447 Å). The O–C distances of 1.321 Å av. in the amidate core compare favourably to literature values.[20,22] This indicates that the resulting amidate bonding motif is best described as an imine-alkoxide mode of bonding. Crystals of **3a** were obtained from saturated cyclohexane at 3 °C, while **3b** and **3c** were obtained from toluene solutions at –40 °C. Complex **3a** crystallizes in the monoclinic space group *P*21/*n* as a nonmerohedral twin (ratio of the two twin components approximately 60 : 40), while **3b** crystallizes with two independent molecules in the unit cell. Complex **3c** crystallizes in a triclinic system. The Ta–Cl bond distance *trans* to the oxygen in **3b** and **3c** is shorter than the two *cis*-Cl's (2.365(2) *vs.* av. 2.422 Å and 2.369(1) *vs.* av. 2.412 Å, respectively). Notably, changing the steric bulk and/or electronic properties of the amidate results in little or no effect on the fundamental coordination geometry of the resulting solid-state structure. However, the Ta–N bond length increases slightly as the steric bulk of the N-substituent is increased (2.274(7) in **3a** *vs*. 2.308(7) Å in **3b**).

Reduction of Cp*Ta(amidate)Cl_3

Following the procedure reported for the reduction of Cp*Ta(amidinate)Cl_3,[15–17] the amidate derivatives **3a–c** were reduced with KC_8 under 4 atm of nitrogen in tetrahydrofuran (THF) at low temperatures (Scheme 2). After filtration over Celite and crystallization in diethyl ether, white crystals were obtained that

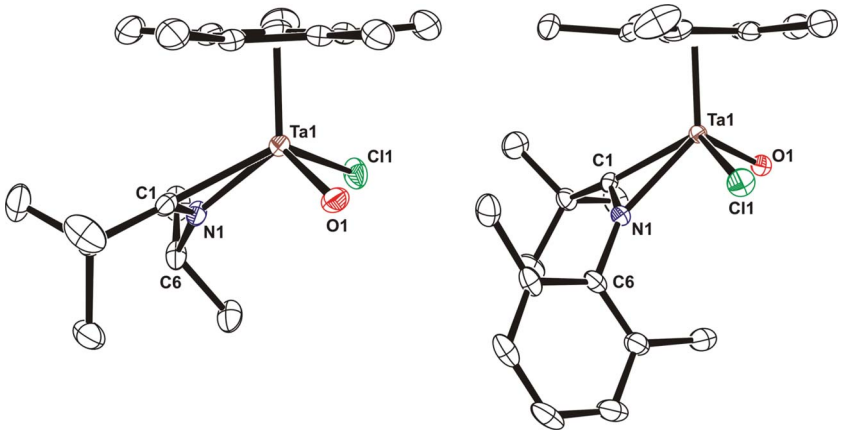
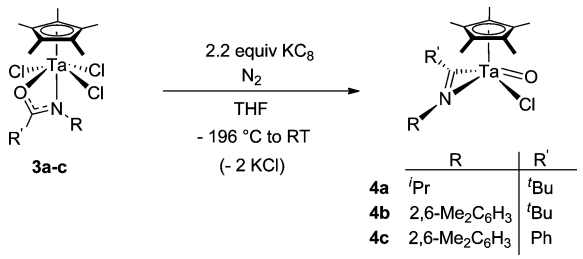


Fig. 2 ORTEP representation of the solid-state molecular structure of **4a** (left) and **4b** (right) (ellipsoids at 50% probability, hydrogen atoms omitted for clarity) with selected bond lengths (Å): **4a**: Ta1–Cl1, 2.420(1); Ta1–O1, 1.738(2); Ta1–N1, 2.113(2); C1–N1, 1.268(3); N1–C6, 1.475(3); **4b**: Ta1–Cl1, 2.406(1); Ta1–O1, 1.750(1); Ta1–N1, 2.119(2); C1–N1, 1.270(2); N1–C6, 1.435(2).

display solution NMR data consistent with reduced symmetry from that of the starting materials. For example, reduction of **3a** generates a species that shows diastereotopic Me's for the *N*-isopropyl group; reduction of **3b** and **3c** results in complexes that also display inequivalent *o*-methyl groups of the N-aryl unit at room temperature. Suitable crystals for X-ray analysis were obtained, which revealed that the amidate complexes have been transformed to iminoacyl derivatives containing a terminal tantalum oxo unit (Fig. 3). ^{13}C NMR spectroscopy revealed a diagnostic peak for the N=C resonance around 235 ppm, in good agreement with related η^2-iminoacyl complexes[23,24] (Scheme 2). The IR spectrum of **4a–c** showed strong bands at 1620 and 900 cm^{-1}, which are consistent with the N=C and the terminal Ta=O vibrations, respectively.[25] The same complexes could be obtained by the use of permethylcobaltocene, Cp_2*Co, as the reducing agent (–1.94 V *vs.* Fc/Fc$^+$ in CH_2Cl_2); interestingly, no reduction was observed with the milder reducing agent Cp_2Co (–1.33 V *vs.* Fc/Fc$^+$ in CH_2Cl_2).



Scheme 2

Crystallographic data for **4a** and **4b** show a distorted square pyramidal geometry with the Cp* ligand situated in the apical position (Fig. 2). The iminoacyl moiety is bound in the η^2-coordination mode, consistent with literature precedent for other early metal derivatives. Complex **4b** crystallized together with a molecule of amide in the unit cell. The Ta=O bond distance in **4a** and **4b** (1.738(2) and 1.750(1) Å, respectively) is in good agreement with the previously reported terminal oxo tantalum complex Cp*Ta=O(η^2-2,6-$Me_2C_6H_3$N=CMe)Cl (1.731(7) Å).[23]

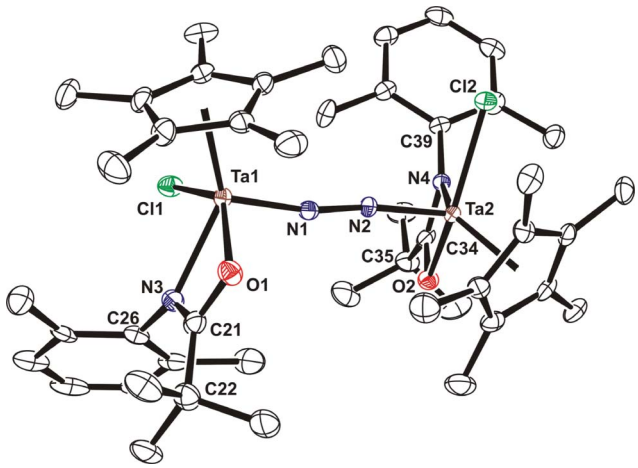


Fig. 3 ORTEP representation of the solid-state molecular structure of **7b** (ellipsoids at 50% probability, hydrogen atoms omitted for clarity) with selected bond lengths (Å), and angles (°): Ta1–N1, 1.802(3); N1–N2, 1.292(4); Ta1–Cl1, 2.421(1); Ta1–O1, 2.158(3); Ta1–N3, 2.218(3); C21–N3, 1.296(5); N3–C26, 1.431(5); O1–C21, 1.299(5); C21–C22, 1.524(6); Ta1–N1–N2, 168.5(3); O1–Ta1–N3, 58.63(11).

The formation of the oxo imino-acyl derivatives **4a–c** *via* reduction of the amidate precursors is a stereoselective process, in which only one diastereomer is observed, and the carbon and the oxygen of the amidate carbonyl are *cis* disposed in the product. We propose that reduction of the Ta(v) amidate complexes **3a–c** produces a Ta(iii) amidate, which subsequently undergoes oxygen extrusion to generate the observed Ta(v) oxo species **4a–c**. Presumably, it is the high oxophilicity of tantalum that promotes this outcome.

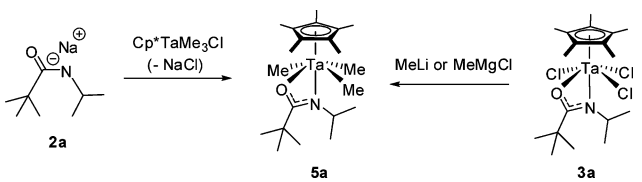
Such isolable terminal oxo species have been targeted synthetically, as group 5 species often result in the isolation of bridging oxo compounds.[23,24,26–30] While the synthesis of terminal oxo complexes is easily accomplished for bis(cyclopentadienyl) compounds of both tantalum and niobium,[31] few other examples of terminal oxo tantalum complexes supported by non-cyclopentadienyl or mono-cyclopentadienyl ligands are known.[27,28] The attempted introduction of terminal oxo ligands *via* hydrolysis reactions of monocyclopentadienyl compounds M(C_5R_5)X_4 (M = Nb, Ta) gives

polynuclear oxo-bridged complexes.[32] However, in the presence of a strong Lewis acid such as $E(C_6F_5)_3$ (E = B, Al),[33–36] molecular aggregation is suppressed *via* adduct formation and complexes of the type $Cp^*MR_2(=O^{\cdot}E(C_6F_5)_3)$ (M = Ta, Nb; R = Cl, CH_2Ph, Me; E = B, Al) can be isolated.[24,37] Furthermore, the only monocyclopentadienyl η^2-iminoacyl oxo complexes reported are formed either by insertion of isocyanides into Ta–C bonds or by reacting the tantalum imido species, Cp*Ta=NAr(Me)Cl (where Ar = 2,6-$Me_2C_6H_3$) with CO.[23,25,38,39] In both cases, the formation of chelated N,O complexes have been proposed as intermediates en route to the observed and characterized Ta oxo species. Thus, this approach starting from discrete amidate complexes, is consistent with these previous literature suggestions.[24,37]

With the observation that amidate ligands are transformed under the reducing conditions normally required for the formation of N_2 complexes, a fundamental question regarding the suitability of amidates as a supporting auxiliary ligand arises. To address this concern, other milder synthetic routes into amidate ligated N_2 complexes were pursued.

Attempts to hydrogenate Cp*Ta(amidate)Me_3 complexes

As already mentioned, a milder but not general method for the preparation of dinitrogen complexes is the reaction of N_2 with certain hydride complexes.[14] For example, hydrogenation of the tantalum(v) trimethyl complex [NPN]$TaMe_3$ (where [NPN] is $[PhP(CH_2SiMe_2NPh)_2]$) generates the dinuclear tetrahydride $([NPN]Ta)_2(\mu\text{-}H)_4$, which reacts spontaneously with N_2 to generate the side-on, end-on dinitrogen complex $([NPN]Ta)_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)(\mu\text{-}H)_2$.[40] In analogy to the formation of [NPN]$TaMe_3$, we examined the preparation of the corresponding derivative, Cp*Ta(amidate)Me_3. As one of the most common methods of introducing an amidate ligand is *via* protonolysis,[41] we first attempted the direct reaction of the amide proligand with Cp^*TaMe_4; unfortunately, only intractable mixtures resulted. We were able to prepare the desired organometallic amidate complexes *via* metathesis methods. The reaction of the known monochloro metal-alkyl complex, Cp^*TaMe_3Cl,[42] with the amidate salt **2a** yielded the desired trimethyl complex **5a** in 60% yield (Scheme 3). The ^{1}H NMR spectrum exhibits a singlet at 1.86 ppm corresponding to the Cp* ligand and two singlets at 0.30 and 0.02 ppm in a 2 : 1 ratio, respectively, attributed to the two *cis* and one *trans* Ta–Me groups. As for **3a–c**, according to ^{1}H and ^{13}C NMR spectra, the ligand coordination mode in **5a** has a NCO plane of symmetry perpendicular to the cyclopentadienyl ring, making the *N*-isopropyl methyl groups equivalent. Alternatively, complex **5a** can be obtained by the reaction of **3a** with 3 equivalents of MeLi or MeMgCl at low temperature. However, this reaction yielded a mixture of the desired **5a** and the tetramethyl Cp* derivative Cp^*TaMe_4 in a 1 : 2 ratio, indicating that the amidate ligands are labile and are prone to displacement.



Scheme 3

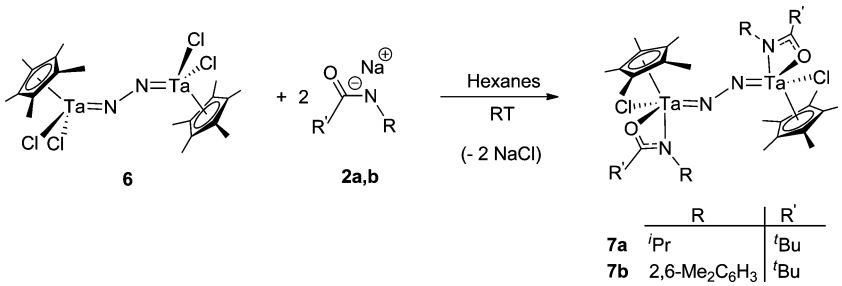
Hydrogenation at normal pressures (1–4 atm) did not result in the formation of hydride complexes; only starting materials were recovered. We did not investigate higher pressures to force the hydrogenolysis process. We also attempted the reaction of $KBEt_3H$ with the amidate trichloro complex **3a**, however, we were unable to isolate or characterize any of the species that were produced.

Amidate supported dinitrogen complexes

Given the outcome of the attempt to form amidate-stabilized dinitrogen complexes by reduction, and the inability to access azophilic hydride complexes, we revised our strategy and examined a preformed dinitrogen complex that already includes the Cp^*TaCl_2 fragment, namely the dinuclear derivative, $[Cp^*TaCl_2]_2(\mu\text{-}N_2)$ (**6**).[43] Reduction of Cp^*TaCl_4 with Na/Hg under N_2, or dehydrochlorination of the hydrazine adduct $[(C_5Me_5)TaCl_4]_2(\mu\text{-}N_2H_4)$, gives the dinuclear dinitrogen complex **6**. Due to the success of the aforementioned salt metathesis reaction (Scheme 1), two equivalents of the amidate sodium salts **2a**,**b** were reacted with **6** to yield the corresponding dinuclear dinitrogen complexes **7a**,**b** (Scheme 4); spectroscopic and analytical data of the resultant complexes are consistent with the proposed structure. For example, the mass spectrum of **7a** and **7b** both show a molecular ion peak at 1014 and 1138 (*m*/*z*), respectively, confirming the formation of dinuclear species with two amidate ligands present, along with two Cp* units and one N_2 ligand, presumably bridging. In addition, the ^{1}H NMR spectrum of **7a** shows a downfield septet corresponding to the CH of the *N*-isopropyl group at 4.48 ppm that integrates for 2H with respect to the 30H of the Cp*, thus suggesting that the complex has the required stoichiometry of Cp* : amidate being 1 : 1. A notable feature in this spectrum is the two sets of signals for the Me's of the *N*-isopropyl groups at 1.39 and 1.19 ppm, which indicates diastereotopicity in the molecule due to the chiral Ta centres. In **7b**, these are two singlets for the *o*-methyl groups of the *N*-aryl unit at 2.68 and 2.04 ppm, which can be attributed to restricted rotation of this group.

Although the high solubility of **7a** in nonpolar solvents prevented us from obtaining crystalline material suitable for solid state analysis, crystals of **7b** suitable for X-ray diffraction could be obtained from a solution of bis(trimethylsilyl)ether and a few drops of toluene at –40 °C (Fig. 3). Complex **7b** crystallizes in the triclinic space group $P\bar{1}$ with two molecules of **7b** and three molecules of toluene present in the unit cell. The N_2 ligand remains bounded in a $\mu\text{-}\eta^1{:}\eta^1$ fashion, as in the dinitrogen precursor **6**. The Ta1–N1 distance, 1.802(3) Å, is consistent with a Ta-imido-like linkage, and the N1–N2 distance, 1.292(4) A°, is similar to that observed in **6** and other reported $\mu\text{-}\eta^1{:}\eta^1\text{-}N_2$ complexes.[44–47] The Ta1–N1–N2 angle of 168.5(3)° is comparable to that of **6** (166.3(4)°). As in the Cp*Ta-amidate chloro complexes **3a–c**, the amidate ligand is bound with the nitrogen *trans* to the Cp* ligand. The Ta–O1 bond length slightly increases compared to **3b** (2.158(3) *vs.* 2.061(6) Å), while the Ta1–N3 bond length is now significantly shorter (2.218(3) *vs.* 2.308(7) Å). The particular stereoisomer in the solid state corresponds to the *meso* diastereomer.

These results illustrate that amidate ligands can indeed support isolable dinitrogen complexes, however, they are incompatible with strong reducing metals, as oxygen extrusion from the amidate moiety occurs.



Scheme 4

Conclusions

In summary, we have described the facile preparation of a new family of Ta(v) amidate complexes of the formula Cp*Ta(amidate)R_3 (R = Me, Cl) *via* salt metathesis. These complexes are structurally analogous to previously characterized Ta-amidinate complexes, although in the case of complexes **3a–c**, the unsymmetrical amidate unit coordinates with the amido nitrogen *trans* to the Cp* moiety.

Upon reduction of **3a–c** under N_2, instead of isolating dinuclear dinitrogen complexes analogous to related amidinate derivatives, we observed the stereoselective formation of a series of terminal tantalum oxo η^2-iminoacyl species **4a–c**. While imino acyl species can be accessed *via* insertion, the oxygen extrusion process described here represents a new method to generate terminal Ta=O units; however, it also reveals a limitation in using amidates as ancillary ligands as they are non-innocent under reducing conditions. This approach for the preparation of terminal tantalum oxo complexes is notable considering that such species have been previously postulated and attempts to introduce terminal oxo ligands in mono-cyclopentadienyl group 5 metal complexes of tantalum and niobium have been particularly elusive.[48–50]

Finally, we have synthesized the first amidate dinitrogen complexes **7a**,**b** by incorporating the amide ligand in the last step of the synthesis, thus avoiding ligand degradation under strong reducing conditions. The preparation of these complexes begs the question of whether amidate ligands can be used under alternative reducing conditions that avoid the use of strong reducing metals.

Experimental

General considerations

All operations were carried out with standard Schlenk and glove-box inert-gas techniques under dry nitrogen. Anhydrous diethyl ether, tetrahydrofuran, hexanes, pentanes and toluene were purchased from Aldrich, sparged with dinitrogen, and passed through columns containing activated alumina and Ridox catalyst before use. Anhydrous diethyl ether and tetrahydrofuran were stored over a sodium mirror. Nitrogen gas was dried and deoxygenated by passage through a column containing activated molecular sieves and CuO. Deuterated benzene was degassed by several freeze-pump-thaw cycles and dried with activated 4-Å molecular sieves. Isopropyl amine, 2,6-dimethylaniline, pivaloyl chloride, benzoyl chloride and pyridin-2-ol were purchased from Aldrich and used as received. $TaCl_5$ (Strem), Cp^*_2Co (Aldrich) and Cp_2Co (Aldrich) were used as received. Amides **2a–c** were prepared according to literature procedures.[51] Cp*$TaCl_4$ (**1**),[52] Cp*$TaMe_4$,[52] $TaMe_3Cl_2$,[53] Cp*$TaMe_3Cl$,[42] KC_8[54] and $[Cp^*TaCl_2]_2(\mu\text{-}N_2)$ (**6**)[43] were prepared according to literature procedures. ^1H and ^{13}C spectra were recorded with a Bruker Avance 300 or Avance 400 spectrometer. Mass spectra were recorded with a Kratos MS-50 spectrometer using an electron-impact (70 eV) source. Samples for IR spectroscopy were prepared as KBr pellets and recorded with a Nicolet 4700 FT-IR spectrophotometer in the region 4000–400 cm^{-1}. The samples for the IR measurements were prepared and handled in a N_2-filled glovebox. Elemental analyses were recorded with a Carlo Erba Elemental Analyzer EA 1108.

Cp*Ta(^{i}PrNC(O)^{t}Bu)Cl_3 (3a)

A THF (40 mL) solution of *N*-isopropyl(*tert*-butyl)amide (1.432 g, 10.00 mmol) was added dropwise to a suspension of sodium bis(trimethylsilyl)amide (1.833 g, 10.00 mmol) in THF (40 mL) at r.t.. The suspension was stirred for 1 h and the solvent, together with the bis(trimethylsilyl)amine formed, was removed *in vacuo*. The white solid was dissolved again in THF (80 mL) and was added *via* cannula to a solution of Cp*$TaCl_4$ (4.580 g, 10.00 mmol) in 80 mL of THF at −30 °C. After stirring at r.t. overnight, the THF was removed *in vacuo*, and the resulting yellow solid was extracted with cyclohexane and filtered through Celite. Concentration and cooling in the fridge yielded 2.48 g of yellow crystalline analytically pure material (44% yield). ^1H NMR (benzene-d_6): δ 4.68 (sept, 1H, NC*H*$(CH_3)_2$), 2.27 (s, 15H, $C_5(CH_3)_5$), 1.82 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NCH(CH_3)$_2$), 1.03 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 181.1 (N*C*(C(CH_3)$_3$)O), 130.6 ($C_5(CH_3)_5$), 52.1 (N*C*H(CH_3)$_2$), 39.4 (NC(*C*(CH_3)$_3$)O), 26.7 NC(C(*C*H_3)$_3$)O), 21.4 (NCH(*C*H_3)$_2$), 12.4 ($C_5(CH_3)_5$). MS(EI), m/z = 563 ([M]$^+$, 62%), 565 ([M+2]$^+$, 62%), 567 ([M+4]$^+$, 22%), 527 ([M]$^+$-Cl, 28%), 529 ([M+2]$^+$-Cl, 20%), 421 ([M]$^+$- (^{i}PrNC(O)^{t}Bu), 34%), 423 ([M+2]$^+$- (^{i}PrNC(O)^{t}Bu), 34%), 126 ([^{i}PrNC(O)^{t}Bu]$^+$-CH_3, 100%). Anal. calcd for $C_{18}H_{31}NCl_3OTa$ (564.75): C 38.28, H 5.53, N 2.48. Found: C 38.17, H 5.49, N 2.50.

Cp*Ta((2,6-$Me_2C_6H_3$)NC(O)^{t}Bu)Cl_3 (3b)

In a similar procedure as for complex **3a**, a THF (60 mL) solution of *N*-2′,6′-dimethylphenyl(*tert*-butyl)amide (2.10 g, 10.23 mmol) was added dropwise to a suspension of sodium bis(trimethylsilyl)amide (1.88 g, 10.23 mmol) in THF (40 mL) at r.t.. The suspension was stirred for 1 h and the solvent, together with the bis(trimethylsilyl)amine formed, was removed *in vacuo*. The white solid was dissolved again in THF (80 mL) and was added *via* cannula to a solution of Cp*$TaCl_4$ (4.685 g, 10.23 mmol) in

80 mL of THF at −30 °C. After stirring at r.t. overnight, the THF was removed *in vacuo*, and the resulting orange solid was extracted with toluene and filtered through Celite. The toluene was removed *in vacuo* and the yellow-orange solid washed with hot hexanes to give 3.612 g (56% yield) of a yellow-orange powder of **3b**. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated toluene solution of **3b** to −40 °C. ^{1}H NMR (benzene-d_6): δ 6.96 (m, 2H, Ar*H*), 6.84 (m, 1H, Ar*H*), 2.80 (s, 6H, Ar(CH_3)), 2.25 (s, 15H, C_5(CH_3)$_5$), 0.96 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 184.2 (N*C*(C(CH$_3$)$_3$)O), 140.9, 134.4, 128.7, 126.0 (Ar), 130.6 (C_5(CH$_3$)$_5$), 41.7 (NC(*C*(CH$_3$)$_3$)O), 26.5 NC(C(*C*H$_3$)$_3$)O), 23.0 (Ar(*C*H$_3$)), 12.5 (C_5(*C*H$_3$)$_5$). MS(EI), *m*/*z* = 625 ([M]$^+$, 18%), 627 ([M+2]$^+$, 18%), 421 ([M]$^+$-((2,6-Me$_2$C$_6$H$_3$)NC(O)^{t}Bu), 94%), 423 ([M+2]$^+$-((2,6-Me$_2$C$_6$H$_3$)NC(O)^{t}Bu), 90%). Anal. calcd for $C_{23}H_{33}NCl_3OTa$ (626.82): C 44.07, H 5.31, N 2.23. Found: C 44.10, H 5.36, N 2.30.

Cp*Ta((2,6-Me$_2$C$_6$H$_3$)NC(O)Ph)Cl$_3$ (3c)

In a similar procedure as for complex **3a**, a THF (40 mL) solution of *N*-2′,6′-dimethylphenyl(phenyl)amide (660 mg, 2.93 mmol) was added dropwise to a suspension of sodium bis(trimethylsilyl)amide (537 mg, 2.93 mmol) in THF (40 mL) at r.t.. The suspension was stirred for 1 h and the solvent, together with the bis(trimethylsilyl)amine formed, was removed *in vacuo*. The white solid was dissolved again in THF (40 mL) and was added *via* cannula to a solution of Cp*TaCl$_4$ (1.342 g, 2.93 mmol) in 60 mL of THF at r.t.. After stirring at r.t. overnight, the THF was removed *in vacuo*, and the resulting yellow-orange solid was extracted with diethyl ether and filtered through Celite. The diethyl ether was removed *in vacuo* and the yellow powder washed with hexanes to give 860 mg (45% yield) of **3c**. Single crystals suitable for X-ray diffraction were obtained by cooling a saturated toluene solution of **3c** to −40 °C. ^{1}H NMR (benzene-d_6): δ 7.52 (m, 2H, Ar*H*), 6.97 (m, 2H, Ar*H*), 6.87 (m, 2H, Ar*H*), 6.77 (m, 2H, Ar*H*), 2.75 (s, 6H, Ar(CH_3)), 2.33 (s, 15H, C_5(CH_3)$_5$). ^{13}C NMR (benzene-d_6): δ 174.3 (N*C*(C(CH$_3$)$_3$)O), 141.4, 134.6, 133.0, 132.4 (Ar), 131.0 (C_5(CH$_3$)$_5$), 129.6, 128.58, 128.56, 127.6, 126.5 (Ar), 22.6 (Ar(*C*H$_3$)), 12.6 (C_5(*C*H$_3$)$_5$). MS(EI), *m*/*z* = 645 ([M]$^+$, 24%), 647 ([M+2]$^+$, 24%), 421 ([M]$^+$-((2,6-Me$_2$C$_6$H$_3$)NC(O)Ph), 100%), 423 ([M+2]$^+$-((2,6-Me$_2$C$_6$H$_3$)NC(O)Ph), 94%), 208 ([(2,6-Me$_2$C$_6$H$_3$)NC(O)Ph]$^+$-CH$_3$, 100%). Anal. calcd for $C_{25}H_{29}NCl_3OTa$ (646.81): C 46.42, H 4.52, N 2.17. Found: C 46.48, H 5.59, N 2.56.

Cp*Ta═O(^{i}PrN═C^{t}Bu)Cl (4a)

Complex **3a** (595 mg, 1.00 mmol) and freshly prepared KC_8 (338 mg, 2.5 mmol) were placed in a glass tube with a teflon valve and then THF (~ 20 mL) was added *via* vacuum transfer at −196 °C. Dinitrogen (1 atm) was added at this temperature and then the glass tube was sealed and warmed to −78 °C. After stirring for 5 h, the reaction mixture was allowed to warm to r.t. and stirred overnight. The black suspension was filtered through Celite and the solvent was removed *in vacuo*. The crude deep green material was then extracted with diethyl ether *via* cannula filtration (red-orange solution). Concentration and cooling at −30 °C yielded 112 mg of white crystalline analytically pure material (23% yield). ^{1}H NMR (benzene-d_6): δ 4.39 (sept, 1H, NC*H*(CH$_3$)$_2$), 1.99 (s, 15H, C_5(CH_3)$_5$), 1.35 (d, $^3J_{HH}$ = 6.8 Hz, 3H, NCH(CH_3)), 1.14 (s, 9H, C(CH_3)$_3$) 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 3H, NCH(CH_3)). ^{13}C NMR (benzene-d_6): δ 242.24 (N*C*(C(CH$_3$)$_3$)), 117.3 (C_5(CH$_3$)$_5$, 55.4 (N*C*H(CH$_3$)$_2$), 40.22 (NC(*C*(CH$_3$)$_3$)), 28.8 (NCH(*C*H$_3$)$_2$), 22.3 NC(C(*C*H$_3$)$_3$)), 11.7 (C_5(*C*H$_3$)$_5$). MS(EI), *m*/*z* = 493 ([M]$^+$, 12%), 450 ([M]$^+$-^{i}Pr, 100%), 394 ([M]$^+$-^{i}Pr-^{t}Bu, 40%), 367 ([M]$^+$-(^{i}PrN═C^{t}Bu), 50%). Anal. calcd for $C_{18}H_{31}NClOTa$ (493.16): C 43.78, H 6.33, N 2.84. Found: C 44.34, H 6.38, N 2.94. IR (KBr, ν, cm^{-1}) = 1624 (vs) [C═N], 898 (vs) [Ta═O].[25]

Cp*Ta═O((2,6-Me$_2$C$_6$H$_3$)N═C^{t}Bu)Cl (4b)

Method **A**: Complex **3b** (626 mg, 1.00 mmol) and freshly prepared KC_8 (338 mg, 2.5 mmol) were placed in a glass tube with a teflon valve and then THF (~ 20 mL) was added *via* vacuum transfer at −196 °C. Dinitrogen (1 atm) was added at this temperature and then the glass tube was sealed and warmed to −78 °C. After stirring for 5 h, the reaction mixture was allowed to warm to r.t. and stirred overnight. The black suspension was filtered through Celite and the solvent was removed *in vacuo*. The crude deep green material was then extracted with diethyl ether *via* cannula filtration (red-orange solution). Concentration and cooling at −30 °C yielded a white crystalline material, which was used for single X-ray crystallography. Method **B**: Complex **3b** (313 mg, 0.5 mmol) and Cp$^*_2$Co (411.7 mg, 1.25 mmol) were placed in a glass tube with a teflon valve and then THF (40 mL) was added *via* cannula at −196 °C. Dinitrogen (1 atm) was added at this temperature and then the glass tube was sealed and warmed to r.t. overnight. The solvent was removed *in vacuo* and the crude brown material was extracted with pentane *via* cannula filtration. The solvent was removed under vacuo and hexane was added. Concentration and cooling at −40 °C yielded 53 mg of a white powder (19% yield). ^{1}H NMR (benzene-d_6): δ 6.83 (m, 3H, Ar*H*), 2.30 (s, 3H, Ar(CH_3)), 2.06 (s, 15H, C_5(CH_3)$_5$), 1.65 (s, 3H, Ar(CH_3)), 1.06 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 243.0 (N*C*(C(CH$_3$)$_3$)), 142.8, 131.1, 128.9, 127.4, 126.5 (Ar), 117.6 (C_5(CH$_3$)$_5$, 42.3 (NC(*C*(CH$_3$)$_3$)), 27.5 NC(C(*C*H$_3$)$_3$)), 19.0, 18.8 (Ar(*C*H$_3$)) 11.8 (C_5(*C*H$_3$)$_5$). MS(EI), *m*/*z* = 557 ([M+2]$^+$, 14%), 555 ([M]$^+$, 34%), 500 ([(M+2)-^{t}Bu]$^+$, 34%), 498 ([M-^{t}Bu]$^+$, 100%), 367 ([M-((2,6-Me$_2$C$_6$H$_3$)N═C^{t}Bu)]$^+$, 14%). Anal. calcd for $C_{23}H_{33}NClOTa$ (555.92): C, 49.69, H 5.98, N 2.52. Found: C 49.48, H 6.07, N 2.55. IR (KBr, ν, cm^{-1}) = 1622 (vs) [C═N], 908 (vs) [Ta═O].[25]

Cp*Ta═O((2,6-Me$_2$C$_6$H$_3$)N═CPh)Cl (4c)

Complex **3c** (515 mg, 0.8 mmol) and freshly prepared KC_8 (270 mg, 2.0 mmol) were placed in a glass tube with a teflon valve and then THF (40 mL) was added *via* cannula at −196 °C. Dinitrogen (1 atm) was added at this temperature and then the glass tube was sealed and warmed to r.t. overnight. The solvent was removed *in vacuo* and the crude material was extracted with diethyl ether *via* cannula filtration. Concentration and cooling at −30 °C yielded 119 mg of a white powder (26% yield). ^{1}H NMR (benzene-d_6): δ 7.38 (m, 2H, Ar*H*), 6.92 (m, 4H, Ar*H*), 6.86 (m, 1H, Ar*H*), 6.66 (m, 1H, Ar*H*), 2.04 (s, 15H, C_5(CH_3)$_5$), 2.02 (s, 3H, Ar(CH_3)), 1.75 (s, 3H, Ar(CH_3)). ^{13}C NMR (benzene-d_6): δ 233.3 (N*C*Ph), 141.9, 133.6, 132.5, 130.4, 129.8, 129.7, 129.3, 129.1, 126.9 (Ar) 117.4 (C_5(CH$_3$)$_5$, 18.7, 18.2 (Ar(*C*H$_3$)),

11.40 ($C_5(CH_3)_5$). MS(EI), m/z = 575 ([M]$^+$, 56%), 470 ([M-2,6-$Me_2C_6H_3$]$^+$, 10%), 208 ([(2,6-$Me_2C_6H_3$)N=CPh]$^+$, 100%). Anal. calcd for $C_{25}H_{29}NClOTa$ (575.90): C 52.14, H 5.08, N 2.43. Found: C 52.72, H 5.13, N 2.41. IR (KBr, ν, cm^{-1}) = 1621 (s) [C=N], 902 (vs) [Ta=O].[25]

Cp*Ta(^{i}PrNC(O)^{t}Bu)Me$_3$ (5a)

A THF (40 mL) solution of the sodium salt of *N*-isopropyl(*tert*-butyl)amide (0.196 g, 1.18 mmol) was added *via* cannula to a solution of Cp*TaMe$_3$Cl (0.470 g, 1.18 mmol) in 40 mL of THF at −30 °C. The reaction mixture was allowed to slowly warm to r.t. and stirred overnight. The THF was removed *in vacuo*, and the resulting yellow solid was extracted in toluene. After removal of the toluene, 0.360 g (60% yield) of a yellow powder was obtained. ^{1}H NMR (benzene-d_6): δ 4.68 (sept, 1H, NCH(CH$_3$)$_2$), 1.86 (s, 15H, C$_5$(CH_3)$_5$), 1.71 (d, $^3J_{HH}$ = 6.4 Hz, 6H, NCH(CH_3)$_2$), 1.08 (s, 9H, C(CH_3)$_3$), 0.29 (s, 6H, Ta-CH_3), 0.02 (s, 3H, Ta-CH_3). ^{13}C NMR (benzene-d_6): δ 176.6 (NC(C(CH$_3$)$_3$)O), 120.4 (C_5(CH$_3$)$_5$), 51.0 (Ta-CH$_3$), 50.6 (Ta-CH$_3$), 45.2 (NCH(CH$_3$)$_2$), 39.5 (NC(C(CH$_3$)$_3$)O), 27.6 NC(C(CH$_3$)$_3$)O), 23.3 (NCH(CH$_3$)$_2$), 11.1 (C_5(CH$_3$)$_5$).

[Cp*TaCl$_2$]$_2$(μ-N$_2$) (6)

^{1}H NMR (toluene-d_8): δ 1.97 (s, 30H, C$_5$(CH_3)$_5$). ^{13}C NMR (toluene-d_8): δ 121.5 (C_5(CH$_3$)$_5$, 11.0 (C$_5$(CH$_3$)$_5$). MS(EI), m/z = 802 ([M]$^+$, 46%), 385 ([Cp*TaCl$_2$]$^+$, 100%).[43]

[Cp*TaCl(^{i}PrNC(O)^{t}Bu)]$_2$(μ-N$_2$) (7a)

In a glove box, a small vial was charged with **7** (40.1 mg, 0.05 mmol), **2a** (16.5 mg, 0.1 mmol) and hexanes (4 mL). After stirring overnight at room temperature, the reaction mixture was filtered through Celite and the filtrate was evaporated to dryness. The brown-red powder was dissolved in the minimum amount of toluene and trimethylsilyl ether was added. After cooling to −40 °C, brown-red needles of **8a** were formed. ^{1}H NMR (benzene-d_6): δ 4.23 (sept, 2H, NCH(CH$_3$)$_2$), 2.07 (s, 30H, C$_5$(CH_3)$_5$), 1.60 (d, $^3J_{HH}$ = 6.5 Hz, 6H, NCH(CH_3)$_2$), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 6H, NCH(CH_3)$_2$), 1.10 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 184.2 (NC(C(CH$_3$)$_3$)O), 117.8 (C_5(CH$_3$)$_5$), 48.4 (NCH(CH$_3$)$_2$), 39.6 (NC(C(CH$_3$)$_3$)O), 27.7 NC(C(CH$_3$)$_3$)O), 23.5 (NCH(CH$_3$)$_2$), 23.3 (NCH(CH$_3$)$_2$), 11.0 (C$_5$(CH$_3$)$_5$). MS(EI), m/z = 1014 ([M]$^+$, 40%).

[Cp*TaCl((2,6-Me$_2$C$_6$H$_3$)NC(O)^{t}Bu)]$_2$(μ-N$_2$) (7b)

In a glove box, a small vial was charged with **8** (28.5 mg, 0.035 mmol), **2b** (16 mg, 0.07 mmol) and hexanes (4 mL). After stirring overnight at room temperature, the reaction mixture was filtered through Celite and the filtrate was evaporated to dryness. The red powder was dissolved in the minimum amount of toluene and trimethylsilyl ether was added. After cooling to −40 °C, red crystalline material of **8b** was obtained. ^{1}H NMR (benzene-d_6): δ 7.05 (m, 2H, ArH), 6.92 (m, 4H, ArH), 2.68 (s, 6H, Ar(CH_3)), 2.11 (s, 30H, C$_5$(CH_3)$_5$), 2.04 (s, 6H, Ar(CH_3)), 1.01 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (benzene-d_6): δ 184.5 (NC(C(CH$_3$)$_3$)O), 142.40, 134.5, 132.2, 128.3, 127.2, 125.4 (Ar), 118.2 (C_5(CH$_3$)$_5$), 41.2 (NC(C(CH$_3$)$_3$)O), 27.6 NC(C(CH$_3$)$_3$)O), 20.4 (Ar(CH$_3$)), 19.2 (Ar(CH$_3$)), 11.1 (C$_5$(CH$_3$)$_5$). MS(EI), m/z = 1138 ([M]$^+$, 32%).

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