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The reduction of pentavalent group 5 compounds with KC_8 or $LiBH_4$: a potpourri of oxidation states[†]

F Albert Cotton[1*], John H Matonic[1], Carlos A Murillo[1,2*], Xiaoping Wang[1]

[1] *Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843-3255 USA;*
[2] *Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica*

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Summary — Attempts to reduce $TaCl_5$ with KC_8 or $LiBH_4$ in the presence of lithium diphenylformamidinato (LiDPhF) or potassium pyridinethiolato (Kpyt) are described. At low temperature the reaction of $TaCl_5$, KC_8 and LiDPhF yields the mononuclear eight-coordinated compound $Ta(DPhF)_4$ **2** which was found to be isostructural with the niobium analog **1**. At room temperature and in the presence of KC_8 and Kpyt the isolated product was $[K(THF)_6][Ta(pyt)_4]$ **3**. Whenever the reactions were carried out with LiDPhF present in an excess of $LiBH_4$, breakage of a C–N bond in the ligand occurred giving imido complexes, such as the mononuclear seven-coordinated $Ta(NPh)(DPhF)_3$ **4** or the dinuclear species $Ta_2(\mu\text{-NPh})_2(\mu\text{-DPhF})_2(\eta^2\text{-DPhF})_2$ **5**. All compounds, **1**–**5**, have been characterized by X-ray crystallographic methods and the results are presented here.

tantalum / niobium / reduction / formamidinato / pyridinethiolato / imido

Résumé — Réduction de composés pentavalents du groupe 5 par KC_8 et $LiBH_4$: un pot pourri d'états d'oxydation. *Des tentatives de réduction de $TaCl_5$ par KC_8 ou $LiBH_4$ en présence du lithium diphénylformamidinato (LiDPhF) ou du potassium pyridinethiolato (Kpyt) sont décrites. A basse température, la réaction de $TaCl_5$, KC_8 et LiDPhF conduit au composé mononucléaire octa-coordiné $Ta(DPhF)_4$,* **2** *dont on observe qu'il est isostructural de l'analogue au niobium,* **1**. *À température ambiante et en présence de KC_8 et Kpyt le produit obtenu est $(K(THF)_6)$ $(Ta(pyt)_4)$,* **3**. *Lorsque ces réactions sont conduites avec LiDPhF dans $LiBH_4$ en excès, une liaison C–N du ligand se coupe pour donner des complexes imido comme le composé mononucléaire hepta-coordiné $Ta(NPh)(DPhF)_3$,* **4** *ou le composé dinucléaire $Ta_2(\mu\text{-NPh})_2(\mu\text{-DPhF})_2(\eta^2\text{-DPhF})_2$,* **5**. *Tous les composés obtenus (***1**–**5***) ont été caractérisés par les méthodes de diffraction des rayons X dont les résultats sont présentés ici.*

tantale / niobium / réduction / formamidinato / pyridinethiolato / imido

Introduction

Formamidinato ligands have been excellent starting materials in producing metal-metal bonded compounds of the type M_2(formamidinato)$_4$ with divalent middle and late transition elements. However, for the early transition elements it was not until 1992 that the first one was prepared, namely $V_2(DTolF)_4$, DTolF = di(p-tolylformamidinato) [1]. No such compound is yet known for the other group 5 elements.

In our studies of the reduction of Nb and Ta, we have found that divalent niobium compounds can be formed in good yields from the reduction of $NbCl_4(THF)_2$ by KC_8 in THF/py [2] but the analogous reactions using $TaCl_5$ yield only trivalent species [3].

We also know that the product of the reaction of $TaCl_5$ and a large excess of $LiBH_4$ with LiDTolF or LiDPhF, (DTolF = di(p-tolylformamidinato, DPhF = diphenylformamidinato) is the trivalent compound $Ta_2(\mu_2\text{-}\eta^4\text{-}B_2H_6)$(formamidinato)$_4$ [4]. In our attempts to reduce group 5 elements in the presence of formamidinato ligands we have also observed that such ligands frequently break to give imido species, if an excess of a hydride reducing agent is present. In this paper we will show some of our results in this field along with the characterization of several formamidinato and related compounds of niobium and tantalum in trivalent or higher oxidation states.

Experimental section

All operations were carried out under an argon atmosphere using standard Schlenk or drybox techniques. Solvents were

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[†] Dedicated to Prof Raymond Weiss.

[*] Correspondence and reprints

purified by conventional methods and distilled under nitrogen from Na/K. Tantalum(V) chloride (resublimed 99.99%) was obtained from Strem. Other chemicals, including HDPhF and pyridine thiol (pytH), were purchased from Aldrich and were used as received. Potassium graphite (KC_8) was prepared by heating at 180 °C a mixture of potassium metal and graphite with a potassium to carbon mole ratio of 1:8 [5]. $NbCl_4(THF)_2$ was made as reported in the literature [6].

Preparations

- *Nb(DPhF)*$_4$ **1**

To a suspension of $NbCl_4(THF)_2$ (0.25 g, 0.66 mmol) in toluene (15 mL) was added a solution of LiDPhF, freshly prepared by adding butyl lithium (1.6 M, 1.6 mL) to a cold solution (−77 °C) of HDPhF (0.514 g, 2.64 mmol). The reaction mixture was stirred for 8 h and was then filtered to remove LiCl. The solution was concentrated under vacuum to a volume of 5 mL and hexanes (20 mL) were slowly layered onto the toluene solution. After 1 week of storage at −10 °C, the crystalline product was collected by filtration and washed with hexanes (2 × 5 mL) (yield 0.375 g, 65%).

- *Ta(DPhF)*$_4$ **2**

To a slurry of $TaCl_5$ (0.54 g, 1.51 mmol) and potassium graphite (0.62 g, 4.6 mmol) in THF (20 mL) was added LiDPhF (3 mmol) in 15 mL THF at −30 °C. After stirring for 4 h, the THF was removed by syringe and the remaining solid was then dried under vacuum. A dark green solid was obtained. It was washed with ether (2 × 10 mL). The solid was extracted with 20 mL toluene. An orange solution was observed. It was filtered and layered with 15 mL of hexanes. Orange crystals of **2** were obtained on standing in the freezer for 2 weeks (yield 0.29 g, 20%).

- *[K(THF)*$_6$*][Ta(pyt)*$_4$*]* **3**

$TaCl_5$ (0.36 g, 1.0 mmol) and KC_8 (0.46 g, 3.4 mmol) were combined in 20 mL diethyl ether. The mixture was stirred at room temperature for 30 min and was then dried under vacuum. THF (20 mL) was then added and the mixture was stirred for 10 min. A brown slurry was observed. After cooling to dry ice temperature, a suspension of the potassium salt of pyridine-2-thiol (Kpyt) (2 mmol) in THF (20 mL) was transferred to the brown slurry. Sodium triethylborohydride ($NaEt_3BH$) (1 mmol, 1 mL of a 1 M THF solution) was then added. The blue suspension obtained was stirred overnight. The color changed to dark brown. After filtration, the filtrate was placed in the freezer. Dark lavender crystals of **3** were collected after 10 days (yield 0.38 g, 35%).

- *Ta(DPhF)*$_3$*(NPh)·C*$_6$*H*$_6$ **4**

$TaCl_5$ (1.46 g, 4.1 mmol) and $LiBH_4$ (0.29 g, 13.3 mmol) were mixed in 20 mL toluene and heated to 105 °C for 24 h. A dark solid formed. After distillation of most of the toluene, THF (20 mL) was added at room temperature. An exothermic reaction was observed. The brown suspension was stirred for 15 min and then cooled to −78 °C. After a solution of LiDPhF (8.2 mmol) in 15 mL THF was transferred to the cold suspension, the mixture was slowly warmed to room temperature and stirred for 4 h. The solvent was removed under vacuum and the solid was extracted with 30 mL benzene/5 mL hexanes. The extract was filtered through 3 cm Celite. The filtrate was divided into two portions. A portion of the filtrate (15 mL) was layered with hexanes (28 mL). Another portion of the filtrate was reduced to half of its original volume and then layered with 30 mL hexanes. Crystals of compound **4** were obtained from both solutions in a week (yield 0.92 g, 24%).

- *Ta*$_2$*(μ-NPh)*$_2$*(μ-DPhF)*$_2$*(η*^{2}*-DPhF)*$_2$ **5**

To $TaCl_5$ (1.46 g, 4.0 mmol) and $LiBH_4$ (0.31 g, 14.2 mmol) was added toluene (40 mL). The resulting suspension was refluxed for 2 days. After cooling to room temperature, a colorless toluene solution and a black precipitate were observed. The toluene solution was removed by syringe and the solid was dried under vacuum. Then THF (30 mL) was added to the solid which was cooled in a dry ice bath. The resulting dark brown solution was stirred for 30 min. LiDPhF (8 mmol) in THF (20 mL) was transferred to the tantalum solution. The mixture was kept stirring for 2 h at dry ice temperature then slowly warmed up to room temperature. After stirring overnight the THF was removed under vacuum. The brown solid was extracted with benzene (30 mL). After filtration, the benzene was eliminated under vacuum. The resulting brown solid was washed with diethyl ether (2 × 10 mL) and then extracted with dichloromethane (30 mL). The brown solution obtained after filtration was reduced to one-half of its original volume and hexanes (30 mL) were layered. After the diffusion of hexanes finished, it was placed in a freezer for a week, then rod-shaped dark brown crystals suitable for single X-ray analysis were obtained (yield 0.39 g, 15%).

X-ray structure determinations

Geometric and intensity data for compound **1** were collected on a Rigaku AFC5R diffractometer equipped with a rotating Cu anode. Data for **2**, **3**, and **5** were gathered at −60 °C on an Enraf-Nonius FAST area detector system, utilizing the software program MADNES [7]. Data for **4** were collected on a CAD4-S diffractometer. Detailed procedures have previously been described [8].

Unit cell refinement for **1** and **4** utilized 25 high angle reflections. For **2**, **3**, and **5** indexing was performed on 50 reflections taken from three 10° ω-rotations in the range $0 \leqslant \omega \leqslant 100°$ and unit cell refinement used 250 reflections in the range $20 \leqslant 2\theta \leqslant 32°$. In each case, the cell dimensions and Laue group was confirmed by axial images. All data were corrected for Lorentz and polarization effects. Three strong reflections measured periodically throughout the data collection for compounds **1** and **4** showed no significant decay. An empirical absorption correction based on six φ-scans was applied for **1** and **4**. For compound **5**, the program SORTAV [9] was used to correct for absorption. Data from the FAST diffractometer were processed into SHELX format using the program ABSURD [10]. Data for **1** were processed using the program TEXSAN [11].

In all structures, the positions of heavy atoms were found in direct methods E-maps using the software solution program in SHELXTL [12]. Subsequent cycles of least-squares refinement followed by difference-Fourier synthesis produced the positions of the remaining non-hydrogen atoms. For purposes of structure factor calculations, hydrogen atoms were placed in idealized positions. Compound **3** crystallized in the chiral space group Pn which was confirmed by the program XPREP of the SHELXTL [12] package. After all non-hydrogen atoms were refined by full-matrix least-squares on F^2, a disorder of the ligands in the $Ta(pyt)_4^-$ anion was observed. The absolute structure of **3** was established from the Flack [13] absolute structure parameter x (0.0624(2)). An 80.3% occupancy factor was found for the major configuration. Anisotropic least-squares refinement of the major configuration along with isotropic refinement of the minor configuration lead to convergence at $R_1 = 0.051$, $wR2 = 0.125$ for $I > 2\sigma(I)$ and $R_1 = 0.067$, $wR2 = 0.138$ for all data. Structural parameters of both configurations are essentially the same.

During the refinement of compound **5**, a phenyl group of each of the two chelating $DPhF^-$ ligands was found to be

Table I. Crystal data and data collection for the structures of Nb(DPhF)$_4$ **1**, Ta(DPhF)$_4$ **2**, [K(THF)$_6$][Ta(pyt)$_4$] **3**, Ta(NPh)(DPhF)$_3$ · C_6H_6 **4** and Ta$_2$(μ-NPh)$_2$(μ-DPhF)$_2$(η^2-DPhF)$_2$ **5**.

Formula	$C_{52}H_{44}N_8Nb$ **1**	$C_{52}H_{44}N_8Ta$ **2**	$C_{44}H_{64}N_4S_4TaKO_6$ **3**	$C_{51}H_{44}N_7Ta$ **4**	$C_{64}H_{54}N_{10}Ta_2$ **5**
M	873.86	961.87	1093.28	935.92	1325.08
Space group	$P2_1/a$	$P2_1/a$	Pn	$P\bar{1}$	$P2_1/n$
a/Å	17.124(2)	17.092(1)	12.751(2)	10.793(2)	10.3860(9)
b/Å	14.418(1)	14.381(2)	12.823(4)	15.256(3)	19.233(1)
c/Å	18.764(2)	18.678(2)	16.217(2)	15.510(2)	13.764(2)
α/°	90	90	90	109.96(2)	90
β/°	110.040(7)	110.400(8)	111.85(1)	97.25(1)	100.795(6)
γ/°	90	90	90	91.18(2)	90
U/Å^3	4352.2(8)	4303.1(8)	2461.1(9)	2375.7(7)	2700.8(5)
Z	4	4	2	2	2
Dc/g cm^{-3}	1.334	1.486	1.475	1.323	1.629
Crystal size (mm^3)	0.25 × 0.25 × 0.30	0.25 × 0.15 × 0.15	0.22 × 0.24 × 0.27	0.21 × 0.22 × 0.28	0.15 × 0.24 × 0.30
μ/cm^{-1}	26.09	26.01	25.11	23.53	41.00
Data collection instrument	Rigaku AFC5R	FAST	FAST	CAD4	FAST
Radiation	Cu $K\alpha$ (λ_α = 1.54184 Å)	Mo $K\alpha$ (λ_α = 0.71073 Å)	Mo $K\alpha$ (λ_α = 0.71073 Å)	Mo $K\alpha$ (λ_α = 0.71073 Å)	Mo $K\alpha$ (λ_α = 0.71073 Å)
Temperature (K)	293(2)	213(2)	213(2)	293(2)	213(2)
Data collection range, θ(°)	2.51–60.08	2.40–23.50	2.34–23.5	2.20–23.95	2.26–25.09
Number of unique data, total	6458	5770	6886	7453	4761
with $F_o^2 > 2\sigma(F_o^2)$	5008	4869	5522	5713	4108
Refined parameters	550	550	640	532	364
Transmission factors, min, max	0.6730, 0.9998	–	–	0.8463, 0.9994	–
R_w^a	0.037	0.040	0.051	0.054	0.032
$wR2^b$	0.088	0.094	0.126	0.152	0.074
Quality-of-fit indicator^c	1.034	1.099	1.111	1.240	1.098

[a] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (a \cdot p)^2 + b \cdot p]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.0426$ and $b = 1.7656$ for **1**; $a = 0.0349$ and $b = 23.114$ for **2**; $a = 0.0751$ and $b = 8.333$ for **3**; $a = 0.101$, $b = 4.959$ for **4** and $a = 0.033$, $b = 9.249$ for **5**.

disordered. The major part of the disordered phenyl group was then refined anisotropically with an occupancy factor of 67.6% and the remaining part was refined isotropically. Final refinement converged to agreement values of $R_1 = 0.032$, $wR2 = 0.074$ for $I > 2(I)$ and $R_1 = 0.041$, $wR2 = 0.082$ for all data.

Other details of data collection and refinement are given in table I. Positional parameters for **1** and **2**, **3**, **4**, and **5** are listed in tables II, III, IV and V, respectively. Selected bond distances and angles for **1** and **2**, **3**, **4**, and **5** are found in tables VI, VII, VIII and IX, respectively. Other crystallographic data are given as supplementary material.

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Nb(DPhF)$_4$, **1** and Ta(DPhF)$_4$, **2**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U*(eq)*
Ta	4545(1)	822(1)	2467(1)	24(1)
Nb	*4535(1)*	*818(1)*	*2462(1)*	*35(1)*
N(1)	4996(3)	2268(4)	2516(3)	32(1)
	4990(2)	*2263(2)*	*2514(2)*	*45(1)*
N(2)	4154(3)	1510(4)	3372(3)	30(1)
	4141(2)	*1520(2)*	*3365(2)*	*41(1)*
N(3)	3210(3)	1188(4)	2253(3)	29(1)
	3203(2)	*1178(2)*	*2249(2)*	*44(1)*
N(4)	4136(3)	1021(4)	1190(3)	31(1)
	4136(2)	*1017(2)*	*1195(2)*	*42(1)*
N(5)	5498(3)	80(4)	3422(3)	31(1)
	5487(2)	*80(2)*	*3415(2)*	*44(1)*
N(6)	5696(3)	1173(4)	2178(3)	29(1)
	5687(2)	*1174(2)*	*2180(2)*	*41(1)*
N(7)	4380(3)	−378(4)	1687(3)	29(1)
	4382(2)	*−380(2)*	*1686(2)*	*44(1)*
N(8)	4185(3)	−318(4)	3118(3)	29(1)
	4174(2)	*−327(2)*	*3115(2)*	*41(1)*
C(2)	3357(4)	1522(4)	2939(4)	29(2)
	3356(2)	*1518(2)*	*2938(2)*	*45(1)*
C(4)	4175(4)	125(5)	1053(4)	32(2)
	4168(2)	*125(3)*	*1067(2)*	*45(1)*
C(6)	5627(4)	2072(4)	2281(4)	31(2)
	5612(2)	*2062(2)*	*2288(2)*	*46(1)*
C(8)	4951(4)	−401(5)	3632(4)	33(2)
	4932(2)	*−404(2)*	*3600(2)*	*46(1)*
C(11)	4880(4)	3143(5)	2782(4)	34(2)
	4887(3)	*3146(2)*	*2788(2)*	*49(1)*
C(12)	4089(5)	3530(5)	2591(4)	41(2)
	4098(3)	*3535(3)*	*2593(2)*	*59(1)*
C(13)	3983(6)	4392(5)	2878(5)	51(2)
	3993(4)	*4395(3)*	*2867(3)*	*80(2)*
C(14)	4645(7)	4878(6)	3340(6)	70(3)
	4662(5)	*4872(3)*	*3340(3)*	*97(2)*
C(15)	5444(6)	4511(6)	3547(6)	60(2)
	5438(4)	*4496(4)*	*3540(3)*	*88(2)*
C(16)	5569(5)	3645(5)	3281(5)	47(2)
	5558(3)	*3630(3)*	*3273(2)*	*65(1)*
C(21)	4473(4)	1925(4)	4095(4)	33(2)
	4452(2)	*1926(2)*	*4086(2)*	*44(1)*
C(22)	5326(4)	1864(5)	4511(4)	41(2)
	5291(3)	*1874(3)*	*4489(2)*	*58(1)*
C(23)	5660(5)	2267(5)	5228(5)	48(2)
	5628(3)	*2274(3)*	*5199(2)*	*68(1)*
C(24)	5169(6)	2727(6)	5558(5)	54(2)
	5136(4)	*2733(3)*	*5516(2)*	*77(1)*
C(25)	4337(6)	2794(6)	5159(5)	60(2)
	4309(4)	*2798(4)*	*5125(3)*	*88(2)*
C(26)	3972(5)	2395(6)	4437(5)	46(2)
	3957(3)	*2389(3)*	*4415(2)*	*74(1)*
C(31)	2389(4)	971(5)	1781(4)	29(2)
	2381(2)	*969(2)*	*1786(2)*	*45(1)*
C(32)	1795(4)	662(5)	2103(4)	36(2)
	1794(2)	*671(3)*	*2100(2)*	*55(1)*
C(33)	970(4)	509(5)	1633(5)	44(2)
	981(3)	*507(3)*	*1643(2)*	*62(1)*
C(34)	729(4)	644(6)	857(5)	48(2)
	746(3)	*629(3)*	*879(3)*	*68(1)*
C(35)	1310(5)	919(6)	530(5)	47(2)
	1318(3)	*905(3)*	*559(2)*	*72(1)*
C(36)	2129(4)	1088(5)	992(5)	44(2)
	2136(3)	*1069(3)*	*1008(2)*	*59(1)*
C(41)	4105(4)	1702(4)	632(4)	30(2)
	4107(2)	*1690(2)*	*645(2)*	*42(1)*
C(42)	3751(4)	2558(5)	676(4)	34(2)
	3758(2)	*2550(3)*	*681(2)*	*52(1)*
C(43)	3695(4)	3237(5)	136(5)	44(2)
	3701(3)	*3214(3)*	*139(2)*	*61(1)*
C(44)	3988(5)	3064(6)	−455(5)	49(2)
	3994(3)	*3049(3)*	*−442(2)*	*69(1)*
C(45)	4368(5)	2231(6)	−479(5)	51(2)
	4365(3)	*2214(3)*	*−469(2)*	*75(1)*
C(46)	4435(5)	1552(6)	57(5)	43(2)
	4430(3)	*1538(3)*	*70(2)*	*60(1)*
C(51)	6362(4)	−79(5)	3776(4)	32(2)
	6347(2)	*−85(3)*	*3772(2)*	*49(1)*
C(52)	6942(4)	602(6)	3799(4)	42(2)
	6924(2)	*590(3)*	*3795(2)*	*57(1)*
C(53)	7791(4)	388(7)	4095(5)	52(2)
	7769(3)	*395(4)*	*4093(2)*	*74(1)*
C(54)	8068(5)	−456(8)	4399(5)	61(3)
	8046(3)	*−459(4)*	*4396(3)*	*86(2)*
C(55)	7504(5)	−1131(7)	4410(6)	65(3)
	7478(3)	*−1120(4)*	*4399(3)*	*92(2)*
C(56)	6653(5)	−949(6)	4088(5)	50(2)
	6638(3)	*−952(3)*	*4074(3)*	*71(1)*
C(61)	6204(4)	821(5)	1801(4)	30(2)
	6202(2)	*832(3)*	*1797(2)*	*45(1)*
C(62)	6481(4)	1380(6)	1307(4)	41(2)
	6468(2)	*1386(3)*	*1321(2)*	*58(1)*
C(63)	7000(4)	1005(6)	963(5)	46(2)
	6991(3)	*1025(4)*	*969(2)*	*69(1)*
C(64)	7245(4)	83(6)	1067(5)	51(2)
	7237(3)	*111(4)*	*1069(3)*	*74(1)*
C(65)	6968(5)	−464(6)	1529(5)	46(2)
	6961(3)	*−446(3)*	*1530(3)*	*67(1)*
C(66)	6455(4)	−111(5)	1881(5)	39(2)
	6449(2)	*−89(3)*	*1888(2)*	*55(1)*
C(71)	4304(4)	−1354(4)	1672(4)	29(2)
	4291(2)	*−1352(2)*	*1663(2)*	*43(1)*
C(72)	4878(4)	−1908(5)	2203(4)	33(2)
	4873(2)	*−1906(3)*	*2186(2)*	*51(1)*
C(73)	4776(5)	−2863(5)	2194(4)	4(2)
	4771(3)	*−2857(3)*	*2175(2)*	*63(1)*
C(74)	4090(5)	−3279(5)	1662(5)	48(2)
	4090(3)	*−3267(3)*	*1644(3)*	*74(1)*
C(75)	3504(5)	−2730(5)	1132(5)	49(2)
	3510(3)	*−2724(3)*	*1122(2)*	*69(1)*
C(76)	3608(4)	−1779(5)	1138(4)	39(2)
	3604(3)	*−1776(3)*	*1136(2)*	*55(1)*
C(81)	3484(4)	−651(4)	3289(4)	29(2)
	3484(2)	*−655(2)*	*3276(2)*	*43(1)*
C(82)	3316(4)	−343(5)	3916(4)	40(2)
	3321(2)	*−366(3)*	*3915(2)*	*56(1)*
C(83)	2617(5)	−686(6)	4057(5)	48(2)
	2628(3)	*−698(3)*	*4055(3)*	*70(1)*
C(84)	2093(5)	−1302(6)	3562(5)	52(2)
	2105(3)	*−1319(4)*	*3566(3)*	*75(1)*
C(85)	2252(5)	−1593(6)	2933(5)	51(2)
	2260(3)	*−1605(3)*	*2929(3)*	*75(1)*
C(86)	2941(4)	−1268(5)	2781(5)	43(2)
	2949(3)	*−1265(3)*	*2783(2)*	*61(1)*

Italicized numbers represent coordinates for Nb while non-italicized numbers represent coordinates for Ta.

Table III. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **3**.

	x	y	z	U*(eq)*
Ta	7456(2)	2519(1)	2208(2)	31(1)
N(1)	6448(12)	3684(11)	1215(8)	37(4)*
N(3)	8828(13)	2169(14)	1724(11)	32(4)*
N(5)	5878(16)	2403(13)	2435(12)	40(5)*
N(7)	8739(14)	1912(10)	3469(10)	40(4)*
S(2)	6219(5)	1792(5)	680(4)	49(2)*
S(4)	9038(4)	3936(3)	2436(3)	40(1)*
S(6)	7158(4)	3889(3)	3292(3)	39(1)*
S(8)	7525(5)	526(3)	2468(3)	50(1)*
C(11)	5872(16)	3105(13)	527(11)	34(4)*
C(12)	4961(20)	3519(20)	−276(14)	59(6)*
C(13)	4867(22)	4604(19)	−243(14)	75(8)*
C(14)	5540(19)	5210(19)	460(13)	59(5)*
C(15)	6297(14)	4673(13)	1163(10)	37(4)*
C(31)	9591(14)	2993(14)	2003(10)	36(4)*
C(32)	10584(19)	2929(23)	1771(15)	53(6)*
C(33)	10777(16)	2164(23)	1336(14)	46(6)*
C(34)	10025(15)	1293(15)	1082(16)	50(5)*
C(35)	9039(15)	1336(15)	1303(12)	54(5)*
C(51)	5877(13)	3235(19)	2972(13)	48(5)*
C(52)	5024(20)	3434(17)	3222(17)	60(6)*
C(53)	4040(31)	2773(40)	2936(39)	80(14)*
C(54)	4041(17)	1932(19)	2398(18)	62(7)*
C(55)	4946(14)	1781(15)	2170(13)	49(4)*
C(71)	8643(15)	857(14)	3448(12)	42(4)*
C(72)	9278(18)	280(15)	4152(15)	62(6)*
C(73)	10069(23)	700(23)	4867(13)	68(7)*
C(74)	10192(20)	1778(18)	4880(14)	60(6)*
C(75)	9559(18)	2378(14)	4179(13)	41(6)*
K	7436(13)	2501(3)	7233(10)	77(1)
O(1)	5454(16)	2628(11)	6776(15)	65(5)
O(2)	9502(16)	2384(10)	7707(15)	60(5)
O(3)	7267(11)	1398(9)	5962(8)	57(3)
O(4)	7701(12)	3612(10)	8472(8)	63(4)
O(5)	7394(9)	3978(10)	6342(8)	54(3)
O(6)	7403(11)	991(12)	8068(9)	73(4)
C(111)	4634(19)	2149(22)	5992(20)	99(8)
C(112)	3528(18)	2167(27)	6197(24)	116(10)
C(113)	3620(22)	2913(29)	6735(37)	207(26)
C(114)	4920(17)	3102(19)	7318(18)	96(7)
C(121)	10315(18)	2873(21)	8434(12)	86(7)
C(122)	11404(23)	2735(19)	8443(22)	91(8)
C(123)	11094(18)	2361(15)	7408(18)	80(6)
C(124)	10054(16)	1859(22)	7238(16)	98(7)
C(131)	7484(16)	382(16)	6044(11)	65(5)
C(132)	7056(19)	−88(16)	5093(15)	78(7)
C(133)	6537(18)	845(20)	4499(14)	95(7)
C(134)	7020(17)	1706(16)	5064(11)	71(5)
C(141)	7494(21)	4726(13)	8390(15)	82(7)
C(142)	7822(34)	5189(22)	9267(16)	141(15)
C(143)	8272(22)	4343(19)	9858(13)	99(7)
C(144)	7887(18)	3346(16)	9359(13)	79(6)
C(151)	6373(17)	4471(13)	5778(13)	74(5)
C(152)	6729(21)	5356(19)	5348(14)	89(7)
C(153)	7947(17)	5551(16)	5938(15)	83(6)
C(154)	8263(19)	4466(16)	6217(14)	87(7)
C(161)	8413(16)	495(13)	8630(13)	65(5)
C(162)	8041(23)	−438(15)	9067(15)	84(7)
C(163)	6855(18)	−619(16)	8449(15)	87(7)
C(164)	6434(16)	498(15)	8114(16)	81(6)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. * Starred atoms have an occupancy of 0.803. Full listings of the atomic coordinates of **3** are available as supplementary material.

Table IV. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **4**.

	x	y	z	U*(eq)*
Ta(1)	1676(1)	8510(1)	7175(1)	40(1)
N(1)	3543(8)	8010(6)	6840(6)	46(2)
N(2)	2031(8)	7898(7)	5700(6)	52(2)
N(3)	2642(8)	8770(6)	8602(5)	47(2)
N(4)	1042(8)	9578(6)	8400(6)	48(2)
N(5)	337(7)	9239(6)	6530(6)	43(2)
N(6)	2287(7)	9887(6)	6957(6)	43(2)
N(7)	795(8)	7471(6)	7117(6)	49(2)
C(1)	3213(10)	7731(7)	5940(7)	46(2)
C(2)	1892(10)	9407(8)	9008(8)	54(3)
C(3)	1121(10)	9933(8)	6574(7)	51(3)
C(4)	4726(10)	7866(8)	7230(7)	50(3)
C(5)	5425(11)	8592(9)	7895(7)	56(3)
C(6)	6616(11)	8465(10)	8278(9)	67(3)
C(7)	7118(12)	7612(13)	7980(10)	79(4)
C(8)	6416(15)	6892(11)	7314(10)	79(4)
C(9)	5193(11)	6995(9)	6930(8)	60(3)
C(10)	1519(10)	7747(7)	4770(7)	44(2)
C(11)	2198(11)	7872(8)	4136(7)	53(3)
C(12)	1648(13)	7749(10)	3255(9)	69(4)
C(13)	415(12)	7501(9)	3002(8)	61(3)
C(14)	−315(11)	7378(9)	3625(8)	62(3)
C(15)	253(10)	7495(8)	4518(8)	52(3)
C(16)	3466(9)	8376(8)	9122(7)	49(3)
C(17)	4160(11)	8952(10)	9957(8)	62(3)
C(18)	4951(14)	8565(12)	10465(9)	85(5)
C(19)	5127(18)	7626(15)	10131(11)	109(6)
C(20)	4468(17)	7093(11)	9328(10)	88(5)
C(21)	3630(12)	7447(9)	8802(8)	61(3)
C(22)	311(10)	10339(8)	8687(7)	48(2)
C(23)	808(13)	11202(9)	9279(9)	71(4)
C(24)	51(22)	11938(11)	9575(14)	114(7)
C(25)	−1184(19)	11825(13)	9253(13)	94(5)
C(26)	−1695(14)	11001(13)	8672(10)	80(4)
C(27)	−963(11)	10235(10)	8358(9)	64(3)
C(28)	−913(9)	9149(8)	6113(7)	44(2)
C(29)	−1418(11)	9708(9)	5655(8)	59(3)
C(30)	−2644(12)	9580(11)	5254(9)	77(4)
C(31)	−3424(10)	8851(11)	5315(9)	72(4)
C(32)	−2948(12)	8308(10)	5769(10)	72(4)
C(33)	−1702(10)	8422(9)	6174(8)	57(3)
C(34)	3193(9)	10579(8)	7068(7)	46(2)
C(35)	4374(9)	10356(8)	6878(8)	50(3)
C(36)	5281(11)	11032(10)	6959(9)	64(3)
C(37)	5000(13)	11954(11)	7208(10)	74(4)
C(38)	3853(14)	12191(9)	7438(10)	74(4)
C(39)	2930(11)	11527(8)	7368(8)	57(3)
C(40)	191(10)	6656(8)	7072(8)	54(3)
C(41)	128(13)	6460(11)	7861(10)	74(4)
C(42)	−459(17)	5628(15)	7831(16)	107(6)
C(43)	−950(17)	4980(10)	6969(17)	103(6)
C(44)	−901(16)	5192(11)	6190(13)	96(5)
C(45)	−349(14)	5995(8)	6227(10)	75(4)
C(46)	5401(33)	5770(18)	4243(22)	161(11)
C(47)	4956(24)	5651(15)	3347(25)	136(9)
C(48)	5705(35)	5352(16)	2683(17)	142(9)
C(49)	6934(32)	5233(18)	3000(24)	144(9)
C(50)	7325(28)	5368(21)	3933(29)	165(11)
C(51)	6511(36)	5621(25)	4489(27)	224(22)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table V. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **5**.

	x	y	z	U*(eq)*
Ta	407(1)	9851(1)	5952(1)	20(1)
N(1)	1953(4)	9241(2)	5477(3)	24(1)
C(1)	2044(5)	9188(3)	4532(4)	26(1)
N(2)	−1230(4)	10509(2)	6215(3)	23(1)
C(11)	2892(5)	8817(3)	6123(4)	28(1)
C(12)	2655(6)	8108(3)	6177(5)	46(2)
C(13)	3583(7)	7694(4)	6772(6)	59(2)
C(14)	4670(7)	7971(4)	7309(6)	59(2)
C(15)	4911(7)	8678(4)	7269(6)	57(2)
C(16)	4012(6)	9102(4)	6686(5)	44(2)
C(21)	−1565(5)	10625(3)	7176(4)	27(1)
C(22)	−2677(6)	10342(3)	7416(5)	41(1)
C(23)	3323(8)	12362(4)	5468(5)	57(2)
C(24)	−2139(8)	10869(4)	9023(5)	57(2)
C(25)	−1038(8)	11135(4)	8786(5)	54(2)
C(26)	−713(6)	11013(3)	7863(4)	38(1)
N(4)	201(4)	9192(2)	7256(3)	28(1)
C(2)	1083(6)	9541(3)	7875(4)	33(1)
N(3)	1662(5)	10059(2)	7461(4)	31(1)
C(31)	2628(5)	10481(3)	8034(4)	32(1)
C(32)	3339(12)	10924(6)	7509(9)	41(3)*
C(33)	4210(13)	11395(6)	8026(11)	54(4)*
C(34)	4448(11)	11444(7)	9010(12)	47(3)*
C(35)	3787(12)	10997(7)	9523(7)	51(3)*
C(36)	2811(12)	10557(6)	9033(7)	49(3)*
C(41)	−548(5)	8691(3)	7662(4)	27(1)
C(42)	−930(6)	8081(3)	7153(4)	36(1)
C(43)	−1624(7)	7584(3)	7555(5)	49(2)
C(44)	−1984(6)	7681(4)	8454(5)	50(2)
C(45)	−1624(7)	8284(4)	8955(5)	52(2)
C(46)	−942(6)	8794(3)	8561(4)	38(1)
N(5)	858(4)	10620(2)	5100(3)	22(1)
C(51)	1663(5)	11209(3)	5197(4)	25(1)
C(52)	1284(6)	11822(3)	5612(4)	36(1)
C(53)	2123(7)	12388(3)	5742(5)	48(2)
C(54)	−2976(7)	10469(4)	8348(5)	54(2)
C(55)	3690(7)	11769(4)	5030(6)	57(2)
C(56)	2872(6)	11197(3)	4890(5)	44(2)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. * Starred atoms have an occupancy of 0.6763. Full listings of atom coordinates are available as supplementary material.

Table VI. Selected bond lengths (Å) and angles (deg) for compounds **1** and **2**.

Ta-N(1)	2.209(5)	Ta-N(2)	2.252(5)	Ta-N(3)	2.237(5)
Nb-N(1)	*2.215(3)*	*Nb-N(2)*	*2.264(3)*	*Nb-N(3)*	*2.237(3)*
Ta-N(4)	2.256(6)	Ta-N(5)	2.225(5)	Ta-N(6)	2.272(5)
Nb-N(4)	*2.257(3)*	*Nb-N(5)*	*2.234(3)*	*Nb-N(6)*	*2.271(3)*
Ta-N(7)	2.212(5)	Ta-N(8)	2.250(5)		
Nb-N(7)	*2.216(3)*	*Nb-N(8)*	*2.264(3)*		
N(1)-Ta-N(2)	75.2(2)	N(1)-Ta-N(3)	96.0(2)		
N(1)-Nb-N(2)	*74.7(1)*	*N(1)-Nb-N(3)*	*96.4(1)*		
N(1)-Ta-N(4)	84.2(2)	N(1)-Ta-N(5)	105.7(2)		
N(1)-Nb-N(4)	*84.4(1)*	*N(1)-Nb-N(5)*	*105.3(1)*		
N(1)-Ta-N(6)	58.8(2)	N(1)-Ta-N(7)	136.4(2)		
N(1)-Nb-N(6)	*58.5(1)*	*N(1)-Nb-N(7)*	*136.3(1)*		
N(1)-Ta-N(8)	145.1(2)	N(2)-Ta-N(4)	132.3(2)		
N(1)-Nb-N(8)	*145.0(1)*	*N(2)-Nb-N(4)*	*132.2(1)*		
N(2)-Ta-N(3)	58.7(2)	N(2)-Ta-N(6)	126.1(2)		
N(2)-Nb-N(3)	*58.9(1)*	*N(2)-Nb-N(6)*	*125.4(1)*		
N(2)-Ta-N(5)	86.2(2)	N(2)-Ta-N(7)	146.6(2)		
N(2)-Nb-N(5)	*86.4(1)*	*N(2)-Nb-N(7)*	*147.26(1)*		
N(2)-Ta-N(8)	72.9(2)	N(3)-Ta-N(4)	82.0(2)		
N(2)-Nb-N(8)	*73.5(1)*	*N(3)-Nb-N(4)*	*81.9(1)*		
N(3)-Ta-N(5)	132.2(2)	N(3)-Ta-N(6)	145.0(2)		
N(3)-Nb-N(5)	*132.4(1)*	*N(3)-Nb-N(6)*	*145.1(1)*		
N(3)-Ta-N(7)	100.3(2)	N(3)-Ta-N(8)	79.3(2)		
N(3)-Nb-N(7)	*100.3(1)*	*N(3)-Nb-N(8)*	*79.4(1)*		
N(4)-Ta-N(5)	141.2(2)	N(4)-Ta-N(6)	72.3(2)		
N(4)-Nb-N(5)	*141.1(1)*	*N(4)-Nb-N(6)*	*72.4(1)*		
N(4)-Ta-N(7)	58.8(2)	N(4)-Ta-N(8)	128.4(2)		
N(4)-Nb-N(7)	*58.8(1)*	*N(4)-Nb-N(8)*	*128.5(1)*		
N(5)-Ta-N(6)	81.0(2)	N(5)-Ta-N(7)	92.5(2)		
N(5)-Nb-N(6)	*80.8(1)*	*N(5)-Nb-N(7)*	*92.5(1)*		
N(5)-Ta-N(8)	58.6(2)	N(6)-Ta-N(7)	86.5(2)		
N(5)-Nb-N(8)	*58.6(1)*	*N(6)-Nb-N(7)*	*86.5(1)*		
N(8)-Ta-N(6)	135.5(1)	N(7)-Ta-N(8)	78.0(2)		
N(8)-Nb-N(6)	*135.3(1)*	*N(7)-Nb-N(8)*	*78.1(1)*		

Italicized numbers represent values for Nb while non-italicized numbers represent values for Ta.

Table VII. Selected bond distances (Å) and angles (deg) for compound **3**.

$[Ta(pyt)_4]^-$			
Ta-N(1)	2.22(1)	Ta-S(2)	2.567(6)
Ta-N(3)	2.22(2)	Ta-S(4)	2.638(5)
Ta-N(5)	2.18(2)	Ta-S(6)	2.611(5)
Ta-N(7)	2.23(2)	Ta-S(8)	2.587(4)
N(1)-Ta-N(7)	158.2(4)	N(5)-Ta-S(2)	82.2(5)
N(1)-Ta-S(2)	64.0(3)	N(5)-Ta-S(4)	136.8(4)
N(1)-Ta-S(4)	81.0(4)	N(5)-Ta-S(6)	63.8(4)
N(1)-Ta-S(6)	81.1(4)	N(5)-Ta-S(8)	83.3(5)
N(1)-Ta-S(8)	139.3(4)	N(7)-Ta-S(2)	137.4(3)
N(3)-Ta-N(1)	101.5(6)	N(7)-Ta-S(4)	81.4(4)
N(3)-Ta-N(7)	81.2(6)	N(7)-Ta-S(6)	81.9(4)
N(3)-Ta-S(2)	82.3(4)	N(7)-Ta-S(8)	62.4(4)
N(3)-Ta-S(4)	61.6(5)	S(2)-Ta-S(4)	123.2(2)
N(3)-Ta-S(6)	135.0(4)	S(2)-Ta-S(6)	134.7(2)
N(3)-Ta-S(8)	82.7(5)	S(2)-Ta-S(8)	76.7(2)
N(5)-Ta-N(1)	81.2(6)	S(6)-Ta-S(4)	74.8(1)
N(5)-Ta-N(3)	161.1(4)	S(8)-Ta-S(4)	132.8(2)
N(5)-Ta-N(7)	103.3(7)	S(8)-Ta-S(6)	124.0(2)
$[K(THF)_6]^+$			
K-O(1)	2.36(3)	K-O(4)	2.38(2)
K-O(2)	2.46(2)	K-O(5)	2.37(2)
K-O(3)	2.44(2)	K-O(6)	2.37(2)
O(1)-K-O(2)	179.5(7)	O(4)-K-O(3)	176.7(9)
O(1)-K-O(3)	91.6(8)	O(5)-K-O(2)	91.0(7)
O(1)-K-O(4)	91.3(8)	O(5)-K-O(3)	88.4(6)
O(1)-K-O(5)	88.6(7)	O(5)-K-O(4)	90.0(5)
O(1)-K-O(6)	89.5(7)	O(5)-K-O(6)	177.3(9)
O(3)-K-O(2)	88.6(7)	O(6)-K-O(2)	90.9(7)
O(4)-K-O(2)	88.5(8)	O(6)-K-O(3)	89.7(6)
O(6)-K-O(4)	92.0(7)		

Table VIII. Selected bond lengths (Å) and angles (deg) for compound **4**.

Ta(1)-N(1)	2.229(8)	Ta(1)-N(5)	2.188(8)
Ta(1)-N(2)	2.242(9)	Ta(1)-N(6)	2.335(8)
Ta(1)-N(3)	2.223(8)	Ta(1)-N(7)	1.801(9)
Ta(1)-N(4)	2.235(9)		
N(1)-Ta(1)-N(4)	133.5(3)	N(2)-Ta(1)-N(6)	81.2(3)
N(3)-Ta(1)-N(1)	80.7(3)	N(5)-Ta(1)-N(6)	58.9(3)
N(3)-Ta(1)-N(4)	59.0(3)	N(4)-Ta(1)-N(6)	79.2(3)
N(5)-Ta(1)-N(1)	131.2(3)	N(7)-Ta(1)-N(6)	162.8(3)
N(5)-Ta(1)-N(3)	135.4(3)	N(1)-Ta(1)-N(2)	59.2(3)
N(5)-Ta(1)-N(4)	77.5(3)	N(1)-Ta(1)-N(6)	87.4(3)
N(7)-Ta(1)-N(1)	103.7(4)	N(4)-Ta(1)-N(2)	155.7(3)
N(7)-Ta(1)-N(2)	93.1(4)	N(3)-Ta(1)-N(2)	139.8(3)
N(7)-Ta(1)-N(3)	94.1(4)	N(3)-Ta(1)-N(6)	100.6(3)
N(7)-Ta(1)-N(4)	101.4(4)	N(5)-Ta(1)-N(2)	80.1(3)
N(7)-Ta(1)-N(5)	104.3(3)		

Table IX. Selected bond lengths (Å) and angles (deg) for compound **5**.

Ta-Ta′	2.6608(5)	Ta-N(5)′	1.983(4)
Ta-N(1)	2.185(4)	Ta-N(5)	1.997(4)
Ta-N(2)	2.203(4)	Ta-N(3)	2.271(4)
		Ta-N(4)	2.241(4)
N(1)-Ta-N(2)	172.1(1)	N(5)′-Ta-N(1)	87.7(2)
N(1)-Ta-N(3)	92.3(2)	N(5)′-Ta-N(2)	87.5(2)
N(1)-Ta-N(4)	97.0(2)	N(5)′-Ta-N(3)	159.5(2)
N(2)-Ta-N(3)	94.4(2)	N(5)′-Ta-N(4)	100.2(2)
N(2)-Ta-N(4)	90.1(2)	N(5)′-Ta-N(5)	96.1(2)
N(4)-Ta-N(3)	59.4(2)	N(5)-Ta-N(3)	104.4(2)
N(5)-Ta-N(1)	87.5(2)	N(5)-Ta-N(4)	163.3(2)
N(5)-Ta-N(2)	86.8(2)		

Primed atoms are generated by an inversion center.

Results and discussion

Chemical reactivity

The two reducing agents we have used more frequently in our attempts to produce tantalum(II) species have been KC_8 and $LiBH_4$. So far we have found that the former is more likely to produce mononuclear compounds in intermediate oxidation states, mostly trivalent, while the latter will react with formamidinato ligands to produce a variety of products in different oxidation states. The final outcome depends on subtle changes in the reaction conditions.

- *Reductions using* KC_8

In general the reactions were carried out by reducing $TaCl_5$ with three equivalents of KC_8 in the presence of an ether and then reacting the resulting products with the appropriate ligands. Table X lists some of the reaction conditions we have used along with the products formed.

When the reduction process is carried out at room temperature we obtained trivalent tantalum compounds such as $[K(THF)_6][Ta(pyt)_4]$ and a variety of crystalline forms of *mer*-$TaCl_3(py)_3$. However, if the reduction is done at low temperatures then the tetravalent tantalum compound $Ta(DPhF)_4$ is isolated in low yields. We presume that at low temperature the reduction to tantalum(III) species is incomplete, thus allowing the formation of **2**. We did not attempt to improve its yield. However, because of the interesting eight-coordinated structure it possesses (vide infra) we decided to synthesize the corresponding niobium compound using a more logical route from $NbCl_4(THF)_2$ and LiDPhF. As expected, the yields of the corresponding tetravalent niobium compound are higher.

- *Reductions using* $LiBH_4$

As shown in table XI, our attempts to produce divalent tantalum species using three or more equivalents of $LiBH_4$ gave an array of products in which the tantalum oxidation state varied from III to V.

Generally $TaCl_5$ was reacted with $LiBH_4$ in toluene and then further reduction was tried by changing the solvents to an ether (THF or Et_2O) and then adding LiDPhF. However it was found that frequently the ligand broke down producing in two cases, **4** and **5**, an imido fragment, namely phenyl imido, which binds strongly to tantalum. The mechanism of such fragmentation is not currently known, but the process has been previously observed in at least one other reaction. When the reduction of $TiCl_4$ was attempted by using two equivalents of $HSn(n\text{-}Bu)_3$ in the presence of LiDPhF, a similar fragmentation of the ligand occurred and crystals of $Ti_2(\mu\text{-}NPh)_2(\mu\text{-}DPhF)_2(DPhF)_2$ [14] were isolated.

It appears that the simultaneous presence of reducing hydrido groups, metal-containing species and LiDPhF leads to ligand breakage. As pointed out before, we do not know the mechanism of the process, but so far we have observed the formation of amido species only when hydrides are used in the reaction. The use of a larger excess of $LiBH_4$ in the reaction (a $TaCl_5/LiBH_4$ ratio of 1:6) leads instead to the formation of $B_2H_6^{2-}$ ion-containing species [4] in which the $B_2H_6^{2-}$ ion formally substitutes the two NPh^{2-} groups which are found in **5**.

At this point it is clear to us that the formation of species of the type $Ta_2(DPhF)_4$ is not likely to be accomplished if the reactions are performed in the presence of $LiBH_4$. A successful synthesis will necessarily require the use of a different type of reducing material.

Structural considerations

- *Eight-coordinate compounds*

Compounds **1** and **2** are isostructural; a diagram of compound **2** is shown in figure 1. There are four chelating formamidinato groups surrounding each metal atom. Long M–N bond distances, attributed to possible steric hindrances from the eight atoms around a metal center, characterize both compounds. The bond

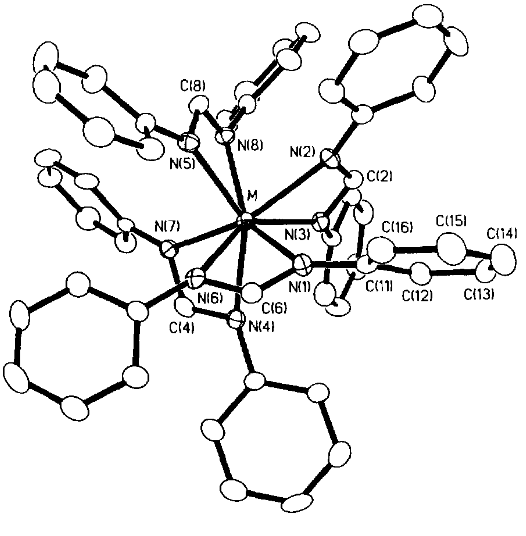


Fig 1. A drawing of the molecular structure of $M(DPhF)_4$, M = Nb and Ta. Non-hydrogen atoms are represented by their 30% probability ellipsoids of **2**.

Table X. Some reaction conditions for the formation of tantalum compounds by addition of ligand to the reduction product of $TaCl_5$ with a threefold excess of KC_8.

Product	*Formal Ta oxidation state*	*Reduction temperature*	*Ligand*	*Solvents used in extraction*	*Reference*
2	IV	−30 °C	LiDPhF	Toluene	This work
3	III	Room temperature	Kpyt	THF	This work
$TaCl_3(py)_3$	III	Room temperature	py	Et_2O/py	[3]

Table XI. Some reaction conditions for the formation of various tantalum formamidinato compounds by reduction of $TaCl_5$ with $LiBH_4$.

Product	*Formal Ta oxidation state*	*$TaCl_5/LiBH_4$ molar ratio*	*Temperature of THF added after toluene removal*	*Solvents used in extraction*	*Reference*
5	IV	1:3	−78 °C	Benzene/CH_2Cl_2	This work
4	V	1:3	Room temperature	Benzene	This work
6*	III	1:6	−78 °C	Benzene/Et_2O	[4]

* Compound **6** is $Ta_2(\mu_2\text{-}\eta^4\text{-}B_2H_6)(DPhF)_4 \cdot 2Et_2O$.

distances and angles are virtually the same for both compounds even though the metals belong to two different transition series.

Compound **3** is the chiral ionic compound, $[K(THF)_6][Ta(pyt)_4]$. As far as we know, the cation, in which six THF molecules surround the potassium ion, has been structurally observed only once before in $[K(THF)_6][Cu_5(PPh_2)_2]$ [15]. However, this fact was not discussed in the report. Sodium analogs have been seen several times in compounds such as $[Na(THF)_6][V(CO)_6]$ [16] and $[Na(THF)_6][(\eta^3\text{-}C_9H_7)_3Ln(\mu\text{-}Cl)Ln(\eta^3\text{-}C_9H_7)_3]$, where Ln is Nd, Sm, and Pr [17]. In $[K(THF)_6][Ta(pyt)_4]$, the potassium atom lies in the center of an octahedron of oxygen atoms (fig 2). The K–O bond lengths range from 2.35 to 2.47 Å. Most of the basal oxygen atoms are coplanar with the potassium ion and the two carbon atoms to which they are bonded. In the anion of **3**, $Ta(pyt)_4^-$ (fig 3), four ligand groups are chelated to the tantalum atom giving an eight-coordinate ion. To our knowledge, this is the first time that such a coordination has been observed in a mononuclear Ta(III) species. Ta–N bond distances range from 2.18 to 2.23 Å, whereas the Ta–S bond distances range from 2.51 to 2.59 Å.

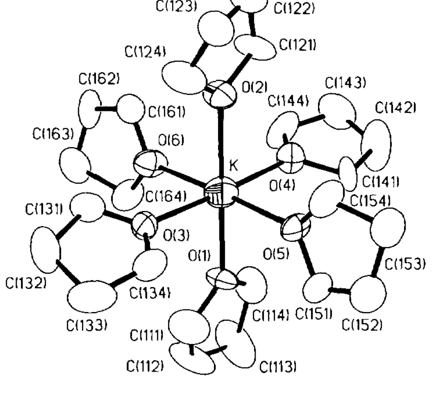


Fig 2. Perspective view of the cation $[K(THF)_6]^+$ in **3**. Nonhydrogen atoms are represented by their 30% probability ellipsoids.

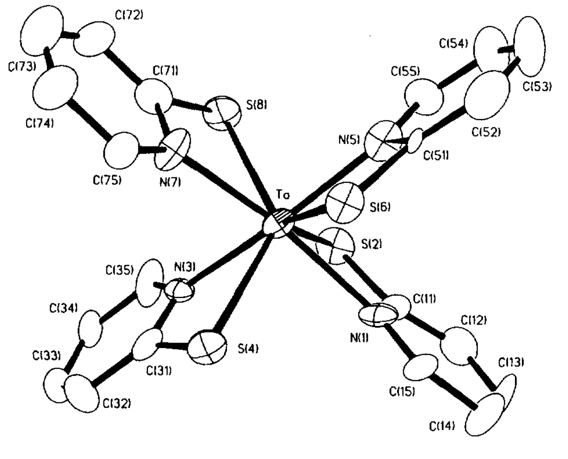


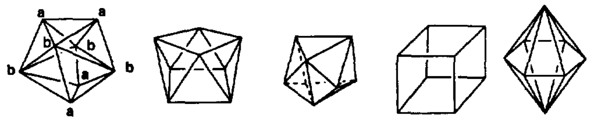
Fig 3. A plot of the major configuration of the anion $Ta(pyt)_4$ in **3** showing the atom labeling scheme. Nonhydrogen atoms are represented by their 40% probability ellipsoids.

The structures of complexes with high coordination numbers have been studied extensively [18]. For a coordination number of eight, many structural types can exist (fig 4). Distorted dodecahedral and square antiprismatic are by far the most common. This fact has been rationalized by theoretical studies [19]. In order to determine the geometry of these complexes, the procedure by Muetterties and Guggenberger was followed [20]. This involves measuring the dihedral angle (δ) between faces that intersect along the 'type *b*' edges of a dodecahedron (see fig 4). The angle φ was also calculated and is defined as the twist in the diagonal trapezoids of a regular dodecahedron as a result of distortion. The trapezoids in **1** and **2** are defined by atoms (N1,N3,N6,N8) and (N2,N4,N5,N7). The values of δ and φ along with that of the idealized polyhedra are given in table XII. The structures of **1** and **2** can best be described as distorted dodecahedron containing idealized D_{2d} (gggg) symmetry. The metal-nitrogen bond

Table XII. Comparison of dodecahedral and square antiprismatic models for **1**, **2** and **3**.

	δ	φ
Nb(DPhF)$_4$, **1**	21.2(3), 26.9(3), 31.1(3), 38.4(4)	16.3(2), 28.8(3)
Ta(DPhF)$_4$, **2**	21.2(4), 27.1(3), 31.9(3), 38.5(3)	16.3(2), 28.6(1)
Ta(pyt)$_4^-$, **3**	32.5(7), 31.1(6), 8.4(7), 7.1(9)	10.6(4), 10.9(6)
Dodecahedron	29.5, 29.5, 29.5, 29.5	0
Square antiprism	52.4, 52.4, 0,0	24.5

distances show short (2.20–2.22 Å) bond lengths representing the *b*-type vertices and long (2.25–2.27 Å) bond lengths representing the *a*-type vertices.



Dodecahedron Square antiprism Bicapped trigonal prism Cube Hexagonal bipyramid

Fig 4. A schematic drawing of some of the most important geometries found in eight-coordinate compounds. The labels on the dodecahedron are explained in the text.

In contrast, the structure of **3** can best be described as a square antiprism. Many factors contribute to the geometry of the ligands about the metal center. It has previously been shown that the energy difference between the dodecahedral and square antiprismatic geometries is small [21]. In the case of [K(THF)$_6$][Ta(pyt)$_4$], the geometry could be influenced by the cation, or the different M–N and M–S bond lengths.

- *Structure of Ta(DPhF)$_3$(NPh)* 4

In this mononuclear compound there are three DPhF groups chelating the tantalum(V) ion as shown in figure 5. An imido group completes the all-nitrogen seven coordination of the metal ion. The core has a distorted pentagonal bipyramidal geometry. The short Ta–N$_{(\mathrm{imido})}$ distance (1.801(9) Å) together with a linear M-N-C (176.6(8)°) unit suggests that a Ta≡N triple bond exists [22]. The Ta-N(6) shows a marked *trans* effect and has the longest Ta–N distance (2.335(8) Å). The remaining Ta–N bond distances are in the range 2.188(8) to 2.242(9) Å which is significantly longer than the distances found in other seven-coordinate formamidinato-tantalum(V) compounds of the type TaCl$_{3-n}$Me$_n$(amidinato)$_2$, n = 0,1 [23] in which the tantalum-nitrogen distances are in the range 2.04 to 2.22 Å with an average of 2.14 Å.

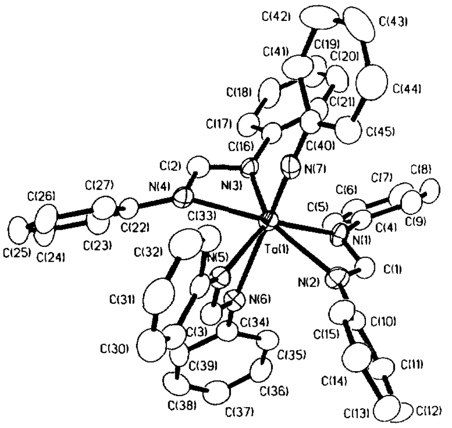


Fig 5. Perspective view of the molecular structure of Ta(DPhF)$_3$(NPh) showing the atom labeling scheme. Non-hydrogen atoms are represented by their 30% probability ellipsoids.

- *Structure of Ta$_2$(μ-DPhF)$_2$(η^2-DPhF)$_2$(μ-NPh)$_2$* 5

The compound is composed of discrete dinuclear molecules in the solid state as shown in figure 6. Each molecule possesses a crystallographically imposed C_i symmetry. The two tantalum(IV) atoms are separated by a distance of 2.6608(5) Å which is consistent with the presence of a Ta–Ta single bond.

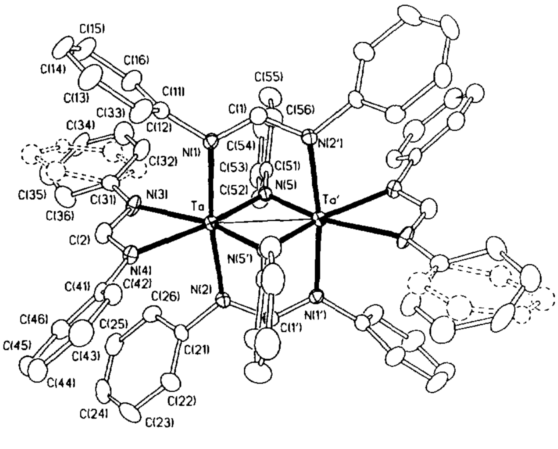


Fig 6. A drawing of the centrosymmetric molecule Ta$_2$(μ-NPh)$_2$(μ-DPhF)$_2$(η^2-DPhF)$_2$ showing a conformational disorder in one of the crystallographically unique phenyl rings. Non-hydrogen atoms are represented by their 30% probability ellipsoids.

This structure is related to that of the titanium analog [14]. One formamidinato group is chelated to each of the tantalum atoms while the other two DPhF$^-$ groups form a bridge to the metal atoms. The nitrogen atoms of the imido groups are symmetrically bonded to both tantalum atoms at an average distance of 1.99 Å which is ca 0.20 Å longer than the Ta–N$_{(\mathrm{imido})}$ found in **4**. A conformational disorder of the phenyl rings defined by the carbon atoms C(32)-C(36) was observed and accounted for during the crystal structure solution.

Supplementary material available

Complete X-ray data for compounds **1**–**5**, including tables of atomic coordinates, interatomic distances, displacement parameters (54 pages), calculated and observed structure factors (115 pages) are available from the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° SUP 90424.

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References

1 Cotton FA, Daniels LM, Murillo CA, *Inorg Chem* (1993) 32, 2881

2 Araya MA, Cotton FA, Matonic JH, Murillo CA, *Inorg Chem* (1995) 34, 5424

3 Cotton FA, Murillo CA, Wang X, *Inorg Chim Acta* (1996) in press

4 Cotton FA, Daniels LM, Murillo CA, Wang X, *J Am Chem Soc*, in press

5 a) Schwindt MA, Lejon T, Hegedus LS, *Organometallics* (1990) 9, 2814
b) Fürstner A, *Angew Chem Int Ed Engl* (1993) 32, 164

6 Pedersen SF, Hartung Jr, JB, Roskamp EJ, Dragovich PS, *Inorg Synth* (1992) 29, 119

7 Pflugrath J, Messerschmitt A, *MADNES*, Munich Area Detector (New EEC) System, Version EEC 11/1/89, with enhancements by Enraf-Nonius Corp, Delft, The Netherlands. A description of MADNES appears in: Messerschmitt A, Pflugrath J, *J Appl Crystallogr* (1987) 20, 30

8 a) Bryan JC, Cotton FA, Daniels LM, Haefner SC, Sattelberger AP, *Inorg Chem* (1995) 34, 1875
b) Scheidt WR, Turowska-Turk I, *Inorg Chem* (1994) 33, 1314

9 Blessing RH, *Acta Cryst* (1995) A51, 31

10 Evans PR, *ABSURD* - Absorption correction program for the area detector. MRC Laboratory of Molecular Biology, Hills Road, Cambridge, UK, (1990)

11 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, (1985)

12 SHELXTL (version 5.03); Siemens Industrial Automation Inc: Madison WI

13 Flack HD, *Acta Cryst* (1983) A39, 876

14 Cotton FA, Wojtczak WA, *Polyhedron* (1994) 13, 1337

15 Eichhöfer A, Fenske D, Holstein W, *Angew Chem Int Ed Engl* (1993) 32, 242

16 Churchill MR, Janik TS, *J Chem Crystallogr* (1995) 25, 597

17 Ye Z, Wang S, Kong D, Huang X, *J Organometal Chem* (1995) 491, 57 and references therein

18 Drew MGB, *Coord Chem Rev* (1977) 24, 179

19 a) Blight DG, Kepert DL, *Inorg Chem* (1972) 11, 1556
b) King RB, *Polyhedron* (1994) 13, 2005

20 Muetterties EL, Guggenberger LJ, *J Am Chem Soc* (1974) 96, 1748

21 Cotton FA, Diebold MP, Roth WJ, *Inorg Chem* (1987) 26, 2889

22 Nugent WA, Mayer JM, *Metal-Ligand Multiple Bonds*, Wiley, New York, 1988, p 22

23 Barker J, Kilner M, *Coord Chem Rev* (1994) 133, 219 and references therein