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Cleavage of Formamidinate Ligands on a Ta═Ta Double Bond: Formation of H_xCNAryl (x = 0 and 1) and Arylimido-Bridged Complexes

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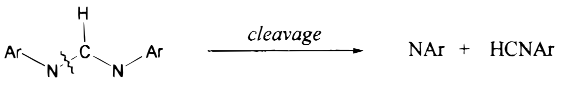
Three complexes which resulted from the C−N bond cleavage reactions of formamidinate anions, $[\text{ArNC(H)NAr}]^-$, have been synthesized and structurally characterized. The reaction of *N,N′*-diphenylformamidinate, DPhF^-, with $(\text{Me}_2\text{S})\text{Cl}_2\text{Ta}(\mu\text{-Me}_2\text{S})(\mu\text{-Cl})_2\text{TaCl}_2(\text{SMe}_2)$ (abbreviated as $\text{Ta}_2\text{Cl}_6(\text{SMe}_2)_3$) in the presence of Zn metal produces the CNPh-containing dinuclear compound $(\eta^2\text{-DPhF})_2\text{Ta}(\mu\text{-NPh})(\mu\text{-}\eta^2\text{-CNPh})\text{Ta}(\eta^2\text{-DPhF})_2\cdot\text{C}_7\text{H}_8$, $\mathbf{1}\cdot\text{C}_7\text{H}_8$. By using DTolF^- and Na/Hg as reducing agent, the isolated product is $(\eta^2\text{-DTolF})\text{Ta}(\mu\text{-NTol})(\mu\text{-}\eta^2\text{-CNTol})(\mu\text{-DTolF})_2\text{Ta}(\eta^2\text{-DTolF})\cdot1.5\text{C}_6\text{H}_{14}$, $\mathbf{2}\cdot1.5\text{C}_6\text{H}_{14}$, where DTolF^- = *N,N′*-di(*p*-tolyl)formamidinate. Both **1** and **2** are isolated in low yields. There is a formal single bond between the tantalum atoms which are bonded to intact formamidinate ions as well as the two fragments which result from the cleavage of a formamidinate ligand, namely arylimido (NAr^{2-}) and (CNAr). In the absence of a reducing agent, the reaction of LiDTolF and $\text{Ta}_2\text{Cl}_6(\text{SMe}_2)_3$ produces $\text{Cl}_2(\eta^2\text{-DTolF})\text{Ta}(\mu\text{-NTol})(\mu\text{-}\eta^2,\eta^2\text{-HCNTol})\text{Ta}(\eta^2\text{-DTolF})_2$, **3**, in high yield. In addition to the tolylimido group, a tolylformimidoyl fragment (HCNTol) binds to the tantalum atom through both carbon and nitrogen atoms in a η^2,η^2 mode. Because of this and the relatively long C−N bond distance (1.42(1) Å), the ligand can be formulated as $[\text{HCNTol}]^{3-}$. Thus the tantalum atoms in **3** have a formal oxidation state of +5, which precludes the presence of a metal-metal bond. Crystal data for $\mathbf{1}\cdot\text{C}_7\text{H}_8$: monoclinic, $I2/a$, $a = 19.437(2)$ Å, $b = 15.587(1)$ Å, $c = 20.401(1)$ Å, and $\beta = 97.840(6)°$. Crystal data for $\mathbf{2}\cdot1.5\text{C}_6\text{H}_{14}$: triclinic, $P\bar{1}$, $a = 13.990(2)$ Å, $b = 15.841(1)$ Å, $c = 19.442(4)$ Å, $\alpha = 98.98(1)°$, $\beta = 104.07(1)°$; $\gamma = 109.59(1)°$. Crystal data for **3**: monoclinic, $P2_1/n$, $a = 17.962(3)$ Å, $b = 15.539(4)$ Å, $c = 19.973(3)$ Å, $\beta = 90.126(7)°$.

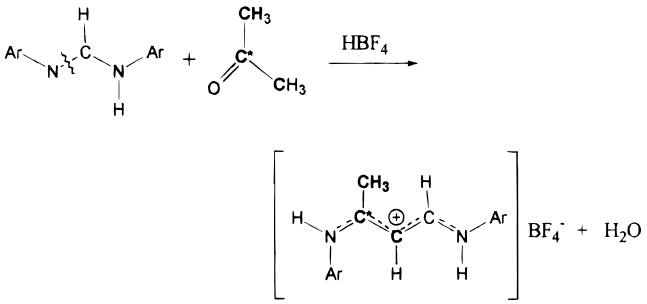
Introduction

Formamidines, ArNC(H)N(H)Ar, and their anions have been widely used as ligands in coordination chemistry,[1] where they are usually found in monodentate,[2] chelating,[3] and bridging modes.[4] The latter are ubiquitous in the lantern-type dinuclear compounds, many of which contain metal to metal bonds. However, we have observed that under suitable conditions they often undergo cleavage at a C−N bond. For example, arylimido-containing compounds have been isolated in the course of attempts to reduce tantalum.[5,6] In addition to the imido group, cleavage of a formamidinate ligand should produce a HCNAr fragment (Ar = phenyl or tolyl) as shown in Scheme 1.

Scheme 1



Scheme 2



Both of the fragments are not necessarily found in the same product because one or the other might combine with other molecules to give different ligands or molecular species. From a melt reaction of VO(acac)_2 and HDPhF, a new *β*-diketonate complex, namely oxobis[6-(phenylamino)hexane-2,4-dionato-*O,O′*]vanadium(IV), has been synthesized.[7] In this reaction, two hydrogen atoms of one of the methyl groups of each acac moiety are replaced by a PhNHCH fragment. The other fragment picks up the two hydrogen atoms to give aniline.

More recently we have reported that vinamidinium compounds can be obtained from the reaction of formamidines and acetone in the presence of Lewis or Brønsted acids.[8] As shown in Scheme 2, the formamidine again undergoes cleavage of a C−N bond. Subsequent insertion of two carbon atoms of an acetone molecule yields vinamidinium salts.[8]

There is one example, $(\eta\text{-dmpm})\text{Cl}_2\text{Ta}\,(\mu\text{-NTol})(\mu\text{-}\eta^2\text{-R})(\mu\text{-dmpm})\text{TaCl}(\eta^2\text{-DTolF})$, R = HCNTol or CNTol, in which both

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fragments of the cleaved formamidinate anion were found in the same molecule.[6] It was obtained in low yield by reduction of $Ta_2Cl_6(SMe_2)_3$ with Zn metal in the presence of LiDTolF and dmpm.

Thinking that the cleavage of the formamidinate ligand in the presence of ditantalum compounds could be a consequence of the reducing agent, we decided to investigate this process further. By changing the reaction conditions, three tantalum complexes containing NAr and CNAr or HCNAr groups have been synthesized. Compound $(\eta^2\text{-DPhF})_2\text{Ta}(\mu\text{-NPh})(\mu\text{-}\eta^2\text{-CNPh})\text{Ta}(\eta^2\text{-DPhF})_2$, **1**, was prepared from the reaction of LiDPhF with $Ta_2Cl_6(SMe_2)_3$ in the presence of Zn metal. In the presence of LiDTolF and Na/Hg, the isolated product is is $(\eta^2\text{-DTolF})\text{Ta}(\mu\text{-NTol})(\mu\text{-}\eta^2\text{-CNTol})(\mu\text{-DTolF})_2\text{Ta}(\eta^2\text{-DTolF})$, **2**. Both compounds are obtained in low yields. However, the absence of the reducing agent allows the isolation of $\text{Cl}_2(\eta^2\text{-DTolF})\text{Ta}(\mu\text{-NTol})(\mu\text{-}\eta^2,\eta^2\text{-HCNTol})\text{Ta}(\eta^2\text{-DTolF})_2$, **3**, in high yield and high purity. Details of the syntheses and structural characterization of compounds **1**−**3** will be discussed.

Experimental Section

Materials and Methods. All operations were carried out under an argon atmosphere using standard Schlenk or drybox techniques. Solvents were purified by conventional methods and distilled under nitrogen from Na/K. Slightly modified literature procedures were used to synthesize HDTolF[9] and $Ta_2Cl_6(SMe_2)_3$.[10] Other chemicals, including HDPhF, were purchased from Aldrich and were used as received. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Perkin-Elmer 16-PC spectrophotometer using KBr pellets. ^1H NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer.

Synthesis of $(\eta^2\text{-DPhF})_2\text{Ta}(\mu\text{-NPh})(\mu\text{-}\eta^2\text{-CNPh})\text{Ta}(\eta^2\text{-DPhF})_2\cdot C_7H_8$ ($1\cdot C_7H_8$). To a mixture of $Ta_2Cl_6(SMe_2)_3$ (0.77 g, 1.0 mmol) and LiDPhF (5.0 mmol) in toluene (30 mL)/THF (5 mL) was added zinc powder (0.90 g, 1.4 mmol) at −30 °C. The mixture was allowed to warm to room temperature and was stirred for 10 h. It was then filtered. Red crystals of compound **1** were obtained by slow diffusion of hexanes (20 mL) into the red brown filtrate at −5 °C. Yield: 0.34 g, 24%. ^1H NMR: δ (C_6D_6/THF-d_8) 9.52 (s, 1H), 9.44 (s, 1H), 9.24 (s, 1H), 8.74 (s, 1H), 8.11 (m, 3H, phenyl), 7.57 (d, 2H, phenyl), 7.34−6.08 (m, 45H, phenyl). IR bands (cm^{-1}): 3057 (s), 2956 (m), 1933 (w), 1865 (w), 1790 (w), 1963 (w), 1667 (w), 1651 (w), 1587 (s), 1538 (s), 1487 (s), 1456 (sh, m), 1403 (w), 1373 (m), 1329 (w), 1285 (s), 1227 (s), 1202 (m), 1172 (sh, m), 1154 (sh, m), 1072 (m), 1027 (m), 998 (w), 957 (m), 916 (w), 893 (w), 825 (w), 756 (s), 733 (sh, m), 689 (s), 631 (w), 612 (w), 593 (w), 538 (m), 522 (m), 466 (m).

Synthesis of $(\eta^2\text{-DTolF})\text{Ta}(\mu\text{-NTol})(\mu\text{-}\eta^2\text{-CNTol})(\mu\text{-DTolF})_2\text{Ta}(\eta^2\text{-DTolF})\cdot 1.5C_6H_{14}$ ($2\cdot 1.5C_6H_{14}$). To a solution of $Ta_2Cl_6(SMe_2)_3$ (1.53 g, 2.0 mmol) in THF (30 mL) was added a suspension of LiDTolF (10.0 mmol) in THF (15 mL) at −78 °C. After stirring for 2 h, the brown mixture was warmed to room temperature and Na/Hg (4.0 mmol of Na/100 g of Hg) was added with a syringe. After overnight stirring, the THF was removed under vacuum and the remaining solid was washed with hexanes (2 × 15 mL). The solid was then extracted with toluene (25 mL). A green brown solution, obtained after filtration, produced dark purple crystals of **2** after layering of *n*-hexane (20 mL) onto the filtrate. Yield: 0.60 g, 19%. ^1H NMR: δ (C_6D_6) 8.84 (s, 1H), 8.79 (s, 1H), 8.27 (s, 2H), 7.58 (d, 2H, tolyl, J_{HH} = 7.4), 7.08−6.69 (m, 32H, tolyl), 6.52 (d, 2H, tolyl, J_{HH} = 7.5), 6.14 (d, 2H, tolyl, J_{HH} = 8.0), 5.79 (d, 2H, tolyl, J_{HH} = 7.8), 2.32 to 1.96 (series of singlet, 30H, tolyl methyl groups) (all *J* values are in Hz). IR bands (cm^{-1}): 3020 (m), 2919 (s), 2860 (m), 1888 (w), 1694 (w), 1667 (m), 1652 (m), 1605 (m), 1533 (s), 1506 (s), 1428 (w), 1356 (m), 1312 (m), 1283 (s), 1205 (s), 1106 (w), 1018 (w), 956 (w), 924 (w), 817 (br, s), 714 (w), 585 (w), 531 (w).

Synthesis of $\text{Cl}_2(\eta^2\text{-DTolF})\text{Ta}(\mu\text{-NTol})(\mu\text{-}\eta^2,\eta^2\text{-HCNTol})\text{Ta}(\eta^2\text{-DTolF})_2$ (3). To a solution of $Ta_2Cl_6(SMe_2)_3$ (0.77 g, 1.0 mmol) in THF (30 mL) was added a suspension of LiDTolF (4.0 mmol) in THF (15 mL) at −78 °C. The mixture was allowed to warm slowly to room temperature and then stirred overnight. The solvent was then removed under reduced pressure and the remaining dark brown solid was first washed with hexanes (2 × 15 mL) and then extracted with toluene (25 mL). The toluene solution was layered with hexanes (20 mL). Brown crystals of **3** were isolated from the solution after it had been held at −5 °C for 10 days. Yield: 1.08 g, 81%. ^1H NMR: δ (C_6D_6) 8.88 (s, 1H), 8.12 (s, 1H), 8.06 (s, 1H), 7.80 (s, 1H), 7.79 (d, 2H, tolyl, J_{HH} = 8.3 Hz), 7.10 to 6.70 (m, 24H, tolyl), 6.51 (d, 2H, tolyl, J_{HH} = 8.3), 6.28 (d, 2H, tolyl, J_{HH} = 8.3), 6.04 (d, 2H, tolyl, J_{HH} = 8.2), 2.29−1.88 (series of singlet, 24H, tolyl methyl groups). IR bands (cm^{-1}): 3184 (w), 3084 (w), 3025 (m), 2921 (s), 2863 (m), 1889 (w), 1694 (s), 1612 (m), 1591 (w), 1537 (s) 1517 (s), 1448 (w), 1341 (s), 1312 (sh, m), 1284 (m), 1268 (s), 1252 (m), 1221 (m), 1127 (w), 1110 (w), 1039 (w), 1016 (w), 970 (w), 817 (s), 531 (w), 508 (m).

Crystallographic Studies. Crystals of each of $\mathbf{1}\cdot C_7H_8$, $\mathbf{2}\cdot 1.5C_6H_{14}$, and **3** were mounted on the tips of glass fibers and cooled under a nitrogen stream on the diffractometer. Data for $\mathbf{1}\cdot C_7H_8$ and $\mathbf{2}\cdot 1.5C_6H_{14}$ were collected on a Nonius FAST area-detector system. Unit cell dimensions were obtained by indexing 250 strong reflections in the 2θ range 18.0−41.8° and confirmed by taking axial images. Details of the use of the FAST in our laboratory have been previously described.[11] These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by the multiple equivalent measurements.[12] Data for **3** were collected on a Nonius CAD4 using well-established techniques, including the use of ψ-scans for absorption correction.[13]

In each case the structure was solved by direct methods and refined using the SHELXTL programs.[14] Although **1** does not have rigorous C_2 symmetry, the molecule lies on a crystallographic 2-fold axis and is therefore somewhat disordered. The axis passes through the symmetric phenylamido group and the midpoint of the Ta−Ta bond, and near the asymmetric CNPh group, therefore causing disorder. Also, three of the four independent phenyl groups on the formamidinate ligands were found to be disordered, the two orientations in each case being slightly displaced from each other and having occupancies of 0.50. In order to facilitate the refinement, these three sets of disordered rings were refined as rigid hexagons which were allowed to rotate and translate as a group, and the displacement parameters were refined isotropically. The ring of the disordered phenylimidoyl group was also modeled as a rigid group, but the atoms refined well with anisotropic displacement parameters. A disordered molecule of toluene was also found in the interstices and was included in the model. Hydrogen atoms were included in calculated positions on the phenyl groups of the metal complex.

The structure of **2** refined cleanly without the disorder problems seen for **1**. All non-hydrogen atoms of the metal complex were refined with anisotropic displacement parameters, and hydrogen atoms were used in calculated positions. Two sites containing *n*-hexane were identified in difference maps, one on a general position and one on an inversion center, disordered but well-behaved.

The refined model for **3** included the position of the hydrogen atom of the HCNTol fragment. All other hydrogen atoms in this structure were used in calculated positions.

Crystal and structure refinement data are summarized in Table 1.

Results and Discussion

Syntheses. In our earlier report it was shown that the reduction of $Ta_2Cl_6(SMe_2)_3$ with an excess of Zn metal in the presence of LiDTolF and dmpm produced fragmentation of a DTolF^- group to give a compound which was formulated as $(\text{dmpm})\text{Cl}_2\text{Ta}(\mu\text{-NTol})(\mu\text{-}\eta^2\text{-R})(\mu\text{-dmpm})\text{TaCl}(\text{DTolF})$, R = HCNTol or CNTol.[6] The unique feature of this reaction is the formation of bridging tolylimide and CNTol- containing frag-

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Table 1. Crystal Data and Structure Refinement for $Ta_2(\mu\text{-}NPh)(\mu\text{-}\eta^2\text{-}C{=}NPh)(DPhF)_4{\cdot}C_7H_8$, **1**$\cdot C_7H_8$, $Ta_2(\mu\text{-}NTol)(\mu\text{-}\eta^2\text{-}CNTol)_2(\mu\text{-}DTolF)_2(DTolF)_2{\cdot}1.5C_6H_{14}$, **2**$\cdot 1.5C_6H_{14}$, and $Ta_2(\mu\text{-}NTol)(\mu\text{-}\eta^2,\eta^2\text{-}HCNTol)Cl_2(DTolF)_3$, **3**

	$C_{72}H_{62}N_{10}Ta_2$	$C_{84}H_{95}N_{10}Ta_2$	$C_{60}H_{60}Cl_2N_8Ta_2$
fw	1429.22	1606.60	1325.96
space group	$I2/a$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	19.437(2)	13.990(2)	17.962(3)
b, Å	15.587(1)	15.841(1)	15.539(4)
c, Å	20.401(1)	19.442(4)	19.973(3)
α, deg	90	98.98(1)	90
β, deg	97.840(6)°	104.07(1)	90.126(7)
γ, deg	90	109.59(1)	90
V, Å^3	6123.0(8)	3802.1(1)	5575(2)
Z	4	2	4
d_{calc}, g/cm^3	1.550	1.403	1.580
abs coeff, cm^{-1}	36.23	29.26	40.64
radiation (monochromated in incident beam), Mo Kα, Å	0.71073	0.71073	0.71073
T, °C	−60	−60	−105
final R indices [I>2F(I)]	R1 = 0.057, wR2 = 0.137	R1 = 0.040, wR2 = 0.106	R1 = 0.032, wR2 = 0.064
R indices (all data)	R1 = 0.071, wR2 = 0.146	R1 = 0.056, wR2 = 0.122	R1 = 0.074, wR2 = 0.082

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2\ [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(F_o^2) + (ap)^2 + bp$, $p = [\mathrm{Max}(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.065$ and $b = 67.9$ for **1**; $a = 0.051$ and $b = 6.07$ for **2**; $a = 0.022$ and $b = 11.6$ for **3**.

ments. In order to explore the role of various factors in the cleavage of the formamidinate ligand, we carried out three other experiments. A reaction was conducted by using only formamidinate as a ligand source (*i.e.* without dmpm):

$$Ta_2Cl_6(SMe_2)_3 + 5LiDPhF + {}^1/_2Zn \xrightarrow{\text{toluene}} (\eta^2\text{-}DPhF)_2Ta(\mu\text{-}NPh)(\mu\text{-}\eta^2\text{-}CNPh)Ta(\eta^2\text{-}DPhF)_2 + 3SMe_2 + 5LiCl + {}^1/_2ZnCl_2 + {}^1/_2H_2 \quad (1)$$

Compound $(\eta^2\text{-}DPhF)_2Ta(\mu\text{-}NPh)(\mu\text{-}\eta^2\text{-}CNPh)Ta(\eta^2\text{-}DPhF)_2$, **1**, was isolated as red crystals in 24% yield. The bridging NCPh (isocyanide) group was characterized both from an X-ray structural analysis (vide infra) and from spectroscopic data. The ^{1}H NMR show sharp singlets which correspond to each of the four methine hydrogen atoms of the chelating formamidinate groups at 9.52, 9.44, 9.24, and 8.74 ppm. Each of those signals integrate to one hydrogen atom. By changing the reducing agent from Zn to Na/Hg, the compound $(\eta^2\text{-}DTolF)Ta(\mu\text{-}NTol)(\mu\text{-}\eta^2\text{-}CNTol)(\mu\text{-}DTolF)_2Ta(\eta^2\text{-}DTolF)$, **2**, was prepared in 19% yield (eq 2). The ^{1}H NMR shows that the compound is diamagnetic. Sharp singlets at 8.84 and 8.79 ppm corresponding to the methine groups of two formamidinate groups. Another signal at 8.27 ppm, which integrates as two protons, corresponds to the other two methine hydrogen atoms.

$$Ta_2Cl_6(SMe_2)_3 + 5LiDTolF + Na/Hg \xrightarrow{\text{THF}} (\eta^2\text{-}DTolF)Ta(\mu\text{-}NTol)(\mu\text{-}\eta^2\text{-}CNTol)(\mu\text{-}DTolF)_2Ta(\eta^2\text{-}DTolF) + 3SMe_2 + 5LiCl + NaCl + Hg + {}^1/_2H_2 \quad (2)$$

However, in the absence of reducing agent, the reaction of LiDTolF with $Ta_2Cl_6(SMe_2)_3$ under mild conditions produced the compound $Cl_2(\eta^2\text{-}DTolF)Ta(\mu\text{-}NTol)(\mu\text{-}\eta^2,\eta^2\text{-}HCNTol)Ta(\eta^2\text{-}DTolF)_2$, **3** (eq 3).

$$Ta_2Cl_6(SMe_2)_3 + 4LiDTolF \xrightarrow{\text{THF}} Cl_2(\eta^2\text{-}DTolF)Ta(\mu\text{-}NTol)(\mu\text{-}\eta^2\text{-}HCNTol)Ta(\eta^2\text{-}DTolF)_2 + 3SMe_2 + 4LiCl \quad (3)$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**$\cdot C_7H_8$

Ta−Ta(A)	2.9411(7)	Ta−N(5)	2.008(6)
Ta−N(1)	2.255(8)	Ta−N(6)	1.85(2)
Ta−N(2)	2.175(8)	Ta−C(6)	2.04(1)
Ta−N(3)	2.157(8)	N(6)−C(6)	1.27(1)
Ta−N(4)	2.280(7)		
N(6)−Ta−N(5)	124.2(4)	N(2)−Ta−N(4)	87.3(3)
N(6)−Ta−C(6)	37.7(5)	N(1)−Ta−N(4)	76.0(3)
N(5)−Ta−C(6)	86.7(3)	N(6)−Ta−Ta(A)	81.4(4)
N(6)−Ta−N(3)	91.1(4)	N(5)−Ta−Ta(A)	42.9(2)
N(5)−Ta−N(3)	104.7(2)	C(6)−Ta−Ta(A)	43.8(3)
C(6)−Ta−N(3)	105.1(2)	N(3)−Ta−Ta(A)	110.7(2)
N(6)−Ta−N(2)	103.8(4)	N(2)−Ta−Ta(A)	110.3(2)
N(5)−Ta−N(2)	98.8(2)	N(1)−Ta−Ta(A)	154.1(3)
C(6)−Ta−N(2)	110.6(2)	N(4)−Ta−Ta(A)	129.3(2)
N(3)−Ta−N(2)	137.9(3)	C(6)−N(6)−C(61)	109(1)
N(6)−Ta−N(1)	78.6(5)	C(6)−N(6)−Ta	79.4(9)
N(5)−Ta−N(1)	153.6(3)	C(61)−N(6)−Ta	171(1)
C(6)−Ta−N(1)	114.1(4)	N(6A)−C(6)−N(6)	142(2)
N(3)−Ta−N(1)	86.1(3)	N(6A)−C(6)−Ta(A)	63.0(8)
N(2)−Ta−N(1)	59.6(3)	N(6)−C(6)−Ta(A)	155(1)
N(6)−Ta−N(4)	141.8(4)	N(6A)−C(6)−Ta	155(1)
N(5)−Ta−N(4)	88.7(2)	N(6)−C(6)−Ta	63.0(8)
C(6)−Ta−N(4)	161.9(2)	Ta(A)−C(6)−Ta	92.4(6)
N(3)−Ta−N(4)	59.3(3)		

[a] Names ending in "A" represent atoms generated by a 2-fold axis.

3 was obtained in high yield and good purity as indicated by NMR, which also showed that it is diamagnetic. Singlets at 8.88, 8.12, 8.06, and 7.80 ppm are assigned to three methine hydrogen signals of the chelating DPhF$^-$ ligands and the solitary hydrogen signal on the HCNTol group. A series of signals in the range 7.8−6.0 ppm are assigned to the aromatic hydrogen atoms of the tolyl groups, and a series of singlets in the range 2.3−1.9 ppm correspond to the hydrogen atoms of the methyl groups. The integration corresponds precisely to the calculated values. The presence of the hydrogen atom in the HCNTol group is probably a consequence of the absence of reducing agent in the reaction mixture which makes the elimination of the hydrogen atom unfeasible. It should be noted that if the hydrogen atom were not present in the HCNTol group, molecule **3** would be paramagnetic. The same would be true if the group were formimidoyl instead of isocyanide in **1** and **2**.

Structural Considerations. Selected bond distances and angles for **1** are presented in Table 2. Compound **1** crystallizes in the monoclinic space group $I2/a$. As shown in Figure 1, there is a crystallographic C_2 axis passing through the atoms C(54), C(51), N5 and the midpoint of the Ta−Ta bond. Each tantalum atom is chelated by two DPhF$^-$ ligands with Ta−N$_{DPhF}$ distances in the range 2.157(8)−2.280(7) Å. The tantalum atoms are bridged by a phenyl imido and a NCPh species. Although the Ta−Ta distance of 2.9411(7) Å is long, it is in the range observed for single metal−metal-bonded tantalum

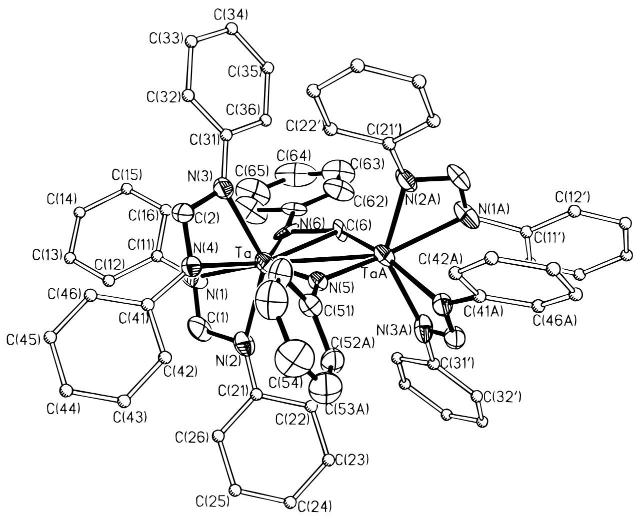

Figure 1. Drawing of the molecular structure of **1**. Only one of the two orientations of the CNPh group is shown. Names ending in "A" represent atoms generated by the 2-fold axis. Primed atoms are the second orientation of a disordered set. The 30% probability ellipsoids are shown for non-hydrogen atoms except for peripheral phenyl groups.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{2}\cdot 1.5C_6H_{14}$

Ta(1)−Ta(2)	2.7825(6)	Ta(2)−C(6)	1.949(7)
Ta(1)−N(2)	2.210(6)	Ta(2)−N(1)	2.221(6)
Ta(1)−N(4)	2.158(6)	Ta(2)−N(3)	2.214(6)
Ta(1)−N(5)	2.001(5)	Ta(2)−N(5)	1.974(6)
Ta(1)−N(6)	2.197(5)	Ta(2)−N(9)	2.353(6)
Ta(1)−N(7)	2.234(6)	Ta(2)−N(10)	2.196(6)
Ta(1)−N(8)	2.236(6)	N(6)−C(6)	1.305(9)
Ta(1)−C(6)	2.162(6)		
N(5)−Ta(1)−N(4)	86.1(2)	N(7)−Ta(1)−N(8)	59.5(2)
N(5)−Ta(1)−C(6)	89.4(2)	C(6)−Ta(2)−N(5)	96.7(2)
N(4)−Ta(1)−C(6)	87.4(2)	C(6)−Ta(2)−N(10)	105.4(2)
N(5)−Ta(1)−N(6)	124.2(2)	C(6)−Ta(2)−N(3)	89.8(2)
N(4)−Ta(1)−N(6)	92.3(2)	N(5)−Ta(2)−N(3)	82.2(2)
C(6)−Ta(1)−N(6)	34.8(2)	N(10)−Ta(2)−N(3)	92.8(2)
N(5)−Ta(1)−N(2)	87.5(2)	C(6)−Ta(2)−N(1)	87.7(2)
N(4)−Ta(1)−N(2)	169.1(2)	N(5)−Ta(2)−N(1)	86.2(2)
C(6)−Ta(1)−N(2)	83.7(2)	N(10)−Ta(2)−N(1)	99.4(2)
N(6)−Ta(1)−N(2)	84.0(2)	N(3)−Ta(2)−N(1)	167.8(2)
N(4)−Ta(1)−N(7)	90.8(2)	Ta(2)−N(5)−Ta(1)	88.9(2)
N(6)−Ta(1)−N(7)	89.1(2)	C(6)−N(6)−Ta(1)	71.1(4)
N(2)−Ta(1)−N(7)	99.4(2)	C(61)−N(6)−Ta(1)	132.9(4)
N(5)−Ta(1)−N(8)	88.6(2)	N(6)−C(6)−Ta(2)	158.8(5)
N(4)−Ta(1)−N(8)	101.6(2)	N(6)−C(6)−Ta(1)	74.1(4)
N(2)−Ta(1)−N(8)	87.1(2)	Ta(2)−C(6)−Ta(1)	85.0(2)

complexes.[4,6] The phenylimido group bridges the tantalum atoms symmetrically with a $\mathrm{Ta{-}N_{imido}}$ distance of 2.008(6) Å. The NCPh fragment is disordered about the crystallographic 2-fold axis. Although intensity statistics clearly indicated a centric distribution, refinement in the noncentrosymmetric space group *Ia* was performed. However, this lowering of the symmetry did not relieve the disorder problem encountered in the structural refinement. The carbon−nitrogen unit of the CNPh group bonds to the tantalum atoms in an edge-on mode, in which the nitrogen atom binds to only one tantalum atom but the carbon atom bridges both of them.

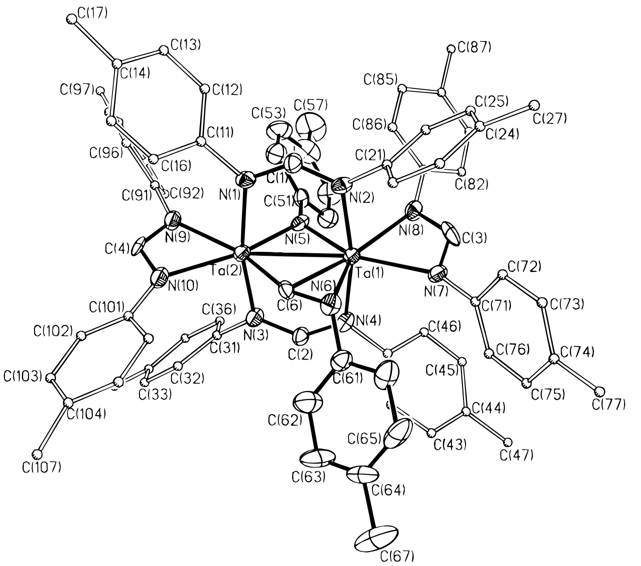

Figure 2. Drawing of the structure of **2** showing the atom numbering scheme. Atoms are represented by their 40% probability ellipsoids. The tolyl carbon atoms of the DTolF groups are shown as small spheres for clarity.

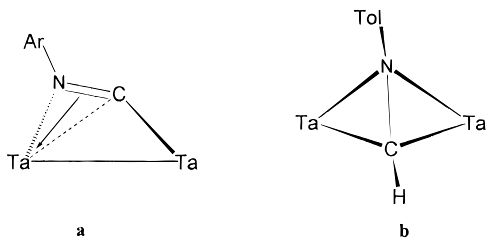

Figure 3. Schematic representation of the bonding of (a) the CNAr fragment to the ditantalum species in **1** and **2** and (b) the $[HCNTol]^{3-}$ in **3**.

Structural parameters for compound **2** are listed in Table 3. Figure 2 shows a perspective view of the molecule. Both chelating and bridging formamidinate ligands are present in this compound. The CNTol and NTol fragments are on general positions and are on different sides of the plane defined by nitrogen atoms of two bridging $DTolF^-$ ligands. The $\mathrm{Ta{-}N_{imido}}$ distances of 2.001(5) and 1.974(6) Å are essentially the same, but the $\mathrm{Ta{-}C_{CNTol}}$ bond distances are different. The longer $\mathrm{Ta{-}C_{CNTol}}$ distance of 2.162(6) Å is 0.2 Å longer than the shorter $\mathrm{Ta{-}C_{CNTol}}$ distance of 1.949(7) Å. The $\mathrm{Ta{-}N_{CNTol}}$ distance of 2.197(5) Å is in the range of $\mathrm{Ta{-}N_{DTolF}}$ single bond lengths. Finally, the asymmetric bonding of the NCTol species to the tantalum atoms can be visualized by considering that the C_{CNTol} atom forms a σ bond with one tantalum atom and bridges to the other one through a donation of π-bonding electrons to the other tantalum atom, as shown in Figure 3a. The bonding of the N−C unit to one tantalum atom should be weaker than the $\mathrm{Ta{-}C_{CNTol}}$ σ bond to the other one. Donation of π-bonding electrons to the metal orbitals also weakens the $\mathrm{C{-}N_{CNTol}}$ double bond, which would account for the C−N distance of 1.305(9) Å observed for the CNTol fragment in **2** being slightly longer than a *normal* C−N double bond. Consequently the ArNC species is probably better described as the corresponding dianion. It should be pointed out that this is consistent with other structural and spectroscopic data. The tetravalent tantalum atoms would possess a single bond between them as indicated by the Ta−Ta distance of 2.7825(6) Å, which is at the short end of the range of single Ta−Ta bonds,[4,5] but this shortness is probably be due to the presence of bridging formamidinate ligands. Another crystalline polymorph of this same compound was isolated, $\mathbf{2}\cdot C_6H_{14}\cdot C_7H_8$, and its structure solved, the only essential difference being the identity of the interstitial solvent. The dimensions of the metal complex are essentially identical to those in $\mathbf{2}\cdot 1.5C_6H_{14}$.[15]

The similarity in the synthetic procedure, the diamagnetism, as well as in the distances and angles in the CNAryl group in **1** and **2** to those found in the compound obtained from the reaction of $Ta_2Cl_6(SMe_2)_3$, LiDTolF, dmpm, and Zn metal[6]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ta(1)−N(8)	2.056(6)	Ta(2)−C(7)	2.073(9)
Ta(1)−N(7)	2.101(6)	Ta(2)−N(7)	2.159(6)
Ta(1)−C(7)	2.152(8)	Ta(2)−N(4)	2.175(6)
Ta(1)−N(1)	2.159(6)	Ta(2)−N(3)	2.186(6)
Ta(1)−N(2)	2.169(6)	Ta(2)−N(5)	2.197(6)
Ta(1)−Cl(2)	2.395(2)	Ta(2)−N(6)	2.230(6)
Ta(1)−Cl(1)	2.418(2)	N(7)−C(7)	1.43(1)
Ta(1)−Ta(2)	3.0025(6)	C(7)−H(7)	0.81(6)
Ta(2)−N(8)	1.959(6)		

N(8)−Ta(1)−N(7)	82.4(2)	C(7)−Ta(2)−N(7)	39.3(3)
N(8)−Ta(1)−C(7)	81.6(3)	N(8)−Ta(2)−N(4)	107.0(2)
N(7)−Ta(1)−C(7)	39.2(3)	C(7)−Ta(2)−N(4)	92.4(3)
N(8)−Ta(1)−N(1)	92.7(2)	N(8)−Ta(2)−N(3)	92.9(2)
C(7)−Ta(1)−N(1)	86.4(3)	N(4)−Ta(2)−N(3)	60.9(2)
N(8)−Ta(1)−N(2)	86.4(2)	N(8)−Ta(2)−N(5)	105.8(2)
N(7)−Ta(1)−N(2)	167.5(3)	N(7)−Ta(2)−N(5)	86.7(2)
N(1)−Ta(1)−N(2)	60.3(2)	N(3)−Ta(2)−N(5)	83.8(2)
N(7)−Ta(1)−Cl(2)	93.4(2)	C(7)−Ta(2)−N(6)	95.9(3)
C(7)−Ta(1)−Cl(2)	93.8(2)	N(7)−Ta(2)−N(6)	87.6(2)
N(1)−Ta(1)−Cl(2)	87.9(2)	N(4)−Ta(2)−N(6)	89.6(2)
N(2)−Ta(1)−Cl(2)	98.0(2)	N(3)−Ta(2)−N(6)	93.3(2)
N(8)−Ta(1)−Cl(1)	93.8(2)	N(5)−Ta(2)−N(6)	59.5(2)
N(7)−Ta(1)−Cl(1)	88.9(2)	C(7)−N(7)−C(71)	129.0(7)
N(2)−Ta(1)−Cl(1)	86.4(2)	Ta(1)−C(7)−Ta(2)	90.6(4)
Cl(2)−Ta(1)−Cl(1)	88.31(8)	Ta(1)−N(7)−Ta(2)	89.6(2)
N(8)−Ta(2)−C(7)	85.9(3)	Ta(1)−N(8)−Ta(2)	96.8(3)
N(8)−Ta(2)−N(7)	83.3(2)	H(7)−C(7)−N(7)	118(5)

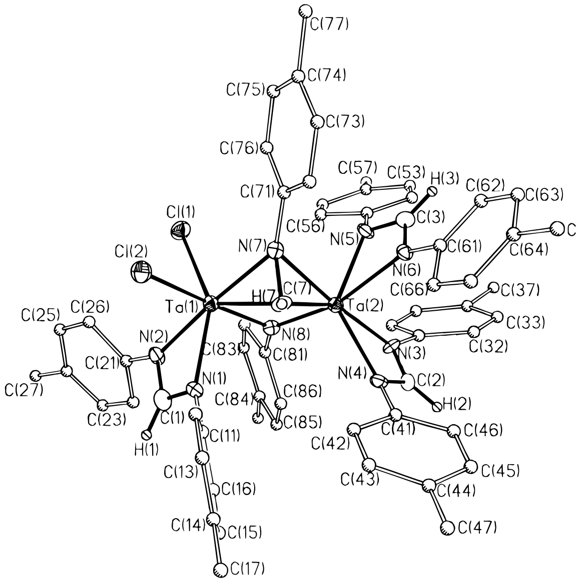

Figure 4. Drawing of the molecular structure of **3**. Tolyl carbon atoms are shown as spheres, and other non-hydrogen atoms are represented by their 30% probability ellipsoids.

means that this previously reported compound should probably be described as (dmpm)Cl_2Ta(μ-NTol)(μ-η^2-CNTol)(μ-dmpm)-TaCl(DTolF), i.e. having no hydrogen atom on the CNTol fragment.

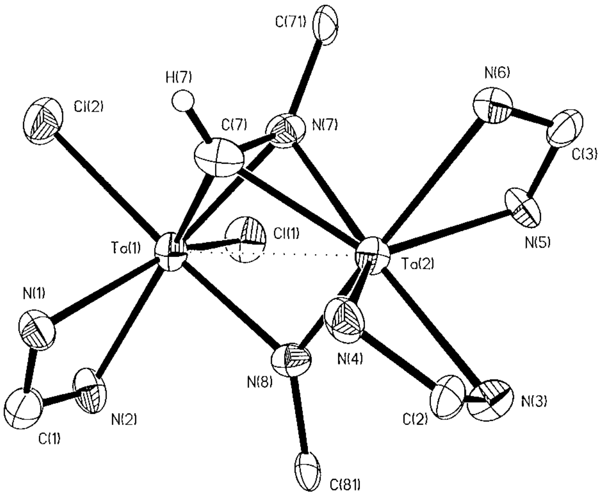

Figure 5. Thermal ellipsoid plot of the core of the structure of **3**. Non-hydrogen atoms are represented by their 30% probability ellipsoids.

Important bond distances and angles for compound **3** are presented in Table 4. The structure is quite different from those discussed earlier, as shown in Figures 3(b) and 4. The coordination about the tantalum atoms differs. One of them is coordinated by two chelating $DTolF^-$ ligands, while the other one is bonded to one chelating $DTolF^-$ and two Cl^- ligands. The Ta−Cl distances of 2.398(2) to 2.417(2) Å are normal for a Ta^V−Cl bond.[5,6] Although the tantalum atoms have quite different coordination environments, they are bridged by both tolylimido and tolylformimidoyl fragments in an essentially symmetrical bonding mode, as shown more clearly in Figure 5. The most significant difference in the structure of compound **3** from those discussed earlier is the presence of a $HCNTol^-$ anion in which both carbon and nitrogen atoms in the C−N unit are connected to two tantalum atoms in a side-on η^2,η^2 bridging fashion, while in the previously discussed compounds the CNAryl unit was in an edge-on η^2,η^1 bridging mode (Figure 3). A signal for the hydrogen atom in the HCNTol group was observed in the ^{1}H NMR spectrum (vide supra) which also showed that compound **3** is diamagnetic. In order to have an even number of electrons in the molecule, the hydrogen atom in the HCNTol group is required. The Ta−C_{HCNTol} distances of 2.152(8) and 2.073(9) Å differ only by 0.08 Å, and the Ta−N_{HCNTol} distances of 2.101(6) and 2.159(6) Å are also very similar to each other. The very long Ta−Ta separation of 3.0025(3) Å argues against any significant metal to metal interaction. Another important difference observed is that the C−N_{HCNTol} bond distance of 1.43(1) Å is longer than in the CNTol groups of compounds **1** and **2**. It is in the range for a C−N single bond. As a formal extreme, the bonding could be formulated as a kind of four membered metallo-C,N-butterfly ring involving two (2c,2e) Ta−C bonds and two (2c,2e) Ta−N bonds in addition to an N−C single bond (Figure 3b). The HCNTol fragment is thus formulated as $[H-C-NTol]^{3-}$ which bridges the Ta^V_2 unit in a symmetrical mode. From this point of view, the reaction of LiDTolF with $Ta_2Cl_6(SMe_2)_3$ is an oxidative addition reaction promoted by a metal−metal double bond.[16] During the reaction, electrons used in metal−metal bonding in $Ta_2Cl_6(SMe_2)_3$ are transferred to form metal to nitrogen and metal to carbon bonds. Cleavage of a C−N bond of a formamidinate ligand occurs along with the breaking of a Ta═Ta bond. Splitting of other types of C−N bonds has precedent in the coordination chemistry of tantalum.[17]

These reactions recall the reaction in which $Ta_2Cl_6(SMe_2)_3$ reacted with a N═N doubly bonded azobenzene compound to give $[TaCl_2(SMe_2)(NPh)_2]_2(\mu\text{-}Cl)_2$. This complex was regarded

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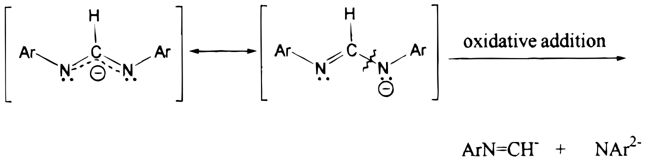
(15) Crystals of **2**·C_6H_{14}·C_7H_8 are triclinic, space group $P\bar{1}$, a =15.476(3) Å, b = 16.385(2) Å, c = 17.611(4) Å, α = 75.41(3)°, β = 78.050(9)°, δ = 81.81(2)°, V = 4209(1) $Å^3$, Z = 2. A model containing 811 parameters was refined against 9052 unique data to converge with R1 = 0.051, wR2 = 0.140, and GOF = 1.06.

(16) Scioly, A. J.; Luetkens, M. L., Jr.; Wilson, R. B., Jr.; Huffman, J. C.; Sattelberger, A. P. *Polyhedron* **1987**, 741.

(17) Gray, S. D.; Smith, D. P.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1992**, *114*, 5462 and references therein.

Scheme 3



as the product of an inorganic double bond metathesis in which Ta═Ta and N═N bonds reacted to furnish two Ta═N bonds.[18]

Concluding Remarks. Three complexes which resulted from a C−N bond cleavage of formamidinate groups have been structurally characterized. These C−N bond cleavage reactions show a pattern as depicted in Scheme 3.

We initially thought that the cleavage of the formamidinate anions was due to the presence of the strong reducing agents in the reaction, but a reaction done in the absence of such agents also cleaves the C−N bond. The appearance of arylimido and formally trivalent $[ArNCH]^{3-}$ groups in compound **3**, which is obtained in large yields, along with the absence of the hydrogen atom of the ArNCH group in compounds **1** and **2** probably indicates that the reducing agent plays a role in the elimination of the hydrogen atom of the HCNAr group. It is likely that the formamidinate ligands are oxidatively adding to the Ta(III)−Ta(III) bond before, during, or in the absence of any reduction.

The important conclusion we draw from the results reported here is that it is very unlikely that a Ta_2(formamidinate)$_4$ species can be formed by reducing ditantalum compounds in high oxidation states in the presence of formamidinate ligands. Other means must be explored, and we are currently doing so.

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Supporting Information Available: Drawings of **1**, **2**, and **3** showing all anisotropic ellipsoids (3 pages). Three X-ray crystallographic files, in CIF format, are available. Access and/or ordering information is given on any current masthead page.

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(18) Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. W. *Polyhedron* **1986**, *5*, 895.