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N$_2$ Functionalization

Carbon–Nitrogen Bond Formation by the Reaction of 1,2-Cumulenes with a Ditantalum Complex Containing Side-On- and End-On-Bound Dinitrogen**

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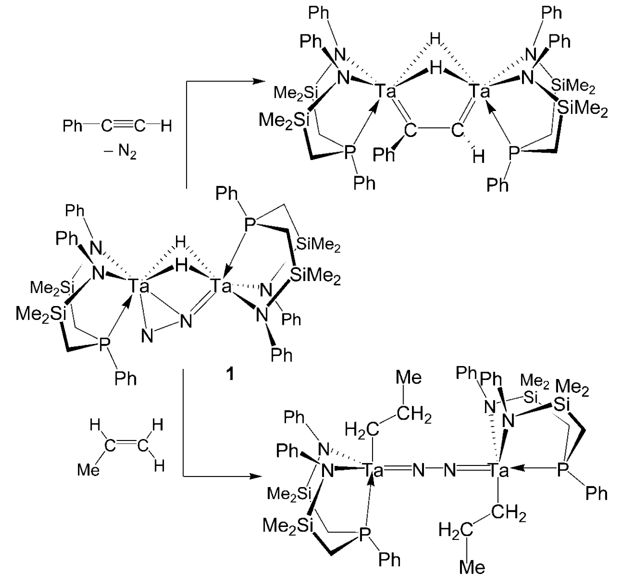
Synthetic ammonia serves as the key precursor for the synthesis of many nitrogen-containing chemicals and is produced by the Haber–Bosch process on the 100 million ton scale annually.[1] Given the energy-intensive nature of this reaction, there is considerable interest in the search for alternative methods to generate nitrogen-containing molecules directly from N_2.[2] One approach towards this goal is the functionalization of coordinated dinitrogen to form new nitrogen–carbon bonds. Typically, reagents such as alkyl halides or triflates can be employed for this purpose.[3] A major drawback of those conversions is the formation of inorganic salts or transition metal halides as byproducts, rendering these reactions atom-inefficient. However, concerted addition reactions that involve the activated dinitrogen unit and substrates with C–X double or triple bonds (X = C, N, O, S) could potentially lead to catalytic cycles for the production of nitrogen-containing heterocycles without any waste products. Unfortunately, only a very few stoichiometric cycloadditions at coordinated N_2 units have been discovered to date.[4] In all cases, highly activated side-on bridging η^2:η^2-N_2 complexes of Group 4 metals have been employed to achieve the desired nitrogen–carbon bond formations by reaction with arylalkynes,[4a] isocyanates,[4b] carbon dioxide,[4c,d] or carbon monoxide[4e] (via migratory insertion). The question we posed was: Could a Group 5 ditantalum dinitrogen complex with the side-on/end-on coordination mode engage in cycloaddition-type processes?

Our initial attempts to try atom-efficient cycloaddition-type chemistry with the previously reported side-on end-on bound dinitrogen in $[\{(NPN)Ta\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^1\text{-}N_2)]$ (**1**; NPN = $PhP(CH_2SiMe_2NPh)_2$)[3d] led to a different behavior. For example, with phenyl acetylene and simple alkenes such as propene, we observed displacement of the N_2 unit or migratory insertion reactions into the tantalum hydrides, respectively (Scheme 1).[3d,5] In contrast, a variety of E–H hydride reagents (EH = R_2BH, R_2AlH, $RSiH_3$) have been shown to add across the side-on/end-on N_2 unit of **1** to generate new functionalized nitrogen fragments and the formation of terminal Ta–H bonds.[6] As these E–H additions can be considered to be additions across a quasi-Ta–N multiple bond,[3d,7] we continued our search for other reagents that could engage in [2+2] chemistry with the side-on/end-on η^2:η^1-N_2 moiety. Herein, we report our studies on the reaction of 1,2-cumulenes of the type X=C=Y (X, Y = NR, O, S) with the dinitrogen complex **1**.



Scheme 1. Reactivity of **1** towards C–C double and triple bonds.

Owing to its low cost and its recent successful application in dinitrogen functionalization with Group 4 metals,[4c,d] CO_2 was chosen as a substrate for preliminary experiments. Parent dinitrogen complex **1** reacts instantaneously with carbon dioxide, but yields intractable solids that have so far resisted characterization. However, the bis(*N*-phenylimino) analogue of CO_2, *N*,*N*′-diphenyl carbodiimide, reacts cleanly with one equivalent of **1** to give **2** as a single product in 70% isolated yield (Scheme 2).[8]

Complex **2** gives rise to two doublets ($^4J_{P,P} = 16.0$ Hz) at $\delta = 3.0$ and 8.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum, verifying that it is an unsymmetrical dinuclear species. Along with a fairly crowded aromatic region and a complicated pattern for the methylene protons, eight resonances for the silyl methyl groups and two signals for the bridging hydrides (at $\delta = 11.9$ and 12.1 ppm) are observed in the proton NMR spectrum. The latter signals show complex splitting patterns, as both

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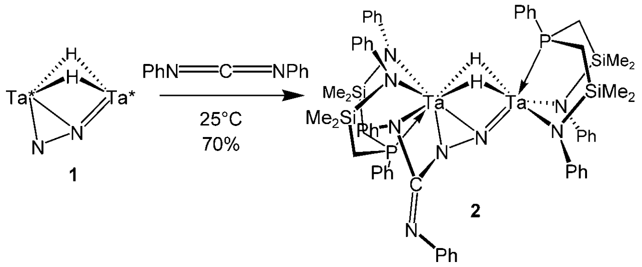


Scheme 2. Reaction of **1** with *N*,*N'*-diphenylcarbodiimide. Ta* = (NPN)Ta, NPN = PhP(CH$_2$SiMe$_2$NPh)$_2$.

hydrides are coupled to each other and to two chemically inequivalent ^{31}P nuclei. In the ^{1}H{^{31}P} NMR spectrum, the hydride signals collapse into two well-resolved doublets ($^{2}J_{H,H} = 13.5$ Hz), which is consistent with a structure that has C_1 symmetry.

X-ray-quality single crystals of **2** were grown from THF/hexanes at −40 °C over several weeks. The refined molecular structure (see Figure 1) is in agreement with the NMR data, although the hydrides could not be located in the diffraction pattern (they were modeled with XHydex instead). What is evident from the single-crystal X-ray structure is that the nitrogen–nitrogen bond is still intact and that the carbodiimide has reacted with the side-on site of the Ta$_2$N$_2$ core (Ta1−N6). The reaction can be categorized as [2+2] cycloaddition between the carbodiimide and the Ta1−N6 bond in **1**. It should be noted that the plane through Ta2-N5-N6-Ta1 is roughly perpendicular to the plane through Ta1-N6-C1-N7, with an angle of 76.73(5)° between the normal vectors of both planes. Therefore, **2a** is a chiral molecule, with both symmetry-related enantiomers present in the unit cell (achiral space group *C*2/*c*). Compared to **1**, only a slight increase in the nitrogen–nitrogen bond length and the Ta1⋯Ta2 distance is observed (**1**: N5−N6 1.319(4), Ta1⋯Ta2 2.830(4) Å; **2**: N5−N6 1.364(8), Ta1⋯Ta2 2.8418(4) Å).

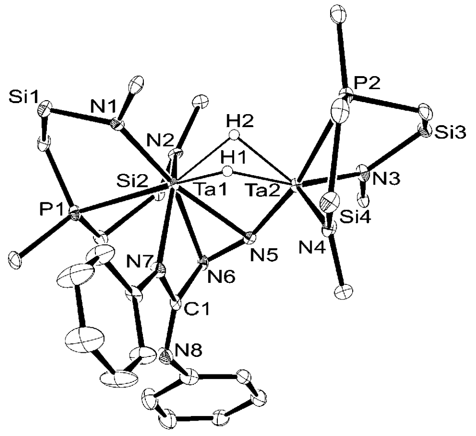
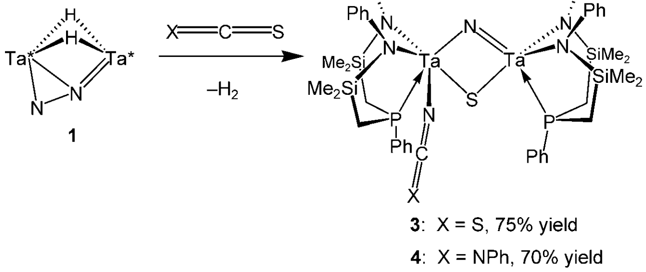


Figure 1. The molecular structure of **2** (ellipsoids set at 30% probability). Silyl methyl groups and carbon atoms of ligand N,P-phenyl rings (except ipso positions) are omitted for clarity. The bridging hydrides were modeled using XHydex (Ta−H ca. 1.83 Å, Ta-H-Ta ca. 102°). Selected bond lengths [Å] and angles [°]: Ta1⋯Ta2 2.8418(4), Ta1−N5 2.213(6), Ta2−N5 1.856(6), Ta1−N6 2.227(6), Ta1−N7 2.187(6), N5−N6 1.364(8), C1−N6 1.475(9), C1−N7 1.357(10), C1−N8 1.288(10); Ta1-N5-Ta2 88.1(2), Ta1-N5-N6 71.6(4), C1-N6-N5 108.7(5), N6-C1-N7 106.8(6), N6-C1-N8 123.8(7), N7-C1-N8 129.1(7).

As found in the E−H additions across the Ta−N bond of **1**, N−N bond cleavage can be induced by elimination of H$_2$, which provides the required two additional electrons for this process. Attempts to induce reductive elimination of molecular H$_2$ from **2** by heating under static vacuum or exposure to UV light were unsuccessful as evidenced by ^{31}P NMR spectroscopy, which showed only unreacted **2** under a variety of conditions.

We expanded the substrates to another analogue of CO$_2$, carbon disulfide. When a −40 °C solution of **1** was treated with CS$_2$, a new product (**3**) formed cleanly and was isolated as yellow powder in 75 % yield.[9] Single crystals suitable for X-ray diffraction were grown at room temperature by diffusion of pentane into a concentrated solution in benzene. The obtained molecular structure revealed the identity of **3** (Scheme 3 and Figure 2) as a dinuclear compound with one bridging sulfide and one bridging nitride. The Ta$_2$NS diamond core in this arrangement is a slightly distorted butterfly fold with a dihedral angle Ta2-N5-Ta1-S1 of 14.473(8)°. Both tantalum–nitride bond lengths are nearly identical (1.88±0.02 Å), and a significant difference between both



3: X = S, 75% yield
4: X = NPh, 70% yield

Scheme 3. Synthesis of **3** and **4** by the reaction of **1** with carbon disulfide and phenyl isothiocyanate, respectively.

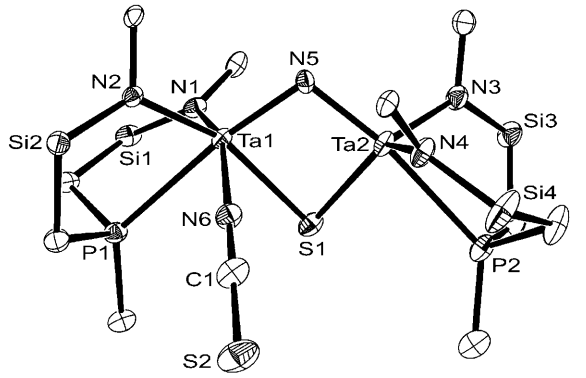
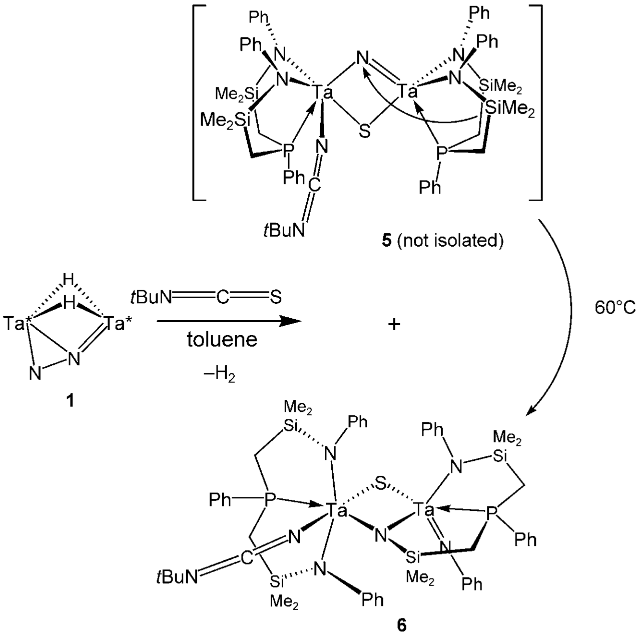


Figure 2. The molecular structure of **3** (ellipsoids set at 30% probability). Silyl methyl groups and carbon atoms of ligand N,P-phenyl rings (except ipso positions) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta1⋯Ta2 3.023(5), Ta1−N5 1.894(5), Ta2−N5 1.864(5), Ta1−S1 2.5038(17), Ta2−S1 2.3168(18), Ta1−N6 2.190(5), N6−C1 1.167(8), C1−S2 1.602(7); Ta1-S1-Ta2 77.57(5), Ta1-N5-Ta2 107.1(2), Ta1-N6-C1 165.4(5), N6-C1-S2 179.5(7).

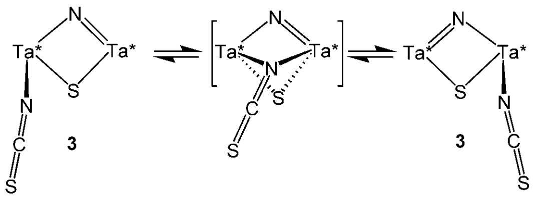
tantalum–sulfide bonds (Ta1−S1 2.5038(17), Ta2−S1 2.3168(18) Å) is noticeable.

The most important information from this crystal structure is the observation that the N−N bond in **1** has been cleaved to furnish the bridging nitride (N5) and a terminal isothiocyanate ligand bound through N6. The latter moiety is almost linear at C1 and N6 (N6-C1-S2 179.5(7)°, Ta1-N6-C1 165.4(5)°) and oriented *trans* to one silylamido nitrogen atom of the NPN ligand. Thus, Ta1 is six-coordinate in the solid state, whereas Ta2 is only five-coordinate, with the coordination polyhedra best described as distorted octahedral and trigonal bipyramidal, respectively.

At room temperature and at −80 °C, solutions of **3** in $[D_8]$toluene exhibit only a singlet at $\delta = -2.7$ ppm in the $^{31}P\{^1H\}$ NMR spectrum, which is not consistent with the solid-state structure of **3**, wherein the {(NPN)Ta} units are inequivalent. Thus, a highly fluxional process that renders both {(NPN)Ta} fragments indistinguishable needs to be invoked. In agreement with the $^{31}P\{^1H\}$ NMR data, four resonances for the silyl methyl groups are observed in the ^1H NMR spectrum. These observations are consistent with an averaged C_s symmetry, indicating that the thiocyanato ligand exchanges rapidly between both tantalum centers (Scheme 4) via a bridging mode reminiscent of a bridging azido moiety.[10]



Scheme 5. Formation of **5** and **6**. Subsequent heating converts **5** into the isolated product **6**.



Scheme 4. Rapid migration (on the NMR timescale) of the thiocyanato ligand in **3** between the two Ta* units upon dissolution.

Solutions of **1** are also reactive towards hetero-1,2-cumulenes, such as carbonyl sulfide (O=C=S), phenyl isocyanate (PhN=C=O), and phenyl isothiocyanate (PhN=C=S). However, similar to that observed for CO_2 the oxygen-containing substrates generated a number of inseparable products and some insoluble materials. Fortunately, the non-oxygen-containing substrate PhN=C=S reacted cleanly to produce **4** as a single product in 70 % isolated yield (Scheme 3). Single crystals of **4** were grown from toluene/hexanes at −40 °C and subjected to X-ray diffraction. The molecular structure of **4** (see the Supporting Information) closely resembles the product **3**, and essential metrical parameters match each other closely. The phenylcyanamido ligand in **4** is almost linear and oriented *trans* to one of the silylamido nitrogen atoms. Similar to **3**, complound **4** is dynamic in solution, and only a single resonance at $\delta = -6.5$ ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum. Even though the NCS and PhNCN ligands of **3** and **4** exhibit this dynamic behavior, we have been unable to remove them from the coordination sphere by further reaction with silyl halides or azides.

That the bridging nitrides mentioned above can actually undergo N−Si bond formations became evident when **1** was reacted with *tert*-butyl isothiocyanate. Monitoring this reaction by $^{31}P\{^1H\}$ NMR spectroscopy revealed that two products, namely **5** (singlet at $\delta = -6.8$ ppm) and **6** (two doublets at $\delta = 10.0$ and 20.7 ppm; $^4J_{P,P} = 37.0$ Hz) formed simultaneously even at low conversions. Upon heating to 60 °C, **5** is converted into **6**, which can then be isolated in 55 % yield (Scheme 5). During this transformation a silylamido bond is cleaved and a terminal *N*-phenylimino fragment is generated at one of the tantalum sites. Such ligand rearrangements involving the labile N−Si bond have been observed previously by us.[6c] At this point it is not clear why the bulky *tert*-butyl group promotes this amide-to-nitride silyl migration.

^1H, ^{13}C, and ^{15}N NMR spectra agree well with the molecular structure of **6**, which could be ascertained by X-ray crystallography (Figure 3). Owing to the rearrangement process, a pronounced asymmetry is found in the molecular structure of **6**, which also affects the structural parameters within the Ta_2SN core. Thus, not only the Ta−S1 but also the Ta−N5 bond lengths are significantly different (Ta1−S1 2.5609(7), Ta2−S2 2.3411(7), Ta1−N5 1.968(2), Ta2−N5 2.107(2) Å). The phenylimino fragment that is bound to Ta2 occupies the apical position square-pyramidal coordination polyhedron of the latter tantalum center. The geometry at the second tantalum atom (Ta1) is best described as distorted octahedral with an intact NPN ligand bound in a meridional fashion. The terminal *tert*-butyl cyanamide that is *trans* to the bridging sulfide is nearly linear at the tantalum-bound nitrogen atom (Ta1-N6-C1 177.8(3)°).

A possible mechanism for the formation of **3**–**5** is given in Scheme 6. Based on the observed reactivity of **1** with PhN=C=NPh to generate **2**, we propose that S=C=S and RN=C=S units initially undergo a [2+2] cycloaddition with the exposed terminal nitrogen–tantalum bond of the side-on N_2 unit to generate intermediate **A**. In the next step, reductive

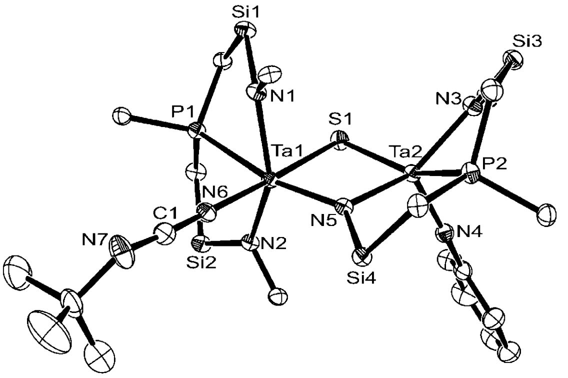
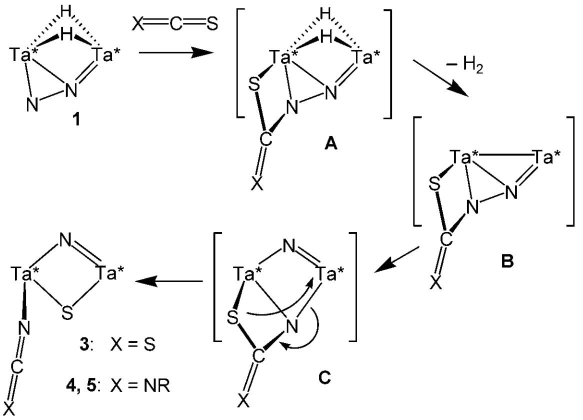


Figure 3. The molecular structure of **6** (ellipsoids set at 30% probability). Silyl methyl groups and carbon atoms of ligand N,P-phenyl rings (except ipso positions) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ta1···Ta2 3.2548(3), Ta1–S1 2.5609(7), Ta2–S2 2.3411(7), Ta1–N5 1.968(2), Ta2–N5 2.107(2), Ta1–N6 2.013(2), Ta2–N4 1.789(2), N5–Si4 1.749(2), N6–C1 1.204(4), C1–N7 1.220(4); Ta1-S1-Ta2 83.08(2), Ta1-N5-Ta2 105.96(9), Ta1-N5-Si4 134.44(12), Si4-N5-Ta2 119.43(12), Ta1-N6-C1 177.8(2), N6-C1-N7 172.8(3).



Scheme 6. Proposed mechanism for the formation of **3**, **4**, and **5**.

elimination of dihydrogen gives rise to a transient Ta^{IV}–Ta^{IV} species (**B**),[6] which in turn undergoes N–N bond cleavage to produce dinuclear **C**. Consecutive cleavage of the C–S bond and one Ta–N bond in the latter moiety produces the observed products **3**, **4** and **5** (see above).

What emerges from our work at this point is that side-on/end-on bound dinitrogen can undergo cycloadditions with cumulated C=X double bonds to generate new carbon–nitrogen bonds. Nevertheless, only the terminal nitrogen atom of the side-on N_2 moiety reacted in the present case. It was also demonstrated that carbodiimides, carbon disulfide, and isothiocyanates are suitable reagents for N_2 functionalization reactions, as isolable products were produced, whereas more established substrates (carbon dioxide and isocyanates) failed to react cleanly.

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Keywords: C–N bond formation · cumulenes · cycloadditions · dinitrogen · tantalum

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[8] An analogous reactivity is observed with *N,N'*-dicyclohexylcarbodiimide; the product of this transformation, however, was resistant to purification. In the case of *N,N'*-bis(*tert*-butyl)carbodiimide, no reaction was observed, even at elevated temperatures.

[9] If the temperature of this addition is too high, N_2 is released and a different product is formed that involved C–S bond cleavage: J. Ballmann, A. Yeo, B. A. MacKay, S. van Rijt, B. O. Patrick, M. D. Fryzuk, *Chem. Commun.* **2010**, *46*, 8794–8796.

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