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Thiolato Dinitrogen (or Hydrazido(4–)) Complexes, $[Ta(SAr)_3(THF)]_2(\mu\text{-}N_2)$ (Ar = 2,6-C_6H_3-*i*-Pr_2, 2,4,6-C_6H_2-*i*-Pr_3), and Phenoxide Analogues. Structural Comparison of $[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ and $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$

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$[TaCl_3(THF)_2]_2(\mu\text{-}N_2)$ reacts with 6 equiv of LiDIPP (DIPP = O-2,6-C_6H_3-*i*-Pr_2) to give $[Ta(DIPP)_3(THF)]_2(\mu\text{-}N_2)$ (**1**) in 60% isolated yield. Crystals of $[Ta(DIPP)_3(THF)]_2(\mu\text{-}N_2)$ belong to the space group *C*2/*c* with *a* = 20.276 (8) Å, *b* = 16.737 (7) Å, *c* = 28.227 (19) Å, *β* = 105.55 (5)°, *V* = 9228 Å^3, and *Z* = 4. The structure contains a hydrazido(4–) μ-N_2 ligand with N–N = 1.32 (1) Å, Ta–N = 1.796 (5) Å, and Ta–N–N = 176.6 (6)°. The μ-N_2 ligand is bound to the metal in an equatorial position of a trigonal bipyramid. $[Ta(TIPT)_3(THF)]_2(\mu\text{-}N_2)$ (**3**; TIPT = S-2,4,6-C_6H_2-*i*-Pr_3) and $[Ta(DIPT)_3(THF)]_2(\mu\text{-}N_2)$ (**4**; DIPT = S-2,6-C_6H_3-*i*-Pr_2) can be prepared analogously in high yield. Crystals of $[Ta(DIPT)_3(THF)]_2(\mu\text{-}N_2)$ (**4**) belong to the space group *Pc*2$_1$*n* with *a* = 13.606 (6) Å, *b* = 23.096 (9) Å, *c* = 28.845 (10) Å, *V* = 9064.5 Å^3, and *Z* = 4. In this relatively poor quality structure N–N = 1.29 (6) Å, Ta–N = 1.90 (6) and 1.72 (6) Å, and Ta–N–N = 166 (5)°. In this case the μ-N_2 ligand is bound in an axial position trans to THF in a trigonal-bipyramidal ligand arrangement about each metal. Neither **1** nor **3** can be prepared by treating $Ta(CHCMe_3)(DIPP)_3(THF)$ or $Ta(CHCMe_3)(TIPT)_3(THF)$ with benzaldehyde azine. **1** reacts readily with benzaldehyde to give benzaldehyde azine in high yield, while **3** gives only ~25% benzaldehyde azine.

Introduction

In spite of the fact that hundreds of dinitrogen complexes are now known,[1] complexes that contain an anionic sulfur ligand are rare. To our knowledge the only reported examples are diethyldithiocarbamate complexes of the type $[M(S_2CNEt_2)_3]_2(\mu\text{-}N_2)$ (M = Nb, Ta)[2a] and complexes of the type *mer*-$[Re(L)(N_2)(PMe_2Ph)_3]$ where L = S_2COEt, S_2PPh_2, or S_2CNR_2.[2b] This is ironic since the molybdenum in nitrogenase, to which dinitrogen possibly binds in order to be reduced, is likely to have sulfur in its coordination sphere.[3] Therefore, it is important to demonstrate that dinitrogen can be found in complexes that contain other types of sulfur ligands (e.g., thiolates) and to structurally characterize such species.

A logical starting point for preparing μ-dinitrogen complexes that contain anionic ligands are complexes of the type $[MCl_3(THF)_2]_2(\mu\text{-}N_2)$ (M = Nb, Ta).[2a,4] The reason is that dithiocarbamate derivatives have been prepared from them[2a] (as noted above), the chlorides in $[TaCl_3(THF)_2]_2(\mu\text{-}N_2)$ have been substituted by *tert*-butoxide ligands to give $[Ta(OCMe_3)_3(THF)]_2(\mu\text{-}N_2)$,[4] and $[Nb(CH_2CMe_3)_3(THF)]_2(\mu\text{-}N_2)$ has been prepared by adding $Mg(CH_2CMe_3)_2$(dioxane) to $[NbCl_3(THF)_2]_2(\mu\text{-}N_2)$.[4] We chose tantalum over niobium in the belief that in circumstances where complexes might be only marginally stable toward loss of dinitrogen, what can be called a ditantalum(5+) hydrazido(4–) complex would be more stable than an analogous niobium complex to "reduction" of the metal to the 3+ oxidation state. We report here the preparation and structural characterization of complexes of the general type $[Ta(XR)_3(THF)]_2(\mu\text{-}N_2)$ where XR is a bulky benzenethiolate or an analogous bulky phenoxide ligand.

Table I. Relevant Bond Distances (Å) and Angles (deg) in $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (**1**)

Ta–N	1.796 (5)	N–Ta–O(1)	108.7 (2)
Ta–O(1)	1.911 (5)	N–Ta–O(2)	109.8 (2)
Ta–O(2)	1.945 (5)	N–Ta–O(3)	109.4 (2)
Ta–O(3)	1.933 (5)	N–Ta–O(4)	91.0 (2)
Ta–O(4)	2.232 (5)	O(1)–Ta–O(3)	93.3 (2)
N–N	1.32 (1)	O(1)–Ta–O(2)	91.6 (2)
Ta–O(1)–C(101)	175.2 (5)	O(1)–Ta–O(4)	160.2 (2)
Ta–O(2)–C(201)	147.2 (4)	O(2)–Ta–O(3)	136.5 (2)
Ta–O(3)–C(301)	160.1 (5)	O(2)–Ta–O(4)	81.5 (2)
Ta–N–N	176.6 (6)	O(3)–Ta–O(4)	79.6 (2)

Results and Discussion

Preparation and Crystal Structure of $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (1). Addition of 6 equiv of lithium 2,6-diisopropylphenoxide to $[TaCl_3(THF)_2]_2(\mu\text{-}N_2)$ in a mixture of ether and THF gives $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (**1**) in ~60% isolated yield as yellow crystals (eq 1). Coordinated THF

$$[TaCl_3(THF)_2]_2(\mu\text{-}N_2) + 6LiDIPP \rightarrow [Ta(DIPP)_3(THF)]_2(\mu\text{-}N_2) \quad (1)$$

$$DIPP = O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$$

exchanges rapidly on the ^1H NMR time scale with free THF in C_6D_6 (according to NMR spectra). Since **1** is so crowded, we assume that THF exchanges in a dissociative manner. All DIPP ligands are equivalent and freely rotating at 25 °C, where intermediate pseudotetrahedral species presumably form. Although **1** did not analyze well (because of THF lability; see Experimental Section), a pyridine adduct could be prepared straightforwardly and did analyze satisfactorily.

X-ray data were collected on a crystal of **1** at –140 °C (see Experimental Section). Three drawings of the structure are shown in Figure 1. Relevant bond distances and angles can be found in Table I.

The molecule has a crystallographically required 2-fold axis that passes through the N–N bond. The configuration about the metal at each end of the molecule is best viewed as a distorted trigonal bipyramid (according to the interligand angles), with the THF ligand (O(4)) and one of the phenoxide ligands (O(1)) being in axial positions. The trigonal-bipyramidal description is also attractive from the point of view of the large Ta–O(1)–C(101) angle of 175.2 (5)° and slightly shorter Ta–O(1) bond length (compared to Ta–O(2) and Ta–O(3)), as if that phenoxide were in a position significantly different (electronically and sterically) compared to the other two.

There is no evidence that replacing chlorides by phenoxide ligands significantly alters the Ta═N—N═Ta core; i.e., the N–N

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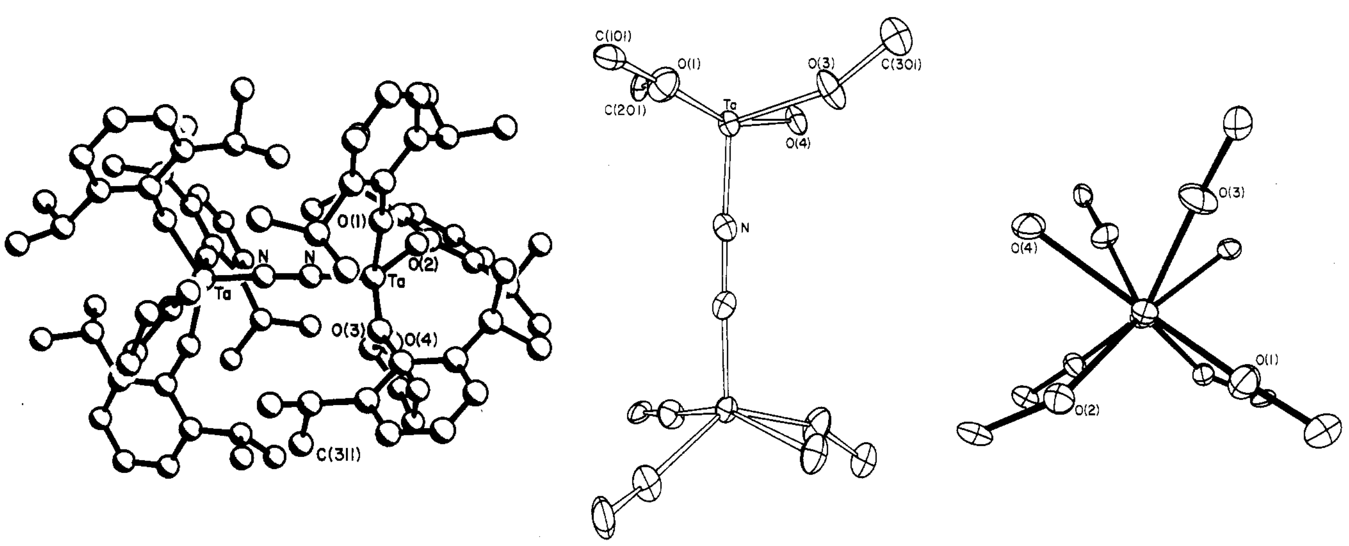

Figure 1. Views of $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (**1**): (left) side-on, with spheres of fixed radius in order to allow structural details to be seen; (middle) central portion from the side; (right) central portion from the end.

Table II. Comparison of M-N Bond Distances (Å), N-N Bond Distances (Å), and M-N-N Angles (deg) in Structurally Characterized Hydrazido(4−) (M=N—N=M) Complexes

compd	M-N	N-N	M-N-N	ref
$[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$	1.837 (8) 1.842 (8)	1.298 (12)	171.43 (65) 172.42 (65)	5
$\{TaCl_3[P(CH_2Ph)_3](THF)\}_2(\mu\text{-}N_2)$	1.796 (5)	1.282 (6)	178.9 (4)	6
$[W(PhC{\equiv}CPh)Cl_2(dme)]_2(\mu\text{-}N_2)$	1.776 (11) 1.735 (11)	1.292 (16)	176.4 (10) 175.6 (10)	7
$[W(\eta^5\text{-}C_5Me_5)Me_3]_2(\mu\text{-}N_2)$	1.763 (18) 1.742 (17)	1.334 (26)	167.0 (16) 170.2 (16)	8
$[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (**1**)	1.796 (5)	1.32 (1)	176.6 (6)	this work
$[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (**4**)	1.90 (6) 1.72 (6)	1.29 (6)	166 (5) 170 (5)	this work

bond length in **1** (1.32 (1) Å) is characteristic of what we believe to be hydrazido(4−) complexes, several examples of which have now been characterized structurally (Table II). The average of the N–N bond lengths listed in Table II is 1.30 Å, and the range is 1.28–1.33 Å; an N–N bond length of 1.30 Å is ~0.1 Å longer than N–N bond lengths in most simple $\eta^1\text{-}N_2$ or $\mu\text{-}N_2$ dinitrogen complexes,[1] consistent with a highly reduced $\mu\text{-}N_2$. The Ta–N bond length and almost 180° Ta–N–N angle are also consistent with this interpretation.

The full view of **1** shown in Figure 1 (left) suggests that it is a relatively crowded molecule in which the six proximal isopropyl groups from the phenoxide ligands fill up the space around the Ta=N—N=Ta core. (There are six N···H contacts of 3.5 Å or less, two of the order of 2.9 Å; they are all noted in the Experimental Section.) The two ends of the molecule are twisted ~110° with respect to one another, as found in $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[5] and $[W(PhC{\equiv}CPh)Cl_2(dme)]_2(\mu\text{-}N_2)$.[7] In all three cases, one could ascribe the approximate orthogonality of the two ends to a minimization of steric interactions, rather than any overriding electronic factors.

It is interesting to compare the structure of **1** with that of $Mo(PhC{\equiv}CPh)(DIPP)_4$.[9] $Mo(PhC{\equiv}CPh)(DIPP)_4$ is also a trigonal-bipyramidal complex with the "substrate" (the acetylene) bound in an equatorial position. The axial Mo–O bond lengths are significantly shorter than equatorial Mo–O bond lengths (1.876 (10) versus 2.004 (10) Å), and the axial M–O–C bond angles, significantly larger than equatorial Mo–O–C angles (160.5 (11) versus 144.4 (10)°). Calling the configuration about each metal in **1** trigonal bipyramidal therefore is consistent with the somewhat shorter Ta–O(1) length and larger Ta–O(1)–C(101) angle compared to other Ta–O lengths and Ta–O–C angles in **1**. It is interesting to note that separate NMR resonances for axial and equatorial DIPP ligands can be observed in $Mo(PhC{\equiv}CPh)(DIPP)_4$,[9] and the axial set cannot rotate freely on the NMR time scale, presumably for steric reasons. In contrast, as we mentioned above, the DIPP ligands in **1** are equivalent on the NMR time scale, most likely as a result of dissociation of THF, although we cannot exclude an intramolecular permutation of the phenoxide ligands in a molecule in which THF remains bound.

We thought it possible that **1** could be prepared by a variation of the reaction between an alkylidene complex and an azine, the type of reaction that led to the discovery of hydrazido(4−) complexes.[4] $Ta(CHCMe_3)(DIPP)_3(THF)$[10] reacts readily with PhCH=N—N=CHPh, but the reaction proceeds only halfway at 25 °C or even after heating to 50 °C for 6 h (eq 2). Almost

$$Ta(CHCMe_3)(DIPP)_3(THF) + PhCH{=}N{-}N{=}CHPh \rightarrow PhCH{=}CHCMe_3 + \underset{\mathbf{2}}{Ta(N{-}N{=}CHPh)(DIPP)_3(THF)} \quad (2)$$

certainly, steric factors weigh heavily in these sterically finely balanced systems and in part prevent further reaction between **2** and $Ta(CHCMe_3)(DIPP)_3(THF)$ to give **1**. (Unfortunately, complexes analogous to $Ta(CHCMe_3)(DIPP)_3(THF)$ that contain a less hindered alkylidene ligand having a β proton are not stable;[10b] a small alkylidene (e.g., propylidene) perhaps would be reactive enough to react further with **2**.) But it is also likely that the the metal alters the reactivity of the other end of the N—N=CHPh ligand system enough so that an alkylidene complex of borderline reactivity will not react with the Ta=N—N=CHPh complex for electronic reasons. For example, conjugation of the

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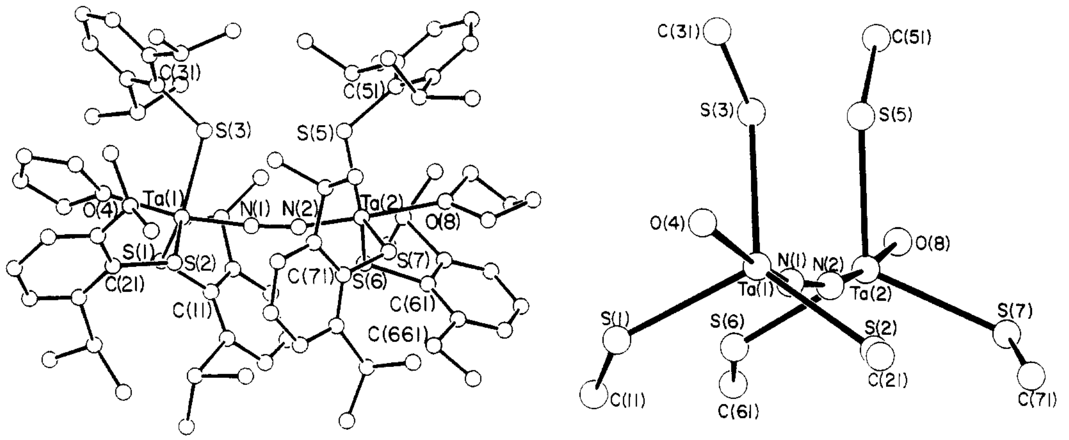


Figure 2. Views of [Ta(S-2,6-C_6H_3-*i*-Pr_2)$_3$(THF)]$_2$(μ-N_2) (**4**): (left) side-on (see Experimental Section for explanation of missing methyl group on C(661)); (right) central portion of **4** from the end.

β-nitrogen lone pair in **2** with the α-nitrogen lone pair, and therefore with the metal, would reduce the basicity of the β-nitrogen lone pair. Since coordination of a nitrogen lone pair to the metal is the likely first step in a reaction of PhCH=N—N=CHPh (or **2**) with an alkylidene complex, **2** should be less reactive. It is important to note in this context, however, that the structure of a molecule in this general class (Mo(OCMe$_3$)$_4$(N—N=CPh$_2$)) shows a *bent* N—N=C bond angle consistent with little conjugation between π systems on N_α and N_β (Mo-N_α-N_β = 168.2 (3)°; N_α-N_β-C = 122.5 (3)°).[11]

Chemical evidence that the μ-N_2 ligand in **1** is a hydrazido(4–) ligand is found in the reaction shown in eq 3, one that has been shown to be characteristic of several hydrazido(4–) complexes.[4]

$$\mathbf{1} + 2\mathrm{PhCHO} \xrightarrow[65\ ^\circ\mathrm{C}]{7\ \mathrm{h}} 2\mathrm{Ta(O)(DIPP)_3} + \mathrm{PhCH{=}N{-}N{=}CHPh}\ (83\%) \quad (3)$$

The first step of the reaction (to give Ta(O)(DIPP)$_3$ and **2**) is fast at 25 °C in benzene-d_6, but several days at 25 °C (or ~7 h at 65 °C) is required (using 6 equiv of benzaldehyde) in order to complete the reaction between benzaldehyde and **2**. These results could be used as evidence that an alkylidene complex is inherently more reactive than an "imido" (Ta=N—N=CHPh) complex in a Wittig-like reaction. The metal-containing product is presumed to be Ta(O)(DIPP)$_3$, the same (by IR spectroscopy and general characteristics) as that generated upon treating Ta(CHCMe$_3$)(DIPP)$_3$(THF) with certain organic compounds containing carbonyl groups.[10]

Benzenethiolate Complexes. The addition of 6 equiv of NaTIPT (TIPT = S-2,4,6-C_6H_2-*i*-Pr_3) to [TaCl$_3$(THF)$_2$]$_2$(μ-N_2) yields [Ta(TIPT)$_3$(THF)]$_2$(μ-N_2) (**3**; eq 4). Although we were not able

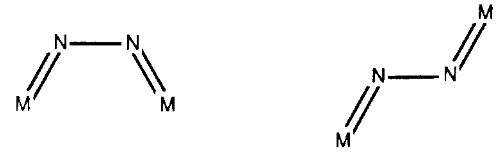
$$[\mathrm{TaCl_3(THF)_2}]_2(\mu\text{-}\mathrm{N_2}) + 6\mathrm{LiSAr} \rightarrow [\mathrm{Ta(SAr)_3(THF)}]_2(\mu\text{-}\mathrm{N_2}) \quad (4)$$

$$\mathrm{SAr} = \mathrm{TIPT}\ (\mathbf{3})\ \text{or DIPT}\ (\mathbf{4})$$

to obtain X-ray-quality crystals of **3**, the analogous DIPT complex (DIPT = S-2,6-C_6H_3-*i*-Pr_2) [Ta(DIPT)$_3$(THF)$_2$]$_2$(μ-N_2) (**4**) finally gave barely adequate crystals after much effort (see Experimental Section for details). Although the X-ray study of **4** is poor, we felt it worthwhile in order to establish the connectivity and overall geometry. A drawing of the entire molecule is shown in Figure 2 (left). Relevant bond distances and angles are listed in Table III.

The geometry about each metal in **4** is essentially trigonal bipyramidal with the three thiolate ligands occupying equatorial positions. Two of the three thiolates are turned away from the central Ta=N—N=Ta core while the phenyl ring of the third is positioned over the Ta=N—N=Ta core. The Ta-S-C angles here are typical of complexes that contain other bulky thiolate ligands,[12] as is the relative orientation of the three equatorial thiolate ligands ("two up, one down").[12a–d] Note that the ends of the molecule are virtually eclipsed (Figure 2 (middle)) and that the bow shape of the Ta=N—N=Ta core forces the phenyl rings in the two thiolates containing S(3) and S(5) to turn away from one another. It does not appear to be possible for steric reasons to bend more than two DIPT ligands (one from each end) over the Ta=N—N=Ta core in **4**. There are five N···H contacts of less than 3.5 Å, as noted in the Experimental Section; interestingly, none is as short as several in **1**.

The Ta=N bond lengths are essentially identical (a result of the large error in each), and the N—N bond again falls in the range (~1.30 Å) expected for hydrazido(4–) complexes (1.28–1.33 Å). It is unfortunate that the error in the N—N bond is so great, as we would like to have been able to compare it meaningfully with the N—N bond in **1**. Note that the Ta=N—N=Ta linkage in **4** is not nearly as linear as it is in **1**, but bow-shaped. (Compare the M-N-N angles in **4** with those in [Ta(CHCMe$_3$)(CH$_2$CMe$_3$)(PMe$_3$)$_2$]$_2$(μ-N_2) and [W(η^5-C_5Me_5)Me$_3$]$_2$(μ-N_2); Table II.) The Ta=N—N=Ta system in **4** in effect appears to be distorting toward one in which the nitrogens π electrons are not strongly donated to the metal, i.e., one of two in general in which the Ta=N—N bond ultimately would approach ~120°, viz.



Steric factors certainly could distort molecules slightly in this manner, but whether electronic factors are also involved remains in doubt; such distortions from linearity are relatively small, and the three cases in which they now have been observed are rather different.

It is interesting to compare the structure of **4** with that of Mo(3-hexyne)(TIPT)$_4$.[9] In each the "substrate" (N_2 or 3-hexyne) is bound in an *axial* position in an essentially trigonal-bipyramidal molecule. In Mo(3-hexyne)(TIPT)$_4$ two of the three TIPT ligands are bent up around the 3-hexyne ligand. (Only two DIPT ligands (one from each end) can bend over the Ta=N—N=Ta core in **4**.) As noted above, in both **1** and Mo(PhC≡CPh)(DIPP)$_4$ the substrate binds in an *equatorial* position. On the basis of these results we can propose that the substrate itself (N_2 or an acetylene) probably does not determine the overall structure as a result of

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some preference to bind in an equatorial versus an axial position (or vice versa) in these particular complexes. It seems more likely that the steric and electronic properties of the phenoxide ligands versus those of the thiolate ligands dictate the position at which substrate will bind.

The reaction between $Ta(CHCMe_3)(TIPT)_3(THF)$[13] and $PhCH{=}N{-}N{=}CHPh$ at 25 °C proceeds as shown in eq 5. As

$$Ta(CHCMe_3)(TIPT)_3(THF) \xrightarrow[-PhCH=CHCMe_3]{+PhCH=N-N=CHPh} \underset{\mathbf{5}}{Ta(N{-}N{=}CHPh)(TIPT)_3(THF)} \quad (5)$$

in the case of the DIPP derivative (eq 2) we have not been able to convert **5** to **3** by further reaction with $Ta(CHCMe_3)(TIPT)_3(THF)$. Some possible reasons for the failure of reactions of this type were discussed earlier. An additional factor in this case is what is believed to be an overall lower reactivity of the Ta=C bond toward olefins in the TIPT complex compared to that in the DIPP complex. For example, although $Ta(CHCMe_3)(DIPP)_3(THF)$ reacts readily with unstrained olefins, $Ta(CHCMe_3)(TIPT)_3(THF)$ does not.[13] Therefore the Ta=C bond in $Ta(CHCMe_3)(TIPT)_3(THF)$ should not react as readily with the carbon–nitrogen double bond in **5** as the Ta=C bond in $Ta(CHCMe_3)(DIPP)_3(THF)$ reacts with the carbon–nitrogen double bond in **2**, if we can assume that this trend in reactivities carries over to other substrates besides olefins.

Preliminary experiments show that **3** reacts only slowly with benzaldehyde in benzene-d_6 to give about a 25% yield of benzaldehyde azine (eq 6), even after heating to 50–60 °C for several hours. We propose that **3** does not react as readily with benzaldehyde as **1** does because of a reduced Wittig-like reactivity of the Ta=N bond when relatively electron-donating thiolates are bound to the metal instead of phenoxides, analogous to the reduced Wittig-like reactivity of the Ta=C bond noted above in thiolate versus that in phenoxide complexes. We believe that side reactions between **3** and benzaldehyde in addition to thermal decomposition of **3** limit the yield of benzaldehyde azine.

$$[Ta(TIPT)_3(THF)]_2(\mu\text{-}N_2) + PhCHO \rightarrow {\sim}25\%\ PhCH{=}N{-}N{=}CHPh \quad (6)$$

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuteriated NMR solvents were passed through a column of activated alumina. 2,6-Diisopropylaniline was purchased commercially.

$[TaCl_3(THF)_2]_2(\mu\text{-}N_2)$ was prepared by treating $Ta(CHCMe_3)Cl_3(THF)_2$ with benzaldehyde azine.[4] $LiDIPP{\cdot}Et_2O$ was prepared by adding butyllithium to 2,6-diisopropylphenol in diethyl ether and isolated straightforwardly as a white crystalline solid. $2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3SH$ was prepared as described in the literature.[14] $NaS\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3$ was prepared from the thiol and sodium metal in diethyl ether.

NMR data are listed in ppm downfield from TMS. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted.

Preparation of $NaS\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$. The procedure used for the preparation of 2,6-diisopropylphenyl bromide outlined here was slightly different from that reported in the literature.[15] 2,6-Diisopropylphenyl bromide was converted into 2,6-diisopropylbenzenethiol by a literature procedure.[16]

A 3-L three-neck flask equipped with an overhead mechanical stirrer, an addition funnel, and a thermometer was charged with 297 g (1.68 mol) of freshly distilled 2,6-diisopropylaniline and 600 mL of water and then cooled to −10 °C with a cold bath. A 750-mL portion of 48% hydrobromic acid was added, causing the reaction mixture to thicken and a white precipitate to form. To this mixture was added dropwise over a period of 90 min a solution of 173 g (2.49 mol) of sodium nitrite in 400 mL of water. The temperature of the reaction was kept below −10 °C. After the reaction was complete, copper powder (11 g, 0.17 mol) was added and the flask (now equipped with a reflux condenser) was heated. After the mixture was refluxed for 2 h, it was extracted with pentane several times. The organic fractions were combined and washed, first with 1 N hydrochloric acid and then with 1 N sodium hydroxide. The organic layer was dried ($MgSO_4$), filtered, and concentrated to give 400 mL of a dark red oil. Virtually all of the dark impurities were removed by passing the oil through a column of silica gel. Distillation yielded 200 g (50%) of 2,6-diisopropylphenyl bromide.

Under an atmosphere of argon, 2,6-diisopropylphenyl bromide (100 g, 0.415 mol) was added to a mechanically stirred suspension of Mg (12 g) in 1200 mL of diethyl ether. After addition was complete, the mixture was refluxed for several hours. The Grignard mixture was cooled to room temperature, and 12 g (0.375 mol) of elemental sulfur was added over a period of 30 min, during which time the temperature of the reaction was maintained at ~30 °C with a cold bath. After the addition was complete, the reaction mixture was stirred for an additional 1 h and then cooled to 0 °C. The temperature was maintained below 5 °C as 400 mL of 2.5 N hydrochloric acid was added slowly. The organic layer was separated, washed with 50 mL of a saturated solution of sodium chloride, and dried over $MgSO_4$. The solvent was removed to give crystalline 2,6-diisopropylbenzenethiol (80% yield). Treatment with sodium metal at room temperature in ether yielded the desired sodium salt straightforwardly.

Preparation of Compounds. $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (1). $LiDIPP{\cdot}Et_2O$ (0.522 g, 2.02 mmol) was added as a solid to $[TaCl_3(THF)_2]_2(\mu\text{-}N_2)$ (0.300 g, 0.34 mmol) dissolved in a mixture of ether and THF (10 mL:2 mL), and the solution was stirred at room temperature for 4 h. As the product formed, the solution turned yellow, and a white precipitate (LiCl) was observed. The mixture was then filtered through Celite, and the solvent was removed in vacuo, leaving a yellow oil. The oil was dissolved in ether, and the solution was cooled to −30 °C to yield yellow crystals (0.323 g, 60%). When **1** is crystallized repeatedly from ether, the partially crystalline product contains much less than 1 equiv of THF/metal. ^1H NMR spectra of such samples do not show a resonance for bound ether. We presume that the metal in such samples is pseudo-four-coordinate. On the basis of qualitative observations, we postulate that ether partially displaces THF upon recrystallization of **1** to yield an analogous etherate that then loses ether readily in the solid state at 25 °C, especially under slight vacuum. ^1H NMR: δ 7.05 (d, H_m), 6.90 (t, H_p), 3.71 (m, THF), 3.57 (septet, $C\textit{H}Me_2$), 1.20 (d, $CH\textit{Me}_2$ and THF). ^{13}C NMR: δ 157.5 (s, C_{ipso}), 137.5 (s, C_o), 123.4 (d, C_m), 122.4 (d, C_p), 71.1 (t, THF), 27.5 (d, $\textit{C}HMe_2$), 25.6 (t, THF), 24.0 (q, $CH\textit{Me}_2$). Anal. Calcd for $TaC_{36}H_{51}O_3N$ (the base-free compound): C, 59.48; H, 7.09; N, 1.93. Found: C, 59.25; H, 7.19; N, 1.63. The analytical sample of **1** had been recrystallized repeatedly from ether and sealed under vacuum for analysis. The pyridine adduct (see below) does not appear to lose pyridine as readily as **1** loses THF.

$[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(py)]_2(\mu\text{-}N_2)$. Pyridine (30 μL, 0.37 mmol) was added to a solution of $[Ta(DIPP)_3(THF)]_2(\mu\text{-}N_2)$ (0.100 g, 0.06 mmol) in ether (5 mL) at room temperature. The solution was stirred for 1 h, during which time the color changed from yellow to orange. The solvent was removed in vacuo and the resulting residue recrystallized from ether at −30 °C to yield orange crystals (an ^1H NMR spectrum of the crude residue showed the yield to be virtually quantitative). ^1H NMR: δ 8.64 (d, py H_α), 7.18–6.82 (multiplet, H_m and H_p), 6.76 (t, py H_γ), 6.49 (t, py H_β), 3.82–3.22 (broad, $C\textit{H}Me_2$), 1.50–0.60 (broad, $CH\textit{Me}_2$). Anal. Calcd for $TaC_{41}H_{56}N_2O_3$: C, 61.10; H, 7.02; N, 3.48. Found: C, 61.13; H, 7.14; N, 3.48.

$Ta(NNCHPh)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)$ (2). A solution of benzaldehyde azine (73 mg, 0.35 mmol) in ether (5 mL) was added to a solution of $Ta(CH\text{-}t\text{-}Bu)(DIPP)_3(THF)$ (0.300 g, 0.35 mmol) in a mixture of ether and THF (15 mL:5 mL) at −30 °C. The solution was stirred at room temperature; there was little color change. After 30 min the solution was filtered through Celite, and the solvent was removed in vacuo. The resulting yellow oil was dissolved in pentane, and the solution was cooled to −30 °C to yield light yellow crystals (0.263 g, 83%). ^1H NMR: δ 7.81 (s, $C\textit{H}Ph$), 7.59 (d, phenyl H_o), 7.14 (d, H_m), 7.05–6.90 (multiplet, H_p and phenyl $H_{m,p}$), 3.93 (m, $C\textit{H}Me_2$ and THF), 1.29 (d, $CH\textit{Me}_2$), 1.09 (m, THF). ^{13}C NMR: δ 157.9 (s, C_{ipso}), 157.3 (d, $\textit{C}HPh$), 137.6 (s, C_o), 135.2 (s, phenyl C_{ipso}), 129.7, 128.8, and 127.1 (unresolved, phenyl $C_{o,m,p}$), 123.5 (d, C_m), 121.9 (d, C_p), 73.3 (t, THF),

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Table III. Relevant Bond Distances (Å) and Angles (deg) in $[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$ (**4**)

Ta(1)–S(1)	2.416 (17)	T(2)–S(5)	2.363 (16)
Ta(1)–S(2)	2.357 (20)	Ta(2)–S(6)	2.461 (19)
Ta(1)–S(3)	2.435 (17)	Ta(2)–S(7)	2.352 (18)
Ta(1)–O(4)	2.206 (40)	Ta(2)–O(8)	2.318 (41)
Ta(1)–N(1)	1.90 (6)	N(2)–Ta(2)–S(5)	87.2 (18)
Ta(2)–N(2)	1.72 (6)	N(2)–Ta(2)–S(6)	88.7 (18)
N(1)–N(2)	1.29 (6)	N(2)–Ta(2)–S(7)	102.9 (19)
N(1)–Ta(1)–S(1)	95.9 (16)	N(2)–Ta(2)–O(8)	173.5 (21)
N(1)–Ta(1)–S(2)	94.8 (17)	S(5)–Ta(2)–S(6)	120.6 (6)
N(1)–Ta(1)–S(3)	81.8 (16)	S(6)–Ta(2)–S(7)	122.8 (6)
N(1)–Ta(1)–O(4)	167.7 (19)	S(5)–Ta(2)–S(7)	115.8 (6)
S(1)–Ta(1)–S(2)	116.6 (6)	Ta(2)–S(5)–C	118.7 (16)
S(2)–Ta(2)–S(3)	130.3 (6)	Ta(2)–S(6)–C	117.2 (17)
S(1)–Ta(1)–S(3)	113.0 (6)	Ta(2)–S(7)–C	112.2 (18)
Ta(1)–S(1)–C	116.9 (18)	Ta(1)–N(1)–N(2)	166.2 (47)
Ta(1)–S(2)–C	116.0 (17)	Ta(2)–N(2)–N(1)	165.9 (48)
Ta(1)–S(3)–C	119.4 (17)		

27.0 (d, *C*HMe$_2$), 25.4 (t, THF), 23.9 (q, CH*Me*$_2$). Anal. Calcd for $TaC_{47}H_{65}N_2O_4$: C, 62.52; H, 7.26; N, 3.10. Found: C, 61.12; H, 7.17; N, 3.02. Poor analytical results are believed to result from some decomposition in the solid state. Satisfactory analytical results were obtained for the pyridine adduct (see below).

Ta(NNCHPh)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_3$(py). Pyridine (30 μL, 0.37 mmol) was added to a solution of Ta(NNCHPh)(DIPP)$_3$(THF) (0.100 g, 0.11 mmol) in ether (10 mL). The solution was stirred at room temperature, and the color changed to a deeper shade of yellow. After 15 min the solvent was removed in vacuo to give a yellow oil. An ^{1}H NMR spectrum of this oil showed only the product. Orange-yellow crystals were obtained by crystallization from pentane at −30 °C. ^{1}H NMR: δ 8.72 (broad, py H$_\alpha$), 7.96 (s, C*H*Ph), 7.62 (d, phenyl H$_o$), 7.2–6.8 (multiplet, H$_m$, H$_p$, and phenyl H$_{m,p}$), 6.79 (broad, py H$_\gamma$), 6.50 (broad, py H$_\beta$), 3.87 (septet, C*H*Me$_2$), 1.19 (d, CH*Me*$_2$). Anal. Calcd for $TaC_{48}H_{62}N_3O_2$: C, 63.36; H, 6.87; N, 4.62. Found: C, 63.28; H, 7.18; N, 4.77.

[Ta(S-2,4,6-C$_6$H$_2$-*i*-Pr$_3$)$_3$(THF)]$_2$(μ-N$_2$) (3). NaTIPT (0.87 g, 3.37 mmol) was added to a suspension of $[TaCl_3(THF)_2]_2(\mu\text{-}N_2)$ (0.50 g, 0.56 mmol) in ether at room temperature. After the reaction mixture was stirred at room temperature for 2 h, it was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The residue was dissolved in pentane and the solution cooled to −30 °C to give yellow-orange crystals (0.75 g, 70%). ^{1}H NMR: δ 7.15 (s, H$_m$), 4.14 (broad, *o*-C*H*Me$_2$), 3.43 (broad, THF), 2.78 (septet, *p*-C*H*Me$_2$), 1.51 (broad, *o*-CH*Me*$_2$), 1.14 (d, *p*-CH*Me*$_2$), 0.68 (broad, THF). Anal. Calcd for $TaC_{49}H_{77}NOS_3$: C, 60.47; H, 7.97; N, 1.44; S, 9.88. Found: C, 59.97; H, 7.83; N, 1.55; S, 9.78.

[Ta(S-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_3$(THF)]$_2$(μ-N$_2$) (4). The preparation of this compound was identical with that of **3**. Prismatic yellow-orange crystals were grown from minimal pentane containing a drop of THF.

Ta(NNCHPh)(S-2,4,6-C$_6$H$_2$-*i*-Pr$_3$)$_3$(THF) (5). A solution of benzaldehyde azine (73 mg, 0.35 mmol) in ether (5 mL) was added to a solution of Ta(CH-*t*-Bu)(TIPT)$_3$(THF) (0.40 g, 0.39 mmol) in ether (10 mL) at room temperature. The solution was stirred for 2 h, during which time the color changed from orange to orange-red. The solvent was removed in vacuo, and the resulting oil crystallized from pentane at −30 °C to yield yellow crystals (0.33 g, 78%). ^{1}H NMR: δ 7.29 (d, phenyl H$_o$), 7.2–7.0 (multiplet, H$_m$ and phenyl H$_{m,p}$), 6.78 (s, C*H*Ph), 4.32 (broad, *o*-C*H*Me$_2$), 4.26 (broad, THF), 2.78 (broad, *p*-C*H*Me$_2$), 1.56 (broad, *o*-CH*Me*$_2$), 1.34 (multiplet, THF), 1.16 (broad, *p*-CH*Me*$_2$). ^{13}C NMR: δ 166.5 (d, *C*HPh), 149.4, 147.4, and 135.8 (s's, C$_{ipso,o,p}$), 134.0 (s, phenyl C$_{ipso}$), 130.6, 128.3, and 127.7 (d's, phenyl C$_{o,m,p}$), 120.6 (d, C$_m$), 75.1 (t, THF), 34.3 (d, *p*-*C*HMe$_2$), 32.9 (d, *o*-*C*HMe$_2$), 25.2 (unresolved, *p*-CH*Me*$_2$), 24.3 (q, *o*-CH*Me*$_2$), 22.7 (unresolved, THF).

Reaction of 1 and 3 with Benzaldehyde. $[Ta(DIPP)_3(THF)]_2(\mu\text{-}N_2)$ (0.10 g, 0.06 mmol) was dissolved in benzene-d_6 (~500 μL), and mesitylene (10 μL, 0.07 mmol) was added as an internal standard. This solution was then divided into two, and benzaldehyde (19 μL, 0.19 mmol) was added to half; the other half was used as a reference. The reaction was monitored by ^{1}H NMR spectroscopy at 25 and 65 °C. An analogous procedure was employed for the reaction between $[Ta(TIPT)_3(THF)]_2(\mu\text{-}N_2)$ and benzaldehyde.

Crystal Structure of [Ta(DIPP)$_3$(THF)]$_2$(μ-N$_2$) (1). Crystals were grown at −30 °C from ether containing ~5% THF, and one with dimensions of approximately 0.15 × 0.20 × 0.15 mm was selected under a stream of cold dinitrogen from a liquid-nitrogen source. Data were collected at −140 °C on an Enraf-Nonius CAD4F-11 κ-geometry diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation (λ = 0.71073 Å). Data collection, reduction, and refinement procedures have been detailed elsewhere.[17] A total of 11 211 reflections ($+h,+k,\pm l$) were collected in the range $3° \le 2\theta \le 55°$, with the 7714 having $F_o > 4\sigma(F_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (473 variables) using the TEXSAN crystallographic software package from Molecular Structure Corp. Final R_1 = 0.052 and final R_2 = 0.062. The anisotropic temperature factor of C(311) was large, probably due to disorder. (We were unable to model this disorder.) One ether molecule of crystallization was found per molecule of $[Ta(DIPP)_3(THF)]_2(\mu\text{-}N_2)$. The oxygen of the ether molecule resides on a center of symmetry, and the methylene carbon atom is disordered. The disorder was modeled with two carbon atoms (C(61A) and C(61B)) each of $^1/_2$ occupancy. Atoms of the ether molecule were refined isotropically. The final difference-Fourier map showed no chemically significant features. Intensity statistics suggested that the structure was centrosymmetric. Crystal data: space group = $C2/c$, a = 20.276 (8) Å, b = 16.737 (7) Å, c = 28.227 (19) Å, β = 105.55 (5)°, V = 9228 Å^3, Z = 4, M_r = 1820.1, ρ(calcd) = 1.310 g cm^{-3}, μ = 25.6 cm^{-1}. A semiempirical absorption correction was applied.

There are six N···H contacts of less than or about 3.5 Å: C(107)–H···N = 3.48 Å; C(207)–H···N = 3.03 Å; C(207)–H···N* = 3.57 Å; C(208)–H$_A$···N = 2.95 Å; C(208)–H$_A$···N* = 2.85 Å; C(208)–H$_B$···N* = 3.29 Å.

Crystal Structure of [Ta(DIPT)$_3$(THF)]$_2$(μ-N$_2$) (4). An orange prismatic crystal of approximate dimensions 0.15 × 0.20 × 0.15 mm was selected under a stream of cold dinitrogen. Data were collected at −65 °C as described above and reduced and refined as described elsewhere.[17] A total of 6092 reflections ($+h,+k,+l$) were collected in the range $3° \le 2\theta \le 45°$, with the 3163 having $F_o > 4\sigma(F_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (269 variables) using SHELX-76. Final R_1 = 0.103 and final R_2 = 0.117. The quality of the final structure is poor because of the marginal quality of the available crystals. After exhaustive attempts it was not possible to locate one of the isopropyl methyl carbons attached to C(661). Benzene rings were refined as rigid planar groups (C–C = 1.395 Å; C–C–C = 120°) pivoting on the ipso carbon atom. The isopropyl groups were also refined as rigid groups (C–C = 1.54 Å; C–C–C = 109°) pivoting on the methyne carbon atom. Only the tantalum atoms were refined anisotropically. The two possible space groups are $Pcmn$ and $pc2_1n$, each a nonstandard setting of $Pna2_1$. The only possible molecular symmetry is a noncrystallographic 2-fold axis passing between the two nitrogen atoms and approximately parallel to the Ta(1)–S(3) and Ta(2)–S(5) bonds. Therefore the structure has been solved and refined in the noncentrosymmetric space group $Pc2_1n$. The centrosymmetric choice is ruled out since the molecule would be required to lie on a site of either $\bar{1}$ or m symmetry, which does not appear to be possible. The final difference-Fourier map showed no chemically significant features. The alternate hand of the structure gave marginally higher R values. Crystal data: space group = $Pc2_1n$, a = 13.606 (6) Å, b = 23.096 (9) Å, c = 28.845 (10) Å, V = 9064.5 Å^3, Z = 4, M_r = 1565.8, ρ(calcd) = 1.147 g cm^{-3}, μ = 24.6 cm^{-1}. A semiempirical absorption correction was applied.

There are five N···H contacts of less than or about 3.5 Å: C(162)–H···N(1) = 3.25 Å; C(162)–H···N(2) = 3.53 Å; C(761)–H···N(2) = 3.23 Å; C(763)–H$_A$···N(1) = 3.10 Å; C(763)–H$_A$···N(2) = 3.21 Å.

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Registry No. **1**, 114220-88-1; **2**, 114198-82-2; **3**, 114198-89-9; **4**, 114198-83-3; **5**, 114198-84-4; $[TaCl_3(THF)_2]_2(\mu\text{-}N)$, 90130-65-7; $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(py)_2](\mu\text{-}N_2)$, 114198-86-6; Ta(CH-*t*-Bu)(DIPP)$_3$(THF), 106034-24-6; Ta(NNCHPh)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_3$(py), 114198-87-7; Ta(CH-*t*-Bu)(TIPT)$_3$(THF), 114198-88-8; NaS-2,6-C$_6$H$_3$-*i*-Pr$_2$, 114198-85-5; N$_2$, 7727-37-9; 2,6-diisopropylaniline, 24544-04-5; sulfur, 7704-34-9; benzaldehyde azine, 588-68-1; benzaldehyde, 100-52-7.

Supplementary Material Available: A fully labeled drawing of $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$, tables of final positional parameters, final thermal parameters, intramolecular bond distances, and intramolecular bond angles for $[Ta(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$, and a table of final positional and thermal parameters for $[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)\}_2(\mu\text{-}N_2)$ (14 pages); listings of final observed and calculated structure factors for both compounds (66 pages). Ordering information is given on any current masthead page.

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