Tantalacyclobutane Complexes Containing the Potentially *C,N,N′*-Coordinating Ligand $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$ (CNN) and Their Reactivity with Carbon Monoxide and *tert*-Butyl Isocyanide. X-ray Molecular Structures of $[Ta\{CH_2CH(Me)CH_2\text{-}1,3\}(CNN)(O\text{-}t\text{-}Bu)_2]$, $[Ta\{CH_2CH(Ph)CH_2\text{-}1,3\}(CNN)(O\text{-}t\text{-}Bu)_2]$, $[Ta\{C(O)((CH_2)_3\text{-}1,3)\}(CNN)(O\text{-}t\text{-}Bu)_2]$, and $[Ta\{C(=N\text{-}t\text{-}Bu)CH_2CH(Ph)CH_2\text{-}1,4\}(CNN)(O\text{-}t\text{-}Bu)_2]$[‖]

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From the reactions of the unsubstituted tantalacyclobutane complex $[Ta\{(CH_2)_3\text{-}1,3\}(CNN)(O\text{-}t\text{-}Bu)_2]$ (CNN = $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$) (**1**) with propene and styrene have been isolated in good yields the substituted tantalacyclobutane complexes $[Ta\{CH_2CH(Me)CH_2\text{-}1,3\}(CNN)(O\text{-}t\text{-}Bu)_2]$ (**2**) and $[Ta\{CH_2CH(Ph)CH_2\text{-}1,3\}(CNN)(O\text{-}t\text{-}Bu)_2]$ (**3**), respectively. The X-ray molecular structures of **2** and **3** show them to be seven-coordinate pentagonal bipyramidal species in which the meridional ligation comprises *C,N,N′*-bonding of the aryldiamine ligand CNN and *σ*-bonding of two carbons of the metallacycle; the two alkoxide groups occupy the apical positions. The organyl substituent of the metallacycle is positioned on the *β*-carbon. Complexes **2** and **3** can both be converted back into **1** by reacting them in Et_2O with ethene. The reaction of **1** with carbon monoxide yields the oxytantalacyclopropane complex $[Ta\{C(O)((CH_2)_3\text{-}1,3)\}(CNN)(O\text{-}t\text{-}Bu)_2]$ (**4**), which has been isolated as an air-stable white solid in 59% yield. The X-ray molecular structure of **4** reveals that the carbon and oxygen atoms of the C=O function are ligated in the meridional plane with further η^3-*C,N,N′*-ligation of CNN and the two alkoxides as found in **2** and **3**. Reaction of the tantalacyclobutane complexes **2**−**4** with 1 equiv of *t*-BuNC affords the 1:1 insertion products $[Ta\{C(=N\text{-}t\text{-}Bu)CH_2CH(R)CH_2\text{-}1,4\}(CNN)(O\text{-}t\text{-}Bu)_2]$ (R = H (**5**), Me (**6**), and Ph (**7**), respectively). Complexes **5** and **7** have been isolated as yellow solids (yields: **5**, 62%; **7**, 50%), while **6** has been prepared and characterized *in situ*. ^1H and ^{13}C NMR spectroscopy of **6** and **7** indicate for each complex the presence of two isomers in solution. The X-ray molecular structure of **7** shows η^2-*C,N*-bonding of the CNN ligand through the aryl C_{ipso} atom and the N(Me) donor atom and, most importantly, the presence of two tantalacyclic rings of different sizes that have a common Ta−C bond. The smaller three-membered ring comprises the metal center with the nitrogen and the α-carbon atom of the η^2-bonded iminoacyl fragment, while the larger five-membered ring is a metallacylopentane system comprising the metal center and four carbon atoms.

Introduction

In a recent paper we reported that the anionic aryldiamine ligand $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2]^-$ (CNN), which has a single *ortho* substituent, can be used to synthesize new tantalum alkylidene complexes $[Ta(=CHR)(CNN)X_2]$ (X = Cl, R = *t*-Bu; X = O-*t*-Bu, R = *t*-Bu, CMe_2Ph) in which CNN functions as a chelating system.[1] In the dichloride complex (X = Cl) the CNN ligand is η^3-*C,N,N′* pseudofacially-bonded to the metal by the aryl C_{ipso} carbon atom and the N(Me) and NMe_2 nitrogen donors both in solution and in the solid state. In solution at room temperature the dialkoxide complexes (X = O-*t*-Bu) have the CNN ligand only η^2-*C,N*-bonded to the metal by the aryl C_{ipso} carbon atom and the N(Me) nitrogen donor. Apparently the dialkoxide complexes, compared to the dichloride species, have a

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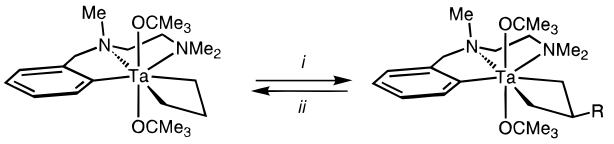
lower Lewis acidity of the metal center due to $p\pi \rightarrow d\pi$ electron donation of the alkoxide lone pairs to the metal center.[2] This difference in bonding of CNN between the dialkoxide and the dichloride species is also reflected in their reactivity. The dichloride complex does not react with ethene and does not show ring-opening metathesis polymerization (ROMP) reactivity with norbornene, whereas the dialkoxide neopentylidene and neophylidene complexes react at room temperature with ethene to form the tantalacyclobutane complex [Ta{$(CH_2)_3$-1,3}(CNN)(O-*t*-Bu)$_2$], **1**. Interestingly, reaction of the dialkoxide neophylidene complex and ethene at 69 °C affords the ethene adduct complex [Ta(H_2C=CH_2)(CNN)(O-*t*-Bu)$_2$].[1] The X-ray molecular structures of the tantalacyclobutane complex **1** and the ethene adduct complex show the CNN ligand to be η^3-*C,N,N*′-bonded to the metal in a meridional fashion. The five-coordinate alkylidene complex [Ta(=CH-*t*-Bu)($C_6H_4CH_2$-NMe_2-2)(O-*t*-Bu)$_2$], which contains an η^2-*C,N* chelating arylamine, also reacts with ethene, but a mixture of unstable products results.[1] The tantalum CNN dialkoxide complex [Ta(=$CHCMe_2Ph$)(CNN)(O-*t*-Bu)$_2$] and **1** are active ROMP catalysts for the polymerization of norbornene and dicyclopentadiene, and though the rate of their reactivity with these strained cyclic olefins is low at room temperature, it is greatly increased at 70 °C. In the case of norbornene polymers are obtained with approximately 90% *trans*-vinylene bonds. In contrast, the reaction of norbornene with the five-coordinate neophylidene complex [TaCl(=$CHCMe_2Ph$)(O-*t*-Bu)$_2$-(PMe_3)] at room temperature is extremely rapid and affords a polymer with 70% *trans*-vinylene double bonds.[1]

We conclude from these results that the outer NMe_2 nitrogen donor of the CNN ligand, even when it is only weakly bonded, hampers approach of an alkene to the alkylidene function. However, the CNN ligand can stabilize reaction products and intermediates, like tantalacyclobutane species and ethene adducts, and is therefore an ideal ligand for the study of elementary reaction processes.

In this paper we report first on reaction of the tantalacyclobutane complex **1** with terminal olefins that affords new isolable β-substituted tantalacyclobutanes. Second, we have investigated insertion reactions of small molecules, i.e. CO and *t*-BuNC, into the metal−carbon bonds of such species. Although much is known concerning the reactions of metal−carbon bonds with CO[3] and isocyanides,[4] the literature concerning metallacycles is comparatively limited.[3a−g,4a−e] We now show that CNN tantalacylobutane complexes undergo insertion reactions with CO and *t*-BuNC to afford interesting stable isolable species containing oxytantalacyclopropane and tantalum η^2-iminoacyl moieties, respectively.

Scheme 1. Synthesis of the C_β-Substituted Tantalacyclobutane Complexes[a]



1 **2**: R = Me **3**: R = Ph

[a] Reaction conditions: *i*, $+C_2H_3R'$, $-C_2H_4$, Et_2O, RT (room temperature); *ii*, $+C_2H_4$, $-C_2H_3R'$, Et_2O, RT.

Results and Discussion

Reactivity of 1 with Propene and Styrene. Reaction of a saturated diethyl ether solution of the known tantalacyclobutane complex [Ta{$(CH_2)_3$-1,3}(CNN)(O-*t*-Bu)$_2$] (CNN = [$C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)$-2]$^-$) (**1**)[1] with propene affords the methyl-substituted tantalacyclobutane complex [Ta{$CH_2CH(Me)CH_2$-1,3}(CNN)-(O-*t*-Bu)$_2$] (**2**), which has been isolated as a white air-sensitive solid in 84% yield (Scheme 1). In the same way reaction of **1** with 1 equiv of styrene affords the phenyl-substituted tantalacyclobutane complex [Ta{$CH_2CH(Ph)CH_2$-1,3}(CNN)(O-*t*-Bu)$_2$] (**3**), which has been isolated as a white solid in 65% yield (Scheme 1). The methyl- and the phenyl-substituted tantalacyclobutane complexes **2** and **3**, respectively, can both be converted back into the unsubstituted tantalacyclobutane **1** by dissolving them in diethyl ether and then saturating the solution with ethene; i.e., it is obvious that these substitution reactions are reversible (*vide infra*). Complexes **2** and **3** are soluble in benzene, toluene, and diethyl ether but are insoluble in pentane or hexane. Needle-shaped colorless crystals of **2** and **3** can be obtained by recrystallization from a saturated diethyl ether solution at −30 °C. The solid powdered tantalacyclobutane complexes **1**−**3** decompose in less than 5 min on exposure to air forming a sticky yellowish mass, but they can be stored intact under a nitrogen atmosphere for months. In solution at room temperature **1**−**3** slowly decompose liberating ethene, propene, and styrene, respectively, together with $C_6H_5CH_2N$-(Me)$CH_2CH_2NMe_2$, i.e. protonated CNN.

Solid-State Structures of 2 and 3. The molecular structures of **2** and **3** together with the adopted num-

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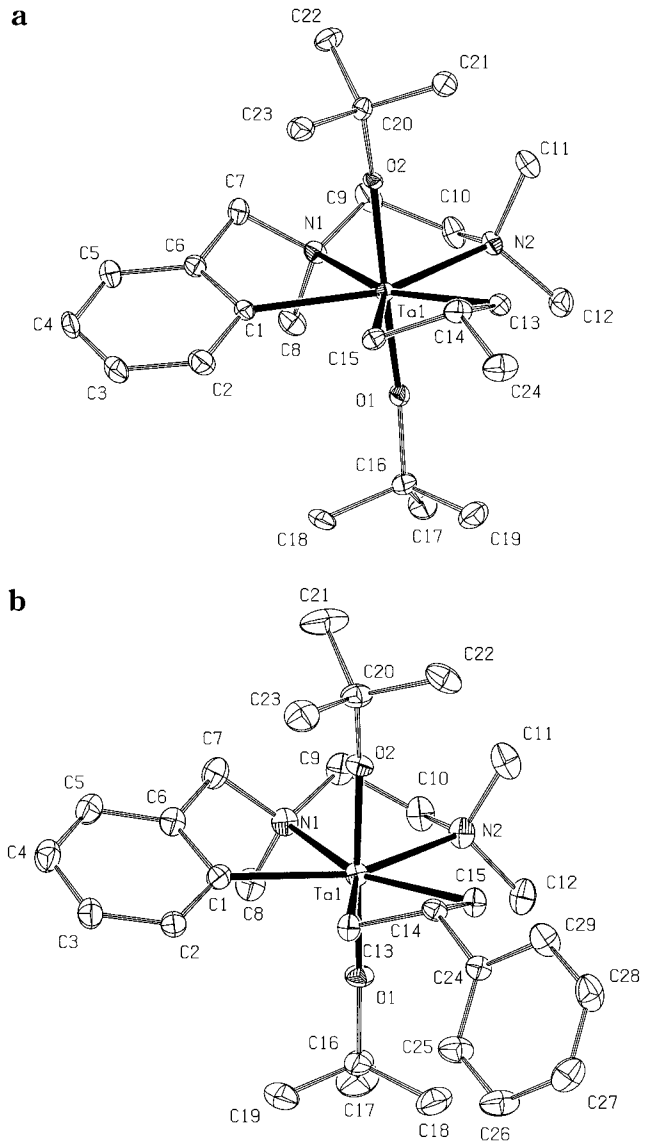


Figure 1. ORTEP thermal motion ellipsoid plot[19] (drawn at 30% probability level) of (a) [Ta{$CH_2CH(Me)CH_2$-1,3}(CNN)(O-*t*-Bu)$_2$] (**2**) and (b) [Ta{$CH_2CH(Ph)CH_2$-1,3}-(CNN)(O-*t*-Bu)$_2$] (**3**) together with adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

bering scheme are shown in Figure 1. The bond distances and angles for **2** and **3** are given in Table 1. Complexes **2** and **3** are mononuclear pentagonal bipyramidal tantalum(V) species with the aryl C_{ipso} carbon, the inner *N*(Me), and the outer *N*Me$_2$ nitrogen donor atoms of the CNN ligand together with the σ-bonded carbons of the metallacycle forming the meridional plane, while the two alkoxide groups are in the apical positions. Overall, both structures show great similarity to the structure of the parent tantalacyclobutane complex **1**.[1] In both **2** and **3** coordination of the inner N(Me) nitrogen donor of CNN makes this nitrogen donor a stereogenic center; Figure 1 shows the *S* configuration**,** but both enantiomers are present in the unit cell. Furthermore, the metallacycle Ta−C(13)−C(14)−C(15) in **2** and **3** has an organyl substituent (Me and Ph, respectively) on the β-carbon (C(14)) of the ring. Accordingly this CH(R) carbon atom is a stable chiral center and each complex can exist in two diastereoisomeric forms. The X-ray structures of both **2** and **3** represent the diastereoisomer in which the R substituent on C(14) is in an equatorial position with the H atom positioned on the side of the meridional plane opposite to that of the methyl group of the inner N(Me) unit. Solutions of **2** and **3** do show the presence of the second possible diastereoisomer (*vide infra*).

Table 1. Bond Distances (Å) and Angles (deg) for 2 and 3

	2	**3**
Ta(1)−O(1)	1.890(3)	1.892(5)
Ta(1)−O(2)	1.896(3)	1.895(5)
Ta(1)−C(1)	2.307(5)	2.287(7)
Ta(1)···C(14)	2.894(5)	2.880(6)
Ta(1)−N(1)	2.425(4)	2.398(6)
Ta(1)−N(2)	2.506(4)	2.482(7)
Ta(1)−C(13)	2.264(5)	2.244(7)
Ta(1)−C(15)	2.238(5)	2.271(6)
C(13)−C(14)	1.517(8)	1.499(9)
C(14)−C(15)	1.529(7)	1.543(10)
C(14)−C(24)	1.524(7)	1.518(9)
O(1)−Ta(1)−O(2)	168.82(15)	169.9(2)
O(1)−Ta(1)−C(13)	92.95(16)	94.6(2)
O(1)−Ta(1)−C(15)	95.61(17)	91.8(2)
O(1)−Ta(1)−C(1)	92.77(17)	94.6(2)
O(1)−Ta(1)−N(1)	86.25(14)	88.0(2)
O(1)−Ta(1)−N(2)	85.62(14)	85.8(2)
N(1)−Ta(1)−C(1)	70.80(17)	70.3(3)
N(1)−Ta(1)−C(15)	147.90(17)	151.6(3)
N(1)−Ta(1)−C(13)	151.44(18)	147.4(2)
N(1)−Ta(1)−N(2)	72.37(14)	73.1(2)
Ta(1)−O(1)−C(16)	159.5(3)	161.9(4)
Ta(1)−O(2)−C(20)	159.5(3)	160.6(5)
Ta(1)−C(13)−C(14)	97.9(3)	98.6(5)
Ta(1)−C(15)−C(14)	98.6(3)	96.2(4)
C(13)−C(14)−C(15)	96.5(4)	97.7(5)
C(13)−Ta(1)−C(15)	60.63(19)	61.0(3)

The Ta- -C_β distances of 2.894(5) and 2.880(6) Å in complexes **2** and **3**, respectively, compare favorably with those of 2.846(19) and 2.868(7) Å found in the two crystal modifications of complex **1**.[1] Within the metallacycle the dihedral angle between the planes C(13)−Ta(1)−C(15) and C(13)−C(14)−C(15) in **2** (25.1(4)°) and **3** (25.7(6)°) are also similar to the corresponding angles found for complex **1** (26.8(6) and 23.1(17)°).[1] In both **2** and **3** the Ta−O distances have values of approximately 1.89 Å.

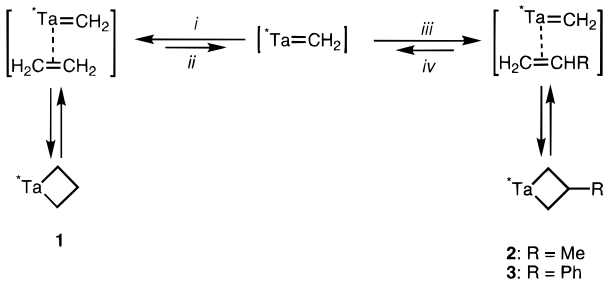
NMR Spectroscopy of the Tantalacyclobutane Complexes 2 and 3. The ^{1}H NMR spectra of **2** and **3** show characteristic resonance patterns associated with the pentagonal bipyramidal structures as shown in Figure 1 (*vide supra*). For example, both **2** and **3** afford two Me resonances for the NMe$_2$ unit, and the Ar*C*H_2N(Me) protons give rise to a well-resolved AB pattern. A complication in the NMR spectra of both **2** and **3** is that there are signals for two diastereoisomers in a 1:10 and 1:12 molar ratio, respectively. These diastereoisomers are due to the presence of two chiral centers, *i.e.* the ArCH_2*N*Me nitrogen donor and the *C*H(R) carbon atom of the metallacyle; the major diastereoisomer is that in which the N(Me) unit has an *S* configuration and the β-substituent is in equatorial position. Due to severe overlap of the signals of the major isomer with the minor isomer in **2** and **3** only the signals of the major isomer have been fully assigned. The ^{1}H and ^{13}C NMR data for the metallacyclic ring of **1**-**3** are listed in Table 2. These data, and in particular the characteristic positions of the protons on the C_α carbon atom (H_α) of the metallacyclic ring that are at higher field than those of the C_β protons (H_β), underline the structural similarity of complexes **1**−**3** in solution. The ^{13}C chemical shift

Table 2. Relevant ^{1}H (200.13 MHz) and ^{13}C (50.32 MHz) NMR Data for the Metallacycles of 1−3[a]

complex	H_α	H_β	C_α[b]	C_β[b]
1[c]	0.61, 0.76, 0.87, 1.58	3.75, 4.69	23.7 (121), 36.7 (120)	25.0 (123)
2	0.29, 0.96, 1.68, 1.95	3.20	36.9 (124), 49.3 (125)	37.1 (129)
3	0.77, 1.12, 1.44, 2.18	4.33	34.7 (124), 46.7 (122)	41.3 (128)

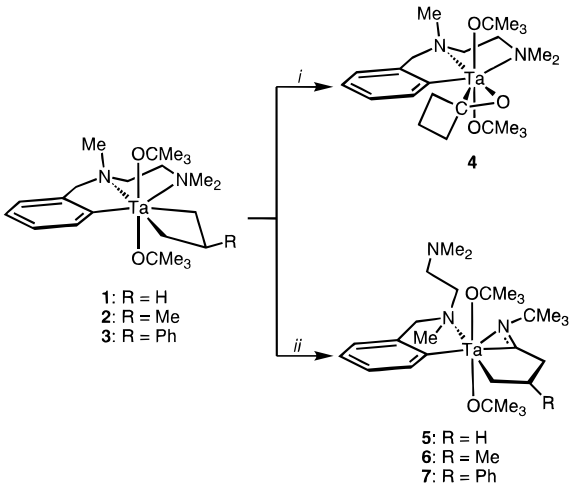
[a] Measured in C_6D_6 at 298 K. Chemical shifts (δ, ppm) referenced to $SiMe_4$. [b] ^1J(C,H) in Hz in parentheses. [c] Data from ref 1.

Scheme 2. Postulated Mechanism for the Formation of Complexes 2 and 3 (*Ta = {Ta(CNN)(O-*t*-Bu)$_2$})[a]



[a] Reaction conditions: *i*, $+C_2H_4$; *ii*, $-C_2H_4$; *iii*, $+C_2H_3R$; *iv*, $-C_2H_3R$.

Scheme 3. Synthesis of Complexes 4-7[a]



[a] Reaction conditions: *i* (**1**), CO, 1 atm, Et_2O, RT, 48 h. *ii* (**1**-**3**): + *t*-BuNC, Et_2O, RT, 1 h.

values for C_α and C_β fall in the range 20−50 ppm, and the ^1J(C,H) values of approximately 125 Hz indicate that the carbon atoms of the metallacycle have more aliphatic (sp^3) than olefinic (sp^2) character. In each complex the absolute differences in chemical shift between the C_α and C_β atoms, i.e. $|\delta(C_\alpha) - \delta(C_\beta)|$, is relatively small (∼10 ppm) and similar small values for $|\delta(C_\alpha) - \delta(C_\beta)|$ were also found by Schrock and co-workers for square-pyramidal tantala- and tungstacyclobutane complexes which contain small C_α−M−C_α angles (∼60°) and relative long M- - -C_β distances (∼2.8 Å). In contrast trigonal-bipyramidal tantala- and tungstacyclobutane complexes which contain large C_α−M−C_α angles (∼80°) and short M- - -C_β distances (∼2.3 Å) show a relatively large value for $|\delta(C_\alpha) - \delta(C_\beta)|$, and it was therefore concluded that there is a direct correlation between $|\delta(C_\alpha) - \delta(C_\beta)|$ and the M- - -C_β distance.[5]

The molecular structures of the pentagonal-bipyramidal tantalacyclobutane complexes described in this paper and in a previous paper[1] are comparable to the square-pyramidal tantalum tungsten complexes mentioned earlier; i.e., they have small C_α−M−C_α angles and long M- - -C_β distances (*vide supra*) and, consistent with earlier reports, they show small differences in chemical shift values between C_α and C_β.

Mechanism for the Formation of 2 and 3. The formation of complexes **2** and **3** from **1** and an alkene is a process which can be reversed by reaction with excess ethene (*vide supra*). On the basis of the experimental observations, we propose a mechanism for the formation of **2** and **3** which is shown in Scheme 2. The first step in this mechanism involves a rearrangement of a metallacyclic complex into an "alkylidene/olefin" intermediate[5a] from which loss of ethene results in the formation of a methylene intermediate (Scheme 2).

Schrock and co-workers were able to trap the methylene intermediate [W(=CH_2)(NAr){$OCMe_2(CF_3)$}(PMe_3)] by addition of PMe_3 to a solution of the tungstacyclobutane complex [W{$(CH_2)_3$-1,3}(NAr){$OCMe_2(CF_3)$}].[5a] Related kinetic studies on the reaction of [W{CH_2CH-(*t*-Bu)CH_2-1,3}(NAr)$(OAr)_2$] with ethene, which gives the unsubstituted tungstacyclobutane complex [W{$(CH_2)_3$-1,3}(NAr){$OCMe_2(CF_3)$}], showed this reaction to be independent of the ethene concentration; i.e., the methylene intermediate forms by a dissociative mechanism as is shown in Scheme 2.[5] In earlier work from our group we proposed that the methylene intermediate as shown in Scheme 2 is involved in the formation of complex **1** from the reaction of alkylidene complexes [Ta(=CHR)(CNN)(O-*t*-Bu)$_2$] (R = *t*-Bu, CMe_2-Ph) with ethene.[1]

In the second step of the proposed mechanism the methylene intermediate can react either with ethene to re-form **1** or in the forward direction with propene or styrene to form **2** or **3**, respectively. In practice because of loss of ethene from the solution the equilibrium shifts completely to the side of the substituted tantalacyclobutane complexes **2** and **3**. Probably for steric reasons the organyl substituent of the olefin becomes located in the products **2** and **3** on the β carbon atom of the metallacyle as far away from the bulky groups attached to the metal center as possible (Scheme 2).

Reactivity of Complexes 1−3 with CO. The unsubstituted tantalacyclobutane **1** reacts with CO at room temperature to afford the oxytantalacyclopropane complex [Ta{C(O)$((CH_2)_3$-1,3)}(CNN)(O-*t*-Bu)$_2$] (**4**), which has been isolated as a white air-stable solid in 59% yield (Scheme 3). Complex **4** is soluble in benzene, toluene, and diethyl ether, but it is insoluble in pentane and hexane. Needle-shaped colorless crystals of **4** were obtained by slow cooling of a saturated diethyl ether solution from +25 to −30 °C. In contrast to the unsubstituted tantalacyclobutane complex **1**, the methyl- and phenyl-substituted tantalacyclobutane complexes **2** and **3**, respectively, react only slowly with CO in benzene-d_6 and after 2 days NMR spectroscopy

(5) (a) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535 and references therein. (b) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, 110, 4964. (c) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, 39, 1.

showed the formation of a mixture of products from which no stable organometallic product could be isolated. In the ^{13}C NMR spectrum of this *in situ* mixture no signals in the region around 100 ppm, indicative for an oxymetallacyclopropane *C*O carbon,[6a−e] were found.

The ^1H NMR spectrum of **4** shows this complex to exist as two isomers in a 10:1 molar ratio. The major product has the aromatic H_{ortho} signal of the CNN ligand at 9.06 ppm whereas the minor product has an aromatic H_{ortho} signal at 9.33 ppm. Unfortunately, most of the resonances of this minor product could not be assigned accurately due to overlap with those of the major product. We believe the two species are mutual isomers which differ in orientation of the oxytantalacyclopropane unit. Overall the ^1H spectrum of the major isomer of **4** is in accordance with a pentagonal bipyramidal structure with the two O-*t*-Bu groups occupying the apical positions as found in the solid-state molecular structure (*vide infra*) illustrated in Figure 4. This spectrum shows, for example, two Me signals for a diastereotopic NMe_2 unit and a well-resolved AB pattern for the $ArCH_2N$ protons. The ^{13}C NMR (50 MHz, C_6D_6, 25 °C) spectrum of **4** shows a signal for the CO carbon atom at 100.6 ppm and CH_2 signals for the cyclobutanone ring are present at 16.79, 49.59 and 51.56 ppm. The "acetone-coordinated" complex $[Ta(Me)_2(\eta^5\text{-}C_5Me_5)\{\eta^2\text{-}C(O)Me_2\}]$ described by Schrock and co-workers has a similar characteristic high-field CO carbon resonance at 111 ppm;[2j] in other oxymetallacyclopropane complexes this resonance falls in the range 80−120 ppm.[6a−e]

The IR spectrum (KBr) of **4** shows a ν(C−O) value for the oxytantalacylopropane fragment at 1181 cm^{-1}, and since noncoordinated cyclobutanone has a ν(C−O) value of 1790 cm^{-1},[7] this value indicates that in **4** there is strong overlap of the C═O π^* acceptor orbital with the occupied frontier orbitals of the [Ta(CNN)(O-*t*-Bu)] fragment. The "acetone-coordinated" complexes $[Ta(Me)_2(\eta^5\text{-}C_5Me_5)\{C(O)Me_2\}]$ and $[WCl_2\{C(O)Me_2\}_2(PMe_2Ph)_2]$ afford similar ν(C−O) values of 1200 and 1230 cm^{-1}, respectively.[3j,6d]

Reactivity of Complexes 1−3 with *t*-BuNC. Addition of 1 equiv of *t*-BuNC to diethyl ether solutions of the tantalacyclobutane complexes **1**−**3** affords the monoinsertion products $[Ta\{C(=N\text{-}t\text{-}Bu)(CH_2CH(R)CH_2\text{-}1,4\}(CNN)(O\text{-}t\text{-}Bu)_2]$ (R = H (**5**), Me (**6**), and Ph (**7**), respectively), see Scheme 3, which contain an η^2-bonded acylamino unit. Complexes **5** (62% yield) and **7** (50% yield) have been isolated as air-sensitive needle-shaped yellow crystals by slow cooling of saturated solutions in pentane and diethyl ether, respectively, from +25 to −30 °C. Due to its high solubility in organic solvents attempts to crystallize **6** from either pentane or diethyl ether were unsuccessful, and this complex has therefore been characterized *in situ* by NMR spectroscopy of a benzene-d_6 solution of **2** to which 1 equiv of *t*-BuNC had been added. The η^2-acylimino complexes **5**−**7** are soluble in benzene, toluene, and diethyl ether.

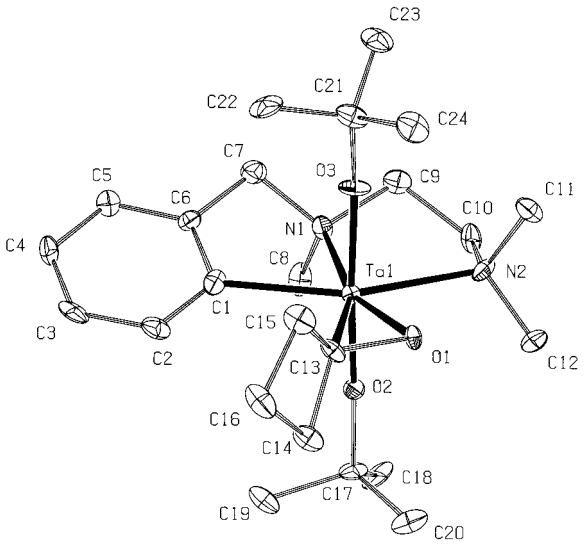


Figure 2. ORTEP thermal motion ellipsoid plot[19] (drawn at 30% probability level) of $[Ta(\eta^2\text{-}C(O)(CH_2)_3)(CNN)(O\text{-}t\text{-}Bu)_2]$ (**4**) together with adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

Spectroscopic Characterization of 5−7. Complexes **5**−**7** have been (primarily) characterized by spectroscopic techniques and a single-crystal structure determination of **7**. Both in the solid state and in solution they are seven-coordinate complexes which contain two tantalacycles of different sizes that share a common Ta−C bond and which have only *C,N*-bonding of the CNN ligand.

The ^1H NMR (300 MHz, C_6D_6, 25 °C) spectra of **5**−**7** show only one Me resonance for the NMe_2 unit of the CNN ligand, and this indicates that this outer NMe_2 nitrogen donor is not coordinated to the metal center in solution. As anticipated the $ArCH_2N(Me)$ protons give rise to a well-resolved AB pattern. As a result of the stereogenity of both the inner N(Me) nitrogen donor and the CH(R) carbon atom of the five-membered metallacyclic ring, two different NMR-distinguishable diastereoisomers are theoretically possible, i.e. *RR/SS* and *RS/SR*, and these isomers are indeed observed in an approximate ratio of 1:1.2 in the ^1H and ^{13}C NMR spectra of **6** and **7**. In the ^{13}C spectra (50 MHz, C_6D_6, 25 °C) of **5**−**7** the signal for the C═N carbon resonates at approximately 230 ppm, and this result is in accordance with literature data for η^2-coordinated iminoacyl carbon atoms.[4b,g,h,j]

The IR spectra (KBr) of complexes **5** and **7** show ν(C═N) absorptions at 1721 and 1726 cm^{-1}, respectively, and these data are in agreement with literature values for iminoacyl complexes.[4i,m] For noncoordinated imines ν(C═N) is found between 1690 and 1640 cm^{-1},[7] and these data for **5** and **7** in KBr indicate that there is an interaction of the C═N π^* acceptor orbital with the occupied frontier orbitals of the $[Ta(CNN)(O\text{-}t\text{-}Bu)_2]$ fragment.

Solid-State Structures of Complexes 4 and 7. The molecular structures of **4** and **7** are shown in Figures 2 and 3, respectively, and relevant bond distances and angles are given in Table 3. The molecular structure of **4** shows it to be a mononuclear pentagonal bipyramidal tantalum species with the aryl C_{ipso} carbon, the N(Me) and NMe_2 nitrogen donors, and the carbon and oxygen atoms of the C═O group (C(13)−O(1))

(6) (a) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 607. (b) Hill, J. E.; Fanwick, F. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771. (c) Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, *12*, 4560. (d) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213. (e) Klein, D. P.; Dalton, D. M.; Méndez, N. Q.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1991**, *412*, C7. (f) Alt, H. G.; Herrmann, G. S.; Thewalt, U. *J. Organomet. Chem.* **1987**, *327*, 237.

(7) Grasselli, J. G.; Ritchy, W. M. *Atlas of Spectral Data and Physical Constants for Organic Compounds*, 2nd ed.; CRC Press: Cleveland, OH, 1975; Vol. III, p 96.

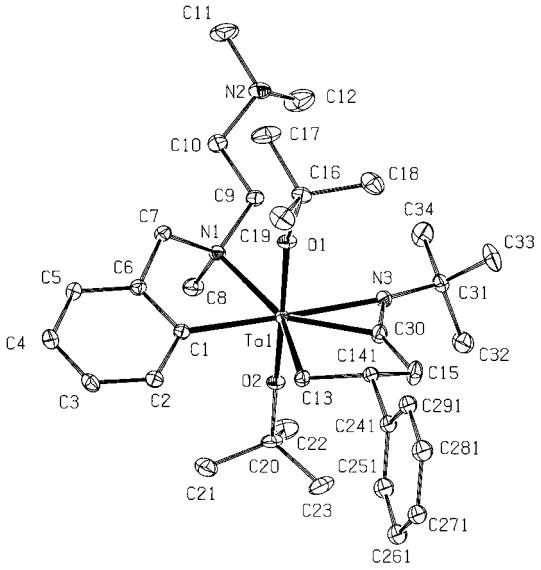


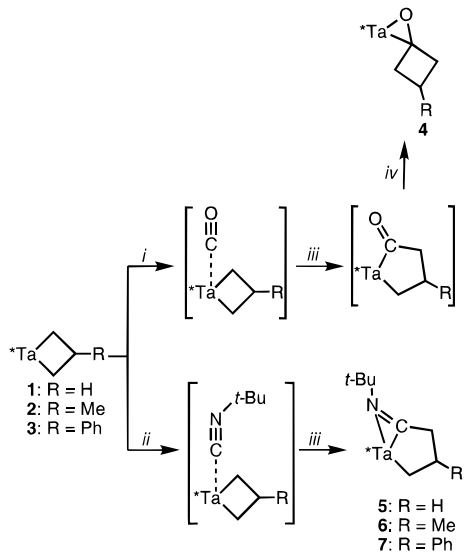
Figure 3. ORTEP thermal motion ellipsoid plot[19] (drawn at 30% probability level) of [Ta{C(═N-*t*-Bu)CH_2CH(Ph)-CH_2-1,4}(CNN)(O-*t*-Bu)$_2$] (**7**) together with adopted numbering scheme. Hydrogen atoms and the minor disorder component have been omitted for clarity.

Table 3. Bond Distances (Å) and Angles (deg) for 4 and 7

4		**7**	
Ta(1)−O(2)	1.885(10)	Ta(1)−O(1)	1.903(3)
Ta(1)−O(3)	1.887(10)	Ta(1)−O(2)	1.890(3)
Ta(1)−C(1)	2.261(15)	Ta(1)−C(1)	2.246(5)
C(13)−O(1)	1.401(17)	C(30)−N(3)	1.236(6)
Ta(1)−N(1)	2.384(15)	Ta(1)−N(1)	2.442(4)
Ta(1)−N(2)	2.424(12)	Ta(1)−C(13)	2.265(5)
Ta(1)−O(1)	1.971(11)	Ta(1)−C(30)	2.099(5)
Ta(1)−C(13)	2.141(17)	Ta(1)−N(3)	2.348(4)
O(2)−Ta(1)−O(3)	166.0(5)	O(1)−Ta(1)−O(2)	169.60(16)
O(2)−Ta(1)−C(13)	96.5(5)	O(2)−Ta(1)−C(30)	89.19(18)
O(2)−Ta(1)−O(1)	95.6(5)	O(2)−Ta(1)−N(3)	87.05(15)
O(2)−Ta(1)−C(1)	92.6(5)	O(2)−Ta(1)−N(1)	88.52(14)
O(2)−Ta(1)−N(1)	86.1(5)	O(2)−Ta(1)−C(1)	91.48(17)
O(2)−Ta(1)−N(2)	84.5(4)	O(2)−Ta(1)−C(13)	96.14(16)
N(1)−Ta(1)−C(1)	71.6(5)	N(1)−Ta(1)−C(1)	74.50(15)
N(1)−Ta(1)−C(13)	160.4(5)	N(1)−Ta(1)−C(13)	156.24(15)
N(1)−Ta(1)−O(1)	159.7(4)	N(1)−Ta(1)−C(30)	133.38(16)
N(1)−Ta(1)−N(2)	75.8(4)	N(1)−Ta(1)−N(3)	101.75(13)
Ta(1)−O(2)−C(17)	165.3(11)	N(3)−Ta(1)−C(30)	31.64(16)
Ta(1)−O(3)−C(21)	163.7(10)	C(13)−Ta(1)−C(30)	70.14(18)
O(1)−Ta(1)−C(13)	39.6(5)		
C(14)−C(13)−C(15)	90.5(12)		
O(1)−C(13)−C(14)	117.7(12)		
O(1)−C(13)−C(16)	142.2(13)		

forming the meridional plane and with the alkoxide groups occupying the axial positions. This structure therefore bears analogy to that of **1**,[1] as well as those of **2** and **3** described above. In **4** the ArCH_2N(Me) nitrogen donor is a stereogenic center with a fixed configuration because of its coordination to the metal center, and Figure 2 shows the *S* configuration. The most interesting aspect of the structure of **4** is the presence of a cyclobutanone system with the keto function "side-on" bonded to the metal center (Ta−C(13) = 2.265(5) Å, Ta−O(1) = 1.903(3) Å). The C(13)−O(1) distance of 1.401(17) Å compares favorably with C−O distances in other oxymetallacyclopropane complexes described in literature that generally fall in the range 1.3−1.4 Å.[6a−f] The four-membered cyclobutanone ring C(13)−C(14)−C(16)−C(15) in **4** is slightly puckered with the angle between the planes described by C(15), C(13), and C(14) and C(15), C(16), and C(14) having a value of 16(2)°.

Scheme 4. Postulated Mechanism for the Formation of Complexes 4-7 (*Ta = {Ta(CNN)(O-*t*-Bu)$_2$})[a]

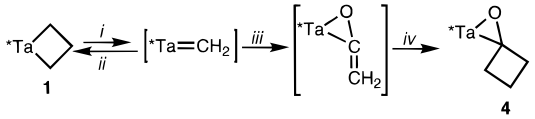


[a] Reaction conditions *i* **1**: CO, R = H. *ii* **1**-**3**: + *t*-BuNC. *iii* insertion. *iv* ring closure.

The structure of **7** (Figure 3) shows it to be a seven-coordinate tantalum(V) species with an overall pentagonal bipyramidal structure in which the O-*t*-Bu groups occupy the apical positions. In the meridional plane the tantalum center is η^2-*C,N*-bonded by the CNN ligand and, most importantly, η^3-*N,C,C* bis-chelate bonded by the C(═N-*t*-Bu)CH_2CH(Ph)CH_2-1,4 unit to form two tantalacycles of different sizes which share a common Ta−C bond. The smaller three-membered ring comprises the metal center with the nitrogen donor N(3) and carbon atom C(30) of the η^2-bonded iminoacyl fragment, while the larger five-membered ring consists of the metal center and the four carbon atoms C(30)−C(15)−C(14)−C(13), i.e. it is a metallacylopentane system. The geometric parameters of the tantalum η^2-iminoacyl unit are normal for early transition metal complexes which contain a side-on-bonded isocyanide substituent.[3b,e,g,h,l,m] In particular the small N(3)−Ta(1)−C(3) bite angle of 31.64(16)° within the iminoacyl fragment is comparable to those found by Peterson *et al.* in the *tert*-butyl isocyanide mono- and di-insertion products [Cp_2Zr{(C═N-*t*-Bu)CH_2Si$Me_2$$CH_2$-1,4}] and [$Cp_2$M{(C═N-*t*-Bu)(C═N-*t*-Bu)CH_2Si$Me_2$$CH_2$-1,5}] (M = Zr, Hf), respectively.[4a−e]

Mechanisms for the Formation of Complexes 4−7. The molecules CO and *t*-BuNC often have a similar chemistry that is related to the isoelectronic structure of C≡O and −N≡C units. It is therefore likely that the formation of the oxytantalacyclopropane complex **4** and the acylimino complexes **5**−**7** follow the same mechanistic pathway, and we propose the most likely pathway to be that shown in Scheme 4. This mechanism involves: (i) a dissociation of the Ta−*N*Me_2 coordination bond and subsequent coordination of a CO or *t*-BuNC molecule to the metal, (ii) insertion of these molecules into the metal−carbon bond to afford an acyl intermediate in the case of CO or the iminoacyl complexes **5**−**7** in the case of *t*-BuNC, and (iii) in the case

Scheme 5. Postulated Mechanism for the Reaction of Tantalacyclobutane Complexes with CO *via* a Ketene Intermediate (*Ta = {Ta(CNN)(O-*t*-Bu)$_2$})[a]



1 4

[a] Reaction conditions: *i*, $-C_2H_4$; *ii*, $+C_2H_4$; *iii*, +CO; *iv*, $+C_2H_4$.

of the acyl intermediate a ring closure to afford the oxytantalacyclopropane complex **4**.

Hoffmann and co-workers found by extended Hückel calculations that an iminoacyl complex[8] is thermodynamically more stable than an acyl complex, and this result was further supported by experimental findings of Sanchez and co-workers.[4m] The reason why the acyl complex does not undergo ring closure in the case of the iminoacyl complex (Scheme 4) might be explained by these earlier results. Finally, further support for the mechanism of Scheme 4 is provided by insertion reactions of CO into the M−C bond of four- and five-membered metallacyclic complexes which afford cyclobutanone[9a−c] and cyclopentanone.[3d,e,9d−f]

Alternative Mechanism for the Formation of Complex 4. On the basis of literature reports,[9c,d,e] an alternative mechanism for the formation of **4** from **1** and CO is possible, and this involves a ketene intermediate as shown in Scheme 5. This mechanism involves formation of a methylene intermediate *via* rearrangement of the metallacycle of **1** into an "alkylidene/olefin" intermediate and subsequent loss of the coordinated ethene as described earlier in the mechanism for the formation of the substituted tantalacyclobutanes **2** and **3**. A ketene intermediate is then formed through a reaction of this methylene intermediate with CO.[10ab] Reaction of ethene, which was initially lost from the "alkylidene/olefin" intermediate but which is still present in solution, with this ketene intermediate gives complex **4**. Although this alternative mechanism (Scheme 5) is possible, it seems less likely as we have not observed the presence of such a ketene intermediate by NMR spectroscopy in the formation of **4**. Futhermore, the synthesis of the complexes **5**−**7**, which can be considered to be the acylimino analogs of the acyl intermediate in the formation of **4**, favors the first mechanism (Scheme 4). Results reported by Van der Heiden and co-workers working with systems similar to ours also oppose this alternative mechanism.[10b] When they reacted CO with the titanium neopentylidene complex [Ti(Cp)(=CH-*t*-Bu)(PMe$_2$CH$_2$CO)(CMe$_2$-*o*-C$_6$H$_4$CMe$_2$)], which contains a bulky phosphinoalkoxide ancillary ligand, they obtained a mixture of two isomeric ketene complexes in which the CO bond of the carbonyl group is bonded in a "edge-on" fashion to the titanium center. However, attempted reaction of this ketene complex with ethene does not give a monosubstituted oxytitanacyclopropane complex as would be expected when a mechanism similar to that shown in Scheme 5 is operative. Instead they found that insertion of CO into the Ti-C bond takes place to afford a bis(alkoxide) complex which contains a 1-oxa-titanacyclopentane unit.[10b]

The reason that carbon monoxide reacts differently with the unsubstituted tantalacyclobutane complex **1** than with the substituted tantalacyclobutane complexes **2** and **3** is not clear. It was therefore very surprising that **1**−**3** do react in exactly the same way with *t*-BuNC to afford in all cases iminoacyl complexes. An important aspect worthy of note is that the reactions of **1**−**3** with CO are seen to be very slow (taking many hours) when compared to the almost instantaneous reactions with *t*-BuNC. An explanation for this behavior might be found in the possible solution equilibrium between a metallacyclic form and an "alkylidene/olefin" form of the tantalacyclobutane. Loss of the olefin from the latter would lead to a methylene species (Scheme 2; *vide supra*). If this equilibrium is more shifted to the side of the "alkylidene/olefin" for the substituted tantalacyclobutane complexes **2** and **3** than for unsubstituted tantalacyclobutane **1** because of steric hinderance of the substituent on the olefin, then complexes **2** and **3** will show more alkylidene character and are therefore more likely to react with CO as shown in Scheme 5 to give a ketene species. For complex **1** it is likely that this equilibrium is shifted more to the metallacyclic side so that reaction with CO, as shown in Scheme 4, affords the oxytantalacyclopropane complex **4**. However, without spectroscopic evidence supporting a mechanism as shown in Scheme 5 this explanation for the difference in reactivity of the tantalacylobutane complexes **1**−**3** with CO is only speculative.

Structural Comparison of the Bonding in the CNN Tantalum Complexes. In this and a previous paper[1] we have reported a series of pentagonal bipyramidal tantalum complexes which show a great structural similarity; i.e. the CNN ligand is meridionally η^3-*C*,*N*,*N*′-bonded to the metal with two alkoxide groups in the apical positions. In the case of the iminoacyl complex [Ta{C(=N-*t*-Bu)(CH$_2$CH(Ph)CH$_2$-1,4}(CNN)(O-*t*-Bu)$_2$] (**7**), the position that is occupied by the NMe$_2$ nitrogen donor of CNN in the other species is now occupied by the nitrogen donor of the imine group and, thus, it too bears a direct structural analogy to these other complexes. The structural similarity of these species finds its origin in the filled frontier orbital of the [Ta(CNN)(O-*t*-Bu)$_2$] fragment. This orbital is positioned in the meridional plane of the pentagonal bipyramidal structure and is available for binding to substrates either in a η^2- or in a σ-fashion and in so doing affords bite angles varying from 70° in the η^2-iminoacyl complex **7** (C−Ta−C) to *ca.* 40° for both the ethene coordination complex [Ta(CNN)(O-*t*-Bu)$_2$)-(CH$_2$=CH$_2$)][1] (C−Ta−C) and the oxytantalacyclopropane complex **4** (C−Ta−O). In this sense the [Ta(CNN)-(O-*t*-Bu)$_2$] fragment is isolobal to a CH$_2$ fragment, and on this basis, the structures of the different organometallic complexes can be simplified to organic molecules, i.e. cyclopropane ([Ta(CNN′)(H$_2$C=CH$_2$)(O-*t*-

(8) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

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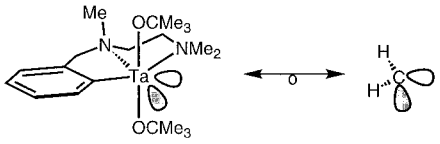
(10) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1995**, *14*, 1278. (c) Miyashita, A.; Ohyoshi, M.; Shitara, H.; Nohira, H. *J. Organomet. Chem.* **1988**, *338*, 103. (d) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, *22*, 1255. (e) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461.

Scheme 6. Isolobal Comparison of the Frontier Orbitals of the {Ta(CNN)(O-*t*-Bu)$_2$} Fragment in the Tantalum Complexes 1−7 with the CH$_2$ Fragment



Bu)$_2$]),[1] cyclobutanes (**1**−**3**), cyclopentanes (**5**−**7**), and an ethylene oxide derivative (**4**).

Conclusions

Our current investigations on the synthesis of Ta(V) species with the ortho-chelating aryldiamine CNN ligand have shown that the [Ta(CNN)] moiety in combination with two alkoxide ligands, i.e. the [Ta(CNN)(O-*t*-Bu)$_2$] fragment, which is isolobal with CH$_2$, provides an excellent fragment for binding of a variety of (hetero)organyl fragments. The Ta−C$_{ipso}$ bond in the [Ta(CNN)(O-*t*-Bu)$_2$] fragment has considerable stability as illustrated by the fact that CO and *t*-BuNC do not insert in this bond but instead into the Ta−C bond of the tantalacyclic unit. This makes the CNN ligand in this Ta(V) chemistry a true spectator ligand; i.e., it does not participate in reactions at the metal center, as is generally found for the commonly used cyclopentadienyl ligands $C_5H_5^-$ (Cp^-) and its derivatives in transition metal chemistry. It is interesting to note that a comparison between the monoanionic CNN and Cp ligands indicates that, from a stereochemical point of view, the CNN ligand is much more versatile in its bonding modes to tantalum. Whereas for Cp η^5-bonding to Ta is usually found we have established that CNN can, in concert with the other ligands in the Ta coordination sphere, bind either as η^3-facial- or η^3-meridional-*C,N,N′* as well as η^2-*C,N*.

Experimental Section

General Methods. All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled prior to use. Elemental analyses were carried out by Dornis und Kolbe, Microanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer; IR spectra were recorded on a Mattson Galaxy FTIR 5000 spectrometer. Complex [Ta{(CH$_2$)$_3$-1,3}(CNN)(O-*t*-Bu)$_2$}] (**1**) was prepared according to a literature procedure.[1] CH$_2$=CHPh and *t*-BuNC were obtained by Aldrich and dried on molecular sieves (4 Å). High-purity ethene, propene, and carbon monoxide were obtained from Aldrich and used as received; resublimed TaCl$_5$ was obtained from Alfa.

[Ta{CH$_2$CH(Me)CH$_2$-1,3}(CNN)(O-*t*-Bu)$_2$] (2). A pale yellow solution of **1** (0.89 g, 1.59 mmol) in Et$_2$O (70 mL) was saturated with propene and stirred for 18 h. Removal of the solvent under reduced pressure afforded an off-white solid which was subsequently washed with cold pentane (3 × 10 mL) and dried under reduced pressure giving pure **2** as a white solid; yield 0.77 g (84%). Small needle-shaped colorless crystals of **2** can be obtained by slow cooling of a saturated diethyl ether solution of **2** from +25 to −30 °C. Complex **2** is obtained as a mixture of two isomers in a ratio of 10:1. Anal. Calcd for $C_{24}H_{45}N_2O_2Ta$: C, 50.17; H, 7.89; N, 4.88. Found: C, 49.88; H, 7.90; N, 4.93. Data for the major isomer: ^{1}H NMR (300.13 MHz, C_6H_6, 25 °C) δ 0.29 (m, 1 H, C*H*$_2$CH(Me)C*H*$_2$), 0.96 (m, 1 H, C*H*$_2$CH(Me)C*H*$_2$), 1.10 (s, 9 H, OC*Me*$_3$), 1.20 (s, 9 H, OC*Me*$_3$), 1.68 (m, 2 H, NC*H*$_2$C*H*$_2$N), 1.73 (d, ^3J(H,H) = 4 Hz, 3 H, CH$_2$CH(*Me*)CH$_2$), 1.95 (m, 1 H, C*H*$_2$CH(Me)C*H*$_2$), 2.08 (s, 3 H, N*Me*), 2.09 (m, 1 H, C*H*$_2$CH(Me)C*H*$_2$), 2.27 (s, 3 H, N*Me*), 2.29 (s, 3 H, N*Me*), 2.45 (m, 1 H, NC*H*$_2$C*H*$_2$N), 2.76 (m, 1 H, NC*H*$_2$C*H*$_2$N), 3.18 (d, ^2J(H,H) = 12 Hz, 1 H, ArC*H*$_2$N), 3.20 (m, 1 H, CH$_2$C*H*(Me)CH$_2$), 4.63 (d, ^2J(H,H) = 12 Hz, 1 H, ArC*H*$_2$N), 7.15−7.23 (m, 2 H, Ar*H*), 7.38 (m, 1 H, Ar*H*), 8.64 (d, ^3J(H,H) = 8 Hz, 1 H, Ar*H*); ^{13}C{^{1}H} NMR (50.32 MHz, C_6H_6, 25 °C) δ 31.7 (OC*Me*$_3$), 31.9 (OC*Me*$_3$; CH$_2$CH(*Me*)CH$_2$), 36.9 (^1J(C,H) = 124 Hz, *C*H$_2$CH(Me)*C*H$_2$), 37.1 (^1J(C,H) = 129 Hz, CH$_2$*C*H(Me)CH$_2$), 47.1 (N*Me*), 49.0 (N*Me*), 49.3 (^1J(C,H) = 125 Hz, *C*H$_2$CH(Me)*C*H$_2$), 50.3 (N*Me*), 56.6 (N*C*H$_2$C*H*$_2$N), 61.6 (N*C*H$_2$C*H*$_2$N), 70.3 (Ar*C*H$_2$N), 78.6 and 78.9 (O*C*Me$_3$), 122.8, 124.6, 126.2, 138.2 and 148.7 (Ar), 191.0 (C$_{ipso}$).

[Ta{CH$_2$CH(Ph)CH$_2$-1,3}(CNN)(O-*t*-Bu)$_2$] (3). To a pale yellow solution of **1** (0.90 g, 1.61 mmol) in Et$_2$O (70 mL) was added H$_2$C=CHPh (0.34 g, 3.23 mmol), and the solution was stirred for 3 d. Removal of the solvent under reduced pressure gave a yellow/white sticky solid which was subsequently washed with cold pentane (3 × 10 mL) and dried under reduced pressure giving **3** as a white solid; yield 0.67 g (65%). The product can be recrystallized by cooling a saturated solution in diethyl ether to −30 °C and is obtained as a mixture of two isomers in a ratio of 10:1. Anal. Calcd for $C_{29}H_{47}N_2O_2Ta$: C, 54.71; H, 7.44; N, 4.40. Found: C, 54.61; H, 7.38; N, 4.32. Data for the major isomer: ^{1}H NMR (300.13 MHz, C_6H_6, 25 °C) δ 0.77 (m, 1 H, C*H*$_2$CH(Ph)C*H*$_2$), 1.07 (s, 9 H, OC*Me*$_3$), 1.12 (s + m, 10 H, OC*Me*$_3$; C*H*$_2$CH(Ph)C*H*$_2$), 1.44 (m, 1 H, C*H*$_2$CH(Ph)C*H*$_2$), 1.64 (m, 2 H, NC*H*$_2$C*H*$_2$N), 2.09 (s, 3 H, N*Me*), 2.18 (m, 1 H, C*H*$_2$CH(Ph)C*H*$_2$), 2.27 (s, 3 H, N*Me*), 2.28 (s, 3 H, N*Me*), 2.40 (m, 1 H, NC*H*$_2$C*H*$_2$N), 2.76 (m, 1 H, NC*H*$_2$C*H*$_2$N), 3.17 (d, ^2J(H,H) = 12 Hz, 1 H, ArC*H*$_2$N), 4.66 (d, ^2J(H,H) = 12 Hz, 1 H, ArC*H*$_2$N), 4.33 (m, 1 H, CH$_2$C*H*(Ph)CH$_2$), 7.17−7.26 (m, 3 H, Ar*H*), 7.37−7.48 (m, 3 H, Ar*H*), 7.85 (d, ^3J(H,H) = 7 Hz, 2 H, *Ph*), 8.63 (t, ^3J(H,H) = 7 Hz, 1 H, C$_6H_4$). ^{13}C{^{1}H} NMR (50.32 MHz, C_6H_6, 25 °C) δ 31.9 (OC*Me*$_3$), 32.0 (OC*Me*$_3$), 34.7 (^1J(C,H) = 124 Hz, *C*H$_2$CH(Ph)CH$_2$), 41.3 (^1J(C,H) = 128 Hz, CH$_2$*C*H(Ph)CH$_2$), 46.7 (^1J(C,H) = 122 Hz, *C*H$_2$CH(Ph)CH$_2$), 47.3 (N*Me*), 49.2 (N*Me*), 50.4 (N*Me*), 56.7 (N*C*H$_2$C*H*$_2$N), 61.7 (N*C*H$_2$C*H*$_2$N), 70.3 (Ar*C*H$_2$N), 78.9 (O*C*Me$_3$), 79.0 (O*C*Me$_3$), 123.0, 124.2, 124.7, 126.3, 126.4, 128.2, 138.3, 148.8 and 160.5 (Ar), 190.6 (C$_{ipso}$).

[Ta{C(O)((CH$_2$)$_3$-1,3)}(CNN)(O-*t*-Bu)$_2$] (4). A pale yellow solution of **1** (1.26 g, 2.2 mmol) in Et$_2$O (50 mL) was saturated with carbon monoxide and stirred for 48 h. The pale yellow solution was concentrated under reduced pressure to *ca.* 15 mL from which **4** crystallized overnight at −30 °C as needle-shaped colorless crystals; yield 0.79 g (59%). Complex **4** is obtained as a mixture of products, possibly two isomers (ratio of major to minor product is 10:1). Anal. Calcd for $C_{24}H_{43}N_2O_3Ta$: C, 48,98; H, 7.36; N, 4.76. Found: C, 49.15; H, 7.31; N, 4.72. Data for the major product: ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C) δ 0.95 (s, 9 H, OC*Me*$_3$), 1.08 (s, 9 H, OC*Me*$_3$), 1.75 (m, 2 H, NC*H*$_2$C*H*$_2$N), 2.27 (s, 3 H, N*Me*), 2.42 (s, 3 H, N*Me*; m, 1 H, NC*H*$_2$C*H*$_2$N), 2.57 (s, 3 H, N*Me*; m, 2 H, C*H*$_2$C*H*$_2$C*H*$_2$), 2.97 (m, 1 H, NC*H*$_2$C*H*$_2$N), 3.32 (d, ^2J(H,H) = 12 Hz, 1 H, ArC*H*$_2$N), 3.4−3.9 (m, 4 H, C*H*$_2$C*H*$_2$C*H*$_2$), 4.62 (d, ^2J(H,H) = 12 Hz, 1 H, ArC*H*$_2$N), 7.30 (m, 2 H, Ar*H*), 7.48 (m, 1 H, Ar*H*), 9.06 (d, ^3J(H,H) = 7 Hz, 1H, Ar*H*); ^{13}C{^{1}H} NMR (50.32 MHz, C_6H_6, 25 °C) δ 16.8 (*C*H$_2$C*H*$_2$C*H*$_2$), 31.1 (OC*Me*$_3$), 31.8 (OC*Me*$_3$), 42.9 (N*Me*), 43.1 (N*Me*), 47.6 (N*Me*), 49.6 (*C*H$_2$C*H*$_2$C*H*$_2$), 51.6 (*C*H$_2$C*H*$_2$C*H*$_2$), 56.5 (NC*H*$_2$C*H*$_2$N), 60.2 (NC*H*$_2$C*H*$_2$N), 70.3 (Ar*C*H$_2$N), 77.7 (O*C*Me$_3$), 77.9 (O*C*Me$_3$), 100.6 (*C*(O)), 123.5, 125.0, 126.6, 142.5 and 148.9 (Ar), 184.7 (C$_{ipso}$); IR (KBr) (cm^{-1}) 1181, ν(C=O).

[Ta{C(=N-*t*-Bu)(CH$_2$)$_3$-1,4}(CNN)(O-*t*-Bu)$_2$] (5). To a pale yellow solution of **1** (0.68 g, 1.2 mmol) in Et$_2$O (50 mL) was added within 1 min a solution of *tert*-butyl isocyanide (136 μL, 1.2 mmol) in Et$_2$O (20 mL) which gave an immediate color change to bright yellow. The solution was stirred for an additional 1.5 h after which the solvent was removed *in vacuo*,

Table 4. Crystallographic Data for 2−4 and 7

	2	3	4	7
		Crystal Data		
formula	$C_{24}H_{45}N_2O_2Ta$	$C_{29}H_{47}N_2O_2Ta$	$C_{24}H_{43}N_2O_3Ta$	$C_{34}H_{56}N_3O_2Ta$
mol wt	574.58	636.65	588.56	719.79
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	17.1133(12)	14.3964(12)	16.818(3)	9.4616(6)
b (Å)	16.128(2)	14.1155(8)	9.520(4)	9.4270(8)
c (Å)	9.0213(6)	17.1913(8)	18.322(4)	38.962(3)
β (deg)	94.173(5)	124.198(8)	122.55(2)	102.773(4)
V (Å^3)	2483.3(4)	2889.5(4)	2472.7(14)	3389.2(4)
D_{calc} (g cm^{-3})	1.537	1.463	1.581	1.411
Z	4	4	4	8
F(000)	1168	1296	1192	1480
μ (cm^{-1})	44.5 (Mo Kα)	37.8 (Mo Kα)	44.2 (Mo Kα)	32.8 (Mo Kα)
cryst size (mm)	0.08 × 0.13 × 0.25	0.5 × 0.5 × 0.5	0.4 × 0.4 × 0.4	0.10 × 0.18 x 0.23
		Data Collection		
θ_{min}, θ_{max} (deg)	1.2, 27.5	1.7, 27.5	1.4, 27.5	0.5, 27.5
SET4 θ_{min}, θ_{max} (deg)	10.32, 13.99 (25 reflcns)	11.16, 13.84 (25 reflcns)	11.86, 13.76 (21 reflcns)	11.43, 13.98 (24 reflcns)
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	ω
$\Delta\omega$ (deg)	1.02 + 0.35 tan θ	0.62 + 0.35 tan θ	1.00 + 0.35 tan θ	0.88 + 0.35 tan θ
hor, ver aperture (mm)	3.65, 4.00	2.60, 4.00	3.00, 4.00	1.91 + 0.95 tan θ, 4.00
X-ray exposure (h)	27	20	27	16
linear decay (%)	3	35	4	2
ref reflcns	$50\bar{2}$, $\bar{4}2\bar{2}$, $\bar{2}3\bar{3}$	$2\bar{4}3$, $\bar{5}23$, $1\bar{3}2$	361, $\bar{7}3\bar{1}$	216, $0\bar{2}9$, $3\bar{1}\bar{1}$
data set	−22 to 22, 0 to 20, −11 to 9	−18 to 17, −18 to 0, −22 to 17	−21 to 19, −12 to 0, −23 to 19	−8 to 12, −12 to 0, −50 to 49
tot. data	9863	9196	6202	8910
tot. unique data	5661	6609	5655	7780
R_{int}	0.036	0.137	0.068	0.036
abs corr range	0.83, 1.36 (DIFABS)	0.70, 1.34 (DIFABS)	0.85, 1.32 (DIFABS)	0.33, 0.53 (PLATON)
		Refinement		
no. of refined params	272	316	280	361
final $R1$[a]	0.0386 [3931, $I > 2\sigma$(I)]	0.0545 [5709, $I > 2\sigma$(I)]	0.0782 [3808, $I > 2\sigma$(I)]	0.0355 [6144, $I > 2\sigma(I)$]
final w$R2$[b]	0.0623	0.1496	0.1846	0.0915
goodness of fit	1.022	1.083	1.078	1.095
w^{-1} [c]	$\sigma^2(F^2) + (0.0179\ P)^2$	$\sigma^2(F^2) + (0.0950P)^2 + 3.72P$	$\sigma^2(F^2) + (0.0615P)^2 + 71.91P$	$\sigma^2(F^2) + (0.0410P)^2 + 6.20P$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.004	0.000, 0.001	0.000, 0.001	0.000, 0.003
min and max resid density (e Å^{-3})	−0.86, 1.02 (near Ta)	−2.29, 4.04 (near Ta)	−2.62, 3.00 (near Ta)	−1.47, 2.40 (near Ta)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] w$R2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

and the resulting a yellow oil was subsequently extracted with pentane (75 mL). The combined extracts were concentrated *in vacuo* to *ca.* 5 mL from which **5** crystallized overnight at −30 °C as needle-shaped pale-yellow crystals; yield 0.48 g (62%). ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C) δ 0.90 (s, 9 H, OC*Me*$_3$), 0.92 (s, 9 H, OC*Me*$_3$), 1.33 (s, 9 H, NC*Me*$_3$), 2.11 (s, 6 H, N*Me*$_2$), 2.3−2.4 (m, 1 H, C*H*$_2$CH$_2$C*H*$_2$), 2.4−2.7 (m, 1 H, CH$_2$C*H*$_2$CH$_2$); 2 H, NC*H*$_2$C*H*$_2$N), 2.71 (s, 3 H, N*Me*), 3.0−3.2 (m, 1 H, C*H*$_2$CH$_2$C*H*$_2$), 3.2−3.3 (m, 1 H, C*H*$_2$CH$_2$C*H*$_2$), 3.3−3.5 (m, 1 H, CH$_2$C*H*$_2$CH$_2$); 2 H, NC*H*$_2$C*H*$_2$N), 3.7−3.8 (m, 1 H, C*H*$_2$CH$_2$C*H*$_2$), 3.92 (d, ^2J(H,H) = 13 Hz, 1 H, ArC*H*$_2$N), 4.38 (d, ^2J(H,H) = 13 Hz, 1 H, ArC*H*$_2$N), 7.1−7.5 (m, 3 H, Ar*H*), 8.74 (d, ^3J(H,H) = 8, 1 H, Ar*H*). ^{13}C{^{1}H} NMR (50.32 MHz, C_6H_6, 25 °C) δ 30.0 (NC*Me*$_3$), 31.9 (OC*Me*$_3$), 32.0 (OC*Me*$_3$), 37.7 (*C*H$_2$CH$_2$*C*H$_2$), 41.8 (*C*H$_2$*C*H$_2$CH$_2$), 46.0 (N*Me*$_2$), 46.3 (N*Me*), 52.7 (*C*H$_2$CH$_2$*C*H$_2$), 55.1 (NC*H*$_2$C*H*$_2$N), 58.1 (NC*H*$_2$C*H*$_2$N), 61.5 (N*C*Me$_3$), 65.1 (Ar*C*H$_2$N), 77.0 (two overlapping O*C*Me$_3$ signals), 124.1, 125.0, 126.3, 138.3 and 147.8 (Ar), 188.9 (C$_{ipso}$), 237.5 (*C*═NCMe$_3$). IR (KBr) (cm^{-1}) 1721, ν(C═N).

[Ta{C(═N-*t*-Bu)CH$_2$CH(Me)CH$_2$-1,4}(CNN)(O-*t*-Bu)$_2$] (6) (*in Situ*). A 5 mm o.d. NMR tube was charged with a solution of **2** (*ca.* 50 mg, 0.08 mmol) in C_6D_6 (1 mL) and 1 equiv (10 μL) of *tert*-butyl isocyanide added with a microsyringe. ^{1}H NMR and ^{13}C NMR showed that the product **6** is formed almost instantly with two isomers A and B formed in a ratio of 1.2:1. Where possible the signals for the two isomers formed have been assigned. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.88 (s, 9 H, OCMe$_3$; A), 0.89 (s, 9 H, OCMe$_3$; B), 0.92 (s, 9 H, OC*Me*$_3$; B), 0.93 (s, 9 H, OC*Me*$_3$; A), 1.29 (s, 9 H, NC*Me*$_3$; B), 1.32 (s, 9 H, NC*Me*$_3$; A), 1.66 (d, ^3J(H,H) = 6 Hz, 6 H, CH$_2$CH(*Me*)CH$_2$; A + B), 2.06 (s, 6 H, N*Me*$_2$); A), 2.13 (s, 6 H, N*Me*$_2$; B), 2.30−2.40 (m, 1 H, C*H*$_2$C*H*(Me)C*H*$_2$; m, 2 H, NC*H*$_2$C*H*$_2$N), 2.40−2.50 (m, 2 H, NC*H*$_2$C*H*$_2$N), 2.59 (s, 3 H, N*Me*; A), 2.80 (s, 3 H, N*Me*; B), 2.90−3.10 (m, 1 H, C*H*$_2$C*H*(Me)C*H*$_2$), 3.15−3.30 (m, 1 H, C*H*$_2$C*H*(Me)C*H*$_2$), 3.40−3.60 (m, 2 H, NC*H*$_2$C*H*$_2$N), 3.73 (d, ^2J(H,H) = 13 Hz, 1 H, ArC*H*$_2$N; A), 3.75−3.90 (m, 3 H, C*H*$_2$C*H*(Me)C*H*$_2$), 4.10−4.20 (m, 1 H, C*H*$_2$C*H*(Me)C*H*$_2$); 1 H, ArC*H*$_2$N), 4.52 (d, ^2J(H,H) = 13 Hz, 1 H, ArC*H*$_2$N), 7.10−7.25 (m, 3 H, Ar*H*), 7.3−7.5 (m, 3 H, Ar*H*), 8.52 (d, ^3J(H,H) = 7 Hz, 1 H, Ar*H*), 8.62 (d, ^3J(H,H) = 7 Hz, 1 H, Ar*H*). ^{13}C{^{1}H} NMR (75.47 MHz, C_6H_6, 25 °C): δ 26.7 (CH$_2$CH(*Me*)CH$_2$), 30.1 (NC*Me*$_3$), 30.1 (NC*Me*$_3$), 31.8 (OC*Me*$_3$), 31.9 (OC*Me*$_3$), 32.1 (OC*Me*$_3$), 32.2 (OC*Me*$_3$), 46.0 (N*Me*$_2$), 46.1 (N*Me*$_2$), 46.2 (CH$_2$CH-(Me)CH$_2$), 46.6 (CH$_2$*C*H(Me)CH$_2$), 47.2 (N*Me*), 47.2 (N*Me*), 48.8 (*C*H$_2$CH(Me)C*H*$_2$), 48.8 (*C*H$_2$CH(Me)C*H*$_2$), 52.7 (*C*H$_2$CH(Me)-*C*H$_2$), 52.8 (*C*H$_2$CH(Me)C*H*$_2$), 56.1 (NC*H*$_2$C*H*$_2$N), 56.9 (NC*H*$_2$-*C*H$_2$N), 58.3 (NC*H*$_2$C*H*$_2$N), 58.9 (NC*H*$_2$C*H*$_2$N), 61.5 (N*C*Me$_3$), 61.6 (N*C*Me$_3$), 65.3 (ArCH$_2$N), 65.5 (ArCH$_2$N), 77.2 (O*C*Me$_3$), 77.3 (O*C*Me$_3$), 124.0, 124.8, 125.9, 126.0, 138.1, 138.2, 147.7 and 147.7 (Ar), 188.8 (C$_{ipso}$), 189.0 (C$_{ipso}$), 234.3 (*C*═NCMe$_3$), 234.4 (*C*═NCMe$_3$).

[Ta{C(═N-*t*-Bu)CH$_2$CH(Ph)CH$_2$-1,4}(CNN)(O-*t*-Bu)$_2$] (7). To a solution of **3** (0.67 g, 1.05 mmol) in Et$_2$O (50 mL) was added *tert*-butyl isocyanide (119 μL, 1.05 mmol) which gave an immediate color change from pale to bright yellow. The solution was stirred for 3 h after which the solution was concentrated under reduced pressure to *ca.* 10 mL from which **7** crystallized overnight at −30 °C as needle-shaped yellow crystals; yield 0.38 g (50%). Complex **7** is obtained as a mixture of two isomers A and B in a ratio of 1.2:1. Anal. Calcd for $C_{34}H_{56}N_3O_2Ta$: C, 56.74; H, 7.84; N, 5.84. Found: C, 56.62; H, 7.73; N, 5.81. Where possible the data for the isomers A

and B are assigned. ^{1}H NMR (300.13 MHz, C_6H_6, 25 °C): δ 0.93 (s, 9 H, OCMe_3; A), 0.95 (s, 9 H, OCMe_3; B), 1.01 (s, 9 H, OCMe_3; B), 1.05 (s, 9 H, OCMe_3; A), 1.31 (s, 9 H, NCMe_3; B), 1.33 (s, 9 H, NCMe_3; A), 2.08 (s, 6 H, NMe_2; B), 2.13 (s, 6 H, NMe_2; A), 2.25−2.40 (m, 2 H, NCH_2CH_2N), 2.40−2.55 (m, 2 H, NCH_2CH_2N; 2 H, CH$_2$CH(Ph)CH$_2$; A + B), 2.62 (s, 3 H, NMe; A), 2.83 (s, 3 H, NMe; B), 3.06−3.10 (m, 2 H, NCH_2CH_2N), 3.15−3.30 (m, 2 H, NCH_2CH_2N; 1 H, ArCH_2N; B), 3.45−3.60 (m, 2 H, CH_2CH(Ph)CH_2), 3.74 (d, ^2J(H,H) = 13 Hz, 1 H, ArCH_2N; A), 3.80−3.95 (m, 1 H, CH_2CH(Ph)CH_2; A), 4.10−4.20 (m, 5 H, CH_2CH(Ph)CH_2; A + B; 1 H, ArCH_2N ; B), 4.56 (d, ^2J(H,H) = 13 Hz, ArCH_2N; A), 7.1−7.4 (m, 12 H, ArH; A + B), 7.71 (d, ^3J(H,H) = 7.2 Hz, 4 H, ArH; A + B), 8.58 (d, ^3J(H,H) = 7 Hz, 1 H, C_6H_4; A), 8.62 (d, ^3J(H,H) = 7.1 Hz, 1 H, C_6H_4; B). ^{13}C{^{1}H} NMR (50.32 MHz, C_6H_6, 25 °C): δ 30.0 (NCMe_3), 30.1 (NCMe_3), 31.9 (OCMe_3), 31.9 (OCMe_3), 32.2 (OCMe_3), 32.3 (OCMe_3), 46.0 (NMe_2), 46.6 (NMe), 46.4 (NMe), 47.9 (CH_2CH(Ph)CH_2), 47.8 (CH_2CH(Ph)CH_2), 52.6 (CH_2CH(Ph)CH_2), 52.8 (CH_2CH(Ph)CH_2), 57.0 (NCH_2CH_2N), 57.9 (NCH_2CH_2N), 58.0 (NCH_2CH_2N), 59.0 (NCH_2CH_2N), 61.6 (NCMe$_3$), 61.7 (NCMe$_3$), 64.6 (CH$_2$CH(Ph)CH$_2$), 64.4 (CH$_2$CH(Ph)CH$_2$), 65.3 (ArCH_2N), 77.1 (OCMe$_3$), 77.5 (OCMe$_3$), 77.6 (OCMe$_3$), 124.1, 125.0, 125.7, 126.2, 127.1, 127.5, 128.4, 128.7, 138.4, 138.3, 147.6 and 151.6 (Ar), 188.8 and 188.6 (C_{ipso}), 233.4 and 233.3 (C=NCMe$_3$). IR (KBr) (cm^{-1}) 1726, ν(C=N).

X-ray Structure Determinations of 2−4 and 7. Crystals suitable for X-ray diffraction were mounted on the tip of a glass fiber and were placed in the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on rotating anode (T = 150 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of a set of well-centered reflections (SET4).[11] Reduced-cell calculations did not indicate higher lattice symmetry.[12] Crystal data and details on data collection and refinement are presented in Table 4. Data were corrected for *Lp* effects and for the observed linear decay of the reference reflections. An analytical absorption correction,[13] as implemented in PLATON,[19] was applied for complex **7**; empirical absorption correction was applied for the other compounds (DIFABS).[14]

The structures of all complexes were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).[15] The structures were refined on F^2, using full-matrix least-squares techniques (SHELXL-96[16] for complex **7** and SHELXL-93[17] for the other complexes); no observance criterion was applied during refinement.

Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms. All methyl hydrogen atoms were refined in a rigid group, allowing for rotation around the C−C or N−C bonds. The C(14)H(Ph) group bonded to C(13) and C(15) is disordered over two positions, approximately related to each other by a local mirror plane through Ta(1), C(13), and C(15). The site occupancy parameter of the major disorder component refined to 0.767(9).

The non-hydrogen atoms were refined with anisotropic thermal parameters, except for the disorder atoms of **7**. The thermal parameters of the minor disorder component atoms were equivalenced to the individually refined isotropic displacement parameters of the major disorder component atoms. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and a factor of 1.2 for all other hydrogen atoms.

Neutral atom scattering factors and anomalous dispersion correction were taken from ref 18. Geometrical calculations and illustrations were performed with PLATON;[19] all calculations were performed on a DECstation 5000 cluster.

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Supporting Information Available: Further details of the structure determinations, including tables of X-ray parameters, atomic coordinates, bond lengths and angles, and thermal parameters (26 pages). Ordering information is given on any current masthead page.

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