A Novel Synthetic Route to Tantalum–Zinc Neophylidyne Complexes Stabilized by *ortho*-Chelating Arylamine Ligands; The X-ray Structure of [TaCl$_2$(μ-C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-CCMe$_2$Ph)ZnCl(THF)]

Marco H. P. Rietveld, Pierre Lohner, Marije G. Nijkamp, David M. Grove, Nora Veldman, Anthony L. Spek, Michel Pfeffer* and Gerard van Koten*

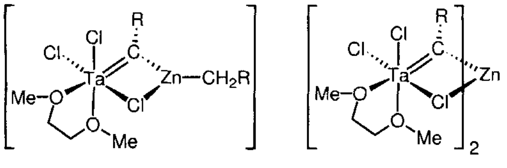
Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday

Abstract: A dimeric tantalum–zinc neophylidyne complex proposed to be [{{TaCl$_2$(μ-CCMe$_2$Ph)(μ-Cl)(THF)$_2$}{Zn(μ-Cl)}}$_2$] (**5a**), which can be prepared easily on a scale of ≈50 mmol, is an ideal starting material for the synthesis of mono- and bis(*ortho*)-chelated arylamine alkylidyne species such as the red Ta–Zn neophylidyne complexes [TaCl$_2$(μ-C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-CCMe$_2$Ph)ZnCl(THF)] (**6**) and [TaCl$_2${μ-C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(μ-CCMe$_2$Ph)ZnCl] (**7**), which have been isolated in high yields. Reaction of **7** with tmeda affords the Ta^{V} alkylidene complex [TaCl(=CHCMe$_2$Ph){C$_6$H$_3$(CH$_2$N(Me)CH$_2$)-2-(CH$_2$NMe$_2$)-6}] (**8**), which shows catalytic activity in the ring-opening metathesis polymerization of norbornene.

Keywords
bridging ligands · intramolecular coordination · organometallic complexes · tantalum · zinc

Introduction

Alkylidyne complexes that contain a metal in its highest possible formal oxidation state are known for metal ions like Mo^{VI}, W^{VI}, Re^{VII} and even Os^{VII}.[1] Some Ta^{V} alkylidyne complexes have also been reported,[2, 3a] including, for example, the Ta–Zn neopentylidyne complexes **1** and **2**[2a] shown schematically in Figure 1. We have recently found that the aryldiamine ligand [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]$^-$ is also suitable for stabilizing tantalum alkylidyne species, and we have reported in a previous paper the tantalum–zinc neopentylidyne complex [TaCl$_2${μ-C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(μ-C*t*Bu)ZnCl] (**3**), in which both a neopentylidyne group and an aryldiamine ligand bridge between the metal atoms of the TaCl$_2$ and ZnCl units.[3a] The reactivity of complex **3** is interesting: for example, the ZnCl$_2$ could be removed from it with tmeda to afford a very reactive alkylidyne species. Addition of tmeda to **3** in the presence of [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-I)]$_2$ led to a new palladium-mediated alkylidyne functionalization reaction that afforded the functionalized alkylidene complex [TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)(=C-*t*Bu{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6})].[3a] This was the first example of a metal-mediated C–C bond formation between a high-oxidation-state Schrock-type alkylidyne complex and a late-transition-metal organometallic complex. This type of carbon–carbon coupling between organopalladium(II) complexes and low-oxidation-state Fischer-type metallacarbynes (the metal being Mo or W) has been extensively studied.[4]



1 **2**

Figure 1. The Ta–Zn neopentylidyne complexes **1** and **2** (R = *t*Bu).

The available syntheses of **3** are associated with some practical problems that hamper the further study of its reactivity. First, the high-yield formation of **3** from the alkylidene complex [TaCl$_2$(=CH*t*Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] and neopentylzinc

---

[*] Prof. Dr. G. van Koten, Dr. M. H. P. Rietveld, M. G. Nijkamp, Dr. D. M. Grove
Debye Institute, Utrecht University
Padualaan 8, 3584 CH Utrecht (The Netherlands)
Fax: Int. code +(30)2523615
e-mail: vankoten@xray.chem.ruu.nl.
Dr. M Pfeffer, P. Lohner
Laboratoire de Synthèses Métallo-Induites, Université Louis Pasteur
4 rue Blaise Pascal, 67000 Strasbourg Cedex (France)
Fax: Int. code +(88)60-7550
e-mail: pfeffer@chimie.u-strasbg.fr
N. Veldman, Dr. A. L. Spek[+]
Bijvoet Center for Biomolecular Research, Utrecht University
Padualaan 8, 3584 CH Utrecht (The Netherlands)
Fax: Int. code +(30)2533940
e-mail: spea@xray.chem.ruu.nl.

[+] For correspondence regarding the crystal structure determination.

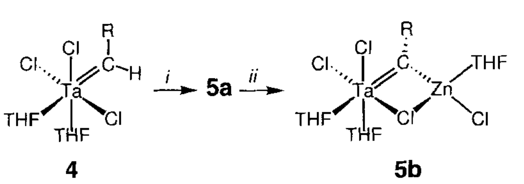
Abbreviations used in this manuscript: THF = tetrahydrofuran (C$_4$H$_8$O); cod = cycloocta-1,5-diene (C$_8$H$_{12}$); dme = 1,2-dimethoxyethane (MeOCH$_2$CH$_2$OMe); tmeda = *N,N,N′,N″*-tetramethylethylenediamine (Me$_2$NCH$_2$CH$_2$NMe$_2$); Cp* = pentamethylcyclopentadienyl ([C$_5$Me$_5$]$^-$); ROMP = ring-opening metathesis polymerization.

chloride takes 5 days to reach completion,[3a] whereas an alternative approach, comprising the transmetallation reaction of **2** with the aryllithium reagent $[\{Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}\}_2]$ affords complex **3** in a poor yield of less than 50%.[3a] Consequently, we searched for a more convenient preparative route for the large-scale synthesis of tantalum alkylidyne complexes containing the $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ ligand. At the same time we changed from a neopentylidyne ($\equiv$C*t*Bu) to a neophylidyne ($\equiv CCMe_2Ph$) functionality not only to reduce costs but also because neophyl derivatives are generally more crystalline and more easily handled than their neopentyl analogues;[5] the methyl groups in the neophylidyne ligand also offer an additional stereochemical NMR probe.

We now report a new, fast, easy and low-cost synthetic procedure for synthesis of Ta–Zn neophylidyne complexes that contain $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ and the mono(*ortho*)-chelating arylamine ligand $[C_6H_4CH_2NMe_2\text{-}2]^-$. One neophylidyne complex stabilized by the latter ligand has been shown by an X-ray molecular structure determination to have zinc and tantalum centres bridged by both the alkylidyne functionality and the aryl C_{ipso} carbon of $[C_6H_4CH_2NMe_2\text{-}2]^-$ with the nitrogen donor atom coordinated to tantalum.

Results and Discussion

Preparation and Characterization of Complexes 5a and 5b: Addition of one molar equivalent of neophylzinc chloride to a purple-red suspension of $[TaCl_3(=CHCMe_2Ph)(THF)_2]$ (**4**) in diethyl ether gave a clear red solution from which a pink-purple precipitate of a new tantalum neophylidyne complex (**5a**) formed (Scheme 1). Crude **5a** was isolated by removal of the solvent under reduced pressure followed by washing with pentane. Unfortunately **5a** has poor solubility in organic solvents such as benzene, chloroform and dichloromethane, and we have not been able to characterize it by solution NMR spectroscopy. Based on its further reactions (see below) we tentatively propose that **5a** has the dimeric formulation shown schematically in Figure 2. Complex **5a** can be prepared in batches of up to ≈50 mmol in approximately one day without any difficulty in conventional Schlenk equipment, and it was used for the high yield preparation of *ortho*-chelated arylamine tantalum–zinc complexes described below.



Scheme 1. Reactivity of complex **4** with neophylzinc chloride (R = CMe_2Ph). Reaction conditions: i) $[ZnCl(CH_2CMe_2Ph)]$, Et_2O, RT, $-CMe_3Ph$. ii) THF, RT.

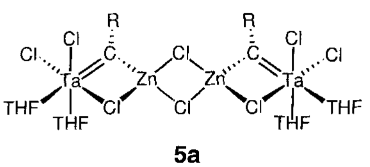


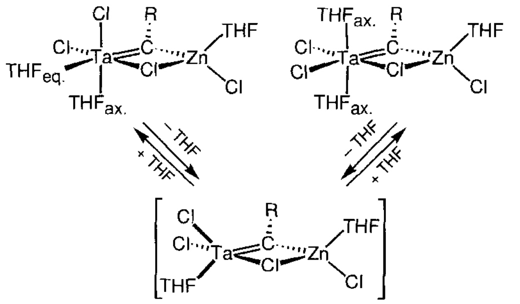
Figure 2. Postulated structure for complex **5a**.

Complex **5a** dissolved in THF to afford, after removal of the solvent under reduced pressure, a new red solid complex **5b** (Scheme 1), which could be obtained as large block-shaped red crystals by recrystallization from a saturated THF solution at −30 °C. Spectroscopic and elemental microanalysis data for **5b** are in agreement with its formulation as a bimetallic Ta–Zn species $[TaCl_2(THF)_2(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)ZnCl(THF)]$. The structure of **5b** proposed in Scheme 1 is similar to that established for $[TaCl_2(dme)(\mu\text{-}CtBu)(\mu\text{-}Cl)ZnCH_2tBu]$ (**1**) (Figure 1).[2a] In this structure of **5b** the neopentyl group and dme of **1** are replaced by a neophyl group and THF, respectively, and the $ZnCH_2tBu$ unit is replaced by a ZnCl(THF) unit. Complex **5b** was soluble not only in the coordinating solvent THF but also in weakly coordinating or noncoordinating solvents like diethyl ether, dichloromethane and benzene. However, in the latter solvents after ca. ten minutes a pink-purple precipitate of what appears to be **5a** formed; this behaviour strongly indicates a solution equilibrium between **5a** and **5b**.

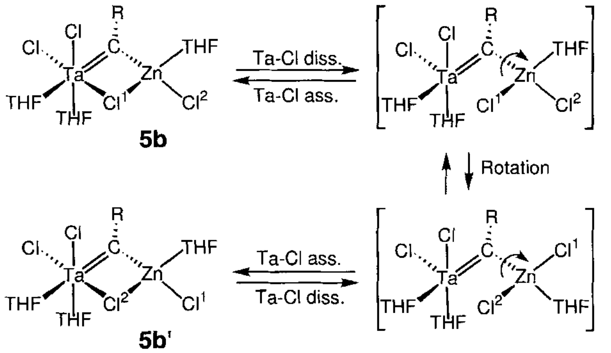
The ^1H NMR (200.13 MHz, CD_2Cl_2) spectrum for **5b** at room temperature shows signals for three THF molecules, of which two are equivalent, and a clearly broadened Me resonance of the CMe_2Ph unit at $\delta = 1.72$; this latter feature points to fluxional behaviour. The ^1H NMR spectrum at −84 °C is very complicated and shows broad signals for at least four different THF molecules but unfortunately, owing to severe overlap of the peaks in this spectrum, a full assignment was not possible. The ^{13}C NMR spectrum of **5b** at −84 °C shows two CMe_2Ph signals at $\delta = 32.8$ and 36.7 and three different THF molecules. Upon raising the temperature the CMe_2Ph signals broaden and eventually become homotopic ($T_c \approx -70\,^\circ C$, $\Delta G^{\neq} = 37\ kJ\,mol^{-1}$); at room temperature there is only one signal at $\delta = 34.6$ for the CMe_2Ph group. In the room temperature ^{13}C NMR spectrum there is a characteristic signal for the alkylidyne α carbon at $\delta = 275.2$; this position is similar to that found for related tantalum–zinc neopentylidyne complexes: for complexes **1** and **2** these resonances occur at $\delta = 277.7$ and 279.5, respectively.[2a]

The temperature-dependent solution NMR data for **5b** indicate a process in which the stereogenic zinc centre racemizes and one pair of THF molecules is rendered equivalent. Two processes, both involving prior THF dissociation either from Zn or from Ta, are feasible. The first process involves dissociation of the THF molecule from the tetrahedrally surrounded stereogenic Zn atom to lead to an intermediate in which the three-coordinate zinc atom adopts a planar geometry. This step is followed by association of THF on the opposite side of this plane to afford a four-coordinate zinc atom with an opposite stereochemistry.

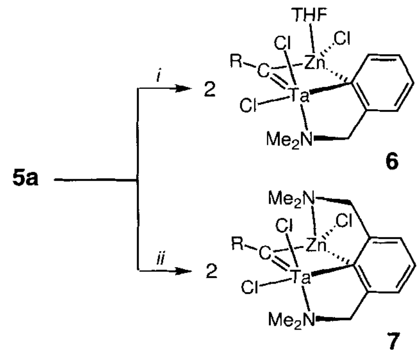
The second process that could also explain the observed complexity of the THF patterns in the ^1H NMR spectrum at low temperature involves addition and dissociation reactions of THF with the tantalum centre (Scheme 2). This type of process was reported by Schrock and co-workers for the octahedral alkylidene complex $[TaCl_3(=CHtBu)(THF)_2]$.[6] In solution there is an equilibrium between two species containing *cis,mer* and *trans,mer* bonded THF molecules that involves a five-coordinate tantalum intermediate (Scheme 2). The fluxionality occurring with **5b** could also be explained by a different type of process, shown in Scheme 3, in which reversible Ta/Cl bond dissociation/association together with rotation of the



Scheme 2. Possible interconversion mechanism of the *cis*- and *trans*-bonded THF molecules on tantalum in complex **5b** (R = CMe_2Ph).



Scheme 3. Proposed mechanism for the racemization of complex **5b** by Ta–Cl dissociation (R = CMe_2Ph).



Scheme 4. Preparation of the Ta–Zn neophylidyne complexes **6** and **7** (R = CMe_2Ph). Reaction conditions: i) $[Zn(C_6H_4CH_2NMe_2\text{-}2)_2]$, Et_2O, −78 °C, $-ZnCl_2$, −2THF. ii) $[\{Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}\}_2]$, Et_2O, −78 °C, −2LiCl, −4THF.

$ZnCl_2(THF)$ unit around the Zn–C bond could afford inversion of the Zn configuration. We have not carried out any detailed experiments to identify the operative mechanism with **5b**, but we suspect that more than one of these processes is operative.

The way in which **5b** is formed from **5a** by simple dissolution in THF led us to the structure proposed for **5a** (Figure 2), based on a dimeric species with the formula $[\{TaCl_2(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)(THF)_2Zn(\mu\text{-}Cl)\}_2]$. In this dimeric structure the two tantalum neophylidyne units are connected by a central $Zn(\mu\text{-}Cl)_2Zn$ unit and consequently the bulky neophyl substituents are well separated from each other. We consider alternative structures for **5a** based on the trimetallic ditantalazinc complex **2** as unlikely.

Preparation and Characterization of Complexes 6 and 7: The reaction of **5a** (vide supra) with $[Zn(C_6H_4CH_2NMe_2\text{-}2)_2]$ affords the complex $[TaCl_2(\mu\text{-}C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}CCMe_2Ph)ZnCl(THF)]$ (**6**), and its reaction with $[\{Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}\}_2]$ similarly affords the species $[TaCl_2\{\mu\text{-}C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\mu\text{-}CCMe_2Ph)ZnCl]$ (**7**). These two new neophylidyne complexes have been isolated as red solids in high yield and have the overall structures shown in Scheme 4. The fact that batches of **7** in quantities of ca. 50 mmol can be prepared without difficulty and in high yield underlines the synthetic potential of **5a** for the preparation of such *ortho*-chelated arylamine stabilized tantalum–zinc complexes. Complexes **6** and **7** are air- and moisture-sensitive but can be stored without noticeable decomposition under a nitrogen atmosphere at room temperature for months. They are soluble in THF and moderately soluble in benzene and toluene, but insoluble in more apolar solvents like diethyl ether, pentane and hexane. Complex **6** crystallizes from a saturated THF solution at −30 °C, while **7** can be recrystallized by layering a benzene solution with pentane. Complex **6** has been characterized in the solid state by an X-ray crystal diffraction study.

Molecular Structure of Complex **6**: The molecular structure of **6** is shown in Figure 3, and relevant bond distances and bond angles are given in Table 1. Complex **6** exists in the solid state as a neutral heterobimetallic species in which the Ta and Zn centres

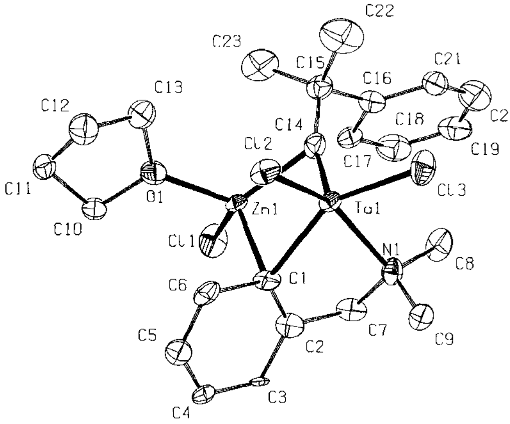


Figure 3. ORTEP plot[14] (drawn at 50% probability level) of $[TaCl_2(\mu\text{-}C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}CCMe_2Ph)ZnCl(THF)]$ (**6**).

Table 1. Selected geometrical data (bond lengths in Å, bond angles in °) for $[TaCl_2(\mu\text{-}C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}CCMe_2Ph)ZnCl(THF)]$ (**6**).

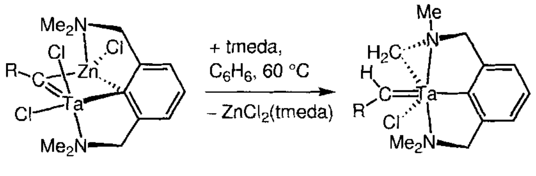
Ta-C14	1.84(2)	Zn-C1	2.27(2)
Ta-N1	2.26(2)	Zn-C14	2.14(2)
Ta-C1	2.23(2)	Zn-O1	1.988(18)
Ta-Cl3	2.346(7)	Zn-Cl1	2.188(7)
Ta-Cl2	2.354(7)	Ta-Zn	2.740(5)
N1-Ta-Cl2	151.7(5)	C14-Ta-N1	51.1(7)
C1-Ta-Cl3	147.5(7)	Zn-C1-Ta	75.0(7)
C1-Ta-C14	103.4(9)	Zn-C14-Ta	86.7(9)
C14-Ta-Cl3	106.0(7)	O1-Zn-C14	115.1(8)
C1-Ta-Cl2	90.6(6)	O1-Zn-C1	106.9(8)
C14-Ta-Cl2	106.5(8)	O1-Zn-Cl1	102.5(5)
Cl3-Ta-Cl2	94.1(2)	C14-Zn-C1	93.0(8)
C1-Ta-N1	75.2(8)	C14-Zn-Cl1	127.3(6)
Cl3-Ta-N1	86.0(5)	C1-Zn-Cl1	110.3(6)

are bridged by the carbyne carbon C(14) of the neophylidyne functionality and the C_{ipso} atom C(1) of the monoanionic arylamine ligand. The four-coordinate zinc atom completes its ligand coordination sphere with a chloride ligand and a donor THF molecule, whereas the five-coordinate Ta^V centre is further ligated by two chloride ligands and the N donor atom of the aryldiamine; the latter is thus μ-*C,N* chelated. The geometry around zinc can be described as being distorted tetrahedral, and that of tantalum is between square pyramidal and trigonal bipyramidal. The structure of **6** is closely related to that of the $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$-stabilized neopentylidyne complex $[TaCl_2\{\mu\text{-}C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\mu\text{-}CtBu)ZnCl]$ (**3**);[3a] in particular, in the bimetallic bridged moiety of **6** the bond distance between tantalum and the alkylidyne C_α carbon, C(14), and the tantalum-zinc distance (with values of 1.84(2) and 2.740(5) Å, respectively) compare closely to those of the corresponding bonds in **3**.[3a]

*NMR spectroscopy of complexes **6** and **7***: The solution ^1H NMR data (300.13 MHz, $CDCl_3$) of **6** are consistent with bidentate *C,N* coordination of the *ortho*-chelating arylamine ligand; coordination of the nitrogen donor and stereogenicity of the tantalum and zinc centres render the CH_2NMe_2 groupings diastereotopic, thus resulting in an AB spin system for the CH_2 hydrogen atoms and two singlets for the NMe_2 groups. The diastereotopic CMe_2Ph unit gives rise to two Me signals at $\delta = 1.66$ and 1.74. In the ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, 25 °C) the resonances for the bridging alkylidyne C_α and the C_{ipso} carbon of the arylamine ligand are found at $\delta = 287.9$ and 171.7, respectively; these values are similar to those found for complex **3**.[3a]

The ^1H NMR spectrum (300.13 MHz, $CDCl_3$, 25 °C) for aryldiamine complex **7** shows this complex to be highly asymmetric, and there are four methyl resonances for the two NMe_2 units and an AX pattern for each of the two CH_2N units; that is, the two *anisochronous* CH_2NMe_2 substituents each contain diastereotopic NMe_2 and CH_2 units. Furthermore, the two resonances for the Me groups of the CMe_2Ph unit at $\delta = 1.72$ and 1.91 are also indicative of the presence of at least one stereogenic centre. These data are in accordance with a structure for **7** (shown in Scheme 4) that is similar to that of **6**, but in which the THF has been replaced by a nitrogen donor of the second CH_2NMe_2 substituent of the aryldiamine ligand. Such an asymmetric structure with two chiral centres, tantalum and zinc, was found earlier for the analogous neopentylidyne complex **3**.[3a] The ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C) spectrum of **7** shows a resonance for the bridging alkylidyne C_α carbon at $\delta = 291.7$, a value which is comparable to that found for complexes **6** (287.9) and **3** (295.4).[3a] The resonance for the C_{ipso} carbon of the aryldiamine ligand at $\delta = 175.4$ shows a highfield shift that indicates a C_{ipso} carbon bridging between tantalum and zinc (nonbridging C_{ipso} carbons are found in the range $190 \leq \delta \leq 210$).[3]

Reactivity of 7 with tmeda: Treatment of the bimetallic neopentylidyne **7** with excess tmeda at 60 °C leads to clean elimination of $[ZnCl_2(tmeda)]$ with concomitant formation of the tantalum neophylidene complex $[TaCl(=CHCMe_2Ph)\{C_6H_3\text{-}(CH_2N(Me)CH_2)\text{-}2\text{-}(CH_2NMe_2)\text{-}6\}]$ (**8**), as depicted in Scheme 5. Monitoring of this NMe C–H activation by ^1H NMR spectroscopy (300.13 MHz, C_6D_6, 60 °C) shows the reaction to be highly selective, though isolated yields of **8** are low (40%) primarily as a result of the difficulty of separating the product from the excess tmeda. Complex **8** is a yellow solid that is readily soluble in benzene and diethyl ether but is only moderately soluble in more apolar solvents like pentane or hexane.



7 **8**

Scheme 5. Formation of complex **8** by treatment of **7** with excess tmeda ($R = CMe_2Ph$).

The ^1H NMR (300.13 MHz, C_6D_6, 25 °C) spectrum for **8** agrees with the structure depicted in Scheme 5, that is, a six-coordinate Ta^V alkylidene species in which a metalla-azacyclopropane moiety $TaCH_2NMe$ is present. For example, there are two Me resonances for a diastereotopic NMe_2 unit, a Me resonance for the $ArCH_2N(Me)CH_2$ unit, and three well-resolved AB patterns for the three CH_2 groups. The Me signals for the diastereotopic CMe_2Ph unit are found as two singlets at $\delta = 1.51$ and 1.54. The ^{13}C NMR spectrum (50.32 MHz, C_6D_6, 25 °C) shows a signal for the C_{ipso} carbon of the aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ at $\delta = 193.1$, which is the same value as found for the neopentylidene analogue of **8**, $[TaCl(=CHtBu)\{C_6H_3(CH_2N(Me)CH_2)\text{-}2\text{-}(CH_2NMe_2)\text{-}6\}]$.[3a] The alkylidene C_α carbon signal at $\delta = 250.5$ has a small $^1J(C,H)$ value of 84 Hz, which is typical for electron-deficient alkylidene complexes.[3, 7] The formation of **8** probably involves a σ-bond metathesis reaction between a carbyne function and a NMe_2 C–H bond in an initially formed tantalacarbyne intermediate. Similar C–H bond activation of a NMe_2 group has been reported for the formation of $[TaCl_2\{C_6H_4(CH(Me)N(Me)CH_2)\text{-}2\}(CH_2Ph)(THF)]$,[8a] $[TaCl_2\{1\text{-}C_{10}H_6(N(Me)CH_2)\text{-}8\}(CH_2Ph)(THF)_2]$[8a] and $[Ir^{III}(C_6H_4NEt(CHMe)\text{-}2\text{-}C,N,C')I(cod)]$.[8b] Recently a related C–H activation reaction has been reported by Royo and co-workers,[8c] who found that addition of one equivalent of $[Li\{C_6H_4CH_2NMe_2\text{-}2\}]$ to the trichloroaryltantalum(v) complex $[TaCp^*Cl_3(C_6H_4CH_2NMe_2\text{-}2)]$ caused C–H bond activation at one of the NMe_2 methyl groups with β-H elimination, leading to the formation of the cyclometalated complex $[TaCp^*Cl_2\{C_6H_4CH_2N(Me)CH_2\text{-}2\}]$. Further reaction of this complex with 2 equivalents of $[Li(C_6H_4CH_2NMe_2\text{-}2)]$ affords the alkylidene complex $[TaCp^*Cl(C_6H_4CH_2NMe_2\text{-}2)\{C_6H_4CH_2N(Me)CH\text{-}2\}]$. This type of C–H activation has also been shown to play a key role in the ligand rearrangements of some Ru^{II} and Ir^I species, namely in the conversion of $[RuCl\text{-}\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}\{\eta^6\text{-}(MeC_6H_4\text{-}4\text{-}iPr\}]$[8d] and $[Ir\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(cod)]$[8e] to the more stable species $[RuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}\{\eta^6\text{-}(MeC_6H_4\text{-}4\text{-}iPr\}]$ and $[Ir\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}(cod)]$, respectively.

Finally, preliminary reactivity studies of alkylidene complex **8** have shown that it has activity as a ROMP catalyst; in 2 days 250 equivalents of norbornene were polymerized to polycyclopentenameric materials containing approximately 50% *cis*-vinylene bonds.

© VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1997 0947-6539/97/0305-0820 $ 17.50+.50/0

Conclusions

Tantalum–zinc neophylidyne complexes containing *ortho*-chelating arylamine ligands are readily accessible and can be obtained in high yield by a new, fast and easy synthetic procedure. We have shown that this procedure is not restricted to the *N,C,N*-terdentate aryldiamine ligand $[\mathrm{C_6H_3(CH_2NMe_2)_2\text{-}2,6}]^-$ but can be extended to *C,N*-bonding arylamine ligand systems. We are currently investigating the C–C bond formation reactions between the high-oxidation-state metal alkylidyne complexes described here and late-transition-metal species; the results of this study will be reported in a subsequent paper.[9]

Experimental Section

General: All experiments were performed in a dry nitrogen atmosphere with 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) and the Service de Microanalyse, Strasbourg (France). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 or AC 300 spectrometer. Complex $[\mathrm{TaCl_3(CH_2CMe_2Ph)_2}]$ was synthesized from $\mathrm{TaCl_5}$ and $[\mathrm{Zn(CH_2CMe_2Ph)_2}]$ in toluene at 0 °C following the literature procedure[10] for its neopentyl analogue at 25 °C. The lower temperature prevents formation of $[\mathrm{TaCl_2(CH_2CMe_2Ph)_3}]$. $[\mathrm{TaCl_3(CH_2CMe_2Ph)_2}]$ was isolated in near-quantitative yields as a yellow oil and characterized by comparison of its spectroscopic data with $[\mathrm{TaCl_3(CH_2}t\mathrm{Bu)_2}]$.[10] The complexes $[\mathrm{Zn(C_6H_4CH_2NMe_2\text{-}2)_2}]$ and $[\{\mathrm{Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}}\}_2]$ were prepared according to literature procedures.[11, 12]

$[\mathrm{TaCl_3({=}CHCMe_2Ph)(THF)_2}]$ (4): Complex **4** was synthesized by a procedure similar to that described for its neopentyl analogue.[6] A solution of $[\mathrm{TaCl_3(CH_2CMe_2Ph)_2}]$ (7.99 g, 14 mmol) in a mixture of $\mathrm{Et_2O}$ (50 mL) and THF (10 mL) was stirred for 12 h and the solvent then removed in vacuo. Washing of the residue with pentane (3 × 30 mL) yielded **4** as a purple microcrystalline solid in >99% yield (8.14 g). ^{1}H NMR (200.13 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta = 1.25$ (m, 8 H; O(CH$_2$CH_2)$_2$), 1.74 (s, 6 H; CMe_2Ph), 3.90 (m, 8 H; O(CH_2CH$_2$)$_2$), 4.06 (s, 1 H; Ta=CH), 7.08 (t, ^3J(H,H) = 8 Hz, 1 H; Ar–H), 7.22 (m, 2 H, Ar–H), 7.62 (d, ^2J(H,H) = 8 Hz, 2 H; Ar–H).

$[\{\mathrm{TaCl_2(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)(THF)_2}\}\mathrm{ZnCl(THF)}]$ (5b): A suspension of $[\mathrm{Zn(CH_2CMe_2Ph)_2}]$ (1.69 g, 5.12 mmol) and $\mathrm{ZnCl_2}$ (0.69 g, 5.06 mmol) in $\mathrm{Et_2O}$ (30 mL) was added over 5 min to a purple-red suspension of $[\mathrm{TaCl_3({=}CHCMe_2Ph)(THF)_2}]$ (**4**) (5.78 g, 10.25 mmol) in $\mathrm{Et_2O}$ (100 mL). After ca. 1 h a clear red solution was formed, and stirring for a further 1 h resulted in the formation of a pink-purple precipitate. This suspension was stirred for 18 h, after which the solvent was removed in vacuo to afford a pale pink-purple solid. This solid, assumed to be the Ta–Zn neophylidyne complex $[\{\{\mathrm{TaCl_2(\mu\text{-}CCMe_2Ph)(\mu\text{-}Cl)(THF)_2}\}\{\mathrm{Zn(\mu\text{-}Cl)}\}\}_2]$ (**5a**), was washed with pentane (2 × 50 mL) and used in the transmetallation reactions described below. Dissolution of **5a** in THF affords a dark red solution. This solution was stirred for 1 h and the solvent then removed under reduced pressure to afford a dark red oil. Washing of this oil with pentane (3 × 20 mL) to remove excess THF and subsequent rigorous drying in vacuo afforded **5b** as a dark red solid; yield 6.58 g (87% calculated from **4**). Block-shaped red crystals of **5b** were obtained by cooling down a saturated solution in THF to –30 °C. Anal. calcd. for **5b**, $\mathrm{C_{22}H_{35}Cl_4O_3TaZn}$: C 35.92, H 4.80; found: C 35.67, H 4.73; ^{1}H NMR (200.13 MHz, $\mathrm{CD_2Cl_2}$, 25 °C): $\delta = 1.72$ (br s, 6 H; CMe_2Ph), 1.82 (m, 8 H; O(CH$_2$CH_2)$_2$), 2.10 (m, 4 H; O(CH$_2$CH_2)$_2$), 3.83 (m, 8 H; O(CH_2CH$_2$)$_2$), 4.51 (m, 4 H; O(CH_2CH$_2$)$_2$), 7.17 (t, ^2J(H,H) = 6 Hz, 1 H; Ar–H), 7.30 (m, 2 H, Ar–H), 7.65 (d, ^2J(H,H) = 5 Hz, 2 H; Ar–H); ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{CD_2Cl_2}$, 25 °C): $\delta = 25.6$ (O(CH$_2$$CH_2$)$_2$), 26.6 (O(CH$_2$$CH_2$)$_2$), 34.6 (C$Me_2$Ph), 56.2 ($CMe_2$Ph), 70.4 (O($CH_2CH_2$)$_2$), 81.1 (O($CH_2CH_2$)$_2$), 126.1 (Ar), 127.1 (Ar), 127.5 (Ar), 153.1 (Ar), 275.2 (Ta≡C).

$[\mathrm{TaCl_2(\mu\text{-}C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}CCMe_2Ph)ZnCl(THF)}]$ (6): A solution of $[\mathrm{Zn(C_6H_4CH_2NMe_2\text{-}2)_2}]$ (2.01 g, 7.20 mmol) in $\mathrm{Et_2O}$ (50 mL) was added to a suspension of **5a** (9.45 g, 7.12 mmol; prepared in situ as described above) in $\mathrm{Et_2O}$ (100 mL) at –78 °C over 5 min. The resulting thick pink suspension was allowed to warm to room temperature and stirred for 3 h, during which time the colour gradually changed to red. Removal of the solvent in vacuo gave a red solid, which was extracted with $\mathrm{C_6H_6}$ (3 × 50 mL). Subsequent removal of $\mathrm{C_6H_6}$ from the combined extracts in vacuo and washing of the solid residue with pentane (2 × 30 mL) and cold $\mathrm{Et_2O}$ (1 × 30 mL) afforded **6** as a red solid; yield 6.92 g (70%). Complex **6** can be recrystallized as block-shaped bright red crystals by cooling down a saturated THF solution from +25 to –30 °C. Anal. calcd. for $\mathrm{C_{23}H_{31}Cl_3NOTaZn}$: C 40.03, H 4.53, N 2.03; found: C 39.88, H 4.50, N 1.95; ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 1.66$ (s, 3 H; CMe_2Ph), 1.74 (s, 3 H; CMe_2Ph), 1.70–1.80 (m, 4 H; O(CH$_2$CH_2)$_2$), 2.48 (s, 3 H; NMe_2), 3.04 (s, 3 H; NMe_2), 3.50–3.65 (m, 4 H; O(CH_2CH$_2$)$_2$), 3.74 (d, ^2J(H,H) = 14 Hz, 1 H, ArCH_2N), 4.88 (d, ^2J(H,H) = 14 Hz, 1 H, ArCH_2N), 7.05–7.40 (m, 6 H; Ar–H), 7.64 (d, ^3J(H,H) = 8 Hz, 2 H; CMe$_2$$Ph$), 7.87 (d, ^3J(H,H) = 7.1 Hz, 2 H, Ar–H); ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 25.1$ (O(CH$_2$$CH_2$)$_2$), 36.1 (C$Me_2$Ph), 32.7 (C$Me_2$Ph), 48.2 (N$Me_2$), 53.3 (N$Me_2$), 56.9 ($CMe_2$Ph), 70.6 (O($CH_2CH_2$)$_2$), 72.6 ($CH_2$N), 125.2 (Ar), 125.7 (Ar), 126.4 (Ar), 126.6 (Ar), 128.2 (Ar), 132.2 (Ar), 150.2 (Ar), 152.0 (Ar), 153.1 (Ar), 171.7 (C_{ipso}), 287.9 (Ta≡C).

$[\mathrm{TaCl_2\{\mu\text{-}C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\mu\text{-}CCMe_2Ph)ZnCl}]$ (7): A solution of $[\{\mathrm{Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}}\}_2]$ (1.70 g, 8.60 mmol) in $\mathrm{Et_2O}$ (50 mL) was added over 5 min to a suspension of **5a** (5.65 g, 4.26 mmol; prepared in situ as described above) in $\mathrm{Et_2O}$ (100 mL) at –78 °C. The suspension was allowed to warm up to room temperature, during which time the colour gradually changed from pink to brown-red. After 3 h the solvent was removed in vacuo and the dark red solid was extracted with $\mathrm{C_6H_6}$ (3 × 50 mL). The solvent was removed from the combined extracts in vacuo and washing of the residue with cold $\mathrm{Et_2O}$ (3 × 10 mL) yielded **7** as a red solid; yield 4.99 g (87%). After recrystallization by layering a benzene solution with pentane, complex **7** is obtained as block-shaped red crystals. Anal. calcd. for $\mathrm{C_{22}H_{30}Cl_3N_2TaZn}$: C 39.14, H 4.48, N 4.15; found: C 39.02, H 4.45, N 4.09; ^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 1.72$ (s, 3 H; CMe_2Ph), 1.91 (s, 3 H; CMe_2Ph), 2.00 (s, 3 H; NMe), 2.12 (s, 3 H; NMe), 2.69 (s, 3 H; NMe), 2.76 (d, ^2J(H,H) = 13 Hz, 1 H, ArCH_2N), 3.24 (s, 3 H; NMe), 3.79 (d, ^2J(H,H) = 13 Hz, 1 H; ArCH_2N), 4.72 (d, ^2J(H,H) = 13 Hz, 1 H; ArCH_2N), 4.86 (d, ^2J(H,H) = 13 Hz, 1 H; ArCH_2N), 7.11–7.17 (m, 3 H; Ar–H), 7.23–7.36 (m, 3 H; Ar–H), 7.73 (d, ^3J(H,H) = 8 Hz, 2 H; CMe$_2$$Ph$); ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 31.7$ (CMe_2Ph), 36.3 (CMe_2Ph), 47.3 (NMe), 47.6 (NMe), 49.0 (NMe), 54.3 (NMe), 56.9 (CMe$_2$Ph), 67.2 (ArCH$_2$N), 71.6 (ArCH$_2$N), 125.8 (Ar), 126.4 (Ar), 126.6 (Ar), 129.0 (Ar), 130.3 (Ar), 131.1 (Ar), 151.4 (Ar), 152.3 (Ar), 153.7 (Ar), 175.4 (C_{ipso}), 291.7 (Ta≡C).

$[\mathrm{TaCl({=}CHCMe_2Ph)\{C_6H_3(CH_2N(Me)CH_2)\text{-}2\text{-}(CH_2NMe_2)\text{-}6\}}]$ (8): To a stirred purple-red solution of **7** (6.81 g, 10 mmol) in $\mathrm{C_6H_6}$ (100 mL) at room temperature was added tmeda (6 mL, 26 mmol). The suspension was first stirred for 1 h at 60 °C and then for 12 h at room temperature, during which the colour gradually changed from purple-red to yellow-brown. The solvent was removed in vacuo and the brown sticky solid residue was extracted with hexane (3 × 100 mL). The combined extracts were concentrated in vacuo to 10 mL, from which **7** crystallized overnight at –30 °C as small needle-shaped yellow crystals. Yield: 2.1 g (40%); Anal. calcd. for $\mathrm{C_{22}H_{30}ClN_2Ta}$: C 49.03, H 5.61, N 5.20; found: C 48.93, H 5.55, N 5.18; ^{1}H NMR (200.13 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta = 1.11$ (s, 1 H; Ta=CH), 1.32 (d, ^2J(H,H) = 10 Hz, 1 H; TaCH_2NMe), 1.51 (s, 3 H, CMe_2Ph), 1.54 (s, 3 H, CMe_2Ph), 2.05 (s, 3 H; NMe), 2.66 (s, 3 H; NMe), 2.73 (s, 3 H; NMe), 3.07 (d, ^2J(H,H) = 10 Hz, 1 H; TaCH_2NMe), 3.18–3.34 (m, 2 H; ArCH_2N), 4.11 (d, ^2J(H,H) = 16 Hz, 1 H; ArCH_2N), 4.40 (d, ^2J(H,H) = 13 Hz, 1 H; ArCH_2N), 6.93–7.03 (m, 3 H; Ar–H), 7.09–7.17 (m, 3 H; Ar–H), 7.40 (d, ^3J(H,H) = 8 Hz, 2 H; CMe$_2$$Ph$); ^{13}C{^{1}H} NMR (50.32 MHz, $\mathrm{C_6D_6}$, 25 °C): $\delta = 32.9$ (CMe_2Ph), 34.1 (CMe_2Ph), 47.1 (NMe), 51.8 (NMe), 52.7 (TaCH$_2$N(Me)), 58.2 (NMe), 73.0 (ArCH$_2$N), 73.5 (ArCH$_2$N), 84.9 (CMe$_2$Ph), 121.4 (Ar), 122.4 (Ar), 125.4 (Ar), 126.01 (Ar), 127.6 (Ar), 129.3 (Ar), 148.7 (Ar), 152.2 (Ar), 153.0 (Ar), 193.1 (C_{ipso}), 250.5 (Ta=CH, ^1J (C,H) = 84 Hz).

X-ray Data Collection and Structure Refinement for Complex 6:[17] Crystals were sampled and handled in inert oil (R 3000). A suitable red crystal was cut to shape and transferred into the cold nitrogen stream (150 K) of an Enraf-Nonius CAD 4T diffractometer with rotating anode. Pertinent data are given in Table 2. Reflection profiles were structured. The somewhat higher than

Table 2. Crystallographic data for **6**.

formula	$C_{23}H_{31}Cl_3NOTaZn$
mol. wt.	690.20
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
a, b, c (Å)	10.110(10), 12.98(2), 19.751(16)
β (°)	105.65(9)
V (Å^3)	2496(5)
Z	4
ρ_{calc} (gcm^{-3})	1.837
$F(000)$ (electrons)	1352
$\mu(Mo_{K\alpha})$ (cm^{-1})	56.8
crystal size (mm)	0.30 × 0.30 × 0.30
T (K)	150
radiation (Å)	$Mo_{K\alpha}$ (monochrom.) 0.71073
$\theta_{min}, \theta_{max}$ (°)	1.9, 25.3
scan type, scan (°)	ω, 0.80 +0.35 tg (θ)
horiz. and vert. aperture (mm)	3.00, 4.00
reference reflection	−3 −3 2
data set	−11:11; −11:0; −23:23
total and unique refls.	7982, 4048
observed refls ($I > 2.0\sigma(I)$)	1877
N_{ref}, N_{par}	4042, 275
R, wR, S [a]	0.0829, 0.2270, 1.04
max. and av. shift/error	0.000, 0.000
min./max. resid. dens. (e/Å^3)	−2.65, 1.90

[a] $w = 1/(\sigma^2(F_o^2) + (0.0632\,P)^2)$, where $P = (F_o^2 + 2F_c^2)/3$.

usual R value reached is related to the nonideal quality of the crystals available. Data were corrected for absorption with the DIFABS[13] algorithm as implemented in PLATON.[14] The structure was solved by automated Patterson/Fourier techniques with DIRDIF-92[15] and refined on F^2 with SHELXL-93.[16] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms with U_{iso}'s related to U_{eq} of the atom to which they are attached. Geometrical calculations and the ORTEP plots were done with PLATON.[14]

Acknowledgements: This work was supported in part (A. L. S. and N. V.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). This research is part of the Human Capital and Mobility European Network "Metal-mediated and Catalyzed Organic Synthesis", and is based on results obtained in Utrecht during the three-month visit of P. L. at the Debye Institute, which was made possible through a grant from the European Community (Scheme Contract No. ERBCHRXCT 930149).

Received: November 5, 1996 [F 515]

---

[1] a) T. Woo, E. Folga, T. Ziegler, *Organometallics* **1993**, *12*, 1289; b) L. G. McCullough, R. R. Schrock, *J. Am. Chem. Soc.* **1984**, *106*, 4067; c) L. G. McCullough, R. R. Schrock, J. C. Dewan, J. C. Murdzek, *ibid.* **1985**, *107*, 5987; d) H. Strutz, J. C. Dewan, R. R. Schrock, *ibid.* **1985**, *107*, 5999; e) R. R. Schrock, D. N. Clark, J. Sancho, J. H. Wengrovius, S. M. Rocklage, S. F. Pedersen, *Organometallics* **1982**, *1*, 1645; f) J. H. Wengrovius, J. Sancho, R. R. Schrock, *J. Am. Chem. Soc.* **1981**, *103*, 3932; g) R. R. Schrock, M. L. Listemann, L. G. Sturgeoff, *ibid.* **1982**, *104*, 4291; h) M. H. Chisholm, D. M. Hoffmann, J. C. Huffman, *Inorg. Chem.* **1983**, *22*, 2903; i) M. R. Churchill, W. J. Youngs, *ibid.* **1979**, *18*, 2454; j) M. H. Chisholm, J. C. Huffman, N. S. Marchant, *J. Am. Chem. Soc.* **1983**, *105*, 6162; k) G. A. Vaughan, R. Toreki, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1993**, *115*, 2980; l) A. LaPointe, R. R. Schrock, *Organometallics* **1995**, *14*, 1875; m) D. S. Edwards, L. V. Biondi, J. W. Ziller, M. R. Churchill, R. R. Schrock, *ibid.* **1983**, *2*, 1505; n) A. LaPointe, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1995**, *117*, 4802; o) A. LaPointe, R. R. Schrock, *Organometallics* **1993**, *12*, 3379.

[2] a) A. W. Gal, H. van der Heijden, *J. Chem. Soc. Chem. Commun.* **1983**, 420; b) H. van der Heijden, A. W. Gal, P. Pasman, A. G. Orpen, *Organometallics* **1983**, *2*, 1505; c) L. Guggenberger, R. R. Schrock, *J. Am. Chem. Soc.* **1975**, *97*, 2935; d) S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs, M. R. Churchill, *ibid.* **1978**, *100*, 5962; e) M. R. Churchill, H. J. Wasserman, H. W. Turner, R. R. Schrock, *ibid.* **1982**, *104*, 1710; f) M. R. Churchill, W. J. Youngs, *Inorg. Chem.* **1979**, *18*, 171; g) L. Li, Z. Xue, G. P. A. Yap, A. L. Rheingold, *Organometallics* **1995**, *14*, 4992.

[3] a) H. C. L. Abbenhuis, N. Feiken, H. F. Haarman, D. M. Grove, E. Horn, A. L. Spek, M. Pfeffer, G. van Koten, *Organometallics* **1993**, *12*, 2227; b) H. C. L. Abbenhuis, N. Feiken, D. M. Grove, J. T. B. H. Jastrzebski, H. Kooijman, P. van der Sluis, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1992**, *114*, 9773; c) H. C. L. Abbenhuis, M. H. P. Rietveld, H. F. Haarman, M. P. Hogerheide, A. L. Spek, G. van Koten, *Organometallics* **1994**, *13*, 3259.

[4] a) P. F. Engel, M. Pfeffer, J. Fischer, *Organometallics* **1994**, *13*, 4751; b) W. Klaui, H. Hamers, M. Pfeffer, A. De Cian, J. Fischer, *J. Organomet. Chem.* **1990**, *394*, 213; c) P. F. Engel, M. Pfeffer, J. Fischer, A. Dedieu, *J. Chem. Soc. Chem. Commun.* **1991**, 1274.

[5] R. R. Schrock, R. T. DePue, J. Feldman, K. B. Yap, D. C. Yang, W. M. Davis, L. Park, M. DiMare, M. Schofield, J. Anhaus, E. Walborsky, E. Evitt, C. Krüger, P. Betz, *Organometallics* **1990**, *9*, 2262.

[6] G. A. Ruprecht, L. W. Messerle, J. D. Fellmann, R. R. Schrock, *J. Am. Chem. Soc.* **1980**, *102*, 6236.

[7] a) C. D. Wood, S. J. McLain, R. R. Schrock, *J. Am. Chem. Soc.* **1979**, *101*, 3210; b) K. C. Wallace, A. H. Liu, J. C. Dewan, R. R. Schrock, *ibid.* **1988**, *110*, 4964; c) R. R. Schrock, *Acc. Chem. Res.* **1986**, *19*, 98, and references cited therein.

[8] a) H. C. L. Abbenhuis, R. Belzen, D. M. Grove, A. J. A. Klomp, G. P. M. Mier, A. L. Spek, G. van Koten, *Organometallics* **1993**, *12*, 210; b) I. C. M. Wehman, I. F. Luitwieler, K. Vatter, D. M. Grove, W. J. J. Smeets, E. Horn, A. L. Spek, G. van Koten, *Inorg. Chim. Acta* **1996**, *252*, 56; c) J. Castro, M. V. Galakhov, M. Gómez, P. Gómez-Sal, P. Royo, *Organometallics* **1996**, *15*, 1362; d) P. Steenwinkel, A. L. Spek, G. van Koten, unpublished results; e) A. A. H. van der Zeijden, G. van Koten, R. Luijk, R. A. Nordemann, A. L. Spek, *Organometallics* **1988**, *7*, 1549.

[9] P. Lohner and M. Pfeffer, personal communication.

[10] C. D. Wood, S. J. McLain, R. R. Schrock, *J. Am. Chem. Soc.* **1979**, *101*, 3210.

[11] A. Osman, R. G. Steevenz, D. G. Tuck, H. A. Meinema, J. G. Noltes, *Can. J. Chem.* **1984**, *62*, 1698.

[12] J. T. B. H. Jastrzebski, G. van Koten, M. Konijn, C. H. Stam, *J. Am. Chem. Soc.* **1982**, *104*, 5490.

[13] N. Walker, D. Stuart, *Acta Crystallogr.* **1983**, *A39*, 158.

[14] A. L. Spek, *Acta Crystallogr.* **1990**, *A46*, C34.

[15] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The DIRDIF program system*, Technical Report of the Crystallographic Laboratory, University of Nijmegen (The Netherlands), **1992**.

[16] G. M. Sheldrick, SHELXL-93. Program for crystal structure refinement, University of Göttingen (Germany), **1993**.

[17] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100013. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).