

the same reaction with aminophosphanes led to addition compounds on the pyrylium moiety, analogously to the known addition of Ph_3P on pyrylium salts.^[1,2] 2) Variation of the substitution pattern of pentamethinium salts which can be realized with both reagents: arsanes can easily introduce a large variety of amino groups; the pyrylium salt governs the substitution on the C_5 -moiety. Using the method described here we were able to synthesize the first phenyl-substituted pentamethinium salts (and 1,5-disubstituted derivatives). Finally, it is important to underline the importance of developing new compounds in the pentamethinium series, which have proven useful in chemistry (dyes and intermediates in azulene synthesis^[1,3], physics (laser, nonlinear optics in the crystal phase^[1,4]) and biology (anthelmintics^[1,5]).

Experimental procedure

1: A solution of 0.540 g (1.32 mmol) of 2,4,6-triphenylpyrylium perchlorate in 10 mL of acetonitrile was treated with 0.162 mL (0.88 mmol) of *tris*(dimethylamino)arsane. The mixture was stirred for two hours at room temperature. The fluorescence due to the pyrylium salt disappeared and the solution became deep red. As_4O_6 was then filtered off. After removal of the solvent, the precipitate was washed with pentane to yield a red powder (yield > 90%). Recrystallization from EtOH (100%) afforded bright red crystals, m.p. 195 °C, which were suitable for an X-ray structure analysis. **2–5** were obtained analogously.

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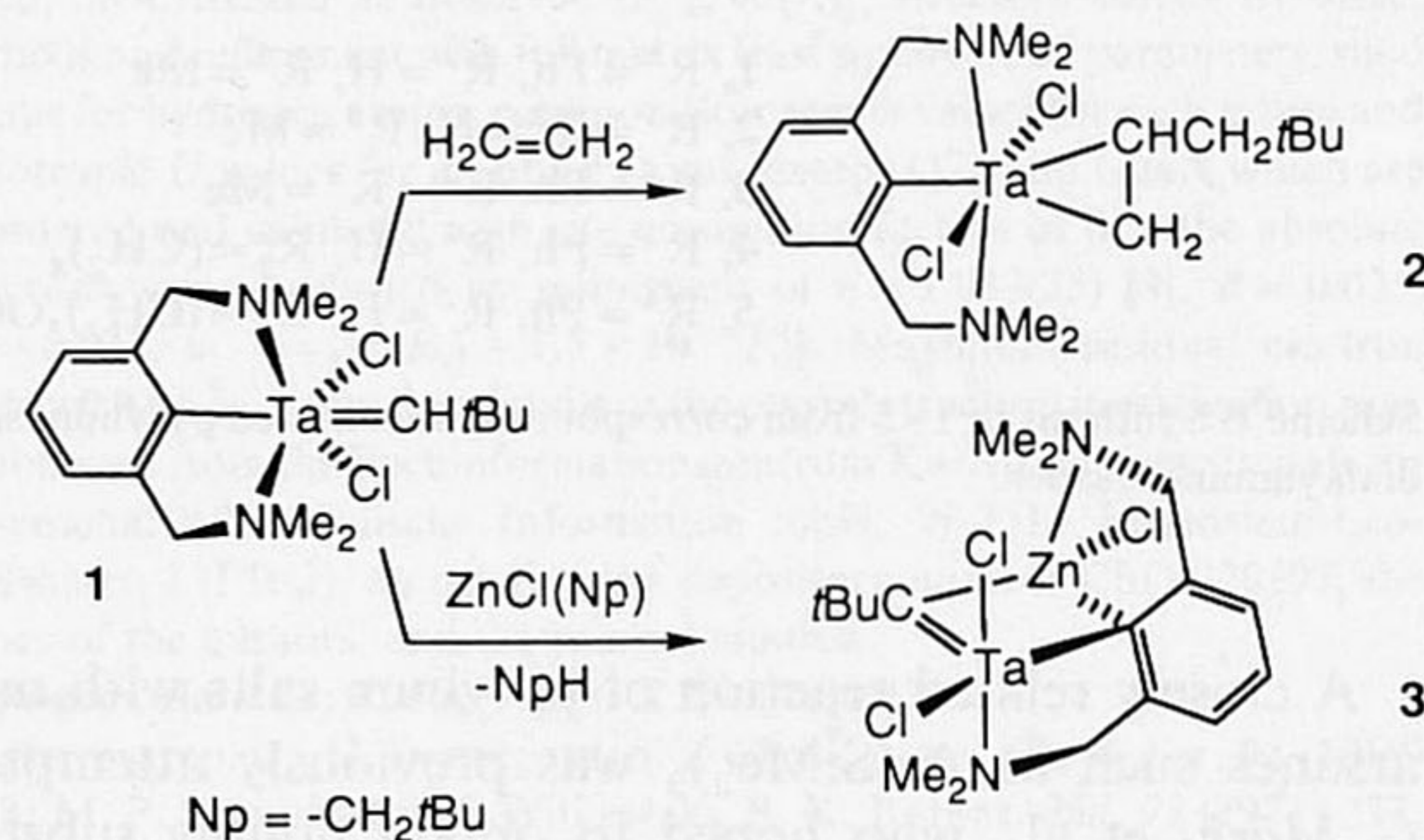
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Effect of Intramolecular Coordination on Tantalum-Alkylidene-Centered Reactions: Synthesis and Structure of a Tantalum-Olefin Adduct and a Tantalum-Zinc-Alkylidene Complex**

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Dedicated to Professor Hans-Georg von Schnering on the occasion of his 60th birthday

Recently, we started to explore the influence of intramolecular Lewis bases on tantalum-alkylidene reactivity. The potentially terdentate, monoanionic ligand $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]^-$ seemed well-suited for this research because of its demonstrated ability to stabilize high oxidation state transition metal centers [e.g. $\text{Fe}^{\text{III}[1]}$ and $\text{Ni}^{\text{III}[2]}$] as well as unusual transition metal intermediates.^[3] We have synthesized a tantalum-alkylidene complex $[\text{TaCl}_2\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}(\text{CHtBu})]$ **1** that contains this spectator ligand.^[4] Here we report the alkylidene-centered reactions of **1** with either an olefin (ethene) or a strong base (neopentylzinc chloride). These reactions (Scheme 1) lead to the formation of a tantalum-olefin adduct and a novel bimetallic tantalum zinc complex, respectively.



Scheme 1. Alkylidene-centered reactivity of **1**.

Treatment of the alkylidene complex **1** with an excess of ethene in pentane at 20 °C affords the neopentylethene adduct **2** which was characterized spectroscopically^[5] and by X-ray structure analysis.^[6] The structure determination (Fig. 1) shows **2** to be a mononuclear, distorted pentagonal bipyramidal tantalum complex. In this complex two chlorine atoms [Cl(1) and Cl(2)] occupy the axial *trans* positions. The equatorial plane contains the C(13) and C(14) atoms of the coordinated olefin together with the C(1), N(1) and N(2) atoms of the terdentate aryldiamine ligand. Both five-membered $\text{Ta}-\text{C}-\text{C}-\text{N}$ chelate rings are puckered. The considerable lengthening of the olefinic bond ($\text{C}(13)-\text{C}(14) = 1.436(10)$ Å) upon coordination to tantalum and the short distances between olefinic carbons C(13) and C(14) and tantalum (2.200(7) and 2.211(7) Å, respectively) make it more

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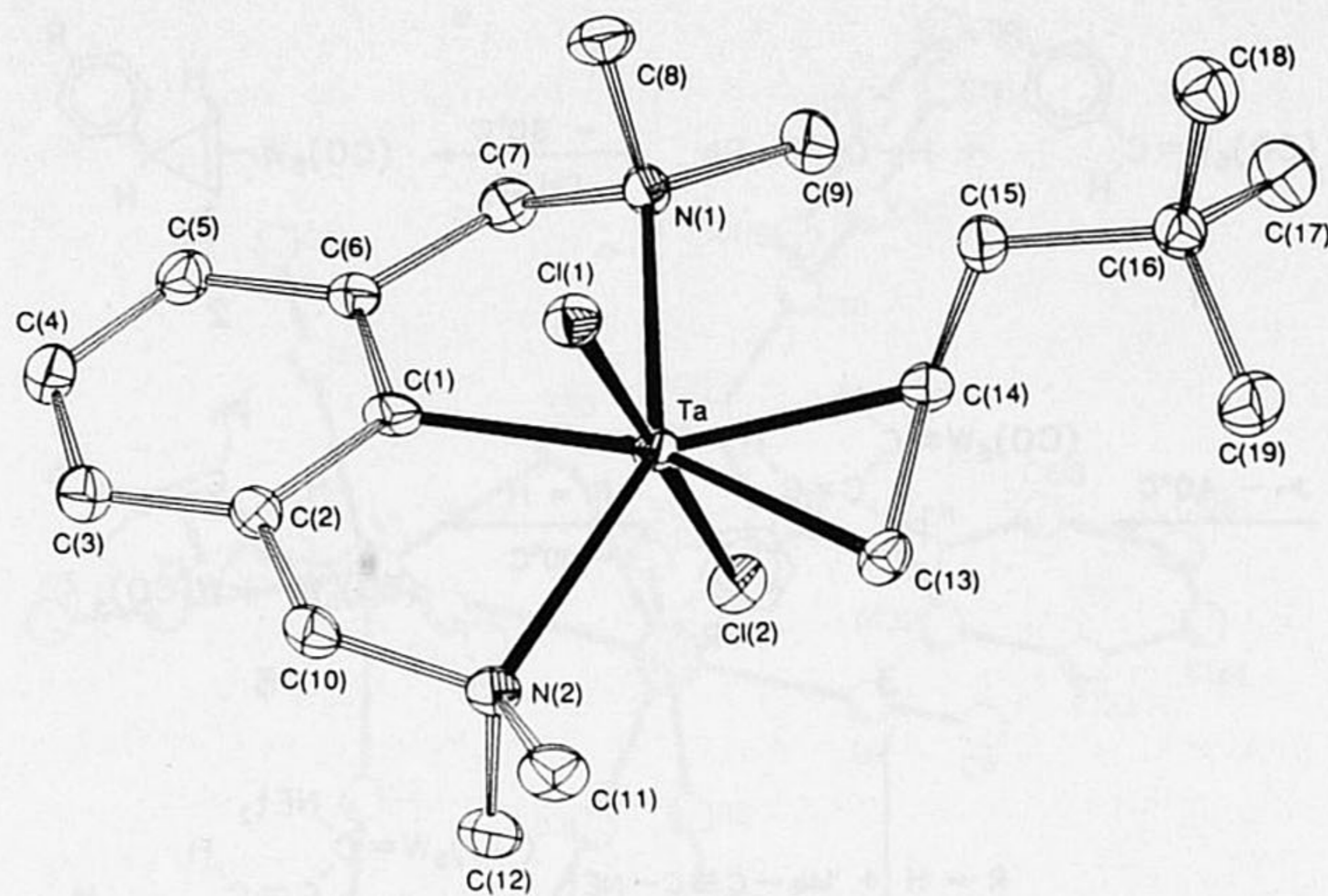


Fig. 1. Thermal motion ellipsoid plot (50% probability level) of **2** in the crystal. Selected bond lengths [Å] and bond angles [°]: Ta-Cl(1) 2.3702(18), Ta-Cl(2) 2.3608(18), Ta-C(1) 2.165(7), Ta-N(1) 2.353(6), Ta-N(2) 2.372(6), Ta-C(13) 2.200(7), Ta-C(14) 2.211(7); Cl(1)-Ta-Cl(2) 178.76(7), N(1)-Ta-N(2) 145.0(2), N(1)-Ta-C(14) 88.5(2), C(13)-Ta-C(14) 38.0(3).

acceptable to describe the structure as a tantalacyclopropane (with tantalum in oxidation state V).

The $^1\text{H-NMR}$ spectrum of **2**^[5] is not temperature dependent to at least 80 °C, indicating a rigid structure of **2** also in solution. Characteristic for the terdentate coordination of the aryldiamine ligand are the four anisochronous NMe resonances at $\delta = 2.35, 2.42, 3.27,$ and 3.45 ; olefinic multiplets shifted to high field at $\delta = 3.10, 4.06,$ and 4.22 are indicative for the η^2 -bonded neopentylethene function. In this function, the value of the olefinic $^1J_{13\text{C}13\text{C}}$ coupling is only 34 Hz (measured in an INADEQUATE $^{13}\text{C}\{^1\text{H}\}$ -NMR experiment), which is more like the $^1J_{\text{sp}^3\text{-C}/\text{sp}^3\text{-C}}$ coupling in alkanes and cyclopropanes than the $^1J_{\text{sp}^2\text{-C}/\text{sp}^2\text{-C}}$ coupling in alkenes.^[7] This finding again argues for the structure of **2** to be described as a tantalacyclopropane species.

Treatment of **1** with neopentylzinc chloride in Et_2O affords the bimetallic complex **3** which was characterized spectroscopically^[5] and by X-ray structure analysis.^[8] The structure determination (Fig. 2) shows **3** to be a tantalum-zinc-

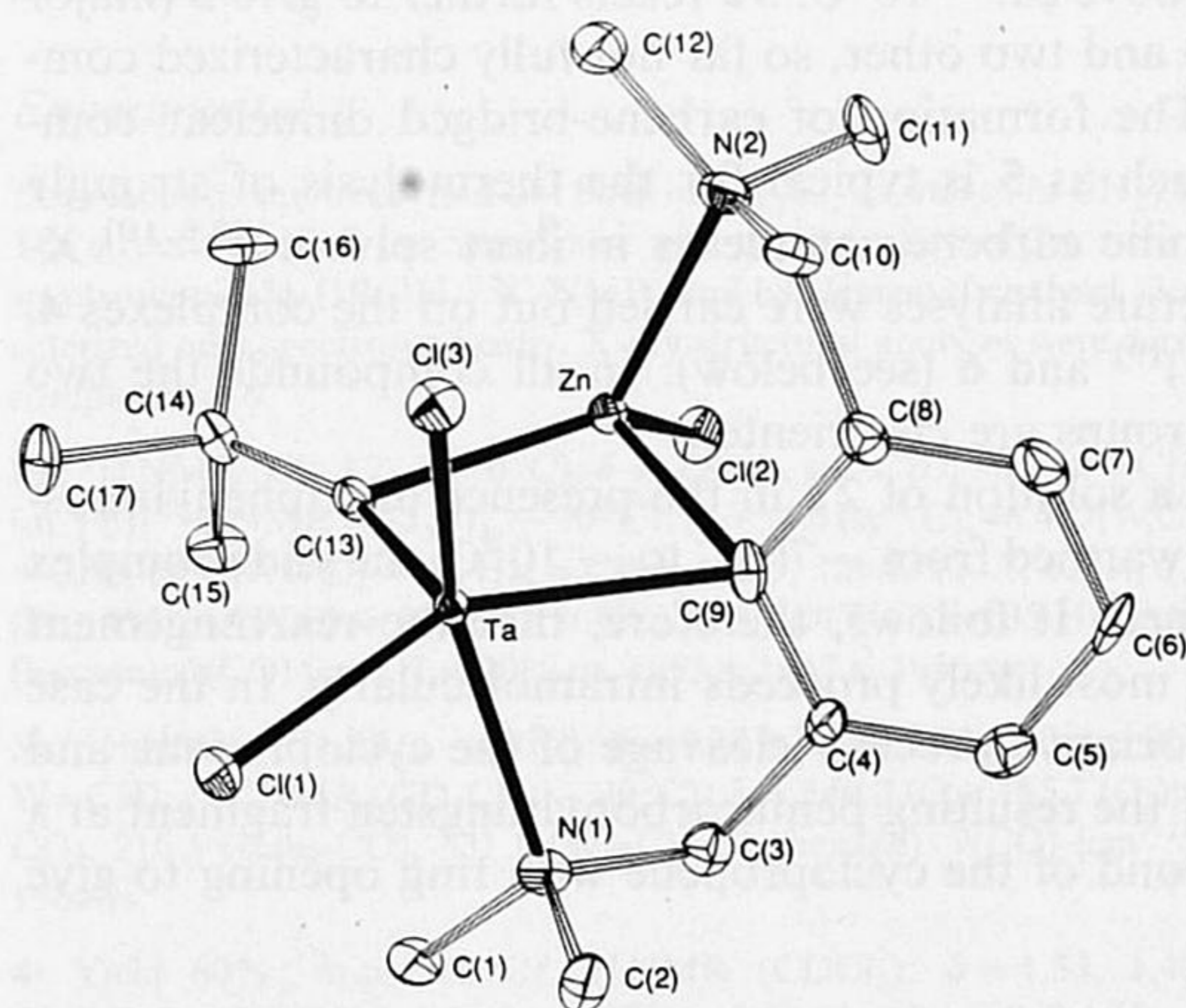


Fig. 2. Thermal motion ellipsoid plot (50% probability level) of **3** in the crystal. Selected bond lengths [Å] and bond angles [°]: Ta-Cl(1) 2.3830(15), Ta-Cl(3) 2.3628(16), Ta-C(9) 2.321(6), Ta-C(13) 1.862(6), Ta-N(1) 2.313(6), Ta-Zn 2.7286(9), Zn-Cl(2) 2.2143(16), Zn-C(9) 2.258(6), Zn-C(13) 2.114(6), Zn-N(2) 2.101(5); Cl(1)-Ta-Cl(3) 91.90(5), Cl(1)-Ta-C(13) 103.04(18), Cl(3)-Ta-C(9) 98.79(16), N(1)-Ta-C(9) 75.0(2), N(2)-Zn-Cl(2) 108.49(15), Cl(2)-Zn-C(9) 117.71(17), Cl(2)-Zn-C(13) 118.51(15).

alkylidene complex that contains a bridging aryldiamine ligand that is nicely positioned to complete the coordination environment of both metal centers. The resulting coordination geometry around zinc is distorted tetrahedral, while the ligand array around tantalum is in between trigonal bipyramidal and square pyramidal (70% along the Berry pseudorotation coordinate towards the latter). The aryl ligand forms an unprecedented asymmetric bridge (via C(9)) between zinc and tantalum: the angle between the Ta-Zn vector and the least squares plane through the aryl carbon atoms is $65.2(2)^\circ$ and deviates strongly from the expected 90° for a symmetrically bridging aryl unit. The structural data are such that it is possible to describe this bond as intermediate between either a two-electron three-center bond or a combination of a Ta-C σ -bond with a coordinative C \rightarrow Zn bond involving electron donation from the filled p-orbital on C(9) to Zn. The latter description is equivalent to the type of bonding that would result from an electrophilic attack of a zinc cation at the *ipso*-carbon atom of the tantalum-aryl moiety.^[10] The very short Ta=C alkylidene bond length (Ta-C(13) = 1.862(6) Å) together with the long Zn-C bond in the alkylidene unit (Zn-C(13) = 2.114(6)) also allow this complex to be described as a tantalum-alkylidyne species stabilized by a Lewis acid-base interaction with a zinc chloride cation. Similar arguments have been used to describe the structural characteristics of $[\{\text{TaCl}_2(\mu\text{-ClBu})(\text{MeOCH}_2\text{CH}_2\text{OMe})\}_2\text{Zn}(\mu\text{-Cl})_2]$.^[11]

Experimental Procedure

2: A purple suspension of 4.03 mmol of **1** [4] in pentane (100 mL) saturated with ethene at 20 °C was stirred for 24 h. The resulting green turbid solution was filtered, and the solvent removed from the filtrate in vacuo to give 3.23 mmol of emerald green **2** (80%). The complex can be crystallized from a minimum of pentane. Correct C,H,N analysis.

3: A purple suspension of 12.3 mmol of **1** [4], 7.12 mmol of ZnCl_2 , and 6.16 mmol of $[\text{Zn}(\text{CH}_2\text{tBu})_2]$ in Et_2O (100 mL) was stirred at 20 °C for five days. The solvent was removed in vacuo and the sticky residue triturated with hexane. The resulting red powder was extracted with 150 mL of warm (50 °C) benzene. The extract was concentrated in vacuo to ca. 50 mL and layered with pentane (200 mL). After storage of the extract at 20 °C for three days, large red crystals of **3** (9.70 mmol, 79%) were isolated. Correct C,H,N analysis.

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- [5] $^1\text{H-NMR}$ (200.13 MHz, C_6D_6 , 25 °C, TMS): **2**: $\delta = 1.33$ (s, 9H; *t*Bu), 2.12 and 2.97 (dd, 2H; CH_2tBu), 2.35, 2.42, 3.27, and 3.45 (s, 12H; NCH₃), 3.10 and 4.06 (m, 2H; $\text{H}_2\text{C}=\text{CH}-$), 4.22 (m, 1H; $\text{H}_2\text{C}=\text{CH}-$), 3.64, 3.68, 4.49, and 4.61 (d, $^2J(\text{H,H}) = 12$ Hz, 4H; CH_2N), 7.10 (dd, 2H; *o*-C₆H₃), 7.27 (t, 1H, *p*-C₆H₃). **3**: $\delta = 1.55$ (s, 9H; *t*Bu), 1.75, 1.94, 2.42, and 2.71 (each s, 12H; NCH₃), 2.26, 2.33, 4.43, and 5.03 (d, $^2J(\text{H,H}) = 13$ Hz, 4H; CH_2N), 6.62 (dd, 2H; *o*-C₆H₃), 6.97 (t, 1H; *p*-C₆H₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, C_6D_6 , 25 °C, TMS): **2**: $\delta = 30.5$ (C(CH₃)₃), 40.7 (C(CH₃)₃), 52.6, 52.8, 54.5, and 55.8 (NCH₃), 58.6 (CH₂C(CH₃)₃), 78.3, and 78.8 (CH₂N), 87.8 (H₂C=CH-), 95.2 (H₂C=CH-), 204.7 (Ar, *ipso*-C); **3**: $\delta = 35.2$ (C(CH₃)₃), 51.2 (C(CH₃)₃), 47.4, 47.9, 48.1, and 54.0 (NCH₃), 67.0, and 71.6 (CH₂N), 175.2 (Ar, *ipso*-C), 295.4 (C*t*Bu).
- [6] Crystal structure data for **2**: C₁₉H₃₃Cl₂N₂Ta, $M = 541.34$, triclinic space group $P\bar{1}$, $a = 8.3199(14)$, $b = 9.041(2)$, $c = 14.054(3)$ Å, $\alpha = 94.531(19)$, $\beta = 90.748(15)$, $\gamma = 92.856(17)^\circ$, $V = 1052.4(4)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.708$ g cm⁻³, $\mu(\text{MoK}\alpha) = 54.2$ cm⁻¹. A block-shaped crystal (ca. 0.6 × 0.2 × 0.1 mm) of **2**, mounted on a glass fibre, was used for data collection on an Enraf-Nonius CAD-4 diffractometer at 100 K with Zr-filtered MoK α radiation ($\theta_{\text{max}} = 30.26^\circ$). The structure was solved with automated Patterson methods followed by peak optimization (SHELXS-86). H-atoms were introduced at calculated positions (C-H = 0.98 Å). An absorption correction was applied (Gaussian integration correction factors range

from 1.69 to 4.51). Full-matrix least-squares refinement of positional and anisotropic thermal parameters of all non-H atoms and an overall isotropic thermal parameter for H atoms converged at a final R value: $0.043 wR = 0.051$; $w^{-1} = \sigma^2(F)$ for 5267 unique reflections with $I \geq 2.5\sigma(I)$ [9].

[7] H. O. Kalinowski, S. Berger, S. Braun in: *Carbon-13 NMR Spectroscopy*, Wiley, Chichester 1988, p. 549.

[8] Crystal structure data for **3**: $C_{17}H_{28}Cl_3N_2TaZn$, $M = 613.11$, orthorhombic space group $P2_12_12_1$, $a = 9.725(2)$, $b = 10.436(2)$, $c = 20.766(3)$ Å, $V = 2107.5(7)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.932$ g cm⁻³, $\mu(\text{MoK}\alpha) = 66.8$ cm⁻¹. A red-brown block-shaped crystal (ca. $0.37 \times 0.63 \times 0.80$ mm) of **3**, mounted on a glass fiber, was used for data collection on an Enraf-Nonius CAD-4-diffractometer at 100 K with Zr-filtered MoK α radiation ($\theta_{\text{max}} = 29.4^\circ$). The structure was solved with Patterson and Fourier techniques (SHELXS-86). H-atoms were introduced at calculated positions (C-H = 0.98 Å). An empirical absorption correction was applied (DIFABS). Full-matrix least-squares refinement converged at a final R value: $0.034 wR = 0.054$; $w^{-1} = \sigma^2(F) + 0.0017(F)^2$ for 4746 unique reflections with $I \geq 2.5\sigma(I)$ [9].

[9] Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW (UK), on quoting the full journal citation.

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Coupling of Alkynes with Carbene Ligands to Tungsten-coordinated Cyclopropenes and Their Stereoselective Isomerization to Vinylcarbene Complexes**

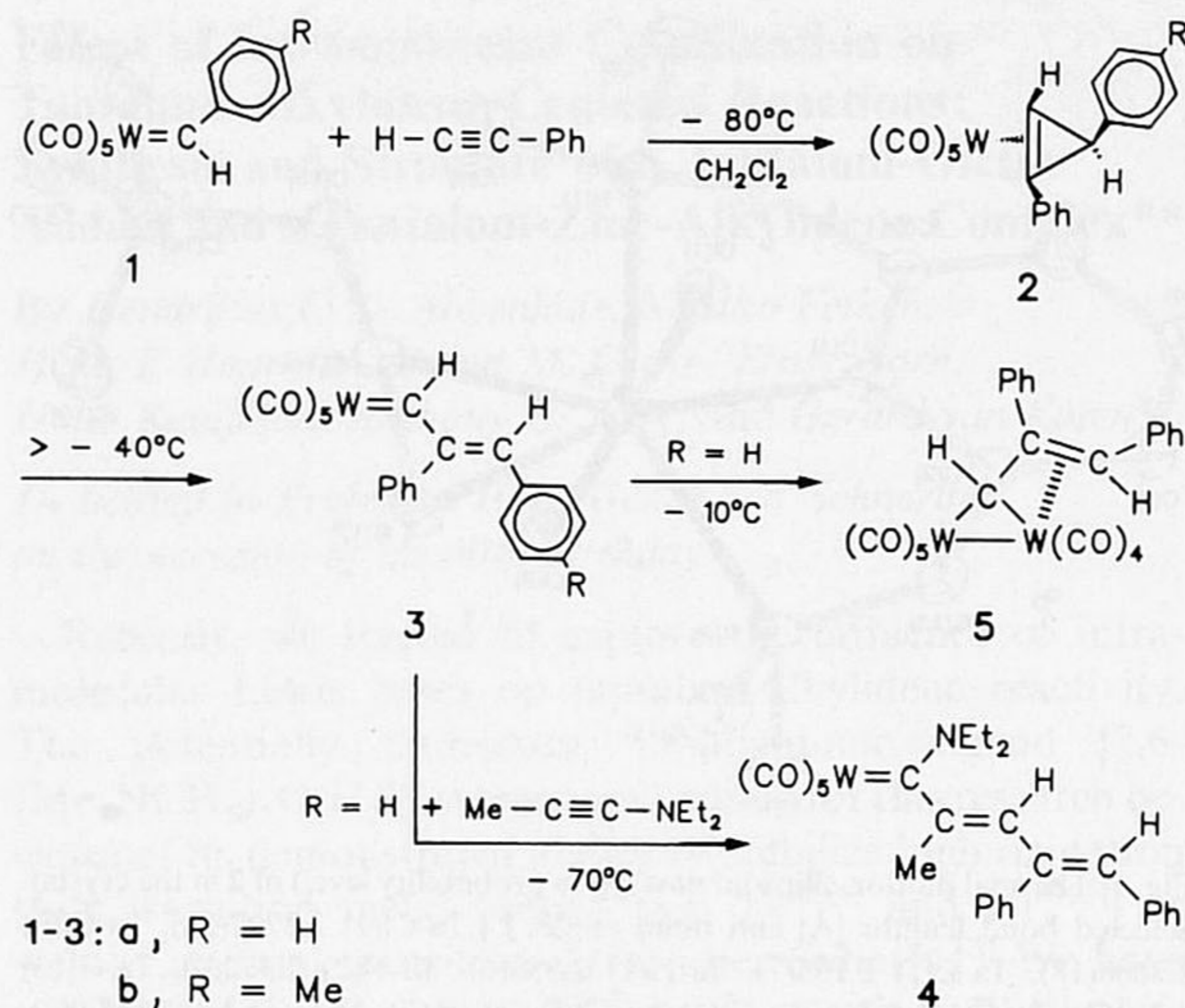
By Helmut Fischer,* Josef Hofmann, and Elvira Mauz

Dedicated to Professor Paul Binger on the occasion of his 60th birthday

Reactions of cyclopropenes with transition metals find many uses in organic synthesis.^[1] For some of the transition metal-catalyzed reactions the sequence cyclopropene \rightarrow cyclopropene complex \rightarrow vinylcarbene complex (or metallacyclobutene) \rightarrow organic product has been postulated.^[2] Both cyclopropene complexes^[3,4] as well as vinylcarbene complexes^[4,5] and metallacyclobutenes^[6] have been prepared from transition metal complexes and cyclopropenes. So far however, it has not been possible to verify the step cyclopropene complex \rightarrow vinylcarbene complex.

Cyclopropene complexes are generally prepared by ligand substitution. Their synthesis from carbene complexes and alkynes has thus far never been reported, though the intermediary formation of a cyclopropene in the reaction of 2-butyne with a cationic benzylidenedicarbonyl(cyclopentadienyl)iron complex has been postulated on the basis of the reaction products.^[7] We now report the synthesis of isolable cyclopropene complexes by addition of alkynes to carbene complexes and the demonstration of stereoselective intramolecular ring opening to give vinylcarbene complexes.

The benzylidene complex **1a**^[8] reacts at -80°C in one to two hours with an equimolar amount of phenylacetylene to give the cyclopropene complex **2a**. This is stable only below ca. -40°C . Above -30°C , **2a** rapidly isomerizes in solution to the vinylcarbene complex **3a**. Upon reaction of **1a** with

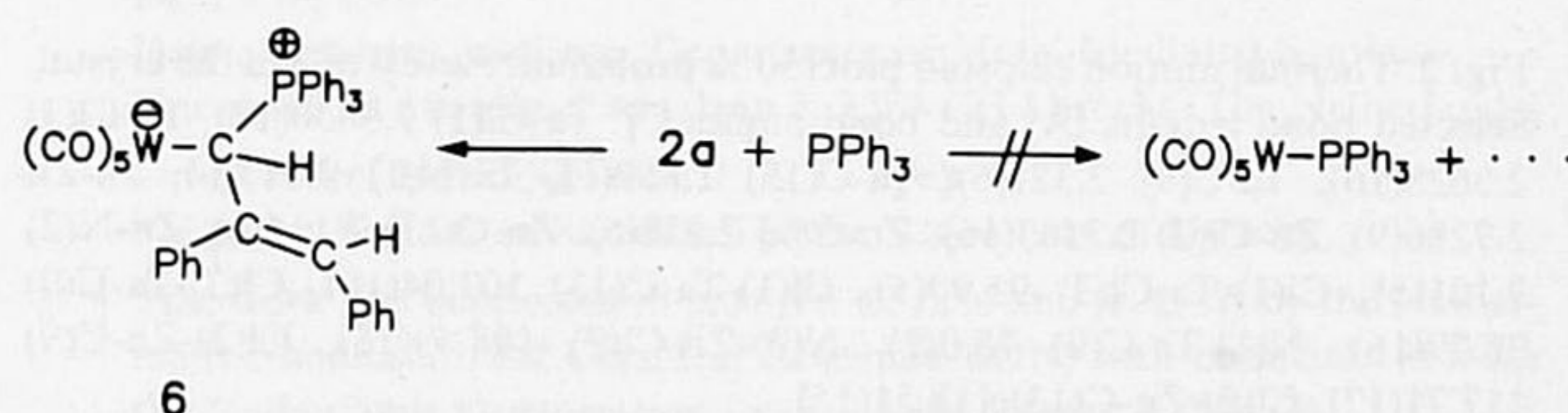


phenylacetylene on a preparative scale, mixtures of **2a** (major product) and **3a** are generally obtained which are difficult to separate. In contrast to **2a** however, **3a** already reacts rapidly at -70°C with diethylpropynylamine to give **4**. The compounds **2a** and **4** can be separated chromatographically at -70°C , hence **2a** is obtainable in pure form in this way.

The structure of the cyclopropene complex **2a** could be confirmed spectroscopically. The IR spectrum indicated a pentacarbonyl complex. The benzylidene-H NMR signal is shifted upfield by more than 14 ppm compared to that in **1a**, while the signal of the original sp-CH atom of phenylacetylene is shifted ca. 2 ppm downfield. The assignments are supported by the spectrum of [D]**2a** (obtained from **1a** and Ph-C \equiv C-D). The ¹³C-NMR spectrum of **2a** shows, in addition to the signals for the CO substituents and the two phenyl groups, signals for three further carbon atoms between $\delta = 34$ and 65, of which two couple with the tungsten atom ($J(\text{W},\text{C}) = 16$ and 19 Hz). Signals at low field ($\delta > 210$), characteristic for carbene complexes, are absent.

According to the NMR spectra the rearrangement of **2a** to **3a** is stereoselective; carbene complexes isomeric with **3a** could not be detected. The structure of **3a** follows unequivocally from the characteristic downfield position of the carbene-H and carbene-CNMR signals ($\delta = 16.64$ and 331.1, resp.). Above ca. -10°C , **3a** reacts further to give **5** (major product) and two other, so far not fully characterized complexes. The formation of carbene-bridged dinuclear complexes such as **5** is typical for the thermolysis of strongly electrophilic carbene complexes in inert solvents.^[8b,10] X-ray structure analyses were carried out on the complexes **4**, **5** (Fig. 1)^[9] and **6** (see below). In all compounds the two phenyl groups are *cis* oriented.

When a solution of **2a** in the presence of triphenylphosphane is warmed from -70°C to -10°C , the ylide complex **6** is formed. It follows, therefore, that the rearrangement **2a** \rightarrow **3a** most likely proceeds intramolecularly. In the case of a dissociative process (cleavage of the cyclopropene and attack of the resulting pentacarbonyltungsten fragment at a C-C σ -bond of the cyclopropene with ring opening to give



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