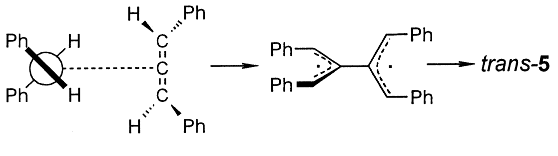
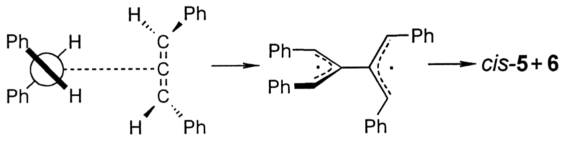
and are transformed to the products without extensive isomerization.

En route to *trans*-**5**, the most likely diradical is **16**, which should be formed on the approach of (*M*)-**4** and (*P*)-**4** with their sterically unhindered faces in the crossed arrangement along their C_2 axes. The corresponding transition state shows equal interactions between the hydrogen atoms of one allene subunit and the phenyl groups of the other with the effect that the phenyl groups of **16** are as far away as possible from the other half of the molecule.



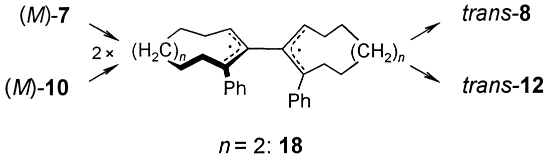
(*M*)-**4** (*P*)-**4** **16**



(*M*)-**4** (*M*)-**4** **17**

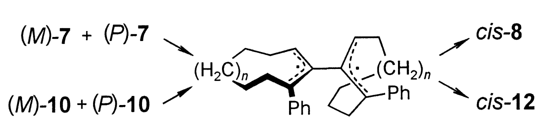
The diradical **17** should be the precursor of *cis*-**5** and **6**. In the corresponding transition state from two homomers of **4**, the hydrogen atoms of the allene subunits approach each other in pairs rather closely. Forced by the steric crowding, one hydrogen atom moves out of the way such that an allyl radical moiety with an *E*,*Z* configuration is generated. With regard to the formation of **5** and **6**, the diradicals **16** and **17** as well as their four diastereomers had been discussed in detail previously, but without a definite conclusion.[2, 12]

Transition states from two allene molecules in the crossed arrangement have to be assumed also for the dimerization of **7** and **10**. However, because of the variety of the possibilities and of the steric interactions—even methylene groups not directly linked to the allene moiety can impair the close contact with the other molecule—the situation is not easily comprehensible. Within the discussed mechanistic concept though, there is no doubt that pairs of homomers of **7** and **10** give rise to the diradicals **18** and **19**, respectively, which eventually collapse to give *trans*-**8** and *trans*-**12**, whereas pairs of enantiomers of **7** and **10** generate the diradicals **20** and **21**, respectively, from which *cis*-**8** and *cis*-**12** result. The non-racemic nature of the *trans* products supports a considerable conformative stability of **18** and **19**, and the only small admixtures of *cis*-**8** and *cis*-**12** confirm their configurative persistence as well, that is only insignificant proportions of **18** and **19** isomerize to **20** and **21**, respectively.



$n = 2$: **18**
$n = 1$: **19**

(absolute configuration unknown)



$n = 2$: **20**
$n = 1$: **21**

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Five-Coordinate Carbides in Ti-Al-C Complexes[**]

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Fifty years after the discovery of catalytic olefin polymerization by Ziegler and Natta, polyolefin products are commodity chemicals. The production of these materials is a significant driving force in our economy; one that continues to inspire research. Over the last twenty years much effort has been directed towards tunable "single-site catalysts".[1–6] The

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vast majority of systems developed and certainly those in commercial practice require the use of Al-based activators. Despite the importance of such alkylaluminum reagents few well-defined products derived from the stoichiometric reactions of early transition metal compounds and Al reagents are known. While Al reagents may act simply as alkylating agents for early transition metal species, there are several examples in which C–H bond activation processes provide novel products. The most familiar example is the Tebbe reagent,[7, 8] $[Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2]$ derived from the reaction of $[Cp_2TiCl_2]$ and $AlMe_3$. Roesky et al. have recently described the formation of the very interesting Zr–Al and Hf–Al clusters $[(Cp^*MMe)(\mu\text{-}F)_2AlMe_2]_2$ and $[(Cp^*M)_3Al_6Me_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)]$.[9, 10] In these cases, it is the attraction of the Al centers to the fluoride ligands that initiates the reactions of $[Cp^*MF_3]$ with $AlMe_3$. Similarly we have recently shown that the interaction of $AlMe_3$ with the S and/or N ligands of $[CpTi(NPR_3)(SR)_2]$ results in the formation of a Ti-thiolate-Al-carbide species.[11] Herein, we demonstrate that the remarkable process of triple C–H bond activation proceeds directly in the reactions of the dialkyl complexes $[CpTi(NPR_3)Me_2]$ with $AlMe_3$. Moreover, the resulting Ti-Al-carbide complexes establish equilibria with excess $AlMe_3$ to provide an unusually facile interconversion bewteen carbide species with distorted tetrahedral and five-coordinate, pseudo trigonal bipyramidal geometries.

The reaction of **1** with more than four equivalents of $AlMe_3$ in toluene or hexane proceeds over 16 h to produce a red

$[CpTi(NPiPr_3)Me_2]$ **1**

crystalline product **2** in 75% yield. In the $^{31}P\{^1H\}$ NMR spectrum of compound **2** there is a single resonance at $\delta = 50.9$. The ^1H and ^{13}C(APT) NMR spectra (ATP = attached proton test) are consistent with the presence of cyclopentadienyl and phosphinimide ligands. Additionally the ^1H NMR spectrum revealed four broad resonance signals near $\delta = 0$ that integrated to approximately 30 hydrogen atoms; this suggests a 4:1 combination of Al and Ti in **2**. Recrystallization of **2** from benzene afforded crystals of the slightly different species **3.** The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a single resonance signal at $\delta = 49.8$ and the ^1H and ^{13}C(APT) NMR spectra are slightly different than those of **2**. In addition, the ^1H NMR spectrum of **3** shows three broad resonances that integrate to 21 hydrogen atoms (near $\delta = 0$) and are attributed to Al-bound methyl groups. The $^{27}Al\{^1H\}$ NMR spectra show three broad resonances at $\delta = 149.0$, 114.0, and 38.0. These data suggest a 3:1 combination of Al and Ti in **3**.

The structue of **3**[12] was confirmed by X-ray crystallography (Figure 1).

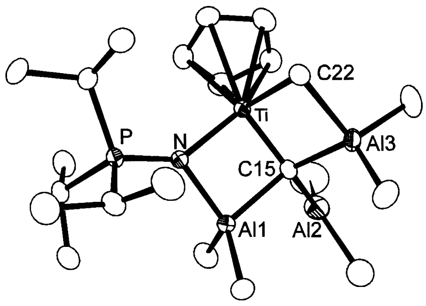


Figure 1. Structure of **3**, (ORTEP drawing 20% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity.

$[CpTi(\mu_2\text{-}Me)(\mu_2\text{-}NPiPr_3)(\mu_4\text{-}C)(\mu_2\text{-}AlMe_2)_2(AlMe_2)]$ **3**

The pseudo "three-legged piano stool" coordination sphere of the Ti center in **3** comprises a cyclopentadienyl ring, a methyl group, a phosphinimide nitrogen atom, and a carbide carbon atom; three aluminum atoms complete the bonding sphere of the carbide unit. Two of the $AlMe_2$ moieties bridge, respectively, the carbide center and the Ti-bound methyl group, and the carbide center and the phosphinimide nitrogen atom bound to the Ti center. The third $AlMe_2$ fragment occupies a terminal position on the carbide center. The most interesting feature is the geometry about the carbide carbon atom. The titanium–carbide (Ti–C15) bond in **3** (1.874(4) Å) is significantly shorter than the terminal Ti–CH_3 bond (2.123(5) Å) in $[Cp(tBu_3PN)TiMe(\mu_2\text{-}CH_3B(C_6F_5)_3)]$.[13] This relatively short Ti–C15 bond, along with the Ti–C22 bond of 2.301(4) Å, infers that the Ti–C15 bond has some degree of multiple-bond character. This view is supported by the flattened geometry of the carbide carbon as evidenced by the Ti-C-Al2 and Al1-C-Al3 angles of 145.4(2) and 122.8(2)°, respectively, in **3**.

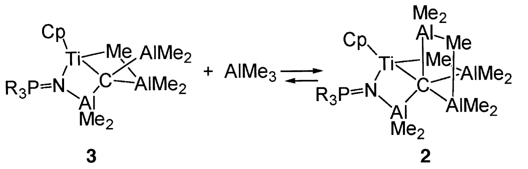
Resonance signals attributed to the carbide carbon atoms of **2** and **3** were not observed in the initial $^{13}C\{^1H\}$ NMR data. This is presumably because of the cumulative effects of the long relaxation time of the quaternary carbon atom, the quadrupolar nature of Al atoms bonded to the carbide, and the low natural abundance of the ^{13}C isotope. However, preparation of **1** employing ^{13}C-labeled [MeMgBr] and subsequent reaction with $AlMe_3$ in toluene results in the formation of labeled **2**. Methyl exchange between **1** and $AlMe_3$ results in a statistical distribution of ^{13}C atoms in the carbide and AlMe sites in **2** and **3**. The resonance signals observed in the $^{13}C\{^1H\}$ NMR spectra of ^{13}C-labeled **2** and **3** at $\delta = 298.1$ and 304.7, respectively, are attributed to the carbides of **2** and **3**.

Compound **3** remains Lewis acidic primarily as a result of the presence of the three-coordinate Al center (Al2). This is demonstrated by the coordination of diethyl ether to the Al2 center of **2**, affording **4**. In [D$_6$]benzene the $^{13}C\{^1H\}$ NMR resonance for the carbide carbon atom in **4** is at $\delta = 312.8$; this

$[CpTi(\mu_2\text{-}Me)(\mu_2\text{-}NPiPr_3)(\mu_4\text{-}C)(AlMe_2)_2\{AlMe_2(OEt_2)\}]$ **4**

reflects a slight change in the coordination environment of the carbide carbon center. It is noteworthy that the ^1H NMR spectrum of **4** is much sharper in the methyl region than those of **2** or **3**, presumably as coordination of diethylether to Al2 precludes methyl exchange processes between the adjacent $AlMe_2$ sites.

Interestingly, the reaction of **2** with excess $AlMe_3$ in benzene indicates that it participates in an already existing equilibrium with **3** [Eq. (1)]. This infers the given formulation of **2**.



(1)

$[\mathrm{CpTi}(\mu_2\text{-Me})(\mu_2\text{-NP}i\mathrm{Pr}_3)(\mu_5\text{-C})(\mu_2\text{-AlMe}_2)_2(\mathrm{AlMe}_2)(\mathrm{AlMe}_3)]$ **2**

Variable-temperature NMR studies established the equilibrium constant for Equation (1) to be 129 M^{-1} at 260 K. The corresponding activation parameters are $\Delta G^{\neq}(260\,\mathrm{K}) = -10.5\,\mathrm{kJ\,mol^{-1}}$, $\Delta H^{\neq} = -57.9\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = -0.183\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$. When ^{13}C-labeled **2** was employed, the carbide resonance was observed at $\delta = 241.2$ in [D$_6$]benzene at 260 K. This shift is considerably upfield of those of **3** or **4** and indicates a dramatic change in the environment of the carbide carbon center in **2**. An interaction of the carbide carbon with the additional equivalent of AlMe$_3$ is proposed. This proposal is further supported by the isolation of compound **6** in 88% yield from the reaction of [CpTi(NPPh$_3$)Me$_2$] (**5**) with an excess of AlMe$_3$. The ^{31}P{^{1}H} NMR spectrum of compound **6** shows a single resonance signal at $\delta = 25.4$ and the ^{1}H NMR data are consistant with the given formulation for **6**.

$[\mathrm{CpTi}(\mu_2\text{-Me})(\mu_2\text{-NPPh}_3)(\mu_5\text{-C})(\mu_2\text{-AlMe}_2)_2(\mathrm{AlMe}_2)(\mathrm{AlMe}_3)]$ **6**

Crystallographic studies of **6**[12] confirmed this structure and established the presence of a five-coordinate carbide center (Figures 2a and b). The gross structural features of **6** are similar to those described for **2**, with an additional equivalent of AlMe$_3$ bonded by the Al4 center to the carbide carbon atom (C24) and by a methyl bridge to the Al3 center. The geometry about the carbide carbon atom in **6** is distorted trigonal bipyramidal. The Ti-C24-Al3 vector is essentially linear with an angle of 175.77(17)°. The angle of these pseudo-axial metal centers to those in the pseudo-equatorial plane range from 78.21(11)–104.82(14)°, while the angles in the trigonal plane vary from 114.45(14) to 130.77(15)°. These distortions are consistent with the presence of strain that arises from the two fused four-membered Ti-C-Al-C and Ti-C-Al-N rings in these complexes.

Hypercoordinate carbide species such as **2** and **6** are rare. Schmidbaur and co-workers[14] have described a gold carbocation [(Ph$_3$PAu)$_5$C]$^+$. This species exhibits a C_{3v}-symmetric trigonal-bipyramidal geometry at the carbon center is similar to that predicted by computational studies for the cations [CH$_5$]$^+$ and [CLi$_5$]$^+$.[15] In recent work, Akiba et al.[16] have described the hypervalent organic carbocation [(MeO)$_2$C{(MeO)$_2$C$_{14}$H$_7$}]$^+$. Compounds **2** and **6** are not to be considered as hypervalent; they are electron-deficient, hypercoordinate species. As such, these are the first neutral compounds in which four- and five-coordinate carbon atoms interconvert in this unprecedented and facile manner.

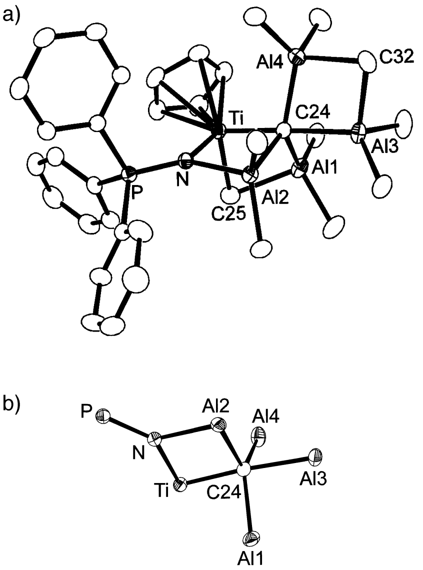


Figure 2. a) Structure of **6** (ORTEP drawing 20% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. b) The carbide coordination sphere of **6** (ORTEP drawing). Selected distances [Å] and angles [°]: Ti-C24 1.975(3), Al4-C24 2.085(3), Al1-C24 2.096(3), Al2-C24 2.150(3), Al3-C24 2.118(3); Ti-C24-Al4 104.82(14), Ti-C24-Al1 83.98(12), Al4-C24-Al1 130.77(15), Ti-C24-Al3 175.77(17), Al4-C24-Al3 78.21(11), Al1-C24-Al3 91.80(12), Ti1-C24-Al2 83.60(11), Al4-C24-Al2 114.45(14), Al1-C24-Al2 114.65(14), Al3-C24-Al2 97.90(12).

Experimental Section

2: A solution of AlMe$_3$ (2.0 M, 2.52 mmol) in hexane (1.26 mL) was added to a solution of complex **1** (0.200 g, 0.630 mmol) in hexane (10 mL). Over 16 h at room temperature a light orange solid precipitated. The solid was isolated by filtration and washed with hexane (1 × 5 mL). ^{1}H NMR (C$_6$D$_6$): $\delta = 6.11$ (br s, 5H; Cp), 1.78 (sept, $^3J_{\mathrm{H,H}} = 7.1$ Hz, 3H; PC*H*(CH$_3$)$_2$), 0.73 (dd, $^3J_{\mathrm{P,H}} = 14.3$ Hz, $^3J_{\mathrm{H,H}} = 7.1$ Hz, 9H; PCH(C*H*$_3$)$_2$), 0.66 (dd, $^3J_{\mathrm{P,H}} = 14.8$ Hz, $^3J_{\mathrm{H,H}} = 7.1$ Hz, 9H; PCH(C*H*$_3$)$_2$), 0.09 (br s, 3H; AlCH$_3$), −0.06 (br s, 9H; AlCH$_3$), −0.26 (br s, 15H; AlCH$_3$), −0.45 (br s, 1H; AlCH$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 50.9$ (br s); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 298.2$ (s; Ti(C)Al$_3$), 109.8 (s; Cp), 26.8 (d, $^1J_{\mathrm{P,C}} = 58.8$ Hz; P*C*HMe$_2$), 16.5 (d, $^2J_{\mathrm{P,C}} = 44.1$ Hz; PCH$_2$(*C*H$_3$)$_2$), 9.9 (s; Ti-CH$_3$), −0.1, −4.8, −6.1 (br s; Al-CH$_3$).

3: Successive recrystallizations of **2** from benzene afforded dark red crystalline **3** in 80% yield. ^{1}H NMR (C$_6$D$_6$): $\delta = 6.19$ (br s, 5H; Cp), 1.84 (sept, $^3J_{\mathrm{H,H}} = 7.1$ Hz, 3H; PC*H*(CH$_3$)$_2$), 0.78 (dd, $^3J_{\mathrm{P,H}} = 14.8$ Hz, $^3J_{\mathrm{H,H}} = 7.1$ Hz, 9H; PCH(C*H*$_3$)$_2$), 0.72 (dd, $^3J_{\mathrm{P,H}} = 14.0$ Hz, $^3J_{\mathrm{H,H}} = 7.1$ Hz, 9H; PCH(C*H*$_3$)$_2$), 0.12 (br s, 3H; AlCH$_3$), −0.10 (br s, 9H; AlCH$_3$), −0.24 (br s, 9H; AlCH$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 49.8$; ^{27}Al{^{1}H} NMR (C$_6$D$_6$) $\delta = 149.00$ (br s), 114.00 (br s), 38.00 (br s); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 304.7$ (s; Ti(*C*)Al$_3$), 109.9 (s; Cp), 27.0 (d, $^1J_{\mathrm{P,C}} = 56.6$ Hz; P*C*H(CH$_3$)$_2$), 16.8 (d, $^2J_{\mathrm{P,C}} = 42.4$ Hz; PCH(*C*H$_3$)$_2$), 10.2 (s; Ti-CH$_3$), −0.6, −4.5 (s; Al*C*H$_3$); elemental analysis calcd (%) for C$_{22}$H$_{47}$Al$_3$NPTi: C 54.43, H 9.76, N 2.89; found: C 54.20, H 9.39, N 2.75.

4: Recrystallization of complex **3** from benzene with the addition of several equivalents of diethyl ether afforded complex **4**. Yield > 95% (by ^{1}H NMR); ^{1}H NMR (C$_6$D$_6$): $\delta = 6.30$ (s, 5H; Cp), 3.48 (quartet, > 4H; OC*H*$_2$CH$_3$), 1.95 (sept, $^3J_{\mathrm{H,H}} = 6.8$ Hz, 3H; PC*H*(CH$_3$)$_2$), 0.84 (t, > 6H; OCH$_2$C*H*$_3$), 0.83 (2 × dd, 18H; PCH(C*H*$_3$)$_2$), 0.18 (s, 3H; AlCH$_3$), −0.05 (s, 3H; AlCH$_3$), −0.08 (s, 6H; AlCH$_3$), −0.19 (s, 9H; AlCH$_3$), −0.38 (s, 3H; AlCH$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 48.9$; ^{27}Al{^{1}H} NMR (C$_6$D$_6$): $\delta = 62.0$ (br s); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 312.8$ (s; Ti(C)Al$_3$), 109.9 (s; Cp), 64.9 (s; O*C*H$_2$CH$_3$), 27.2 (d, $^1J_{\mathrm{P,C}} = 58.8$ Hz; P*C*H(CH$_3$)$_2$), 17.2 (d, $^2J_{\mathrm{P,C}} = 44.1$ Hz; PCH(*C*H$_3$)$_2$), 13.3 (s; OCH$_2$*C*H$_3$), 10.6 (s; Ti-CH$_3$), −1.1, −2.4, −3.7, −4.9, −7.8 (s; AlCH$_3$).

6: Addition of a solution of AlMe$_3$ (2.0 M, 0.810 mmol) in hexane (0.41 mL) to a stirred pale yellow solution of **5** (68 mg, 0.162 mmol) in benzene (4 mL) led to the immediate formation of orange solution formed immediately. Stirring for 16 h gave a dark orange-rust solution which was evaporated to dryness to give an orange-red solid. Yield: 0.088 g (88 %). ^{1}H NMR (C_6D_6): $\delta = 7.43$ (m, 6H; C_6H_5), 7.01 (m, 9H; C_6H_5), 5.83 (s, 5H; Cp), 0.50 (br s, 3H; CH_3), -0.03 (br s, 12H; $AlCH_3$), -0.21 (s, 6H; $AlCH_3$), -0.39 (m, 9H; $AlCH_3$); $^{31}P\{^1H\}$ (C_6D_6): $\delta = 25.2$ (s); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 134.2$, 132.1, 129.3, 127.3 (PC_6H_5), 113.2 (s; Cp), Al- and Ti-bound methyl resonances are unobserved. Elemental analysis calcd (%) for $C_{34}H_{50}Al_4NPTi$: C 61.91, H 7.64, N 2.12; found: C 61.65, H 7.37, N 2.01.

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[12] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141319, and -141320. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Diffraction experiments were performed on a Siemens SMART System CCD diffractometer and solved by employing the SHELX-TL software package. Data for complex **3**: Orthorhombic, space group *Fdd*2; $a = 33.064(5)$ $b = 36.522(7)$, $c = 9.8244(19)$ Å, $V = 11863(4)$ Å^3, $Z = 16$, $R = 0.0449$, $Rw = 0.1103$, GOF = 1.104. Data for complex **6**: Orthorhombic, space group *Pbca*; $a = 18.825$ (3), $b = 18.7742(3)$, $c = 23.9904(4)$ Å, $V = 8479.0(2)$ Å^3, $Z = 8$, $R = 0.0517$, $Rw = 0.1291$. GOF = 1.034.

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The First Example of an Equilibrium between a Carbene and an Isomeric Carbyne Transition Metal Complex**

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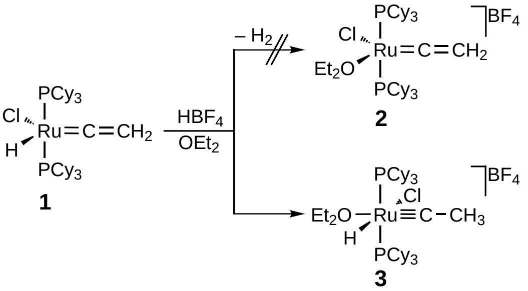
Dedicated to Professor Herbert W. Roesky
on the occasion of his 65th birthday

By attempting to generate a cationic, possibly solvated, vinylideneruthenium(II) complex with a 14-electron configuration at the metal center, we recently found that the reaction of the starting material **1** with HBF_4 in dichloromethane/diethyl ether leads to the formation of the ruthenium carbyne **3** instead of the anticipated ruthenium vinylidene **2** [Eq. (1)].[1] Although compound **3** is a highly efficient catalyst for olefin metathesis, including the cross-olefin metathesis of cyclopentene with methyl acrylate to afford multiply unsaturated esters $CH_2(C_5H_8)_nCHCO_2Me$ ($n = 1-3$), the lifetime of the cationic species containing a Ru≡C bond is rather limited.[1, 2] We therefore set out to prepare more stable ruthenium(II) carbynes and discovered in the course of these studies the first example of an equilibrium between a cationic metal carbene and the isomeric cationic metal carbyne.



(1)

The dichloro(vinylidene)ruthenium(II) complex **4**[3] reacts with excess of HCO_2Na or CH_3CO_2Na in THF or acetone to give exclusively the monosubstituted products **5** and **6** in 77 and 82 % yield, respectively [Eq. (2); L = P*i*Pr$_3$]. The corresponding benzoato(chloro) complex **7** can be prepared from **4** and $PhCO_2H$ (ratio 1:1) in the presence of NEt_3. The reaction of **4** with either CF_3CO_2Na or CF_3CO_2K in THF or acetone leads, however, even after prolonged stirring, to a mixture containing **4**, **8** (major components), and the disubstituted compound **9** (minor component). Treatment of **4** with one

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