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Intermolecular coupling reactions of inversely polarized carbene ligands starting from the $Cp^*_2Ti{=}C{=}CH_2$ intermediate and chromium carbene complexes

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Abstract

The titanaallene intermediate $[Cp^*_2Ti{=}C{=}CH_2]$ (**2**), generated thermally from $Cp^*_2Ti(CH{=}CH_2)CH_3$ (**1**), reacts with methoxyalkylcarbene complexes $(CO)_5Cr{=}C(OCH_3)R$ (**3**) [R = CH_3 (**a**), CD_3 (**b**), Et (**c**)] by CC-coupling of the carbene ligands to give the heterodinuclear complexes $Cp^*_2TiCH_2C(=C(OCH_3)R)C(=Cr(CO)_5)O$ (**4**) and $Cp^*_2TiCH_2C(=C(\mu{-}OCH_3)R)C(=Cr(CO)_4)O$ (**5**). An unusual isomerization of the exocyclic double bond, which occurs by thermal conversion **4c** → **5c**, can be explained considering ionic resonance forms. The addition of one CO molecule to **5c** leads to a displacement of the methoxy coordination. On the other hand, the aminocarbene complex $(CO)_5Cr{=}C(NH^iPr)CH_3$ (**8**), which is less electrophilic than alkoxycarbenes, reacts with **2** to give a dinuclear dititanacyclobutene complex (**9**). Its blue-violet colour is probably caused by a twist around the single bond C(β)–C(β) of the dititanacyclobutene unit. © 1998 Elsevier Science S.A.

Keywords: Intermolecular coupling; Carbene complexes; Titanium complexes; Chromium complexes; Vinylidine complexes

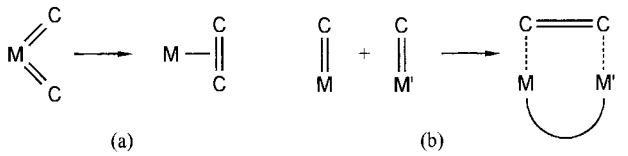
1. Introduction

A large number of transition metal alkylidene complexes has been synthesized since Fischer described the first example exhibiting an MC double bond in 1964 [1,2]. There is still intense interest in this class of molecules from the standpoint of both its specific bonding type and reactivity. Applications have been developed not only in organic synthesis [3–12] but also in the field of catalytic processes [13–18]. Carbon–carbon bond formation is the essential step in these reactions. An experimentally and theoretically important reaction is the formation of CC double bonds by intramolecular coupling of carbene ligands (Scheme 1a) [19–29].

We recently reported the first example of an intermolecular coupling reaction (Scheme 1b) of inversely polarized carbene ligands [30,31]. The reaction of the α-C-nucleophilic vinylidene complex $[Cp^*_2Ti{=}C{=}CH_2]$ **2** with the electrophilic methoxymethyl carbene complex $(CO)_5Cr{=}C(OCH_3)CH_3$ **3a** yields the dinuclear complexes **4a** and **5a** (Scheme 2), which were formed in an unusual metal-centred CC-coupling reaction and isolated as red crystals. Further reactions should demonstrate the use of this new type of C–C bond formation. Herein we describe the synthesis of dinuclear complexes from reaction of the titanaallene species **2**, which is generated as an intermediate from **1** by thermal methane elimination [32–35], with alkoxy- or aminocarbene complexes of the Fischer type.

2. Results and discussion

As deduced from deuterium-labelling experiments, the removement of the chromium bound carbene ligand and carbene–carbene coupling seem to be the essential reaction steps for the formation of **4** and **5**. Treatment of



Scheme 1.

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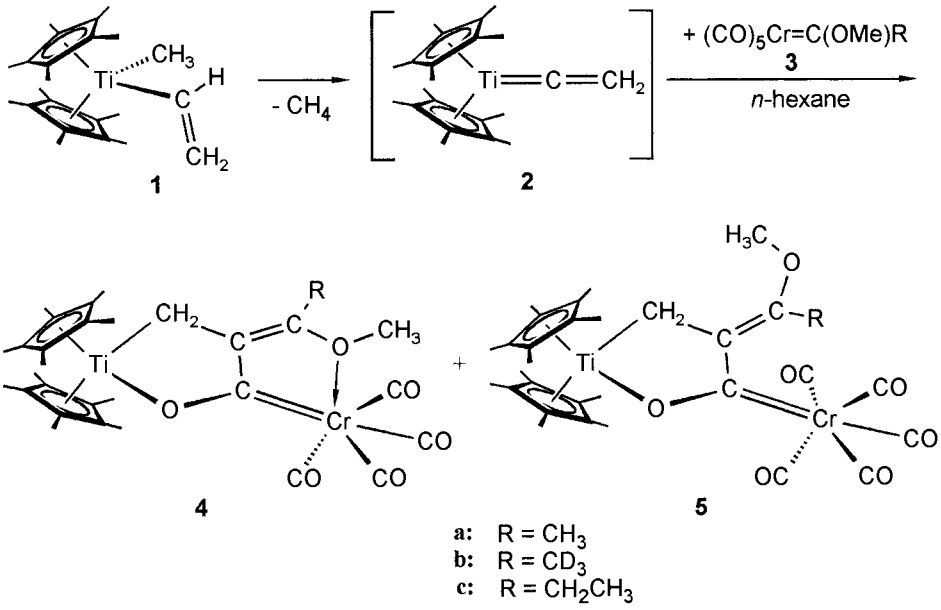


Scheme 2.

1 with $(CO)_5Cr{=}C(OCH_3)CD_3$ **3b** leads to the formation of **4b** and **5b** (Scheme 2), which were isolated as red solids after chromatographic workup and characterized by ^{1}H NMR spectroscopic data in comparison with the known data for **3a**/**4a** (Table 1).

The analogous ethyl substituted complexes **4c**/**5c** are obtained by reaction of **1** with $(CO)_5Cr{=}C(OCH_3)CH_2CH_3$ **3c**. Chromatographic separation was performed by eluting **4c** with *n*-hexane/methylene chloride (2:1) and **5c** with methylene chloride. Spectroscopic data are consistent with the structures shown in Scheme 2. The signals of the carbene carbon atoms are detected in the ^{13}C NMR spectrum at $\delta = 326.6$ (**4c**) and 335.9 (**5c**).

Typically for the observed change in position of the substituents of the exocyclic double bond in **4** relative to **5** the resonances of the ethyl-CH_2 protons are found in the ^{1}H NMR spectrum at $\delta = 3.61$ (**4c**) and $\delta = 2.31$ (**5c**). In addition, the characteristic shift to lower field of the OCH_3 carbon signal in the ^{13}C NMR spectrum is in accordance with a methoxy coordination in **5c** ($\delta = 55.4$ (**4c**), 65.4 (**5c**)). For the $Cr(CO)_4$- and the $Cr(CO)_5$-fragments with local C_{2v}- or C_{4v}-symmetry the expected pattern of CO-stretching vibration bands are observed (Table 1).

Chromatographic workup afforded not only **4c**/**5c** but also the hydroxy compound $Cp^*_2Ti(OH)Cl$ **6** as byproduct. It was obtained, when THF is used as eluent after complete separation of **5c** and isolated as red-brown solid. The constitution of **6** was confirmed ^{1}H and ^{13}C NMR spectroscopically (O*H*: $\delta = 8.15$ $C_5(CH_3)_5$: $\delta = 1.93$) and by means of precision mass determination. Probably, **6** is formed by reaction of **1** or its thermolysis product $Cp^*(\eta^6\text{-}C_5(CH_3)_5)TiCH{=}CH_2$ [36] with methylene chloride at the surface of the aluminium oxide used for chromatography.

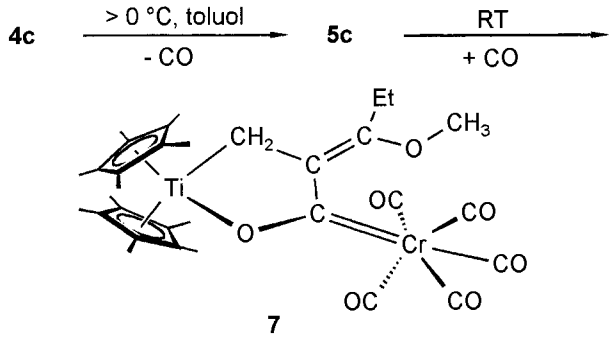
Remarkably, the stability of **4c** and **5c** is significantly decreased compared to the corresponding methyl substituted complexes. While the conversion **4a** → **5a** takes place at 60°C, formation of **5c** from **4c** is already detectable at 0°C IR- and NMR-spectroscopically (Scheme 3). A half-life of 2 h was determined for **4a** → **5a** by means of ^{1}H NMR measurements.

Obviously, the sterically demanding ethyl group facilitates the CO-dissociation and following isomerization, which occurs in the course of the observed conver-

Table 1
Selected spectroscopic data of complexes **4**, **5** and **7** (NMR measurements in $CDCl_3$, IR mesurements in KBr)

	^{1}H NMR (^{13}C NMR)				IR
	R	R	O–CH_3	Ti–CH_2	ν(CO) (cm^{-1})
4a	CH_3	2.89 (17.5)	3.77 (54.6)	2.08 (66.0)	2043, 1963, 1926, 1889, 1876
4b	CD_3	2.81[a]	3.76	2.07	2043, 1964, 1925, 1899, 1875
4c	CH_2CH_3	1.32/3.61 (12.5/22.8)	3.77 (55.4)	2.04 65.4	2044, 1957, 1902, 1868
5a	CH_3	1.90 1.26[b] (13.0)	3.97 3.34[b] (65.3)	1.87 1.77[b] (55.7)	1987, 1873, 1865, 1821
5b	CD_3	1.22[b]	3.33[b]	1.77[b]	1994, 1876, 1828
5c	CH_2CH_3	1.04/2.31 (10.8/19.0)	3.97 (65.4)	1.87 54.0	1986, 1873, 1863, 1827
7	CH_2CH_3	1.15/2.49 (11.3/12.9)	3.88 (54.5)	1.89 (64.2)	2044, 1956, 1901, 1868[c]

[a] Content of deuterium 77%.
[b] In C_6D_6.
[c] In CH_2Cl_2.



Scheme 3.

sion. The very unusual isomerization can be explained considering ionic resonance forms of the intermediately generated tetracarbonyl complex **A** (Scheme 4), which leads to partial loss of double bond character.

Ionic resonance forms are known to play an important role for heterodinuclear complexes [37–40]. A comparable isomerization was described by Aumann for the vinylcarbene complex $(CO)_5Cr{=}C(OEt)CH{=}C(H)R$ [41].

5c is also unstable in solution (half-life at room temperature: 20 h). As shown by NMR measurements the pentacarbonyl complex **7** is formed accompanied by partial decomposition of **5c**. **7** was synthesized alternatively by treatment of **5c** with CO (1 atm) in solution, but could not be obtained in analytically pure form due to its instability in the absence of carbon monoxide. NMR- and IR-spectroscopic data are consistent with the shown constitution with a methoxy group directed but not coordinated to the pentacarbonyl chromium fragment.

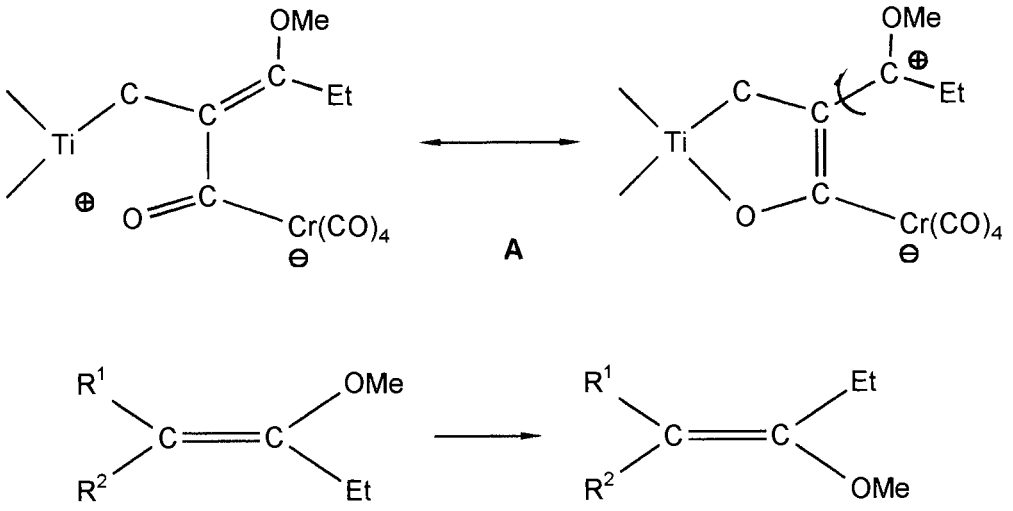
An extension of the reaction discussed above using other alkoxy carbene complexes with electronic properties differing from **3** was not possible so far. No reaction takes place using $(OC)_5W{=}C(OCH_3)CH_3$ or $(OC)_5Cr{=}C(OCH_3)(C_6H_4\text{-}CH_3\text{-}p)$. With $(OC)_5Cr{=}C{=}C{=}C(N^iPr_2)C_6H_5$ or $(OC)_5Cr{=}C(OEt)(C{\equiv}CPh)$ paramagnetic products were formed, which could not be characterized. The unreactivity of the used wolfram complex probably corresponds with a more difficult CO-dissociation relative to chromium complexes. CO-dissociation seems to be decisive for the synthesis of **4**, **5** and **7**.

In contrast, when using aminocarbene complexes, a different type of reaction is found. Compared with analogous alkoxycarbenes, aminocarbene complexes are characterized by a lowered α-C electrophilicity and higher stability due to a stronger π-donor ability of the nitrogen atom.

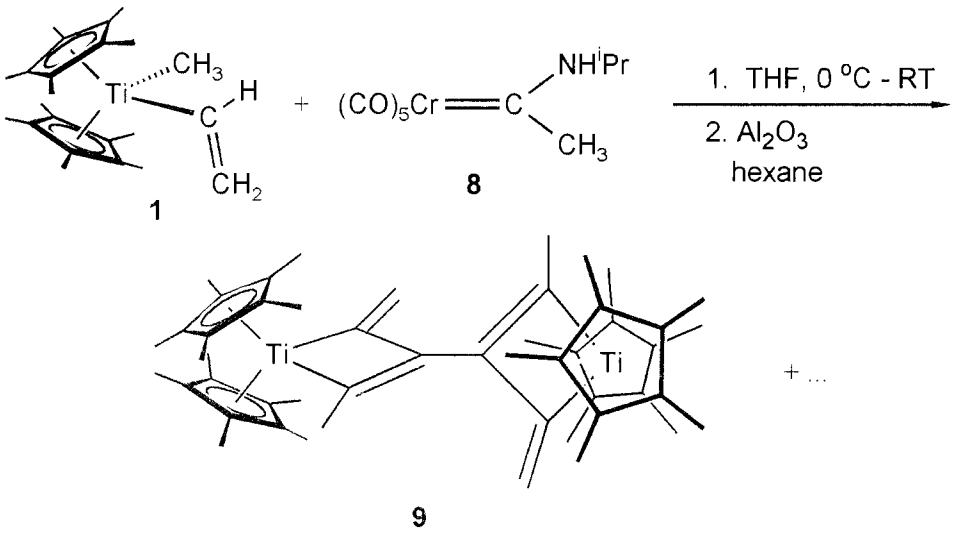
Treatment of $(OC)_5Cr{=}C(NH^iPr)CH_3$ **8** with **1** in THF and chromatographic workup resulted in the formation of the homodinuclear titanium complex **9** (Scheme 5), which was isolated from a blue solution in *n*-hexane as red-violet crystals. NMR spectroscopic data, mass spectrum ($m/z = 767$, $M^+ + 1$) and correct elemental analysis confirm the unexpected formation of the dititanacyclobutene complex.

In the ^1H NMR spectrum of **9**, a singlet for the methyl protons at $\delta = 2.20$, a doublet for the methylene protons at $\delta = 4.54$ and a broad singlet at $\delta = 5.72$ are observed. The occurrence of two signals for the Cp^*-methyl protons at $\delta = 1.84$ and 1.87 indicates noncoplanar titanacyclobutene rings. In the same way, the signals of the Cp^*-carbon atoms are split ($C_5(CH_3)_5$: $\delta = 12.5$ and 12.6; $C_5(CH_3)_5$: $\delta = 119.7$ and 119.9).

A single crystal X-ray structural analysis of **9** confirmed the constitution shown in Scheme 5 and revealed a twist around the internal C(β)–C(β) single bond of



Scheme 4.

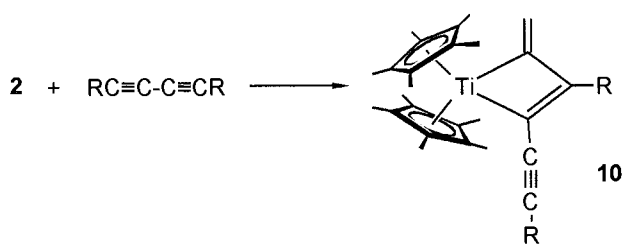


Scheme 5.

about 50°. Similar twist angles were determined for complexes exhibiting chalcogen bridged bis(cyclopentadienyl)titanium fragments [42,43]. A detailed discussion of the structure of **9** was not possible due to the poor quality of the obtained set of data.

The blue-violet colour of **9**, which is very unusual for Ti(IV)-compounds, is probably caused by the twist around the C(β)–C(β) bond deduced from NMR- and X-ray analysis data. As known for diphenyl systems [44], a twist around the single bond due to steric hindrance leads to a reduced conjugation between the chromophoric groups, which results in a hypsochromic shift of the adsorption in the UV spectrum. Considering this and the fact that all known mononuclear methylene–titanacyclobutene complexes **10** (Scheme 6) are red coloured compounds [45], we assume that there is a conjugation between the four membered rings in **9**, though reduced by twisting. So, in the UV spectrum of **9** compared with **10**, not only a bathochromic shift of the maximum adsorption from 280 to 365 nm but also the existence of an additional adsorption of lower intensity at 605 nm is observed.

Formally, the formation of **9** can be interpreted as cycloaddition reaction of two titanaallene molecules **2** with one hexadiene molecule. However, reactions of **1** with RC≡C-C≡CR exclusively led to the formation of cycloaddition products with a regioselectivty shown in Scheme 6 [46]. Further cycloaddition reaction of the acetylide C≡C-bond in the α-position of the mononuclear complexes is precluded due to the steric demand of the Cp* rings.



Scheme 6.

Other aminocarbene complexes were used to get more insight into the reaction, which leads to the formation of **9**. Remarkably, treatment of $(CO)_5Cr{=}C(NH^iPr)CD_3$ or $(CO)_5Cr{=}C(NH^iPr)Et$ with **1** resulted in the formation of **9** as the only detectable product. These results defeated the assumption, that the C–CH_3-groups of the cyclobutene fragment in **9** stem from the carbene alkyl fragment of **8**. Moreover, no characterizable products were obtained by treatment of the aminocarbene complexes $(CO)_5Cr{=}C(NHPh)CH_3$ or $(CO)_5W{=}C(NH^iPr)CH_3$ with **1**.

3. Experimental

The preparation and handling of the described compounds were performed under rigorous exclusion of air and moisture under a nitrogen atmosphere, using a standard vacuum line and Schlenk techniques. All solvents were dried with the appropriate drying agents and distilled under a nitrogen atmosphere. Deuterated solvents were degassed by freeze–pump–thaw cycles and dried over molecular sieves (3, 4 Å) prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents (benzene-d_6, $\delta = 7.15$ ppm for ^1H NMR spectroscopy; benzene-d_6, $\delta = 127.96$ ppm for ^{13}C NMR spectroscopy). Mass spectroscopic analyses were performed on a Finnigan MAT 95 mass spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer

1720X FT-IR spectrometer. Elemental analyses were carried out at the Analytische Laboratorien in Lindlar, Germany. The following compounds were prepared by literature known procedures: $Cp_2^*Ti(CH{=}CH_2)_2CH_3$ **1** [40], $(CO)_5Cr{=}C(OCH_3)CD_3$ **3b** [47,48], $(CO)_5Cr{=}C(OCH_3)CH_2CH_3$ **3c**, [49] aminocarbene complexes [50].

3.1. Synthesis of *4b* and *5b*

The syntheses were performed analogous to literature [30,31]. 300 mg **1** (0.833 mmol), 150 mg **3b** (degree of deuterium labeling: 77%) (0.593 mmol], 20 ml *n*-hexane. Yields: 80 mg **4b** as red solid (0.128 mmol, 21%], 30 mg **5b** as red-brown solid (0.05 mmol, 8%]. **4b**: IR (KBr): $\nu = 2043$ cm^{-1} s, 1964m, 1925s, 1899vs, 1875vs [ν(CO)], 1554m [ν(C=C)]. ^{1}H NMR ($CDCl_3$, 250 MHz, 25°C): $\delta = 1.90$ (s, 30 H, $C_5(CH_3)_5$], 2.07 (s, 2H, CH_2), 2.81 (m, degree of deuterium labeling: 77%], 3.76 (s, 3 H, OCH_3]. **5b**: IR (KBr): $\nu = 1994$ cm^{-1} s, 1876 br vs, 1828vs [ν(CO)], 1342m. ^{1}H NMR (C_6D_6, 500 MHz, 25°C): $\delta = 1.22$ (m, degree of deuterium labeling: 77%], 1.73 (s, 30 H, $C_5(CH_3)_5$], 1.77 (s, 2H, CH_2), 3.33 (s, 3 H, OCH_3].

3.2. Synthesis of *4c* and *5c*

To a solution of 330 mg **3c** (1.25 mmol) in 10 ml *n*-hexane, was added a solution of 480 mg **1** (1.33 mmol) in 20 ml *n*-hexane at a temperature of −30°C. The resulting solution was allowed to warm up to room temperature and changed its colour from yellow to red. After stirring for 5 h at room temperature (formation of products is controlled by IR-spectroscopy) the solvent was removed in vacuo, the residue solved in 3 ml methylene chloride and chromatographed on aluminium oxide (neutral, 100–125 mesh). With *n*-hexane/methylene chloride (2:1) a red solution was obtained, which was evaporated in vacuo until **4c** precipitates as red solid. Elution with methylene chloride afforded a deep red solution. After addition of 10 ml *n*-hexane the solution was evaporated until **5c** precipitates as red solid. Further elution with THF afforded a deep red solution, which was evaporated to dryness. The residue was dissolved in 1 ml methylene chloride and 5 ml *n*-hexane were added. The solution was evaporated until **6** precipitates as a red-brown solid. **4c** and **5c** were crystallized from a toluene solution at a temperature of −23°C. Yields: 160 mg **4c** (0.25 mmol, 20%), 70 mg **5c** (0.12 mmol, 10%), 20 mg **6** (0.05 mmol, 4%). **4c**: red crystals, mp: 179–188°C (dec.). IR (KBr): $\nu = 2044$ cm^{-1} s, 1957m, 1902vs, 1868s [ν(CO)], 1556m [ν(C=C)]. ^{1}H NMR ($CDCl_3$, 500 MHz, −30°C): $\delta =$ 1.32 [t, 3 H, $^3J_{HH} = 7.4$ Hz, CH_2–CH_3], 1.91 [s, 30 H, $C_5(CH_3)_5$], 2.04 [s, 2 H, CH_2], 3.61 [q, 2 H, $^3J_{HH} = 7.4$ Hz, CH_2-CH_3], 3.77 [s, 3 H, OCH_3]. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, −30°C): $\delta = 11.9$ [$C_5(CH_3)_5$], 12.5 [CH_2–CH_3], 22.8 [CH_2–CH_3], 55.4 [OCH_3], 65.4 [CH_2], 124.9 [$C_5(CH_3)_5$], 154.2 [C=CEt(OCH_3)], 170.8 [C=CEt(OCH_3)], 218.6 (*cis*-CO), 224.4 (*trans*-CO), 326.5 (C=Cr). SIMS-MS (Cs^+, 20 kV, 3-nitrobenzyl alcohol): positive ions *m/z* (%): 608 (2) [M^+ − CO], 524 (10) [M^+ − 2CO], 496 (10) [M^+ − 5CO], 445 (30) [M^+ − Cr(CO)$_5$ + 1], 318 (100) [$(C_5(CH_3)_5)_2Ti^+$]; negative ions *m/z* (%): 636 (17) [M^+], 608 (40) [M^+ − CO], 580 (4) [M^+ − 2CO], 344 (52) [$Cp_2^*TiC_2H_2^+$], 317 (100) [$Cp_2^*Ti - 1$]]. Anal. Calcd. for $C_{32}H_{40}O_7CrTi$ (636.2): C, 60.41; H, 6.29; Found: C, 60.45; H, 6.58.

5c: Red crystals, mp: 164–166°C (dec.). IR (KBr): $\nu = 1986$ cm^{-1} s, 1873sh, 1863vs, 1827s [ν(CO)], 1343s. ^{1}H NMR ($CDCl_3$, 500 MHz, −30°C): $\delta = 1.04$ [t, 3 H, $^3J_{HH} = 7.6$ Hz, CH_2–CH_3], 1.87 [s, 2 H, CH_2], 1.95 [s, 30 H, $C_5(CH_3)_5$], 2.31 [t, 2 H, $^3J_{HH} = 7.6$ Hz, CH_2–CH_3] 3.97 [s, 3H, OCH_3]. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, −30°C): $d = 10.8$ [CH_2–CH_3], 12.1 [$C_5(CH_3)_5$], 19.0 [CH_2–CH_3], 54.0 [CH_2], 65.4 [OCH_3], 125.4 [$C_5(CH_3)_5$], 145.1 [C=CEt(OCH_3)], 174.2 [C=CEt(OCH_3)], 218.2, 230.1, 235.4 [*cis*-Cr(CO)$_4$], 335.9 (C=Cr). MS (70 eV), *m/z* (%): 609 (1) [$M^+ + 1$], 318 (100) [$(C_5(CH_3)_5)_2Ti^+$]. Anal. Calcd. for $C_{31}H_{40}O_6CrTi$ (608.5): C, 61.18; H: 6.57; Found: C, 59.65; H, 6.60.

6: Red-brown solid (not purified). ^{1}H NMR ($CDCl_3$, 500 MHz, 25°C): $\delta = 1.93$ [s, 30H, $C_5(CH_3)_5$], 8.15 [s, 1 H, OH]. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25°C): $\delta = 11.9$ [$C_5(CH_3)_5$], 124.4 [$C_5(CH_3)_5$]. MS (70 eV): 370 (1) [M^+], 353 (4) [M^+ − OH], 335 (1) [M^+ − Cl], 317 (3) [$Cp_2^*Ti^+ - 1$]. Exact mass calcd. for $C_{20}H_{31}ClOTi$: 370.1543, Found: 370.1544.

3.3. Synthesis of *7*

A solution of 140 mg **5c** in 2 ml $CDCl_3$ was frozen at a temperature of −196°C and the reaction vessel (Vol = 100 ml) was evacuated. After addition of CO (1 atm), the solution was allowed to warm up to room temperature and stirred for 1 h. (quantitative yield according to ^{1}H NMR spectrum). IR (CH_2Cl_2): $\nu = 2044$ cm^{-1} m, 1956m, 1901s + 1868s [ν(CO)], 1555m [ν(C=C)]. ^{1}H NMR ($CDCl_3$, 500 MHz, 25°C): $\delta = 1.15$ [t, 3 H, $^3J_{HH} = 7.4$ Hz, CH_2–CH_3], 1.89 (s, 2 H, CH_2), 1.93 [s, 30 H, $C_5(CH_3)_5$], 2.49 [q, 3 H, $^3J_{HH} = 7.4$ Hz, CH_2–CH_3], 3.88 [s, 3 H, OCH_3]. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25°C): $\delta = 11.3$ [CH_2-CH_3], 11.9 [$C_5(CH_3)_5$], 12.9 [CH_2-CH_3], 54.5 [OCH_3], 64.2 [CH_2], 125.0 [$C_5(CH_3)_5$], 146.5 [C=CEt(OCH_3)], 166.5 [C=CEt(OCH_3)], 219.9 (*cis*-CO), 225.9 (*trans*-CO), 328.9 (C=Cr).

3.4. Synthesis of *9*

Typical reaction with $(CO)_5Cr{=}C(NH^iPr)CH_3$ **8**: A solution of 200 mg **8** (0.722 mmol) in 10 ml THF was

added to a solution of 490 mg **1** (1.361 mmol) in 20 ml THF at a temperature of −30°C. The solution was slowly warmed up to room temperature and changed in colour to red. After stirring for 20 h the solvent was evaporated in vacuo, the residue was solved in 2 ml Et_2O and rapidly chromatographed on aluminium oxide (neutral, 100–125 mesh). With *n*-hexane a blue solution was obtained, which was reduced in volume to 3 ml and stored at −23°C. At this temperature **9** was obtained as red-violet crystals (mp: 169–171°C), which become metallic-grey upon drying (yield 80 mg, 0.10 mmol, 14% rel. to **8**).

The reaction with $(CO)_5Cr{=}C(NH^iPr)CD_3$ was performed analogously using 130 mg aminocarbene complex (0.464 mmol), 330 mg **1** (0.917 mmol), 30 ml THF. (Ausb. 60 mg, 17%). The reaction with $(CO)_5Cr{=}C(NH^iPr)Et$ was performed analogously using 250 mg aminocarbene complex (0.859 mmol), 500 mg **1** (1.389 mmol), 35 ml THF (yield 30 mg, 0.04 mmol, 5%). ^{1}H NMR (C_6D_6, 500 MHz, 25°C°C): $\delta =$ 1.84 (s, 30 H, $C_5(CH_3)_5$), 1.87 [s, 30 H, $C_5(CH_3)_5$], 2.20 [s, 6 H, CH_3], 4.54 (d, 2 H, $^2J_{HH} = 1.5$ Hz, $=CH_2$), 5.72 (br s, 2 H, $=CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25°C): $\delta = 12.5$ [$C_5(CH_3)_5$], 12.6 [$C_5(CH_3)_5$], 23.7 [CH_3], 100.6 [$=CH_2$], 103.9 [$C{=}C{-}CH_3$], 119.7 [$C_5(CH_3)_5$], 119.9 [$C_5(CH_3)_5$], 209.8 [$C{-}CH_3$], 218.2 [$C{=}CH_2$]. SIMS-MS (Cs^+, 20 kV, 3-nitrobenzyl alcohol): positive ions *m/z* (%): 767 (4) [$M^+ + 1$], 707 (<1) [M^+-4 CH3 + 1], 383 (22) [1/2 M^+], 367 (12) [1/2 M^+ − CH2], 318 (100) [$(C_5(CH_3)_5)_2Ti^+$]. Anal. Calcd. for $C_{50}H_{70}Ti_2$ (766.3): C, 78.36; H, 9.13; Found: C, 78.13; H, 9.28. UV spectrum (*n*-hexane): 365 nm, 540 nm (shoulder), 605 nm.

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