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Facile synthesis of a ruthenium carbene complex with a *cis*-chelating diphosphinoethane ligand

Martin A.O. Volland, Bernd F. Straub, Irene Gruber, Frank Rominger, Peter Hofmann *

Organisch-Chemisches Institut der Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

The neutral carbene complex (^{t}Bu$_2$PCH$_2$CH$_2$P^{t}Bu$_2$-κ^2*P*)Cl$_2$Ru=CHPh (**1**) with bis(di-*t*-butylphosphino)ethane (dtbpe) as a *cis*-chelating ligand is easily accessible from commercially available *trans*-(PCy$_3$)$_2$Cl$_2$Ru=CHPh by phosphine exchange. Its structure in the solid state was determined by single crystal X-ray diffraction. Structural features of this compound in solution were elucidated by various NMR experiments. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Carbene complexes; Metathesis; Homogenous catalysis

1. Introduction

The development of well-defined molybdenum [1] and ruthenium [2] carbene complexes has led to wide application of these compounds as precatalysts for olefin metathesis reactions [3] in organic synthesis and polymer chemistry.

Recently, we have introduced the first Grubbs type ruthenium(II)carbene complexes (dtbpm-κ^2*P*)Cl$_2$Ru=CHR with a rigid *cis*-coordination of the electron-rich, sterically demanding bis(di-*t*-butylphosphino)methane ligand (^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$, dtbpm) [4]. Chloride abstraction from these neutral ruthenium carbenes has led to a novel class of dinuclear ruthenium(II)carbene dications [(dtbpm-κ^2*P*)(μ-Cl)Ru=CHR]$_2^{2+}$ with unprecedented catalytic activity in ring-opening metathesis polymerization (ROMP) reactions [5]. Monomeric, solvent-coordinated cationic carbene complexes [(dtbpm-κ^2*P*)ClRu=CHR(solv)]$^+$, formed by dissociation of the dinuclear units, are believed to represent the catalytically active species [5,6].

2. Results and discussion

A variation of the phosphine ligand, in order to examine the effect of the P–Ru–P bite angle upon metathesis activity of these complexes, seemed interesting and made us attempt the syntheses of analogous dtbpe complexes. Increasing the P–Ru–P angle from ca. 75° towards 90° by employing bis(di-*t*-butylphosphino)ethane (dtbpe) instead of bis(di-*t*-butylphosphino)methane (dtbpm), should not only facilitate chloride ligand dissociation due to a stronger *trans* influence and due to additional steric pressure exerted by the bulky *t*-butyl substituents [7], but might also cause an enhanced tendency to form monomeric carbene cations in solution.

Although complexes (dtbpe-κ^2*P*)Cl$_2$Ru=CHR are independently accessible by the same route as their dtbpm analogs [4], i.e. via the novel unsaturated, dinuclear dihydride [(dtbpe-κ^2*P*)(μ-Cl)RuH]$_2$ [8], we have found a much more facile access to the benzylidene complex (dtbpe-κ^2*P*)Cl$_2$Ru=CHPh (**1**) by a simple ligand exchange reaction, which does not operate for the diphosphinomethane analogue [10]. The ruthenium carbene **1** is isolated as a green, air-stable, microcrystalline, analytically pure solid in 71% yield upon reacting commercially available (PCy$_3$)$_2$Cl$_2$Ru=CHPh with dtbpe [9] at 80°C in toluene (Scheme 1).

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* Corresponding author. Tel.: +49-6221-548502; fax: +49-6221-544885.

E-mail address: ph@phindigo.oci.uni-heidelberg.de (P. Hofmann).

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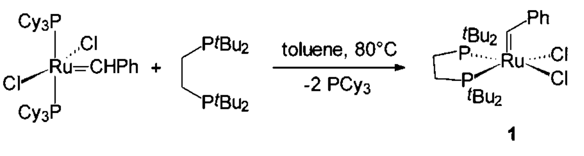

Scheme 1.

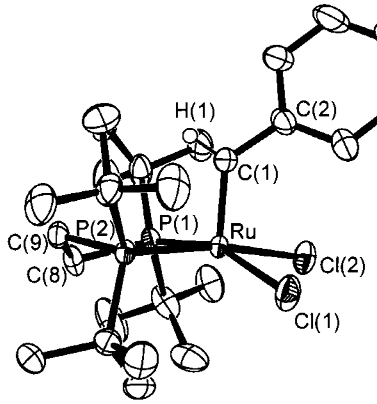

Fig. 1. ORTEP diagram (50% probability) of the solid state structure of **1**. Hydrogen atoms except for H(1) of the carbene moiety are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C(1) 1.836(3), Ru–P(1) 2.351(1), Ru–P(2) 2.352(1), Ru–Cl(1) 2.400(1), Ru–Cl(2) 2.407(1), P(1)–Ru–P(2) 86.1(1), Cl(1)–Ru–Cl(2) 87.4(1), P(1)–Ru–Cl(1) 160.1(1), P(2)–Ru–Cl(2) 170.1(1).

Compound **1** has been fully characterized in solution and in the solid state (Fig. 1) [11].

In the square pyramidal complex **1** the carbene moiety occupies the apical position, whereas the chlorides and the chelating phosphine are in the basal plane. Most notably, the P(1)–Ru–P(2) angle of 86.1(1)° in **1** is enlarged by approximately 12° compared to the dtbpm systems [4,5].

In CD_2Cl_2 solution at 25°C the $C(CH_3)_3$ groups of the dtbpe ligand display two doublets in the ^{1}H-NMR spectrum at $\delta = 1.11$ (^3J(P,H) = 12.3 Hz) and 1.49 (^3J(P,H) = 12.6 Hz), corresponding to the ^{t}Bu groups of the dtbpe ligand. In order to specify these resonances more precisely, a NOESY experiment was carried out. The carbene moiety Ru=CH can only lead to cross peaks with the ^{t}Bu groups in *cis* arrangement to it and thus allows their assignment.

Furthermore it should be noted that due to the nonplanar structure of the chelate ring (cf. X-ray structure) all ^{t}Bu groups are diastereotopic. In fact, VT ^{1}H-NMR spectra indicate that the ^{t}Bu groups *cis* to the carbene moiety are inequivalent on the NMR time scale at low temperatures due to a ring inversion process ($\Delta G^{\ddagger}_{183\ \mathrm{K}} = 35.9 \pm 1.7$ kJ mol^{-1}) of the ruthenacyclopentane. The ^{t}Bu groups *trans* to the carbene unit remain equivalent on the ^{1}H-NMR time scale down to 169 K. Additionally, the rotational barrier ($\Delta G^{\ddagger}_{172\ \mathrm{K}} = 30.9 \pm 1.5$ kJ mol^{-1}) of the phenyl ring around the C(1)–C(2) axis was deduced from the ^{1}H-NMR coalescence of the signals of the diastereotopic *ortho* hydrogen atoms of the phenyl ring (Fig. 2).

Unlike the neutral diphosphinomethane carbene complexes (dtbpm-κ^2P)$Cl_2Ru{=}CHR$ (R = $CH{=}CMe_2$, ^{i}Pr, $CH{=}CPh_2$, $CH{=}C(CH_2)_5$) [4,5], **1** does not polymerize norbornene at ambient temperature, probably due to the reduced chelate ring strain and thus less facile phosphine dissociation. However, as found previously for the four membered chelate system, chloride abstraction from **1** with a Lewis acid such as trimethylsilyl triflate leads to highly active ROMP catalysts, which readily polymerize even weakly strained olefins such as cyclooctene [5]. Their structure and catalytic activity in ROMP as well as ring closing metathesis (RCM) reactions will be reported separately.

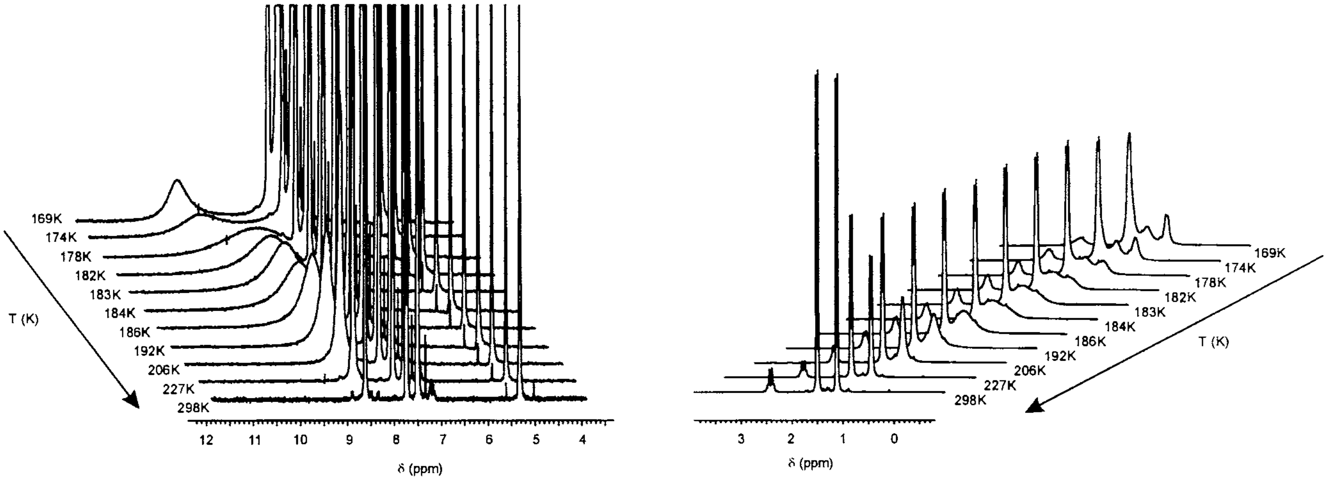

Fig. 2. VT ^{1}H-NMR spectra of **1** in CD_2Cl_2; left: coalescence of the diastereotopic *ortho*-hydrogen signals of the phenyl ring; right: coalescence of the *t*-butyl signals *cis* to the carbene unit. A CH_3OH sample was used to calibrate the temperature.

3. Conclusions

In conclusion, complex **1** is another convenient precursor for highly efficient, cationic ruthenium metathesis catalysts with *cis*-phosphine ligation. It is easily obtained from commercially available compounds in a one-step ligand replacement reaction. Complex **1** offers the possibility to examine the influence of the P–Ru–P bite angle upon catalytic activity. Moreover, C_2-symmetric chelating diphosphines are potential catalyst ligands for asymmetric metathesis reactions and we are pursuing research along these lines.

4. Experimental

All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. NMR spectra were recorded using a Bruker DRX 300 spectrometer. Abbreviations used are: s = singlet, d = doublet, t = triplet and m = multiplet. A ZAB-2F instrument was used for the high-resolution mass spectrum (HRES-MS).

4.1. Synthesis of (dtbpe-κ^2P)$Cl_2Ru{=}CHPh$ (**1**)

In a Schlenk tube 600 mg (0.729 mmol) of $(PCy_3)_2Cl_2Ru{=}CHPh$ (Strem Chemicals) and 283 mg (0.889 mmol, 1.22 equivalents) of bis(di-*t*-butylphosphino)ethane (dtbpe) in 20 ml toluene are heated to 80°C under an atmosphere of argon for 45 min. At ambient temperature the solution is concentrated in vacuo to 2 ml, then cooled to -78°C and the microcrystalline green precipitate is separated from the mother liquor by cannula filtration. The precipitate is washed with 1.5 ml toluene (filtration at -78°C), subsequently with hexane (3 × 5 ml) at ambient temperature and then dried in vacuo, yielding 300 mg (71%) (dtbpe-κ^2P)$Cl_2Ru{=}CHPh$ as a light green microcrystalline air-stable solid. Elemental analysis for $C_{25}H_{46}Cl_2P_2Ru$ Calc.: C, 51.72; H, 7.99; P, 10.67; Found: C, 51.90; H, 7.98; P, 10.56%; m.p. (dec.) 255°C; ^{1}H-NMR (298 K, CD_2Cl_2, 300.1 MHz): δ 1.11 (d, $^3J(P,H) = 12.3$ Hz, 18H, $C(CH_3)_3$), 1.49 (d, $^3J(P,H) = 12.6$ Hz, 18H, $C(CH_3)_3$), 2.28–2.51 (m, 4H, $P(CH_2)_2P$), 7.50 (‘t’, $^3J(H,H) = 7.5$ Hz, 2H, *m*-Ar–*H*), 7.74 (t, $^3J(H,H) = 7.5$ Hz, 1H, *p*-Ar–*H*), 8.62 (d, $^3J(H,H) = 7.5$ Hz, 2H, *o*-Ar–H), 16.79 (t + sat, $^3J(P,H) = 14.6$ Hz, $^1J(C,H) = 150$ Hz, 1H, Ru=C*H*); $^{13}C\{^1H\}$-NMR (298 K, CD_2Cl_2, 75.5 MHz) δ 23.9 (‘dd’, $J(P,C) = 16.6$ Hz, $J(P',C) = 13.3$ Hz, $P(CH_2)_2P$), 29.6 (s, $C(CH_3)_3$), 30.8 (s, $C(CH_3)_3$), 38.1 (m, $N = 40.0$ Hz, $C(CH_3)_3$), 128.4 (s, *m*-Ar–*C*), 131.4 (s, *o*-Ar–*C*), 132.4 (s, *p*-Ar–*C*), 149.2 (s, *ipso*-Ar–*C*), 304.5 (t, $^2J(P,C) = 13.3$ Hz, Ru=*C*H); $^{31}P\{^1H\}$ NMR (298 K, CD_2Cl_2, 121.5 MHz) δ 92.4 (s); HRES-MS (EI +): Calc. for $(C_{25}H_{46}Cl_2P_2Ru)^+$ $m/z = 580.1495$; Found $m/z = 580.1494$ ($\Delta = +0.2$ ppm) correct isotopic pattern for $(C_{25}H_{46}Cl_2P_2Ru)^+$: m/z (Calc./Found intensity): 574 (11,11); 576 (11,11); 577 (29,26); 578 (38,37); 579 (62,63); 580 (100,100); 581 (51,52); 582 (95,93); 583 (29,30); 584 (36,33).

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[10] Reaction of dtbpm with $(PCy_3)_2Cl_2Ru{=}CHPh$ under analogous conditions does not lead to the formation of (dtbpm-κ^2P)$Cl_2Ru{=}CHPh$ (cf. also [4]).

[11] (a) Crystal data: Turquoise green crystals of **1**, containing 0.5 equivalents of toluene, suitable for X-ray analysis were obtained by slowly cooling a solution of **1** in boiling toluene. Data were collected on a Bruker SMART CCD instrument and the structure solution was performed using SHELXTL V5.10 [12,13]. (b) Crystal data: $C_{25}H_{46}Cl_2P_2Ru \cdot 0.5\ C_7H_8$, $M = 626.60$ g mol^{-1}, monoclinic, space group $P2_1/n$, $a = 10.1004(1)$, $b = 18.6621(3)$,

$c = 16.3801(1)$ Å, $\beta = 95.196(1)°$, $V = 3074.87(6)$ Å^3, $Z = 4$, $\mu = 0.803$ mm^{-1}, 31 355 reflections measured at 200(2) K, 7058 independent reflections ($R_{int} = 0.0549$), 5725 reflections observed ($I > 2\sigma(I)$), 339 parameters refined, final agreement factors $R_1 = 0.033$, $wR_2 = 0.066$.

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