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A tertiary phosphine that is too bulky: preparation of catalytically less active carbene and vinylidene ruthenium(II) complexes

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Dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

Abstract

Tricyclooctylphosphine $PCoc_3$ (**1**), which has been prepared from PCl_3 and cyclooctyl Grignard reagent, reacts under an atmosphere of H_2 with the dimer $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$ (**2**) to give the hydrido(dihydrogen) complex $[RuHCl(H_2)(PCoc_3)_2]$ (**4**); in contrast, treatment of **2** with PPh_3 under the same conditions affords $[RuHCl(PPh_3)_3]$ (**3**). The reaction of **4** with acetylene in the presence of $MgCl_2$ and water leads to the formation of the ruthenium carbene $[RuCl_2(=CHCH_3)(PCoc_3)_2]$ (**5**) in 70% isolated yield. In the absence of $MgCl_2$ and water, **4** reacts with acetylene at low temperature to give the hydrido(vinylidene) complex $[RuHCl(=C=CH_2)(PCoc_3)_2]$ (**6**) almost quantitatively. Compounds **5**, **6** and $[RuH(\kappa^2\text{-}O_2CCF_3)(=C=CH_2)(PCoc_3)_2]$ (**7**), the latter being obtained from **6** and CF_3CO_2K by ligand exchange, are poor catalysts for ROMP and cross olefin metathesis.

Keywords: Ruthenium; Carbene complexes; Vinylidene complexes; Hydride complexes; Dihydrogen complexes

1. Introduction

After it was convincingly illustrated that the carberuthenium(II) complexes $[RuCl_2(=CHR)(PCy_3)_2]$ first reported by Grubbs et al. [1] are excellent catalysts for olefin metathesis [2], numerous attempts have been made to modify the coordination sphere of the metal in these five-coordinate molecules with the hope to find an even better application profile [3]. With regard to the type of the phosphine ligand, it was found that the corresponding bis(triphenylphosphine)- and bis(triisopropylphosphine)ruthenium derivatives are catalytically less active than the bis(tricyclohexylphosphine) counterpart [1c,1d] which was explained by the reduced size of PPh_3 and P^iPr_3 compared with PCy_3 [4]. Since there are to the best of our knowledge no reports about using even more bulky tertiary phosphines than PCy_3 as ligands for the carberuthenium catalysts, we set out to prepare tricyclooctylphosphine $PCoc_3$ for which no preparative procedure was known [5]. In the present paper we describe the synthesis of some hydrido, carbene and vinylidene compounds with $Ru(PCoc_3)_2$ as the molecular core and show that they are catalytically less active than the related $Ru(PCy_3)_2$ complexes.

2. Results and discussion

The stepwise procedure for the preparation of $PCoc_3$ (**1**) is outlined in Eq. (1). After we failed to obtain cyclooctylchloride from cyclooctanol and $ZnCl_2$–HCl [6], we used the related bromide as precursor for the Grignard reagent and treated PCl_3 with $c\text{-}C_8H_{15}MgBr$ in ether–toluene. The phosphine **1** was isolated as a colorless viscous oil and characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. The relatively modest yield of **1** is probably due to the known tendency of Grignard compounds containing larger cycloalkyl groups to generate the corresponding cycloalkanes by radical-type reactions [7].

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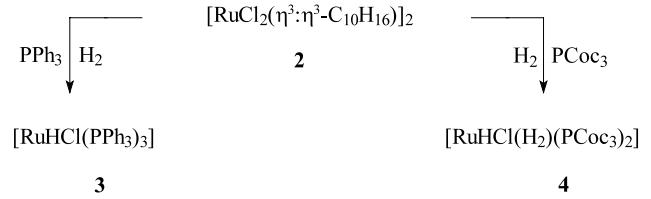
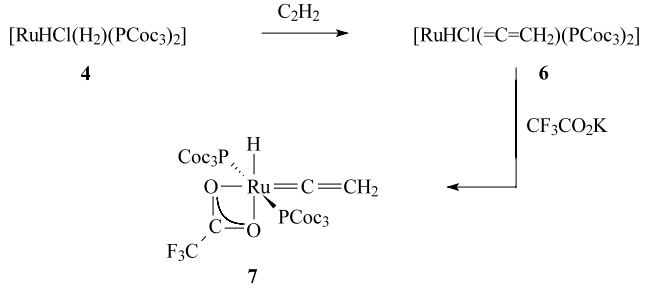
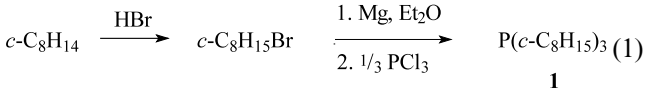


Scheme 1.

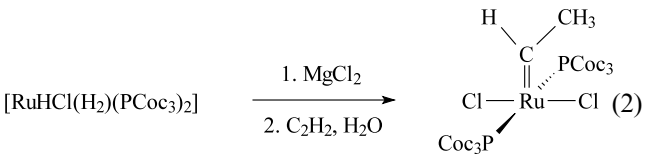


Scheme 2.



The reaction of $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})]_2$ (**2**), which we had already used as starting material for the preparation of $[RuHCl(H_2)(P^iPr_3)_2]$ and $[RuHCl(H_2)(PCy_3)_2]$ [8], with **1** in a solvent mixture of isopropanol and toluene leads, under an atmosphere of dihydrogen, to the bis(tricyclooctylphosphine)ruthenium(II) complex **4** in 68% isolated yield (Scheme 1). Typical spectroscopic features of the light yellow, air-sensitive solid are the Ru–H stretching modes in the IR spectrum at 2104, 2056 and 1905 cm^{-1} and the high-field resonance at δ −16.0 in the ^{1}H-NMR spectrum, the latter being at room temperature a broad singlet as is also found for other ruthenium(II) compounds with $RuH(H_2)$ as a molecular fragment [9]. In contrast to **1**, triphenylphosphine reacts with **2** in the presence of dihydrogen to give the hydride complex **3** in excellent yield. Attempts to prepare $[RuHCl(H_2)(PR_3)_2]$ with $PR_3 = P^iPr_2Ph$, PCy_2Me by using the same methodology as applied to **4** failed.

Similarly to $[RuHCl(H_2)(P^iPr_3)_2]$ and $[RuHCl(H_2)(PCy_3)_2]$, the $Ru(PCoc_3)_2$ counterpart **4** also reacts with acetylene in dichloromethane at −80 °C to afford quantitatively the hydrido(vinylidene) complex **6**. If the reaction of **4** with acetylene is carried out in the presence of $MgCl_2$ and water, instead of **6** the carbene(dichloro) derivative **5** is obtained (Eq. (2)). Key to the structural assignment of **5** from the ^{1}H-NMR spectrum are the quartet at δ 19.54 for the =CH and the doublet at δ 2.72 for the carbene CH_3 protons. The ^{13}C-NMR spectrum of **5** displays a signal at δ 314.3 for the Ru=C carbon atom, the position of which is nearly identical to that of $[RuCl_2(=CHCH_3)(P^iPr_3)_2]$ [10]. With regard to the formation of **5** from **4** as the precursor, we assume that in the first step **4** reacts with acetylene to give the hydrido(vinylidene) compound **6** which in the presence of a chloride source such as $MgCl_2$ generates the anionic vinylruthenium(II) species $[RuCl_2(CH{=}CH_2)(PCoc_3)_2]^-$. The reaction of this intermediate with water could give **5**. In this context we note that recently the first dicationic ruthenium carbene $[Ru(=CHCH_3)(CH_3CN)_2(PCy_3)_2]^{2+}$ (with BF_4^- or $B(Ar_f)_4^-$ as the counterion; $Ar_f = 3,5$-bis(trifluoromethyl)phenyl) has been prepared in our laboratory by protonation of the vinylruthenium(II) monocation $[Ru(CH{=}CH_2)(CH_3CN)_2(PCy_3)_2]^+$ with HBF_4 or Brookhart's acid in dichloromethane [11].



The vinylidene complex **6**, which is formed from **4** and acetylene in the absence of a protic reagent, is a brown, moderately air-sensitive solid which is readily soluble in all common organic solvents. We assume, in agreement with ab initio DFT calculations by Eisenstein et al. for the related compounds $[RuHCl(=C{=}CHR)(P^tBu_2Me)_2]$ [12], that **6** possesses a distorted trigonal–bipyramidal geometry with the two phosphines in the apical positions. The reaction of **6** with CF_3CO_2K leads to an exchange of the anionic ligand and results in the formation of the carboxylato complex **7** in 87% isolated yield (Scheme 2). The bidentate coordination of the $CF_3CO_2^-$ anion is indicated by the IR spectrum of **7** in which the symmetric and asymmetric ν(OCO) stretching modes appear in the region characteristic for $M(\kappa^2\text{-}O_2CR)$ compounds [13]. The ^{1}H-NMR spectra of **6** and **7** show the hydride resonance as a triplet at, respectively, δ −15.95 (for **6**) and −12.61 (for **7**) while the ^{13}C-NMR spectra of **6** and **7** display in the low-field region the signals for the α- and β-carbon atoms of the vinylidene ligand at, respectively, δ 326.4 and 86.9 (for **6**) and δ 334.4 and 86.5 (for **7**). All these resonances are split into triplets due to P,H and P,C couplings.

The hope that the five-coordinate carbene- and vinylideneruthenium complexes **5** and **6** with phosphine ligands, which are more bulky than PCy_3, would be catalytically more active than the $Ru(PCy_3)_2$ counterparts was not fulfilled. Neither in ROMP of *cis*-cyclooctene nor that of dicyclopentadiene could the ruthenium carbene **5** compete with $[RuCl_2(=CHCH_3)(PCy_3)_2]$ in catalytic activity under identical conditions. Similarly, the hydrido(vinylidene) derivative **6**, in the

presence of HBF_4 in ether, does not catalyze with the same rate as the cation $[RuHCl(\equiv CCH_3)(OEt_2)(PCy_3)_2]^+$, formed from $[RuHCl(=C=CH_2)(PCy_3)_2]$ and ethereal HBF_4 [14], the ring-opening metathesis of cyclopentene with methyl acrylate. The conclusion is that among the tertiary phosphines PR_3 the compound with R = cyclohexyl obviously provides the most favorable conditions for generating, from $[RuCl_2(=CHR')(PR_3)_2]$ as the precursor, a 14-electron species $[RuCl_2(=CHR')(PR_3)]$ that is supposed to be the active catalyst in various types of olefin metathesis [2*m*].

3. Experimental

All experiments were carried out under an atmosphere of Ar by Schlenk techniques. NMR spectra were recorded at room temperature (r.t.) on Bruker AC 200 and AMX 400 instruments and IR spectra on a Perkin–Elmer 1420 IR spectrometer. Melting points were determined by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; q, quartet; m, multiplet; br, broadened signal; $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$. The starting material **2** [15] was prepared as described in the literature. Cyclooctylbromide was prepared following a modified procedure to that given by Willstätter and Waser [16]. The reaction of *cis*-cyclooctene with HBr was carried out in water (4 h, 80 °C) instead of AcOH as solvent. The fractional distillation gave first unreacted *cis*-cyclooctene, then cyclooctane, and finally cyclooctylbromide (b.p. 86 °C at 7 mbar) with a yield of 73%.

3.1. Preparation of tricyclooctylphosphine ($PCoc_3$) (1)

In a three-necked flask equipped with a reflux condenser and a dropping funnel 6.1 g (0.25 mol) of Mg filings were covered with 20 ml of ether and activated by addition of 1.80 ml (0.21 mol) of 1,2-dibromoethane. After addition of 30 ml of ether, the mixture was treated dropwise with a solution of 40.0 g (0.21 mol) of cyclooctylbromide in 60 ml of ether and then heated for 1 h under reflux. After the solution (containing the Grignard reagent with a concentration of 0.78 M) was cooled to r.t., it was filtered and the filtrate was added dropwise to a solution of 2.25 ml (25.7 mmol) of PCl_3 in 200 ml of $C_6H_5CH_3$ at −50 °C. After 2/3 of the solution with the Grignard reagent was added, the C_3H_6O–dry ice bath was removed. While the formation of an off-white precipitate was observed, ca. 100 ml of the solvent was distilled off. The remaining solution was kept at 0 °C and treated with 20 ml of aq. HCl. After the reaction was finished, three phases separated which were investigated by spectroscopic techniques. The ^{31}P-NMR spectra revealed that solely the rather viscous middle phase contained an organophosphorus compound. This phase was treated with 20 ml of ether, 20 ml of water and as long as with KOH until the aq. phase reached pH 9. The ethereal phase was separated, and the aq. phase was furthermore extracted twice with 10 ml of ether. The combined ethereal solutions were evaporated in vacuo to give a colorless viscous oil which did not crystallize even upon storing at −20 °C for days; yield 54 g (22%). ^{1}H-NMR (200 MHz, C_6D_6): δ 2.00–1.81, 1.76–1.73, 1.58–1.48 (all m, 45H, C_8H_{15}). ^{13}C-NMR (50.3 MHz, C_6D_6): δ 31.8 [d, $^2J(P,C) = 14.5$ Hz, C2 and C8 of C_8H_{15}], 31.2 [d, $^1J(P,C) = 22.2$ Hz, C1 of C_8H_{15}], 27.5 [d, $^3J(P,C) = 6.2$ Hz, C3 and C7 of C_8H_{15}], 27.3, 26.8 (both s, C4–C6 of C_8H_{15}). ^{31}P-NMR (81.0 MHz, C_6D_6): δ 30.7 (s).

3.2. Preparation of $[RuHCl(PPh_3)_3]$ (3) from 2

A suspension of 105 mg (0.17 mmol) of **2** in 10 ml of C_3H_8O was treated with 357 mg (1.36 mmol) of PPh_3 at r.t. After the Ar atmosphere was partially replaced by dihydrogen (0.8 bar), the solution was warmed to 60 °C and stirred for 30 min at this temperature. A small quantity of a violet solid was precipitated. After the solution was cooled to 20 °C and stored for 12 h, the obtained violet solid was separated from the mother liquor, washed twice with 10 ml of C_3H_8O and dried in vacuo; yield 292 mg (93%). The compound was characterized by comparing the ^{1}H- and ^{31}P-NMR spectroscopic data with those given in the literature [17].

3.3. Preparation of $[RuHCl(H_2)(PCoc_3)_2]$ (4)

A suspension of 204 mg (0.33 mmol) of **2** in 10 ml of C_3H_8O was treated with 9.5 ml of a 0.30 M solution of **1** (2.89 mmol) in $C_6H_5CH_3$ at r.t. After the Ar atmosphere was partially replaced by dihydrogen (0.8 bar), the reaction mixture was warmed to ca. 50 °C and stirred for 10 min at this temperature. The obtained red solution was cooled to 20 °C, the solvent was removed in vacuo, and the oily residue was treated with 10 ml of C_3H_6O. After ca. 1 h a light yellow solid precipitated, which was separated from the mother liquor, washed three times with 10 ml of C_3H_6O and dried in vacuo; yield 396 mg (68%), m.p. (dec.) 102 °C. Anal. Found: C, 66.33; H, 10.73. Calc. for $C_{48}H_{93}ClP_2Ru$: C, 66.36; H, 10.79%. IR (KBr): ν(RuH) 2104, 2056, 1905 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 2.52, 2.16, 1.72–1.45 (all m, 90H, C_8H_{15}), −16.0 [br s, 3H, RuH(H_2)]. ^{13}C-NMR (100.6 MHz, C_6D_6): δ 34.1 (vt, $N = 14.6$ Hz, C1 of C_8H_{15}), 31.5, 27.7, 27.6, 26.4 (all s, C_8H_{15}). ^{31}P-NMR (162.0 MHz, C_6D_6): δ 76.7 (s).

3.4. Preparation of $[RuCl_2(=CHCH_3)(PCoc_3)_2]$ (5)

A solution of 200 mg (0.23 mmol) of **4** in 10 ml of THF was treated with an excess of $MgCl_2$ (200 mg, 2.10

mmol). The suspension was cooled to −40 °C, the Schlenk tube was evacuated and then filled with C_2H_2. Under continuous stirring, the reaction mixture was slowly warmed to r.t., which led to a gradual change of color from yellow to pale brown. The solution was treated with 0.1 ml (5.55 mmol) of water, and after it was stirred for 20 min at 25 °C, the solvent was removed in vacuo. The residue was extracted with 15 ml of C_5H_{12}, and the extract brought to dryness in vacuo to give a red–violet solid; yield 151 mg (70%), m.p. (dec.) 89 °C. Anal. Found: C, 65.03; H, 9.77. Calc. for $C_{50}H_{94}Cl_2P_2Ru$: C, 64.63; H, 10.20%. ^{1}H-NMR (400 MHz, C_6D_6): δ 19.54 [q, $^3J(H,H) = 5.6$ Hz, 1H, Ru=C*H*CH$_3$], 3.06 (br s, 6H, C_8H_{15}), 2.72 [d, $^3J(H,H) = 5.6$ Hz, 3H, Ru=CHC*H*$_3$], 2.10 (br m, 12H, C_8H_{15}), 1.75–1.44 (m, 72H, C_8H_{15}). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 314.3 [t, $^2J(P,C) = 6.3$ Hz, Ru=*C*HCH$_3$], 48.5 (s, Ru=CH*C*H$_3$), 30.8 (vt, $N = 16.3$ Hz, C1 of C_8H_{15}), 27.6 (vt, $N = 8.6$ Hz, C_8H_{15}), 30.9, 27.9, 25.9 (all s, C_8H_{15}). ^{31}P-NMR (162.0 MHz, C_6D_6): δ 62.9 (s).

3.5. Preparation of [RuHCl(=C=CH$_2$)(PCoc$_3$)$_2$] (6)

A Schlenk tube containing a solution of 84 mg (0.10 mmol) of **4** in 10 ml of CH_2Cl_2 was cooled to −80 °C, shortly evacuated and then filled with acetylene. A quick change of color from yellow to red brown took place. After the solution was stirred for 30 s, the solvent was evaporated in vacuo. A brown solid remained, which was washed with small quantities of C_5H_{12} (0 °C) and dried; yield 88 mg (99%), m.p. (dec.) 122 °C. Anal. Found: C, 67.18; H, 10.34. Calc. for $C_{50}H_{93}ClP_2Ru$: C, 67.27; H, 10.50%. IR (KBr): ν(Ru=C=CH$_2$) 2064, ν(RuH) 1900 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 2.94 (m, 6H, PCH), 2.70 [t, $^4J(P,H) = 3.1$ Hz, 2H, Ru=C=CH$_2$], 2.47–2.22 (m, 12H, C_8H_{15}), 1.92–1.41 (m, 72H, C_8H_{15}), −15.95 [t, $^2J(P,H) = 16.7$ Hz, 1H, RuH]. ^{13}C-NMR (100.6 MHz, C_6D_6): δ 326.4 [t, $^2J(P,C) = 14.0$ Hz, Ru=*C*=CH$_2$], 86.9 [t, $^3J(P,C) = 3$ Hz, Ru=C=*C*H$_2$], 33.1 (vt, $N = 15.0$ Hz, C1 of C_8H_{15}), 31.4, 31.0, 27.7, 27.6, 27.5, 26.4, 26.3 (all s, C_8H_{15}). ^{31}P-NMR (81.0 MHz, C_6D_6): δ 64.8 (s).

3.6. Preparation of [RuH(κ^2-O$_2$CCF$_3$)(=C=CH$_2$)(PCoc$_3$)$_2$] (7)

A solution of 196 mg (0.22 mmol) of **6** in 10 ml of THF was treated with 335 mg (2.2 mmol) of CF_3CO_2K and stirred for 10 min at r.t. The solvent was evaporated in vacuo, the residue was extracted twice with 10 ml of C_6H_6 each, and the combined extracts were brought to dryness in vacuo. An olive–green solid was obtained, which dissolves in C_6H_6 to give a yellow solution; yield 185 mg (87%), m.p. (dec.) 44 °C. Anal. Found: C, 63.98; H, 9.48. Calc. for $C_{52}H_{93}F_3O_2P_2Ru$: C, 64.37; H, 9.66%. IR (KBr): ν(Ru=C=CH$_2$) 2072, ν(RuH) 1907, $\nu(OCO_{as})$ 1629, 1602, $\nu(OCO_{sym})$ 1466, 1444 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 2.86 [t, $^4J(P,H) = 3.0$ Hz, 2H, Ru=C=CH$_2$], 2.71 (m, 6H, PCH), 2.48–2.19 (m, 12H, C_8H_{15}), 1.90–1.39 (m, 72H, C_8H_{15}), −12.61 [t, $^2J(P,H) = 16.0$ Hz, 1H, RuH]. ^{13}C-NMR (100.6 MHz, C_6D_6): δ 334.4 [t, $^2J(P,C) = 13.0$ Hz, Ru=*C*=CH$_2$], 163.1 [q, $^2J(C,F) = 36.9$ Hz, CF_3CO_2], 115.4 [q, $^1J(C,F) = 286$ Hz, CF_3CO_2], 86.5 [t, $^3J(P,C) = 3$ Hz, Ru=C=*C*H$_2$], 33.2 (vt, $N = 14.8$ Hz, C1 of C_8H_{15}), 31.5, 31.0, 27.8, 27.6, 27.5, 26.0, 25.9 (all s, C_8H_{15}). ^{19}F-NMR (188.0 MHz, C_6D_6): δ −75.4 (s). ^{31}P-NMR (81.0 MHz, C_6D_6): δ 64.6 (s).

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