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Synthesis and single-crystal X-ray structure of $[(DMPE)_2Ru(C_2H_4)CH_3]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$

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Abstract

The reaction of *cis*-$(DMPE)_2Ru(CH_3)_2$ with $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$ afforded the ruthenium cation $[(DMPE)_2RuCH_3]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$. This cation underwent reaction with ethylene at room temperature to give the stable adduct *trans*-$[(DMPE)_2Ru(C_2H_4)CH_3]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$, **1**. The single crystal X-ray structure of **1** is reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cation; Ethylene; Olefin complex; DMPE

1. Introduction

Current efforts to develop new types of Ziegler–Natta polymerization catalysts based on late transition metals are motivated, at least in part, by the belief that weakly oxophilic late transition metals will exhibit enhanced tolerance toward polar functional groups such as alcohols, aldehydes and ketones [1]. The use of catalysts based on these metals should thus permit the direct introduction of functional groups into polymer backbones (via the monomer) under mild reaction conditions. Cationic nickel- and palladium-based metal alkyls with bulky imine ligands have been observed to polymerize olefins to moderately high molecular weights and high crystallinities [2]. Furthermore, recent studies have shown that iron dichlorides possessing bulky ligands can polymerize ethylene to high molecular weights in the presence of methylaluminoxane cocatalyst; the degree of activity varies with the polymerization conditions and the ligand structure [3].

Although few reports of olefin polymerization via coordinative insertion into ruthenium–alkyl bonds are known [4], we have been exploring the development of ruthenium-based Ziegler–Natta catalysts because ruthenium is not only isoelectronic with iron, but is also known to efficiently initiate the ring opening metathesis polymerization (ROMP) of cyclic olefins that contain polar functionalities [5]. In the present work, we targeted the synthesis of *cis*-$(DMPE)_2Ru(CH_3)_2$ (DMPE = dimethylphosphinoethane, $Me_2PCH_2CH_2PMe_2$) as a catalyst precursor. We anticipated that removal of one of the methyl groups attached to Ru in this complex would generate a metal center that possessed two basic features common to known Ziegler–Natta polymerization catalysts: (1) electron deficiency to encourage coordination of olefins and (2) an alkyl group *cis* to the vacant site to permit insertion and thus propagation [6]. This paper describes the reaction of *cis*-$(DMPE)_2Ru(CH_3)_2$ with the methyl abstraction agent $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$ to generate the resulting cationic complex $[(DMPE)_2RuCH_3]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$. Subsequent reaction of this complex with ethylene yields a novel olefin adduct that is fully characterized.

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2. Results and discussion

We synthesized the targeted catalyst precursor, *cis*-$(DMPE)_2Ru(CH_3)_2$, by modification of the reported procedure [7]. We then attempted to polymerize ethylene by exposing the olefin to *cis*-$(DMPE)_2Ru(CH_3)_2$ in the presence of the borate salt $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$. This salt is known to abstract methyl groups from late transition metal complexes [2]. Indeed, exposure of 0.9 equivalents of the salt to *cis*-$(DMPE)_2Ru(CH_3)_2$ in either methylene chloride or tetrahydrofuran generated the cationic monoalkyl intermediate $[(DMPE)_2RuCH_3]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$, whose structure was supported by ^1H- and ^{31}P-NMR spectroscopy. The single resonance at 37.6 ppm in the ^{31}P-NMR spectrum suggests that all four phosphines are equivalent in solution. The coordination site *trans* to the methyl group is more likely filled by either the diethyl ether moiety derived from the borate salt or a THF moiety when this solvent is employed in the reaction.

Exposure of one atmosphere of ethylene to the cationic monoalkyl intermediate yielded the stable ethylene complex *trans*-$[(DMPE)_2Ru(C_2H_4)CH_3]^+[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$, **1**. Apparently, an incoming molecule of ethylene displaces the coordinating ether moiety to produce the *trans* ethylene complex. We characterized the structure of **1** using single crystal X-ray diffraction. A thermal ellipsoid drawing of the cationic portion of **1** is shown in Fig. 1; the selected bond lengths and bond angles are shown in Table 1. The ethylene group (C1 and C2) and the methyl group (C3) were refined isotropically and found to be disordered into each other at essentially 50:50 occupancy. All atoms involved in this area were refined using variable distance constraints. The structure is pseudo-octahedral with the ethylene moiety occupying the apical position *trans* to the methyl group. The bond distances for Ru–C(1), Ru–C(2), and Ru–C(3) are 2.36, 2.36, and 2.16 Å, respectively. The bond distance of C(1)–C(2) is slightly elongated at 1.40 Å with respect to the known 1.33 Å bond length of ethylene [8].

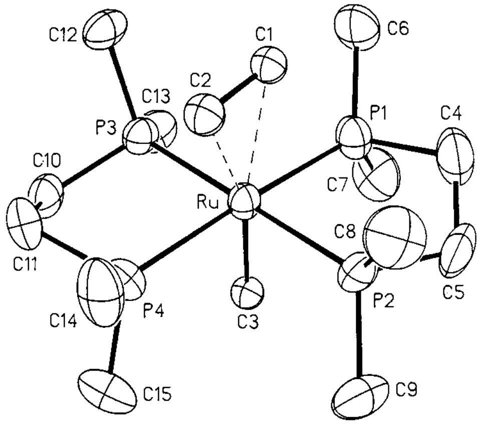

Fig. 1. Thermal ellipsoid drawing of *trans*-$[(DMPE)_2Ru(C_2H_4)CH_3]^+$. Thermal ellipsoids are 40% equiprobability envelopes with the hydrogen atoms omitted.

Table 1
Selected bond distances (Å) and angles (°) for complex **1**

Bond distances			
Ru–P(1)	2.332(3)	Ru–C(1)	2.363(11)
Ru–P(2)	2.329(2)	Ru–C(2)	2.363(9)
Ru–P(3)	2.343(2)	Ru–C(3)	2.156(13)
Ru–P(4)	2.341(3)	C(1)–C(2)	1.404(17)
Bond angles			
P(1)–Ru–P(2)	84.2(1)	P(1)–Ru–C(1)	75.9(3)
P(1)–Ru–P(3)	96.0(1)	P(2)–Ru–C(1)	89.6(4)
P(2)–Ru–P(3)	179.8(2)	P(3)–Ru–C(1)	90.5(3)
P(1)–Ru–P(4)	174.7(1)	P(4)–Ru–C(1)	109.4(3)
P(3)–Ru–P(4)	83.7(1)	P(1)–Ru–C(2)	110.1(3)
P(2)–Ru–C(2)	88.3(4)	P(3)–Ru–C(2)	91.6(4)
P(4)–Ru–C(2)	75.2(3)	C(1)–Ru–C(2)	34.6(4)
P(1)–Ru–C(3)	87.7(4)	P(2)–Ru–C(3)	92.3(4)
P(3)–Ru–C(3)	87.7(4)	P(4)–Ru–C(3)	87.0(4)
C(1)–Ru–C(3)	163.2(5)	C(2)–Ru–C(3)	162.2(5)

Although there are known examples of olefin adducts of half-sandwich arene ruthenium alkyl or hydride complexes [9], there are, to our knowledge, no examples of octahedral ruthenium (II) alkyl olefin complexes that possess either oxygen, nitrogen, sulfur, or phosphine ligands. Only one example of an octahedral ruthenium (II) hydride olefin complex, *trans*-$[(DPPE)_2Ru(C_2H_4)(H)]^+[OC_6H_4\text{-pMe}\cdot 2HOC_6H_4\text{-pMe}]^-$ has been reported [10]. It thus appears that we have synthesized the first example of a ruthenium (II) alkyl olefin complex having the type of coordinating ligands described above.

Neither oligomerization nor polymerization of ethylene was observed using this system despite attempts to vary the reaction conditions (e.g. by increasing the pressure of ethylene to 2.6 atmospheres in the presence of weakly coordinating ligands such as acetonitrile and pyridine) [11]. The lack of catalysis is likely due to the preferred structure of the cationic ruthenium *trans* olefin complex resulting from olefin addition to the vacant site *trans* to the methyl group. We are currently exploring alternative ruthenium-based catalyst systems, in which the alkyl moiety and the vacant site are forced to maintain a *cis* relationship upon coordinative unsaturation.

3. Experimental

The syntheses were performed using standard Schlenk and glove-box techniques. All solvents were dried by passage through alumina and degassed by freeze–pump–thaw methods prior to use. The compounds dimethylmagnesium [12], dirutheniumtetraacetate chloride [13] and diethyloxonium tetrakis[tri(fluoromethyl)phenyl]borate [14] were prepared according to literature procedures. DMPE was purchased from Strem Chemicals and used as received. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 spectrometer operating at 300 MHz (for ^{1}H) and 121 MHz (for ^{31}P). Elemental analyses were performed by National Chemical Consulting.

3.1. *cis*-(DMPE)$_2$Ru(CH$_3$)$_2$

An aliquot of Mg(CH$_3$)$_2$ (4.50 ml of a 1.24 M solution in diethyl ether; 5.58×10^{-3} mol) was added to a solution of 1.04 g of Ru$_2$(OCOCH$_3$)$_4$Cl (2.19×10^{-3} mol) and 1.76 ml of DMPE (1.05×10^{-2} mol) in 70 ml of THF. The solution was stirred at room temperature for 2 h. The orange solution was filtered, dried, and extracted with hexane. The crude product was purified by sublimation (160°C, 40 torr). Yield: 0.661 g; 35% of a white powder. ^{1}H-NMR (CD$_2$Cl$_2$; 300 MHz; 293 K): δ −0.97 (m, 6 H, $J_{\mathrm{PH}} = 3.3$ Hz) Ru–CH$_3$, 1.02 (d, 6 H, $J_{\mathrm{PH}} = 4.5$ Hz), 1.07 (d, 6 H, $J_{\mathrm{PH}} = 6$ Hz), 1.08 (s, 6 H), 1.22 (t, 6 H, $J_{\mathrm{PH}} = 2.7$ Hz), Me$_2$PCH$_2$CH$_2$PMe$_2$, 1.44 (m, 4 H), 1.58 (m, 4 H), Me$_2$PCH$_2$CH$_2$PMe$_2$. ^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$; 121 MHz; 293 K): δ 33.9 (t), 45.7 (t), ($J_{\mathrm{pp}} = 19$ Hz). The ^{1}H-NMR data are consistent with those previously reported for this compound, which was synthesized via an alternative pathway [15].

3.2. [(DMPE)$_2$RuCH$_3$]$^+$[(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$

An aliquot of [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$[H(OEt$_2$)$_2$]$^+$ (6.0 mg; 1.4×10^{-5} mol) was added to a solution of 12.5 mg (1.25×10^{-5} mol) of *cis*-(DMPE)$_2$Ru(CH$_3$)$_2$ in CD$_2$Cl$_2$ (0.5 ml). ^{1}H-NMR (CD$_2$Cl$_2$; 300 MHz; 293 K): δ −1.40 (quint, 3 H, $J_{\mathrm{PH}} = 7.5$ Hz) Ru–CH$_3$, 1.37 (s, 12 H), 1.50 (s, 12 H) Me$_2$PCH$_2$CH$_2$PMe$_2$, 1.78 (m, 8 H) Me$_2$PCH$_2$CH$_2$PMe$_2$, 7.57 (s, 4 H), 7.73 (s, 8 H) C$_6$H$_3$(CF$_3$)$_2$. ^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$; 121 MHz; 293 K): δ 37.6 (s).

3.3. *trans*-[(DMPE)$_2$Ru(C$_2$H$_4$)CH$_3$]$^+$[(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$B]$^-$

An aliquot of [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$[H(OEt$_2$)$_2$]$^+$ (0.31 g; 3.1×10^{-4} mol) was added to a solution of 0.15 g (3.5×10^{-4} mol) of *cis*-(DMPE)$_2$Ru(CH$_3$)$_2$ in CH$_2$Cl$_2$ (2 ml) under 1 atm of ethylene at room temperature. The solution was stirred for 5 min and cooled to −76°C to obtain champagne-colored crystals (0.23 g; 1.8×10^{-4} mol; 58% yield). ^{1}H-NMR (CD$_2$Cl$_2$; 300 MHz; 293 K): δ −0.62 (quint, 3 H, $J_{\mathrm{PH}} = 8.1$ Hz) Ru–CH$_3$, 1.25 (s, 12 H), 1.32 (s, 12 H) Me$_2$PCH$_2$CH$_2$PMe$_2$, 1.65 (m, 8 H) Me$_2$PCH$_2$CH$_2$PMe$_2$, 1.98 (m, 4 H) Ru–C$_2$H$_4$, 7.57 (s, 4 H), 7.73 (s, 8 H) C$_6$H$_3$(CF$_3$)$_2$. ^{31}P{^{1}H}-NMR (THF-d$_8$; 121 MHz; 293 K): δ 41.7 (s). Anal. Calc. for C$_{15}$H$_{39}$P$_4$-Ru$^+ \cdot$C$_{32}$H$_{12}$BF$_{24}^-$: C, 43.15; H, 3.91. Found: C, 43.25; H, 3.72.

3.4. Experimental data for the X-ray crystal structure determinations

Collection of the X-ray data was carried out on a crystal of dimensions 0.30 mm × 0.45 mm × 0.70 mm using a Nicolet R3m/V automatic diffractometer. The sample was placed in a stream of dry nitrogen gas at −50°C, and the radiation used was Mo–K$_\alpha$ monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 2. Intensities were measured using the omega scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant variation. During data reduction, Lorentz and polarization corrections were applied, however, no absorption correction was made. The structure was solved by interpretation of the Patterson map, which revealed the position of the Ru atom. Remaining non-hydrogen atoms were located in subsequent difference

Table 2
Summary of crystallographic parameters for complex **1**

	Complex
Formula	C$_{15}$H$_{39}$P$_4$Ru$^+ \cdot$C$_{32}$H$_{12}$BF$_{24}^-$
Formula weight	1307.74
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	19.402(6)
b (Å)	22.945(10)
c (Å)	24.571(8)
Z	8
V (Å^3)	10938
D (g cm^{-3})	1.59
Absorption coefficient (cm^{-1})	5.07
Temperature	−50°C
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)
Collection range	$4° \leq 2\theta \leq 45°$
Scan width (°)	$1.25 = (K_{\alpha_2} - K_{\alpha_1})$
Scan speed range (° cm^{-1})	2.0 to 15.0
Total data collected	7103
Independent data, $I = 3\sigma(I)$	4395
Total variables	646
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.055
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma_w\|F_o\|^2]^{1/2}$	0.045
Weights	$\sigma(F)^{-2}$

Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for all of them. The ethylene and methyl carbon atoms were, however, refined only isotropically.

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