

Synthesis and Reactivity of (DPPE){[(C₆H₅)(C₆H₄)PCH₂CH₂P(C₆H₅)₂]RuCl}

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Summary: The compound *trans*-(DPPE)₂RuCl₂ (**1**) undergoes reaction in neat trimethylaluminum to afford two products: *trans*-(DPPE)₂RuCH₃Cl (**2**) and (DPPE)-[(C₆H₅)(C₆H₄)PCH₂CH₂P(C₆H₅)₂]RuCl (**3**). Mechanistic studies suggest that the ortho-metalation reaction proceeds via the cationic intermediate [(DPPE)₂RuCH₃]⁺ (**5**). The X-ray crystal structures of complex **3** and the cation of [(DPPE){[(C₆H₅)(C₆H₄)PCH₂CH₂P(C₆H₅)₂]Ru}]⁺[PF₆]⁻ (**6**) are reported.

Transition-metal compounds in combination with Lewis acids are known to polymerize¹ or oligomerize² olefins. Late-transition-metal compounds are of current interest in the development of new types of Ziegler–Natta catalysts because they are less oxophilic than earlier transition metals, which should lead to an enhanced tolerance of polar functional groups.^{3,4} Cationic nickel- and palladium-based metal alkyls were recently found to polymerize olefins to high-molecular-weight and highly crystalline polymers.³ Although ruthenium-based catalysts have been shown to be effective in the metathesis polymerization of cyclic olefins (where they are tolerant of functional groups and aqueous environments),⁴ there are few examples of olefin polymerization/oligomerization via a coordinative insertion mechanism in Ru-based systems.⁵

Our research focuses on the development of ruthenium alkyls for olefin polymerization. One of our early targets has been *cis*-(DPPE)₂RuCH₃Cl, whose synthesis is reported in the literature.⁶ Following the reported procedure, we heated *trans*-(DPPE)₂RuCl₂ in neat AlMe₃ at 80 °C for 5 min, which generated an oily red residue. After washing with ethanol, analysis of the resulting yellow solid surprisingly revealed a mixture of two compounds: the monoalkylated *trans*-(DPPE)₂RuCH₃-Cl (**2**)⁷ and the ortho-metalated (DPPE)(C₆H₅)(C₆H₄)-

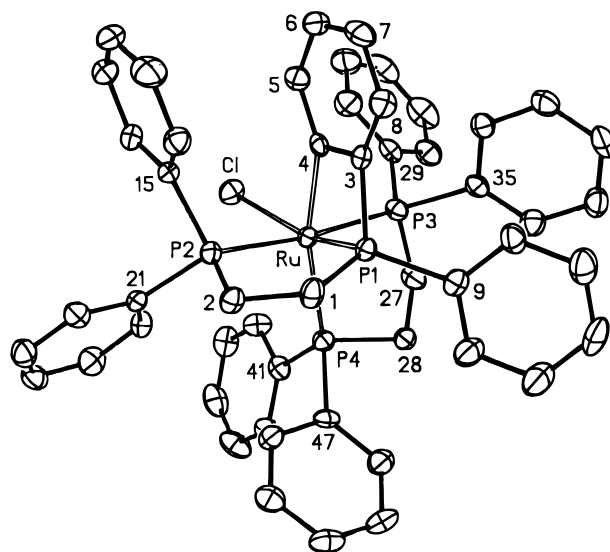


Figure 1. ORTEP drawing (40% probability level) of (DPPE){[(C₆H₅)(C₆H₄)PCH₂CH₂P(C₆H₅)₂]RuCl} (**3**). Parameters: Ru–P(1) = 2.260(1), Ru–P(2) = 2.331(1), Ru–P(3) = 2.371(1), Ru–P(4) = 2.383(1), Ru–C(4) = 2.12(4), Ru–Cl = 2.488(1) Å; P(1)–Ru–C(4) = 67.7(2), P(2)–Ru–C(4) = 84.6(1), P(3)–Ru–C(4) = 89.3(1), P(4)–Ru–C(4) = 164.6(2), Cl–Ru–C(4) = 92.6(2)°.

PCH₂CH₂P(C₆H₅)₂RuCl (**3**)⁸ in about a 1:9 ratio, respectively, rather than the reported *cis*-(DPPE)₂RuCH₃Cl.⁶ When the reaction was conducted at 90 °C, compound **3** was the sole product; conversely, when the temperature was held at 40 °C, compound **2** was the major product (≥95%). Also, **3** can be generated directly from **2** by heating the precursor to 90 °C in neat AlMe₃.

The structure of **3** was determined by single-crystal X-ray diffraction, which revealed a distorted octahedron with the ortho-metalated ruthenium–carbon bond *cis* to the chloride (Figure 1). The Ru–C(sp²) distance is 2.12 Å, which is consistent with those observed in ortho-metalated complexes such as Ru(C₆H₄PPh₂)(PPh₃)(η⁵-C₅H₅) and related compounds.^{9,10} The bond angles in

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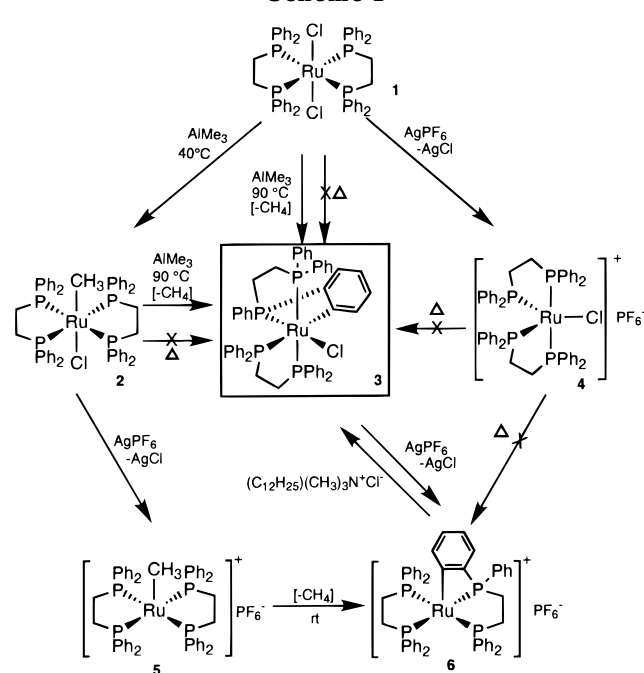
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(7) Prepared separately by heating 0.50 g of **1** (5.2 × 10⁻⁴ mol) in neat AlMe₃ (1.5 mL) for 5 min at 40 °C. Yield: 34% of pale yellow crystals (recrystallized from CH₂Cl₂/Et₂O). ¹H NMR (CD₂Cl₂; 300 MHz; 293 K): δ -1.9 (quint, 3 H, Ru–CH₃, J_{PH} = 5.4 Hz), 2.5 (m, 8 H, Ph₂PCH₂CH₂PPh₂), 6.5–8.0 (m, 40 H, Ph₂PCH₂CH₂PPh₂). ³¹P{¹H} NMR (CD₂Cl₂; 121 MHz; 293 K): δ 57.0 (s). Anal. Calcd for C₅₃H₅₁Cl₂P₄Ru: C, 67.16; H, 5.39. Found: C, 66.89; H, 5.17.

(8) Prepared separately by heating 0.50 g of **1** (5.2 × 10⁻⁴ mol) in neat AlMe₃ (1.5 mL) for 5 min at 90 °C. The red oily product was washed with hexane and stirred with EtOH. The resulting yellow precipitates were extracted with benzene, and recrystallized from CH₂Cl₂/Et₂O. Yield: 68% of yellow crystals. Crystal data: C₅₂H₄₇ClP₄Ru, *M*_r = 932.32; orthorhombic; *Pna*2₁; *a* = 16.366(3) Å, *b* = 20.657(5) Å, *c* = 12.773(3) Å; *V* = 4318 Å³; *Z* = 4; *D* = 1.43 g/cm³. ¹H NMR (CD₂Cl₂; 300 MHz; 293 K): δ 5.0–4.6 (m, 8 H, Ph₂PCH₂CH₂PPh₂), 7.7–9.8 (m, 39 H, Ph₂PCH₂CH₂PPh₂). ¹³C NMR (CD₂Cl₂; 75.5 MHz; 293 K): δ 29.0 (m), 29.1 (m), 22.3 (m), 24.1 (m), 122.3–134.0 (m). ³¹P{¹H} NMR (CD₂Cl₂; 121 MHz; 293 K): ABCD pattern, δ 12.7 (m), 32.2 (m), 41.2 (dd), 43.6 (dd), 48.7 (dd), 51.5 (dd). Mp: 314 °C dec. Anal. Calcd for C₅₂H₄₇ClP₄Ru: C, 66.92; H, 5.04. Found: C, 66.61; H, 5.10.

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Scheme 1



the four-membered metallacycle are typical of those reported in the literature;¹¹ compound **3**, for example, has a P–Ru–C angle of 67.7°.

In experiments at room temperature, exposure of **3** in C₆D₆ to HCl generated *cis*- and *trans*-(DPPE)₂RuCl₂.¹² Exposure of **3** in CD₂Cl₂ to H₂ generated *trans*-(DPPE)₂RuHCl.¹³ Complex **3** did not, however, appear to react in CD₂Cl₂ with 1 atm of either CO or CH₂=CH₂.

Examples of the ortho-metallation of aryl phosphine ligands during the alkylation of ruthenium are well-known.^{10,11,14} The exact mechanism of the ortho-metallation reaction, however, has not been firmly established. We undertook several studies in an effort to probe the mechanistic details of our system (Scheme 1).

The three cationic compounds [(DPPE)₂RuCl]⁺[PF₆][−] (**4**),¹⁵ [(DPPE)₂RuCH₃]⁺[PF₆][−] (**5**),¹⁶ and [(DPPE){(C₆-H₅)(C₆H₄)PCH₂CH₂P(C₆H₅)₂}Ru]⁺[PF₆][−] (**6**)¹⁷ were cleanly obtained by the reaction of **1–3**, respectively, with AgPF₆ in CH₂Cl₂. Analysis by single-crystal X-ray diffraction shows that the cation of **6** exists as a distorted square pyramid with the orthometalated

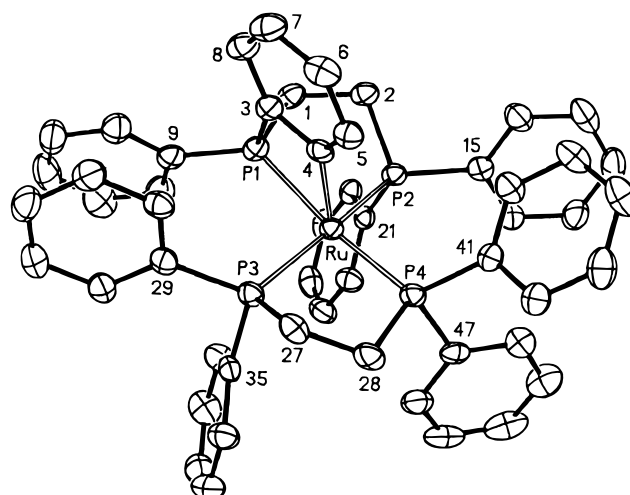


Figure 2. ORTEP drawing (40% probability level) of [(DPPE){(C₆H₅)(C₆H₄)PCH₂CH₂P(C₆H₅)₂}Ru]⁺ (cation of **6**). Parameters: Ru–P(1) = 2.340(1), Ru–P(2) = 2.349(1), Ru–P(3) = 2.319(1), Ru–P(4) = 2.332(1), Ru–C(4) = 2.12(5) Å; P(1)–Ru–C(4) = 68.3(1)°, P(2)–Ru–C(4) = 100.2(1)°, P(3)–Ru–C(4) = 88.2(1)°, P(4)–Ru–C(4) = 98.0(1)°.

carbon in an apical position (Figure 2). The Ru–C(sp²) distance is 2.05 Å, which is shorter than the analogous bond in **3**.

The structural relationship between the phenyl groups and the chloride atoms in **1** and **3** prohibits direct thermal elimination of HCl from **1** as the mechanism for generating **3**. Similarly, direct thermal elimination of CH₄ from **2** is untenable (see Scheme 1). The generation of **3** might proceed *via* dissociation of one of the DPPE phosphines in **1** followed by the oxidative addition of an aryl C–H bond with consequent reductive elimination of CH₄ and reattachment of the phosphine. Heating compound **1** in refluxing benzene or toluene in the absence of AlMe₃, however, fails to generate **3** (Scheme 1). Consequently, phosphine dissociation, if it were to occur, would appear to require the assistance of AlMe₃. Since, however, the enthalpy of formation of arylphosphine–AlX₃ adducts is only weakly favorable,¹⁸ and the abstraction of chlorine from metal complexes by alkylaluminum compounds is well-documented,¹⁹ the role of AlMe₃ is probably to abstract a chlorine (rather than a phosphine) from **1**. These factors suggest a mechanism alternative to phosphine dissociation for the generation of **3**.

There remain at least four plausible mechanisms by which **3** might be produced during the attempted synthesis of *cis*-(DPPE)₂RuCH₃Cl from **1**. The first involves isomerization of **1** to *cis*-(DPPE)₂RuCl₂ followed

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(16) Prepared by reacting 0.050 g of **2** (5.3 × 10^{−5} mol) with 0.013 g of AgPF₆ (5.3 × 10^{−5} mol) in 15 mL of CH₂Cl₂ at room temperature for 1 min. ¹H NMR (CD₂Cl₂; 300 MHz; 293 K): δ −0.9 (quint, 3 H, Ru–CH₃, J_{PH} = 6 Hz), 2.4–2.7 (m, 8 H, Ph₂PCH₂CH₂PPh₂), 6.8–7.4 (m, 40 H, Ph₂PCH₂CH₂PPh₂). ³¹P{¹H} NMR (CD₂Cl₂; 121 MHz; 293 K): δ 56.4 (s). These data strongly support a square-pyramidal structure for **5**. Theoretical studies also support this geometry: Rachidi, I. E.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, 14, 671. Reihl, J. F.; Eisenstein, O.; Pellissier, M. *Organometallics* **1992**, 11, 729.

(17) Prepared by reacting 0.100 g of **3** (1.07 × 10^{−4} mol) with 0.028 g of AgPF₆ (1.1 × 10^{−4} mol) in 20 mL of CH₂Cl₂ at room temperature for 30 min. The solvent was removed under vacuum, and the residue was washed with hexane and then recrystallized from CH₂Cl₂/Et₂O. Yield: 90% of red crystals. Crystal data: C₅₂H₄₇F₆P₃Ru, M_r = 1041.5; monoclinic; P2₁/c; a = 13.379(3) Å, b = 26.742(6) Å, c = 14.685(3) Å; V = 5003 Å³; Z = 4; D = 1.50 g/cm³. ¹H NMR (CD₂Cl₂; 300 MHz; 293 K): δ 2.5–3.2 (m, 8 H, Ph₂PCH₂CH₂PPh₂), 5.8–7.7 (m, 39 H, Ph₂PCH₂CH₂PPh₂). ¹³C NMR (CD₂Cl₂; 75.5 MHz; 293 K): δ 22.5 (dd), 24.3 (dd), 28.5 (m), 122.5–134.4. ³¹P{¹H} NMR (CD₂Cl₂; 121 MHz; 293 K): ABCD pattern, δ 5.7 (dd), 7.7 (dd), 51.2 (dd), 53.2 (dd), 63.5 (dd), 65.4 (dd), 66.1 (dd), 68.1 (dd). A satisfactory analysis could not be obtained. Anal. Calcd for C₅₂H₄₇F₆P₃Ru: C, 59.97, H, 4.51. Found: C, 59.23; H, 4.46.

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by concerted thermal elimination of HCl. The second involves alkylation of **1** to generate *cis*-(DPPE)₂RuCH₃Cl, which then undergoes concerted thermal elimination of CH₄. The third involves loss of Cl[−] from **1** to generate the cation of **4**, which then undergoes concerted thermal elimination of HCl to generate **6** followed by readdition of Cl[−]. The fourth involves alkylation of **1** and loss of Cl[−] to generate the cationic intermediate **5**; this intermediate then undergoes concerted thermal elimination of CH₄ followed by readdition of Cl[−].

Although we have no evidence for the presence of either *cis*-(DPPE)₂RuCl₂ or *cis*-(DPPE)₂RuCH₃Cl under the reaction conditions, we explored the likelihood of generating **3** from these intermediates by examining the reactivity of two closely related complexes where the chloride and methyl ligands are constrained to be *cis*; these complexes employ the tetradentate phosphine ligand tris(2-(diphenylphosphino)ethyl)phosphine (PP₃): (PP₃)RuCl₂²⁰ and (PP₃)RuCH₃Cl.²¹ Stirring these complexes at room temperature in CH₂Cl₂ for 2 days nor refluxing in toluene for 24 h nor heating the solids to 100 °C for 2 days produced any trace of the analog to **3**. Although the arylphosphine ligands used here are different from those in Scheme 1, these results are nevertheless consistent with the notion that neither *cis*-(DPPE)₂RuCl₂ nor *cis*-(DPPE)₂RuCH₃Cl is the direct precursor to **3**.

In other experiments (Scheme 1), compounds **1** and **2** failed to give **3** upon refluxing in benzene or toluene for several hours or in CH₂Cl₂ for 3 days. Compound **4** failed to give either **3** or **6** upon refluxing in benzene, toluene, or CH₂Cl₂ for 1 day. The latter observations strongly suggest that the pathway to **3** does not proceed through **4**. Square-pyramidal **5** gradually underwent ortho metalation at room temperature in CD₂Cl₂ to give **6**. Compound **6** converted to **3** upon exposure to dodecyltrimethylammonium chloride at room temperature in CD₂Cl₂. Taken as a whole, these results are consistent only with the fourth mechanism. Furthermore, the observation of a red oily product upon the

reaction of *trans*-(DPPE)₂RuCl₂ with AlMe₃ is consistent with the formation of a cationic intermediate; the cations of **4**–**6** are red.

The reaction of **6** with dodecyltrimethylammonium chloride can be used to rationalize the observation that treatment of the red oily product with ethanol gives the yellow compound **3**. The AlMe₃Cl present in the mixture reacts with ethanol to give Al(OEt)₃ and Cl[−]. The free Cl[−] reacts with **6** to give **3**. This process probably involves rearrangement of a phosphine in **6** followed by the addition of Cl[−] *cis* to the ortho-metalated bond. Simple addition of Cl[−] to the vacant *trans* site in **6** is likely hindered by the presence of bulky chelating ligands in the equatorial position of the square-pyramidal structure; the two phenyl groups appear to block the vacant *trans* site.²²

In conclusion, exposure of *trans*-(DPPE)₂RuCl₂ to AlMe₃ forms *trans*-**2** and ortho-metalated **3**. We propose that the mechanism of the ortho metalation proceeds *via* the unsaturated cationic intermediate **5**. The direct observation and apparent ortho metalation of **5** provides, to our knowledge, the first experimental evidence for the existence of this type of intermediate in the ortho-metalation chemistry of ruthenium.²³

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Supporting Information Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters and figures giving unit cell views for **3** and **6** and a space-filling structure for **6** (25 pages). Ordering information is given on any current masthead page.

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(21) Prepared by reacting 1.1 equiv of MeLi with 0.30 g of (PP₃)-RuCl₂ (3.6 × 10^{−4} mol) for 2 h at room temperature in benzene. The solvent was removed under vacuum, and the residue was washed with hexane and then recrystallized from CH₂Cl₂/Et₂O. Yield: 34% of pale yellow crystals. ¹H NMR (C₆D₆; 300 MHz; 293 K): δ −0.3 (m, 3 H, Ru-CH₃), 1.4–1.9 (m, 6 H, P(CH₂CH₂PPh₂)₃), 2.5–2.7 (m, 6 H, P(CH₂CH₂PPh₂)₃), 6.5–8.4 (m, 30 H, P(CH₂CH₂PPh₂)₃). ¹³C NMR (C₆D₆; 75.5 MHz; 293 K): δ 3.3 (m), 4.1 (m), 26.0–30.3 (m), 127.8–142.0 (m). ³¹P{¹H} NMR (C₆D₆; 121 MHz; 293 K): δ 40.7 (t), 46.9 (t), 154.3 (t). A satisfactory analysis could not be obtained. Anal. Calcd for C₄₃H₄₅ClP₄Ru: C, 62.80; H, 5.48. Found: C, 61.86; H, 5.50.

(22) The space-filling structure generated from the crystallographic data shows that the two phenyl groups on the phosphine block the empty site *trans* to the ortho-metalated carbon–Ru bond. A view of the space-filling structure is included with the Supporting Information.

(23) Although a coordinatively unsaturated cation was proposed as an intermediate in a related ortho-metalation reaction,¹⁴ no experimental evidence was provided to support its existence.