Organometallics **1997,** *16,* 5613−5615

Synthesis and Reactivity of $(DPPE)\{(C_6H_5)(\overline{C_6H_4)PCH_2CH_2P(C_6H_5)_2\}}RuCl$

Kayo Umezawa-Vizzini and T. Randall Lee*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received July 24, 1997[⊗]

*Summary: The compound trans-$(DPPE)_2RuCl_2$ (**1**) undergoes reaction in neat trimethylaluminum to afford two products: trans-$(DPPE)_2RuCH_3Cl$ (**2**) and $(DPPE)\{(C_6H_5)(\overline{C_6H_4)PCH_2CH_2P(C_6H_5)_2\}}RuCl$ (**3**). Mechanistic studies suggest that the ortho-metalation reaction proceeds via the cationic intermediate $[(DPPE)_2RuCH_3]^+$ (**5**). The X-ray crystal structures of complex **3** and the cation of $[(DPPE)\{(C_6H_5)(\overline{C_6H_4)PCH_2CH_2P(C_6H_5)_2\}}Ru]^+[PF_6]^-$ (**6**) are reported.*

Transition-metal compounds in combination with Lewis acids are known to polymerize[1] or oligomerize[2] 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]

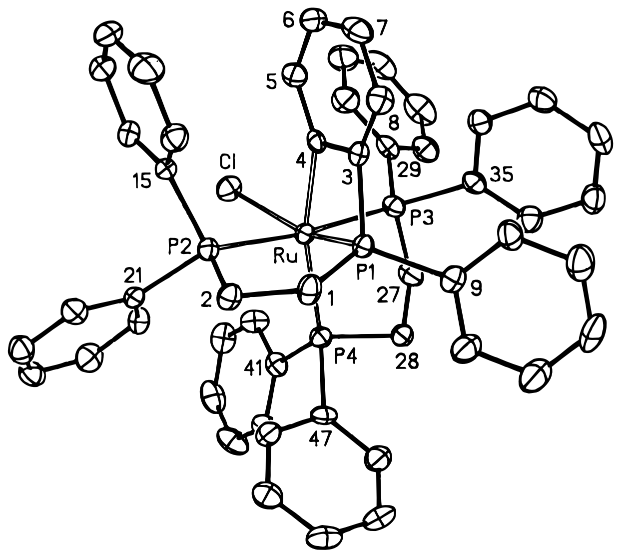


Figure 1. ORTEP drawing (40% probability level) of $(DPPE)\{(C_6H_5)(\overline{C_6H_4)PCH_2CH_2P(C_6H_5)_2\}}RuCl$ (**3**). Parameters: Ru−P(1) = 2.260(1), Ru−P(2) = 2.331(1), Ru−P(3) = 2.371(1), Ru−P(4) = 2.383(1), Ru−C(4) = 2.12(4), Ru−Cl = 2.488(1) Å; P(1)−Ru−C(4) = 67.7(2), P(2)−Ru−C(4) = 84.6(1), P(3)−Ru−C(4) = 89.3(1), P(4)−Ru−C(4) = 164.6(2), Cl−Ru−C(4) = 92.6(2)°.

Our research focuses on the development of ruthenium alkyls for olefin polymerization. One of our early targets has been *cis*-$(DPPE)_2RuCH_3Cl$, whose synthesis is reported in the literature.[6] Following the reported procedure, we heated *trans*-$(DPPE)_2RuCl_2$ in neat $AlMe_3$ 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*-$(DPPE)_2RuCH_3Cl$ (**2**)[7] and the ortho-metalated $(DPPE)(C_6H_5)(\overline{C_6H_4)PCH_2CH_2P(C_6H_5)_2Ru}Cl$ (**3**)[8] in about a 1:9 ratio, respectively, rather than the reported *cis*-$(DPPE)_2RuCH_3Cl$.[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 $AlMe_3$.

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(sp^2) distance is 2.12 Å, which is consistent with those observed in ortho-metalated complexes such as $\overline{Ru(C_6H_4}PPh_2)(PPh_3)(\eta^5\text{-}C_5H_5)$ and related compounds.[9,10] The bond angles in

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

(1) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123.

(2) Jones, J. R.; Symes, T. J. *J. Chem. Soc. C* **1971**, 1124. Kawakami, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 21.

(3) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664. Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(4) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345.

(5) James, B. R.; Markham, L. D. *J. Catalysis* **1972**, *27*, 442. Konita, S.; Yamamoto, A.; Ikeda, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 101.

(6) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1963**, 6017. Ginsberg, A. P.; Lindsell, W. E. *Inorg. Chem.* **1973**, *12*, 1983.

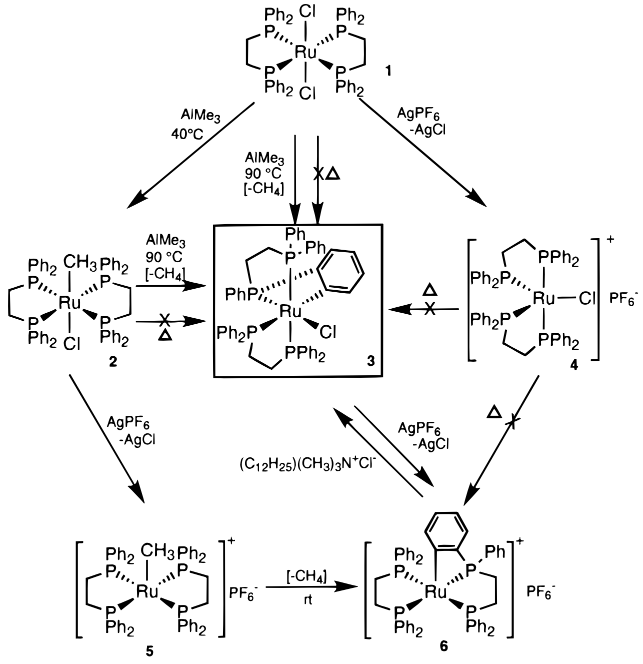
(7) Prepared separately by heating 0.50 g of **1** (5.2×10^{-4} mol) in neat $AlMe_3$ (1.5 mL) for 5 min at 40 °C. Yield: 34% of pale yellow crystals (recrystallized from CH_2Cl_2/Et_2O). ^1H NMR (CD_2Cl_2; 300 MHz; 293 K): δ −1.9 (quint, 3 H, Ru−CH_3, J_{PH} = 5.4 Hz), 2.5 (m, 8 H, $Ph_2PCH_2CH_2PPh_2$), 6.5−8.0 (m, 40 H, $Ph_2PCH_2CH_2PPh_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 121 MHz; 293 K): δ 57.0 (s). Anal. Calcd for $C_{53}H_{51}Cl_2P_4Ru$: 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 $AlMe_3$ (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 CH_2Cl_2/Et_2O. Yield: 68% of yellow crystals. Crystal data: $C_{52}H_{47}ClP_4Ru$, M_r = 932.32; orthorhombic; $Pna2_1$; a = 16.366(3) Å, b = 20.657(5) Å, c = 12.773(3) Å; V = 4318 Å^3; Z = 4; D = 1.43 g/cm^3. ^1H NMR (CD_2Cl_2; 300 MHz; 293 K): δ 5.0−4.6 (m, 8 H, $Ph_2PCH_2CH_2PPh_2$), 7.7−9.8 (m, 39 H, $Ph_2PCH_2CH_2PPh_2$. ^{13}C NMR (CD_2Cl_2; 75.5 MHz; 293 K): δ 29.0 (m), 29.1 (m), 22.3 (m), 24.1 (m), 122.3−134.0 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 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 $C_{52}H_{47}ClP_4Ru$: C, 66.92; H, 5.04. Found: C, 66.61; H, 5.10.

(9) Bruce, M. I.; Cifuentes, M. P.; Humphrey, G.; Poczman, E.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *338*, 237.

S0276-7333(97)00631-6 CCC: $14.00

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 C_6D_6 to HCl generated *cis*- and *trans*-$(DPPE)_2RuCl_2$.[12] Exposure of **3** in CD_2Cl_2 to H_2 generated *trans*-$(DPPE)_2RuHCl$.[13] Complex **3** did not, however, appear to react in CD_2Cl_2 with 1 atm of either CO or $CH_2{=}CH_2$.

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

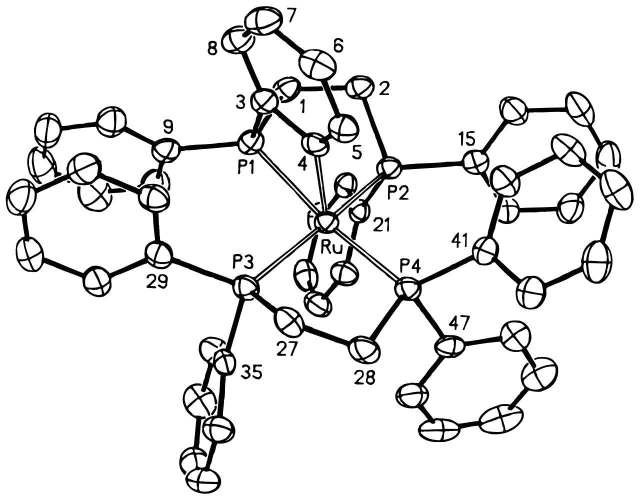


Figure 2. ORTEP drawing (40% probability level) of $[(DPPE)\{(C_6H_5)(C_6H_4)PCH_2CH_2P(C_6H_5)_2\}Ru]^+$ (cation of **6**). Parameters: Ru−P(1) = 2.340(1), Ru−P(2) = 2.349(1), Ru−P(3) = 2.319(1), Ru−P(4) = 2.332(1), Ru−C(4) = 2.12(5) Å; P(1)−Ru−C(4) = 68.3(1)°, P(2)−Ru−C(4) = 100.2(1)°, P(3)−Ru−C(4) = 88.2(1)°, P(4)−Ru−C(4) = 98.0(1)°.

The three cationic compounds $[(DPPE)_2RuCl]^+[PF_6]^-$ (**4**),[15] $[(DPPE)_2RuCH_3]^+[PF_6]^-$ (**5**),[16] and $[(DPPE)\{(C_6H_5)(C_6H_4)PCH_2CH_2P(C_6H_5)_2\}Ru]^+[PF_6]^-$ (**6**)[17] were cleanly obtained by the reaction of **1**−**3**, respectively, with $AgPF_6$ in CH_2Cl_2. Analysis by single-crystal X-ray diffraction shows that the cation of **6** exists as a distorted square pyramid with the orthometalated carbon in an apical position (Figure 2). The Ru−C(sp^2) 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 CH_4 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 CH_4 and reattachment of the phosphine. Heating compound **1** in refluxing benzene or toluene in the absence of $AlMe_3$, however, fails to generate **3** (Scheme 1). Consequently, phosphine dissociation, if it were to occur, would appear to require the assistance of $AlMe_3$. Since, however, the enthalpy of formation of arylphosphine−AlX_3 adducts is only weakly favorable,[18] and the abstraction of chlorine from metal complexes by alkylaluminum compounds is well-documented,[19] the role of $AlMe_3$ 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*-$(DPPE)_2RuCH_3Cl$ from **1**. The first involves isomerization of **1** to *cis*-$(DPPE)_2RuCl_2$ followed

---

(10) Advasio, V.; Diversi, P.; Ingrosso, G.; Lucherini A.; Marchetti, F.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1992**, 3385. Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti F.; Adovasio, V.; Nardelli, M. *J. Chem. Soc. Dalton Trans.* **1990**, 1779.

(11) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 797. Chappell, S. D.; Engelhardt, L. M.; White, A. H. *J. Organomet. Chem.* **1993**, *462*, 295. Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467.

(12) Mason, R.; Meek, D. W.; Scollary, G. R. *Inorg. Chim. Acta* **1976**, *16*, L11.

(13) James, B. R.; Wang, D. K. W. *Inorg. Chim. Acta* **1976**, *19*, L17.

(14) Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1991**, 203.

(15) Chin, A.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278.

(16) Prepared by reacting 0.050 g of **2** (5.3×10^{-5} mol) with 0.013 g of $AgPF_6$ (5.3×10^{-5} mol) in 15 mL of CH_2Cl_2 at room temperature for 1 min. ^1H NMR (CD_2Cl_2; 300 MHz; 293 K): δ −0.9 (quint, 3 H, Ru−CH_3, J_{PH} = 6 Hz), 2.4−2.7 (m, 8 H, $Ph_2PCH_2CH_2PPh_2$), 6.8−7.4 (m, 40 H, $Ph_2PCH_2CH_2PPh_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 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 $AgPF_6$ (1.1×10^{-4} mol) in 20 mL of CH_2Cl_2 at room temperature for 30 min. The solvent was removed under vacuum, and the residue was washed with hexane and then recrystallized from CH_2Cl_2/Et_2O. Yield: 90% of red crystals. Crystal data: $C_{52}H_{47}F_6P_5Ru$, M_r = 1041.5; monoclinic; $P2_1/c$; a = 13.379(3) Å, b = 26.742(6) Å, c = 14.685(3) Å; V = 5003 Å^3; Z = 4; D = 1.50 g/cm^3. ^1H NMR (CD_2Cl_2; 300 MHz; 293 K): δ 2.5−3.2 (m, 8 H, $Ph_2PCH_2CH_2PPh_2$), 5.8−7.7 (m, 39 H, $Ph_2PCH_2CH_2PPh_2$). ^{13}C NMR (CD_2Cl_2; 75.5 MHz; 293 K): δ 22.5 (dd), 24.3 (dd), 28.5 (m), 122.5−134.4. $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 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 $C_{52}H_{47}F_6P_5Ru$: C, 59.97, H, 4.51. Found: C, 59.23; H, 4.46.

(18) Levason, W.: McAuliffe, C. A. *Coord. Chem. Rev.* **1976**, *19*, 173.

(19) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J. *J. Am. Chem. Soc.* **1985**, *107*, 7219. Tebbe, F. N.; Parshall, S. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

by concerted thermal elimination of HCl. The second involves alkylation of **1** to generate *cis*-$(DPPE)_2RuCH_3Cl$, which then undergoes concerted thermal elimination of CH_4. 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 CH_4 followed by readdition of Cl^-.

Although we have no evidence for the presence of either *cis*-$(DPPE)_2RuCl_2$ or *cis*-$(DPPE)_2RuCH_3Cl$ 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 (PP_3): $(PP_3)RuCl_2$[20] and $(PP_3)RuCH_3Cl$.[21] Stirring these complexes at room temperature in CH_2Cl_2 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*-$(DPPE)_2RuCl_2$ nor *cis*-$(DPPE)_2RuCH_3Cl$ 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 CH_2Cl_2 for 3 days. Compound **4** failed to give either **3** or **6** upon refluxing in benzene, toluene, or CH_2Cl_2 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 CD_2Cl_2 to give **6**. Compound **6** converted to **3** upon exposure to dodecyltrimethylammonium chloride at room temperature in CD_2Cl_2. 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*-$(DPPE)_2RuCl_2$ with $AlMe_3$ 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 $AlMe_3Cl$ 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*-$(DPPE)_2RuCl_2$ to $AlMe_3$ 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]

Acknowledgment. The National Science Foundation (CAREER Award to T.R.L.; Grant No. CHE-9625003), the Camille and Henry Dreyfus Foundation (New Faculty Award to T.R.L.; Grant No. NF-93-040), the University of Houston Limited Grant-In-Aid program, and the University of Houston Environmental Institute provided generous support for this research. We thank Dr. James Korp for technical assistance with X-ray crystallographic analyses, and we thank our colleagues Tom Albright, David Hoffman, and June-Ho Jung for helpful comments.

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.

OM970631A

---

[20] Bianchini, C.; Perez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.

[21] Prepared by reacting 1.1 equiv of MeLi with 0.30 g of $(PP_3)RuCl_2$ (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 CH_2Cl_2/Et_2O. Yield: 34% of pale yellow crystals. ^1H NMR (C_6D_6; 300 MHz; 293 K): δ −0.3 (m, 3 H, Ru−CH_3), 1.4−1.9 (m, 6, H, P($CH_2CH_2PPh_2)_3$), 2.5−2.7 (m, 6 H, P($CH_2CH_2PPh_2)_3$), 6.5−8.4 (m, 30 H, P($CH_2CH_2PPh_2)_3$). ^{13}C NMR (C_6D_6; 75.5 MHz; 293 K): δ 3.3 (m), 4.1 (m), 26.0−30.3 (m), 127.8−142.0 (m). $^{31}P\{^1H\}$ NMR (C_6D_6; 121 MHz; 293 K): δ 40.7 (t), 46.9 (t), 154.3 (t). A satisfactory analysis could not be obtained. Anal. Calcd for $C_{43}H_{45}ClP_4Ru$: 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.