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Reactions of (η^5-Indenyl)Ru(PPh_3)$_2$Cl with CH_2Cl_2 and $CHCl_3$: Formation of (η^5-Indenyl)Ru{$CH_2PPh_2(C_6H_4)$}(PPh_3) and (η^5-Indenyl)Ru(PPh_3)(CO)Cl

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*Summary: A cyclic phosphorus ylide complex, (η^5-indenyl)Ru{$CH_2PPh_2(C_6H_4)$}(PPh_3) (**2**), and (η^5-indenyl)Ru(PPh_3)(CO)Cl (**3**) were formed in the reactions of (η^5-indenyl)Ru(PPh_3)$_2$Cl (**1**) with CH_2Cl_2 and $CHCl_3$ in the presence of KOH and 2-propanol, respectively.*

(η^5-Indenyl)Ru(PPh_3)$_2$Cl (**1**) and related half-sandwich ruthenium complexes have been known as versatile catalysts in many useful transformations.[1] Recently, we have found it is an effective catalyst for the racemization of secondary alcohols in the presence of bases,[2] which can be coupled with enzymatic acetylation for dynamic kinetic resolution of the racemic alcohols to chiral acetates.[3] As an unexpected result from this study, formation of a noble cyclic ruthenium phosphorus ylide complex, (η^5-indenyl)Ru{$CH_2PPh_2(C_6H_4)$}(PPh_3) (**2**), was observed when dichloromethane was used as a solvent. This result implicates the C−Cl bond activation and led us to the investigation for the reaction of **1** with various haloalkanes in the presence of potassium hydroxide and 2-propanol (Scheme 1).[4,5]

Complex **2** was obtained in 95% yield by mixing a solution of complex **1** in CH_2Cl_2 and a solution of KOH in 2-propanol for 6 h at room temperature. Characteristic peaks for diastereotopic methylene protons were shown at 0.72 and 1.34 ppm in the ^{1}H NMR spectrum of **2**. By a separate experiment with CD_2Cl_2, it was confirmed that the source of the methylene unit is dichloromethane. Recrystallization of **2** provided single crystals suitable for X-ray diffraction analysis. The molecular structure of **2** revealed the incorporation of a methylene moiety between Ru and P and the orthometalation of the triphenylphosphine ligand to form a five-membered cyclic phosphorus ylide structure (Figure 1). The indenyl ligand is bound to the ruthenium in an η^5-fashion and shows no significant distortion. The bond distance between the ruthenium and the ylide carbon is 2.17 Å, which is almost the same as that found in a linear phosphorus ylide ruthenium complex.[6]

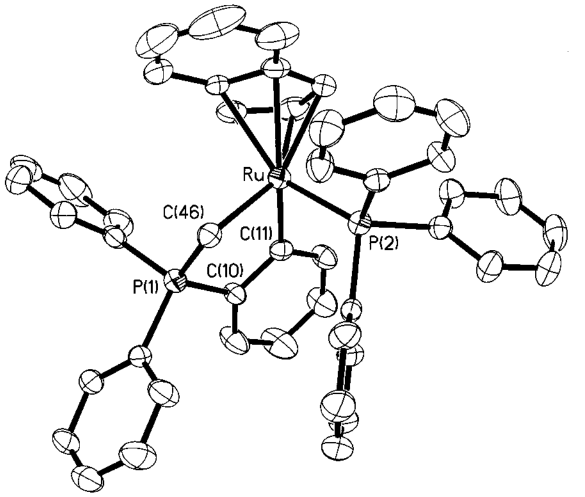

Figure 1. ORTEP drawing (50% probability) of the structure of **2** at 293 K. Selected bond distances (Å): Ru−C(46) = 2.170(4), Ru−C(11) = 2.055(4), Ru−P(2) = 2.2564(13), C(46)−P(1) = 1.743(4), P(1)−C(10) = 1.768(4), C(10)−C(11) = 1.403(6). Selected bond angles (deg): C(46)−Ru−C(11) = 85.6(2), C(46)−Ru−P(2) = 88.36(12), C(11)−Ru−P(2) = 91.30(11), Ru−C(46)−P(1) = 104.9(2), C(46)−P(1)−C(10) = 106.0(2), P(1)−C(10)−C(11) = 112.3(3), C(10)−C(11)−Ru = 120.3(3).

To investigate the scope of the phosphorus ylide complex forming reaction,[7,8] dibromomethane, diiodomethane, 1,2-dichloroethane, and chloroform were subjected to the reaction with **1** (Scheme 1). Simple

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(2) Koh, J. H.; Jeong, H. M.; Park, J. *Tetrahedron Lett.* **1998**, *39*, 5545.

(3) Koh, J. H.; Jung, H. M.; Kim, M.-J.; Park, J. *Tetrahedron Lett.* **1999**, *40*, 6281.

(4) For the activation of haloalkanes by metal complexes, see: (a) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2000**, *41*, 6071. (b) Humann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chem.* **1999**, *38*, 115. (c) Oliván, M.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 566. (d) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543. (e) Weinberger, B.; Tanguy, G.; Abbayes, H. D. *J. Organomet. Chem.* **1985**, *280*, C31.

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(6) Burrell, A. K.; Clark, G. R.; Rickard, C. E. R.; Roper, W. R.; Wright, A. H. *J. Chem. Soc., Dalton Trans.* **1991**, 609.

(7) For a review of metal phosphorus ylide complexes, see: Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

(8) For examples of the formation of cyclic metal phosphorus ylide complexes through orthometalation, see: (a) Koch, J. L.; Shapley, P. A. *Organometallics* **1999**, *18*, 814. (b) Caballero, C.; Chávez, Göknur, Ö.; Löchel, I.; Nuber, B.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1989**, *371*, 329. (c) Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1984**, *273*, C17. (d) Illingsworth, M. L.; Teagle, J. A.; Burmeister, J. L.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1983**, *2*, 1364.

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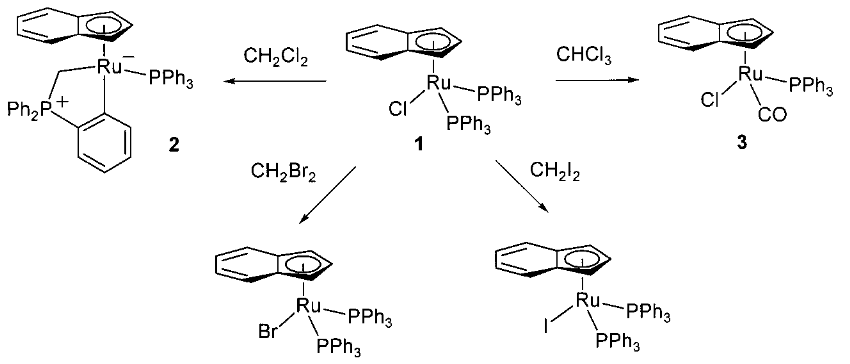
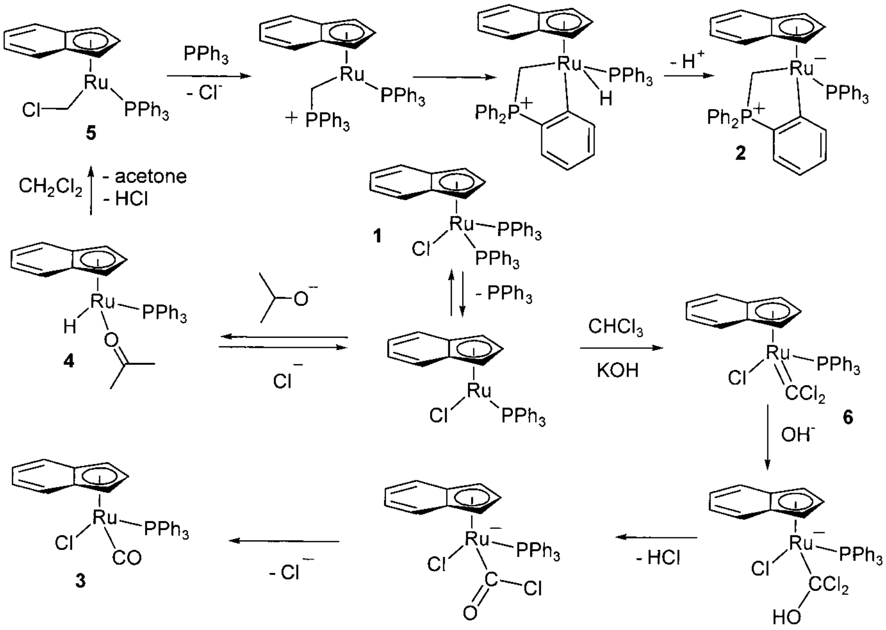
Scheme 1. Reactions of 1 with Haloalkanes



Scheme 2. Proposed Pathways for the Formation of 2 and 3



substitution of the chloride ligand in **1** occurred in the reactions with dibromomethane and diiodomethane to give (η^5-indenyl)Ru(PPh$_3$)$_2$Br and (η^5-indenyl)Ru(PPh$_3$)$_2$I in 55% and 82% yields,[2,9] respectively, while starting complex **1** was recovered from the reaction with 1,2-dichloroethane. Meanwhile, (η^5-indenyl)Ru(PPh$_3$)(CO)-Cl (**3**) was produced in 60% yield in the reaction with dry chloroform. For the formation of **3**, participation of hydroxide ion was speculated, and, in fact, the yield of **3** increased up to 89% by the use of wet chloroform and excess KOH. The spectral data of **3** were consistent with the replacement of one phosphine ligand with CO. Furthermore, the formation of CpRu(PPh$_3$)(CO)Cl in the reaction of CpRu(PPh$_3$)$_2$Cl under conditions similar to that for **3** supported the replacement, which has been synthesized from CpRu(PPh$_3$)$_2$Cl under CO pressure.[10]

In attempts to observe any intermediate for the formation of **2** and **3** by ^{1}H and ^{31}P NMR, only starting ruthenium complex **1** and the final products **2** and **3** were observed. A speculated intermediate, (η^5-indenyl)-Ru(PPh$_3$)$_2$H, was inert under conditions similar to that for the transformation of **1** to **2**. However, interestingly, (η^5-indenyl)Ru(PPh$_3$)$_2$H was slowly converted to a mixture of **1** and **2** when the reaction temperature was raised to 40 °C.

A proposal for the formation of **2** and **3** is shown in Scheme 2. The key step for **2** would be the generation of labile acetone complex **4** with losing one phosphine ligand,[11] from which detachment of acetone provides a coordinatively unsaturated intermediate to activate the C−Cl bond of dichloromethane.[12] The inhibition effect of additional PPh$_3$ was clearly observed,[13] and the results from the experiments with (η^5-indenyl)Ru-(PPh$_3$)$_2$H support that the dissociation of PPh$_3$ rather than indenyl ring slippage would be more responsible for generating coordinatively unsaturated intermediates. From chloromethyl intermediate **5**, intramolecular nucleophilic substitution and orthometalation followed by deprotonation led to the formation of **2**.[8,14] Meanwhile, dichlorocarbene complex **6** would be a key intermediate for **3**,[15] of which carbene carbon is attacked by

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[9] Oro, L. A.; Ciriano, M. A.; Campo, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *289*, 117.

[10] Davies, S. G.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1984**, 993.

[11] Gamasa, M. P.; Gimeno, J.; Gonzalez-Bernardo, C.; Martín-Vaca, B. M.; Monti, D.; Bassetti, M. *Organometallics* **1996**, *15*, 302.

[12] The use of potassium *tert*-butoxide instead of 2-propanol/KOH was not effective for the production of **2** in the reaction of **1** with dichloromethane.

[13] Under the conditions described in the Experimental Section, complex **2** was not formed when PPh$_3$ (3 equiv) was added.

[14] It is also possible that complex **2** is formed via the formation of a carbene complex from the chloromethyl intermediate. See refs 4c and 8c.

Table 1. Crystallographic Data for 2

formula	$C_{46}H_{38}P_2Ru$	radiation (λ, Å)	0.71073
mol wt	753.77	$F(000)$	386
space group	$P1$	μ, mm^{-1}	0.272
a, Å	9.669(2)	T, K	293(2)
b, Å	11.245(2)	scan mode	ω
c, Å	17.375(4)	no. of meads rflns	3309
α, deg	102.05(3)	no. of indep rflns	3206
β, deg	90.95(3)	refinement mothod	full-matrix least-squres on F^2
γ, deg	94.60(3)	goodness of fit on F^2	1.105
V, Å^3	1840.5(6)	final R indices ($I > 2\sigma(I)$)	R1 = 0.0272, wR2 = 0.0620
Z	1	R indices (all data)	R1 = 0.0333, wR2 = 0.0685
d_{calcd}, g cm^{-3}	0.678		

hydroxide, followed by deprotonation and elimination of chlorides to afford the carbonyl ligand.

In summary, we have found the activation of dichloromethane by (η^5-indenyl)Ru(PPh_3)$_2$Cl in the presence of KOH and 2-propanol to form a novel cyclic ruthenium phosphorus ylide complex. In addition, easy ways to prepare (η^5-indenyl)Ru(PPh_3)(CO)Cl and CpRu(PPh_3)(CO)Cl have been introduced from the reactions of chloroform with (η^5-indenyl)Ru(PPh_3)$_2$Cl and CpRu(PPh_3)$_2$Cl, respectively.

Experimental Section

All manipulations except workup and purification were carried out under an atmosphere of argon using standard Schlenk techniques. Et_2O, THF, and hexane were distilled from sodium-benzophenone ketyl. Dichloromethane and chloroform were distilled from P_2O_5. (η^5-Indenyl)Ru(PPh_3)$_2$Cl and (η^5-indenyl)Ru(PPh_3)$_2$H were prepared according to the literature procedures.[9]

If not otherwise stated, all NMR spectra were recorded on a Bruker AM 300 or DPX 300. Chemical shifts are given in δ ppm downfield from tetramethylsilane as an internal standard and from aqueous 85% phosphoric acid solution (δ 0, ^{31}P) as an external standard. IR spectra were taken for the thin films of samples on NaCl plates. Mass spectral analysis was recorded on a JEOL JMS-AM505WA and is reported in units of mass to charge (*m*/*e*). Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Center for Biofunctional Molecules at Pohang University of Science and Technology.

(η^5-Indenyl)Ru{$CH_2PPh_2(C_6H_4)$}(PPh_3) (2). To a solution of **1** (82 mg, 0.10 mmol) in CH_2Cl_2 (2.0 mL) was added a solution of KOH (30 mg, 0.50 mmol) in 2-propanol (0.80 mL, 10 mmol). After being stirred for 6 h at room temperature, the reaction mixture was concentrated, and the residue was chromatographed to give 72 mg (95%) of orange solid **2**, which was then recrystallized from a mixture of Et_2O and hexane. Mp: 185 °C (dec). ^{1}H NMR (C_6D_6): δ 0.72 (ddd, J = 12.4 Hz, 9.7 Hz, 8.3 Hz, 1H), 1.34 (dd, J = 12.1 Hz, 12.1 Hz, 1H), 3.85 (s, 1H), 5.06 (t, J = 2.5 Hz, 1H), 5.14 (s, 1H), 6.62−7.14 (m, 30 H), 7.56 (m, 2H), 8.00 (m, 1H). ^{13}C NMR (C_6D_6): δ −10.0 (dd, J = 25.5 Hz, 7.9 Hz), 64.4 (d, J = 13.3 Hz), 68.4, 92.4, 106.6, 107.7, 119.5 (d, J = 12.6 Hz), 122.0 (d, J = 3.4 Hz), 122.4, 123.8, 127.1 (d, J = 2.6 Hz), 127.8 (d, J = 8.7 Hz), 128.4 (d, J = 7.6 Hz), 128.6 (d, J = 7.0 Hz), 128.8, 129.8, 130.8 (dd, J = 11.0 Hz, 8.7 Hz), 132.1 (d, J = 9.1 Hz), 132.2 (d, J = 2.4 Hz), 132.9 (d, J = 9.1 Hz), 134.4 (d, J = 17.1 Hz), 134.9, 138.7 (d, J = 34.9 Hz), 140.2, 141.9, 145.5 (dd, J = 14.8 Hz, 4.8 Hz), 194.7 (dd, J = 31.1 Hz, 17.1 Hz). ^{31}P NMR (C_6D_6): δ 32.9 (d, J = 3.2 Hz), 68.6 (d, J = 3.2 Hz). MS (FAB, *m*/*e*): 754 (M^+). Anal. Calcd for $C_{46}H_{38}P_2Ru$: C, 73.29; H, 5.08. Found: C, 72.95; H, 5.18.

X-ray Crystallography. A suitable crystal coated with Paratone was mounted on a Siemens SMART diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD detector. Data collection was performed with a detector distance of 6 cm. The raw data collected were processed to produce conventional intensity data by the program SAINT. The intensity data were corrected for Lorenz and polarization effects. The structure was solved by a combination of Patterson and difference Fourier methods provided by the program package SHELEXTL. All the non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and included in the final cycle of refinement. Crystallographic data of **2** are summarized in Table 1.

(η^5-Indenyl)Ru(PPh_3)(CO)Cl (3). To a solution of **1** (30 mg, 0.040 mmol) in degassed and wet $CHCl_3$ (3.0 mL) was added a solution of KOH (32 mg, 0.57 mmol) solution in 2-propanol (0.3 mL). After being stirred for 40 h at 30 °C, the reaction mixture was concentrated, and the residue was chromatographed to give 19.3 mg (89%) of yellow solid **3**, which was then recrystallized from a mixture of THF and hexane. Mp: 211 °C (dec). ^{1}H NMR (C_6D_6): δ 3.72 (s, 1H), 5.03 (t, J = 2.54 Hz), 5.45 (s, 1H), 6.59−7.60 (m, 18H). ^{13}C NMR (C_6D_6): δ 67.6, 73.8 (d, J = 43.5 Hz), 90.9, 114.5, 115.2, 123.1, 126.1, 128.7, 129.0, 129.1, 130.6, 134.4, 134.5, 134.9, 205.2 (d, J = 89.4 Hz). ^{31}P NMR (C_6D_6): δ 48.88 (s). IR (NaCl, cm^{-1}): ν(CO) 1944 (s). MS (FAB, *m*/*e*): 542 (M^+). Anal. Calcd for $C_{28}H_{22}ClOPRu$: C, 61.99; H, 4.20. Found: C, 61.46; H, 3.96.

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Supporting Information Available: Structural diagrams with full atom labeling and tables of bond distances, angles, anisotropic parameters, and atomic coordinates for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For examples of using chloroform and KOH for in situ generation of metal carbonyl complexes, see: Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 3846, and references therein.