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Phosphorane Migration from Ruthenium to the Cyclopentadienyl Ring

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Ruthenium phosphorane complexes, $Cp(CO)_2Ru\{\overline{P(OC_6H_4Z})_2\}$ (Z = NMe, O), react with lithium diisopropylamide (LDA) to give $Li[\{\eta^5\text{-}C_5H_4\overline{P(OC_6H_4Z})_2\}(CO)_2Ru]$ (**5**). In this reaction, one of the protons on the Cp ring is abstracted by LDA and then migration of the phosphorane fragment to the Cp ring takes place. Treatment of **5** with RX (CH_3I, $PhCH_2Cl$, Ph_3SnCl, $HOCOCF_3$, CD_3I) yields $\{\eta^5\text{-}C_5H_4\overline{P(OC_6H_4Z})_2\}(CO)_2RuR$ (**2**). The structure of one of the products, $\{\eta^5\text{-}C_5H_4\overline{P(OC_6H_4N}Me)_2\}(CO)_2RuCH_2Ph$, was determined by X-ray analysis. A reaction of a cationic phosphite complex, $[Cp(CO)_2Ru\{\overline{P(OC_6H_4N}Me)(OC_6H_4NMeH)\}]BF_4$ (**6**), with 2 equiv of LDA also gives **5**. However, the following addition of RX at −30 °C gives the unexpected phosphorane-migration complex $\{\eta^5\text{-}C_5H_4\overline{P(OC_6H_4N}Me)_2\}(CO)_2RuR$, which contains one O atom and one N atom in apical positions and in equatorial positions as well. The complex gradually isomerizes to a thermally more stable apical oxygen-equatorial nitrogen isomer (**2**).

Introduction

The formation and structure of hypervalent compounds of main-group elements continue to be an area of lively interest, and the results have been reviewed.[1−9] Their reactivities have also been investigated.[4,7−12] However, migration of a hypervalent fragment[13] has not been reported for any kind of hypervalent element. Recently we reported base-induced migration of a phosphorane fragment from iron to the cyclopentadienyl ring in $Cp(CO)_2Fe\{\overline{P(OC_6H_4Y)(OC_6H_4Z})\}$[14] (Cp = η^5-C_5H_5; Y, Z = NMe, N$\underline{H, O}$). This is the first example of a hypervalent fragment migration. We also reported syntheses and structures of ruthenium−phosphorane complexes.[15] This paper reports the second example of a hypervalent fragment migration: that is, a phosphorane migration for $Cp(CO)_2Ru\{P(OC_6H_4Z)_2\}$ (Cp = η^5-C_5H_5; Z = NMe, O) (Although the complex should be described as $Cp(CO)_2Ru\{\overline{P(OC_6H_4Z})_2\}$, the tie line is omitted for this type of complex in this paper for clarity.) The migration involves some interesting findings which have not been observed in the case of the related iron complexes.

Results and Discussion

Reactions of $[Cp(CO)_2Ru\{P(OC_6H_4Z)_2\}]$ with LDA and Then RX. The reaction procedures and characterization of the product are described with $Cp(CO)_2Ru\{P(OC_6H_4NMe)_2\}$ (**1**) as an example. Treatment of a yellow solution of **1** with 1 equiv of freshly prepared lithium diisopropylamide (LDA) at −78 °C in THF gave an orange solution. Successive addition of MeI gave a pale yellow suspension from which a white powder was obtained by purification using a silica gel column. For the following reasons, we concluded that a migration product of a phosphorane fragment to a Cp ligand (**2a**) was obtained. (i) The ^{31}P NMR spectrum exhibits a singlet at −47.27 ppm, which is ca. 40 ppm higher in magnetic field than that of **1**. (ii) The ^1H NMR spectrum shows a multiplet pattern and the ^{13}C NMR spectrum

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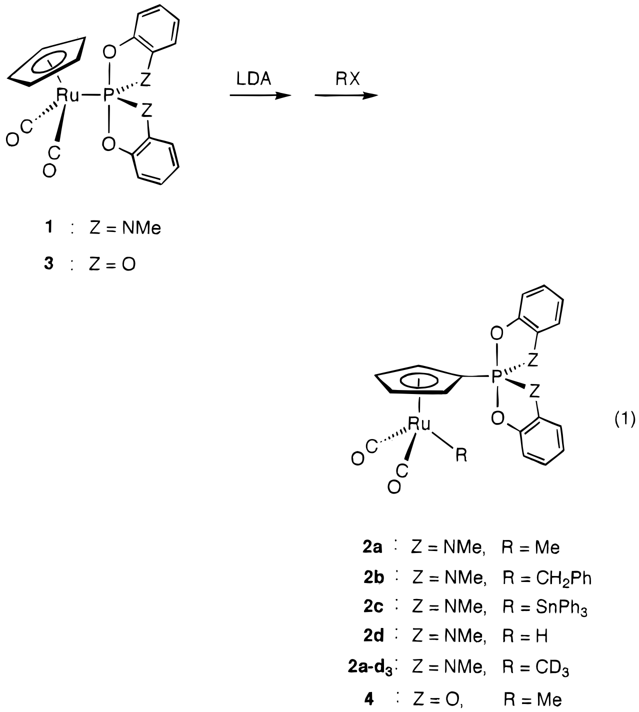
exhibits five doublets in the Cp region, suggesting that the product has a phosphorus-substituted Cp ligand. (iii) A singlet is observed at 0.27 ppm in the ^{1}H NMR spectrum and a singlet at −31.64 ppm in the ^{13}C NMR spectrum, indicating that a methyl group is bonded to the ruthenium atom. (iv) In the IR spectrum, two absorption bands due to ν_{CO} are observed at 2020 and 1959 cm^{-1}. These spectroscopic features are very similar to those for the corresponding iron complex.[14]

The reaction of **1** with LDA and then $PhCH_2Cl$, Ph_3SnCl, $HOCOCF_3$, and CD_3I in place of CH_3I gave **2b**−**d** and **2a-d$_3$**, respectively (eq 1). The formation of **2a-d$_3$** clearly demonstrates that the methyl group on Ru for **2a** comes from added MeI, not from the NMe group in the phosphorane fragment. The structure of **2b** was confirmed by an X-ray analysis (vide infra). These complexes correspond to the migration products of a phosphorane fragment from a ruthenium atom to the Cp ring. The reaction of **3**, having four O and one Ru atoms on the hypervalent phosphorus, with LDA and then MeI also led to the formation of the phosphorane-migration product **4**. These results show that the phosphorane migration reaction seems to be general. Diastereotopic β- and γ-carbon resonances in the Cp ring in the ^{13}C NMR spectra were observed for complexes **2**, whereas **4** did not show such resonances. Therefore, Berry pseudorotation may be slower for complexes **2**, if it occurs at all, whereas it does occur faster for **4** than the NMR time scale. This tendency is the same as that exhibited by the corresponding iron complexes.[14]



1 : Z = NMe
3 : Z = O

2a : Z = NMe, R = Me
2b : Z = NMe, R = CH_2Ph
2c : Z = NMe, R = $SnPh_3$
2d : Z = NMe, R = H
2a-d$_3$: Z = NMe, R = CD_3
4 : Z = O, R = Me

Crystal Structure of 2b. The structure of **2b** was determined by X-ray diffraction analysis. The ORTEP drawing is displayed in Figure 1. The crystal data and the selected bond distances and angles are summarized in Tables 1 and 2, respectively.

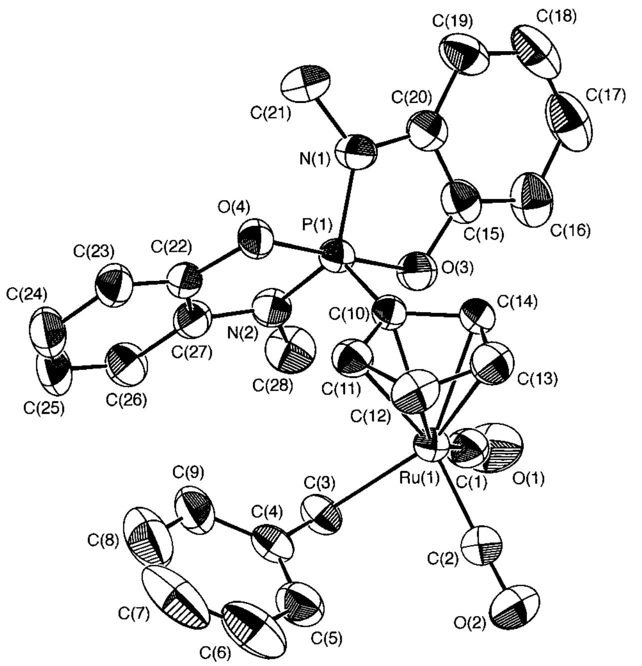


Figure 1. ORTEP drawing of **2b** (50% probability ellipsoids) showing the numbering system. All hydrogen atoms are omitted for clarity.

Table 1. Summary of Crystal Data for 2b

formula	$C_{28}H_{25}N_2O_4PRu$
fw	585.56
cryst syst	monoclinic
space group	$P2_1/c$
cell constants	
a, Å	10.753(3)
b, Å	29.180(7)
c, Å	8.015(3)
β, deg	94.32(3)
V, Å^3	2508(1)
Z	4
D_{calcd}, g cm^{-3}	1.70
μ, cm^{-1}	7.11
cryst size, mm	0.62 × 0.27 × 0.12
radiation	Mo Kα (λ = 0.710 73 Å)
scan technique	ω
scan range, deg	$3 < 2\theta < 53$
scan rate, deg min^{-1}	6.0
no. of unique data	5122
no. of unique data, $F_o > 3\sigma(F_o)$	3662
R	0.034
R_w	0.037

The X-ray structure clearly shows that **2b** is a migration product of a phosphorane fragment from Ru to the Cp ring. The ruthenium atom is coordinated by a monosubstituted Cp ligand in an η^5 fashion, two terminal CO ligands, and a benzyl ligand. The geometry around the phosphorus atom is almost trigonal bipyramidal with two oxygens in the apical positions and with two nitrogens and one carbon in the equatorial positions: P1, N1, N2, and C10 make a plane (the sum of the angles around P1 is 360.0°), and the O3−P1−O4 angle is 179.0°. Comparison of the structures of **1**[15] and **2b** reveals that the P−O bond is ca. 0.05 Å shorter and the P−N bond is ca. 0.02 Å shorter for **2b** than for **1**. This tendency has been observed in the corresponding iron case.[14] The bond distances and the bond angles around the phosphorane phosphorus for **2b** are almost the same as those for the corresponding iron complex $\{C_5H_4P(OC_6H_4NMe)_2\}Fe(CO)_2(CH_2Ph)$.[14] The apical axis (O3−P1−O4) is slightly tilted from the Cp plane. The torsion angles (O4−P1−C10−C11 = 28.2°, O3−P1−C10−C14 = 33.1°) are also similar to those of the

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2b

Bond Distances			
Ru1−C1	1.856(3)	N1−C20	1.406(4)
Ru1−C2	1.852(3)	N1−C21	1.452(5)
Ru1−C3	2.184(3)	N2−C27	1.398(3)
P1−O3	1.709(2)	N2−C28	1.467(4)
P1−O4	1.713(2)	C3−C4	1.487(4)
P1−N1	1.694(3)	C10−C11	1.431(4)
P1−N2	1.704(2)	C10−C14	1.453(4)
P1−C10	1.799(3)	C11−C12	1.424(4)
O1−C1	1.139(4)	C12−C13	1.428(4)
O2−C2	1.147(4)	C13−C14	1.394(5)
O3−C15	1.365(3)	C15−C20	1.385(4)
O4−C22	1.374(3)	C22−C27	1.396(4)
Bond Angles			
C1−Ru1−C2	89.5(2)	P1−N2−C27	113.5(2)
C1−Ru1−C3	89.7(2)	P1−N2−C28	128.8(2)
C2−Ru1−C3	87.4(2)	C27−N2−C28	117.3(2)
O3−P1−O4	179.0(1)	Ru1−C1−O1	177.0(3)
O3−P1−N1	89.0(1)	Ru1−C2−O2	177.3(2)
O3−P1−N2	90.7(1)	Ru1−C3−C4	112.9(2)
O3−P1−C10	90.5(1)	P1−C10−C11	127.1(2)
O4−P1−N1	90.3(1)	P1−C10−C14	127.0(2)
O4−P1−N2	89.1(1)	C11−C10−C14	105.8(2)
O4−P1−C10	90.4(1)	C10−C11−C12	109.3(3)
N1−P1−N2	124.8(2)	C11−C12−C13	106.9(3)
N1−P1−C10	116.9(1)	C12−C13−C14	109.1(3)
N2−P1−C10	118.3(1)	C10−C14−C13	108.8(3)
P1−O3−C15	114.3(2)	O3−C15−C20	112.0(3)
P1−O4−C22	114.5(2)	N1−C20−C15	110.4(3)
P1−N1−C20	113.9(2)	O4−C22−C27	110.9(2)
P1−N1−C21	128.7(3)	N2−C27−C22	111.4(2)
C20−N1−C21	117.1(3)		

corresponding iron complex. These results indicate that the geometry around the phosphorane phosphorus is not affected by whether a transition metal is Ru or Fe.

Consideration of Phosphorane Fragment Migration Process. To elucidate the migration process, we examined the product in the reaction of **1** with LDA. Although the several attempts to isolate the product were unsuccessful due to its instability, the spectroscopic data of the reaction mixture enabled us to identify the product (**5**) as shown in Scheme 1.

Scheme 1

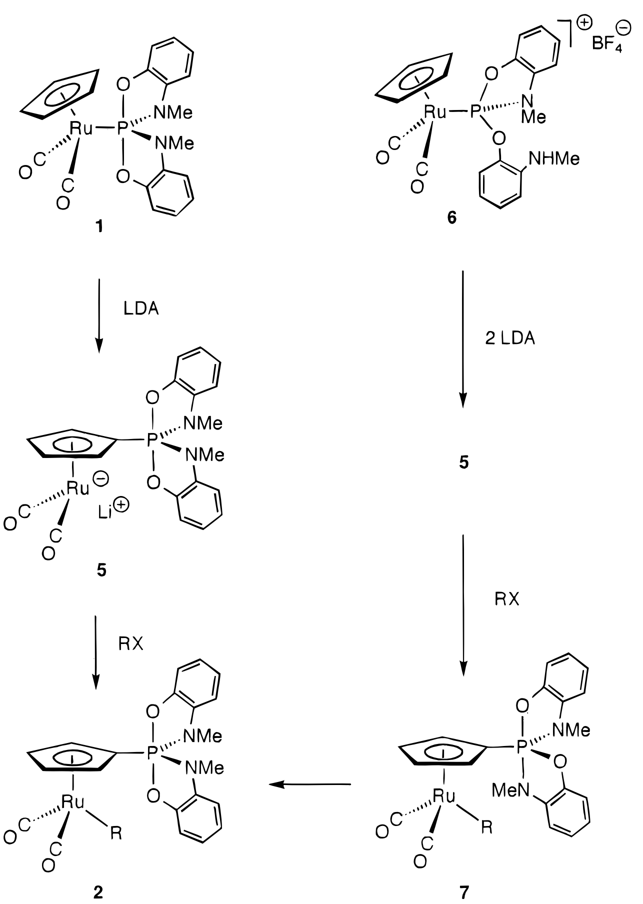
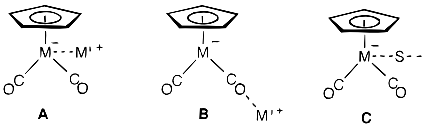


Chart 1



The IR spectrum shows 5 absorption bands in the ν_{CO} region (1916 (s), 1898 (s), 1836 (s), 1815 (m), 1775 (m) cm^{-1}). These values are more than 120 cm^{-1} lower in frequency than those for **1**, indicating a formation of an anionic ruthenium complex, $[(\eta^5\text{-}C_5H_4\{P(OC_6H_4NMe)_2\})(CO)_2Ru]^-$. In the case of $M'[(\eta^5\text{-}C_5R_5)(CO)_2M]$ (R = H: M′ = Li, Na, K: M = Fe;[16] R = Me: M′ = Li: M = Os[17]), it has been proposed that each complex exists as a mixture containing three kinds of ion pairs, an M···M′ contact ion pair (**A**), an M−CO···M′ ion pair with a metal carbonyl oxygen interaction (**B**), and a solvent-separated ion pair (**C**) (see Chart 1). However, there is no report about a ruthenium analogue.[18] Thus, we prepared $Li[Cp(CO)_2Ru]$ from $Cp(CO)_2RuH$ and n-BuLi in a THF solution and measured its IR spectrum. Five absorptions were observed at 1907 (s), 1889 (m), 1826 (s), 1801 (m), and 1759 (m) cm^{-1}. The pattern is very close to that for the Fe and Os complexes. From an interpretation of the precedents,[16,17] absorptions at 1907 and 1826 cm^{-1} can be assigned to the Ru···Li contact ion pair (**A**), those at 1889 and 1759 cm^{-1} to the Ru−CO···Li ion pair (**B**), and those at 1889 and 1801 cm^{-1} to the solvent-separated ion pair (**C**). The IR absorption bands for **5** also resemble those for $Li[Cp(CO)_2Ru]$. Therefore, it may be reasonable that absorptions at 1916 and 1836 cm^{-1} are assigned to **A**, those at 1898 and 1775 cm^{-1} to **B**, and those at 1898 and 1815 cm^{-1} to **C**. It should be noted here that the Ru···Li contact ion pair is a dominant species, as judged from their relative intensities.

The ^{31}P NMR spectrum of **5** shows a singlet at −42.88 ppm, which is at a higher field by ca. 35 ppm than that of **1**. Similar spectroscopic changes were observed in the case of the iron complexes. The chemical shift is consistent with the formation of a phosphorane-migrated anionic ruthenium complex. The ^{13}C NMR spectrum[19]

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(17) Kawano, Y.; Tobita, H.; Ogino, H. *Organometallics* **1994**, *13*, 3849.

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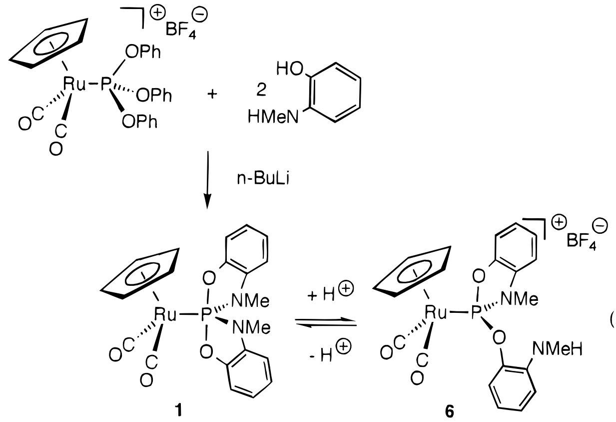
(19) ^{13}C NMR (δ, THF): 32.20 (s, NCH_3), 83.71 (d, J_{PC} = 18.2 Hz, PC_5H_4), 83.98 (d, J_{PC} = 18.3 Hz, PC_5H_4), 86.29 (d, J_{PC} = 17.1 Hz, PC_5H_4), 86.41 (d, J_{PC} = 18.3 Hz, PC_5H_4), 90.36 (d, J_{PC} = 253.9 Hz, PC_5H_4), 107.57 (d, J_{PC} = 7.4 Hz, OC_6H_4N), 108.36 (d, J_{PC} = 12.2 Hz, OC_6H_4N), 118.30 (s, OC_6H_4N), 119.43 (s, OC_6H_4N), 136.38 (d, J_{PC} = 20.8 Hz, OC_6H_4N), 147.67 (s, OC_6H_4N), 212.79 (s, CO).

shows five doublets due to the Cp ring. The coupling constant (253.9 Hz) of the doublet at 90.36 ppm is large compared with coupling constants of the other four resonances. This certainly indicates a direct P−C bond. There are only six resonances assignable to phenyl rings, showing that two OC_6H_4NMe groups are magnetically equal. The phosphorane phosphorus is reasonably expected to have two O atoms in apical positions and two N atoms and one Cp carbon atom in equatorial positions. This shows that an apical−equatorial arrangement around the hypervalent phosphorus is retained during its migration from Ru to the Cp ring.

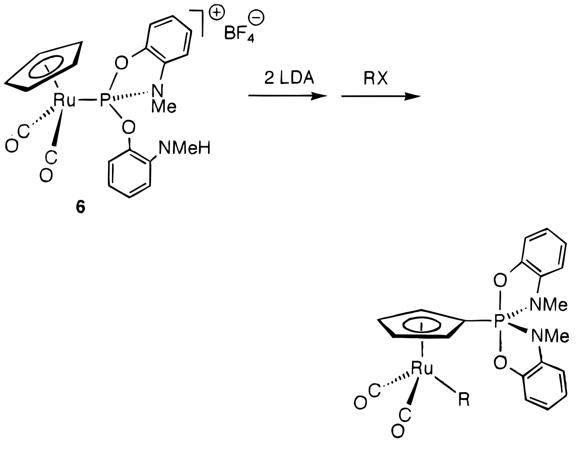
The migration may be initiated by a proton abstraction on the Cp ring by LDA, followed by migration of the phosphorane fragment to give **5**. The driving force of this migration can be thought to arise from the more stable $Cp(CO)_2Ru^-$ derivative than a species having an anion on the Cp ring.

Reaction of $[Cp(CO)_2Ru\{P(OC_6H_4NMe)(OC_6H_4NMeH)\}]BF_4$ (6) with LDA and Then RX. We previously reported that the reaction of $[Cp(CO)_2Ru\{P(OPh)_3\}]BF_4$ with *o*-$C_6H_4(OH)(NMeH)$ and n-BuLi in THF gives a phosphorane complex (**1**), which then reacts with PhOH present in the solution to yield the cationic complex $[Cp(CO)_2Ru\{P(OC_6H_4NMe)(OC_6H_4NMeH)\}]BF_4$ (**6**) (eq 2).[15] The complexes **1** and **6** may exist in equilibrium, but **6** is readily precipitated out from the THF solution. The isolated **6** reacts with a base to give **1**. Therefore, a phosphorane migration is presumed to be attained in the reaction of **6** with 2 equiv of LDA and then RX. As is expected, the migration reaction takes place to give **2** (eq 3).



1 **6** (2)

During the reaction we encountered interesting findings. In the reaction of **6** with 2 equiv of LDA, formation of **5** is inferred from the ^{31}P and ^{13}C NMR spectra. Upon addition of MeI to the solution at −30 °C, a singlet at −42.88 ppm due to **5** in the ^{31}P NMR spectrum disappears and a new singlet appears at −28.91 ppm. The ^{13}C NMR spectrum[20] shows 12 resonances due to phenyl rings in addition to 1 RuMe resonance, 5 Cp resonances, and 1 CO resonance. These spectroscopic data indicate that the product is **7a**, shown in Scheme 1 (R = Me), where the phosphorane phosphorus has one O atom and one N atom in apical positions and in equatorial positions as well. When the solution is warmed to room temperature, **7a** is gradually converted into **2a**. An iron complex corresponding to **7a** has not been detected clearly in the reaction of $[Cp(CO)_2Fe\{P(OC_6H_4NMe)(OC_6H_4NMeH)\}]BF_4$ with 2 equiv of LDA and then MeI.



6 **2** (3)

Addition of Ph_3SnCl, $HOCOCF_3$, and CD_3I at −30 °C to **5** produced from **6** and 2 equiv of LDA gives a similar ^{31}P NMR chemical shift: −30.76 ppm (**7c**), −29.18 ppm (**7d**), and −28.98 ppm (**7a-d$_3$**), respectively. Warming the solution to room temperature results in the formation of **2c**, **2d**, and **2a-d$_3$**, respectively.

In contrast, it is surprising that a reaction of MeI with **5** derived from **1** and LDA does not give **7**. Complex **7** is of interest because an amino group occupies an apical position, though an NR_2 group is reported to have stronger equatophilicity than an OR group. An unusual trigonal-bipyramidal isomer has been reported by Akiba and co-workers for an organophosphorane which has an apical carbon−equatorial oxygen (**8** in Chart 2).[21] The ^{31}P NMR chemical shift of **8** (−3.5 ppm) is at a lower field by 15.3 ppm than that of the thermally more stable isomer **9** (−18.8 ppm). The value and the relative magnetic-field relation are in fair agreement with those obtained in our case: the chemical shift of **7** is at a lower field by 18.4 ppm than that of **2**.

To obtain a clue to the formation of **7**, we examined the following reaction. After the formation of **5** from **6**, 12-crown-4 was added to the THF solution and then RX was added at −30 °C. The product in this reaction was **2**, and **7** was not detected at all. It was also observed that addition of 12-crown-4 to a THF solution containing **7** does not apparently affect the isomerization rate to **2**. These results indicate that Li^+ plays an important role when **5** reacts with RX. It seems to be related to the fact that a contact ion pair is a dominant species for **5**. However, how Li^+ is involved in this reaction is not clear at present.

Conclusion

We recently reported the first example of hypervalent phosphorane migration to the Cp ring for iron complexes

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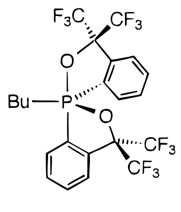
[20] ^{13}C NMR (δ, THF): −30.11 (s, $RuCH_3$), 88.40 (d, $J_{PC} = 15.9$ Hz, PC_5H_4), 88.70 (d, $J_{PC} = 17.1$ Hz, PC_5H_4), 95.97 (d, $J_{PC} = 238.1$ Hz, PC_5H_4), 98.29 (d, $J_{PC} = 20.8$ Hz, PC_5H_4), 100.25 (d, $J_{PC} = 15.9$ Hz, PC_5H_4), 104.77 (d, $J_{PC} = 8.6$ Hz, OC_6H_4N), 107.69 (d, $J_{PC} = 9.7$ Hz, OC_6H_4N), 110.21 (d, $J_{PC} = 12.3$ Hz, OC_6H_4N), 110.89 (d, $J_{PC} = 12.2$ Hz, OC_6H_4N), 116.64 (s, OC_6H_4N), 119.34 (s, OC_6H_4N), 121.24 (s, OC_6H_4N), 122.99 (s, OC_6H_4N), 134.97 (d, $J_{PC} = 22.0$ Hz, OC_6H_4N), 138.55 (d, $J_{PC} = 17.0$ Hz, OC_6H_4N), 141.79 (s, OC_6H_4N), 147.39 (s, OC_6H_4N), 201.78 (s, CO). Detailed assignments of the NCH_3 resonances were not possible due to interference by resonances of the solvent and $HN(i\text{-}Pr)_2$ existing in the solution.

[21] Kojima, S.; Kajiyama, K.; Nakamoto, M.; Akiba, K. *J. Am. Chem. Soc.* **1996**, *118*, 12866.

Chart 2



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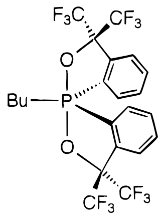

9

$Cp(CO)_2Fe\{P(OC_6H_4Z)_2\}$ (Z = NR, O). The reaction is proposed to be initiated by a proton abstraction on the Cp ring by a Lewis base, followed by migration of the phosphorane fragment to the Cp ring via a metalated hypervalent hexacoordinated phosphorus species as an intermediate. It is generally accepted that a bond between a transition metal and a main-group element becomes strong on going down in the periodic table for transition metals in the same group. In this paper we examined a phosphorane migration for ruthenium complexes, $Cp(CO)_2Ru\{P(OC_6H_4Z)_2\}$, with the expectation of obtaining or detecting the proposed intermediate. The results showed the second hypervalent fragment migration, but the reaction did not enable us to detect an expected intermediate. However, we encountered formation of the unexpected phosphorane migration complex $\{\eta^5\text{-}C_5H_4P(OC_6H_4NMe)_2\}(CO)_2RuR$, which contains one O atom and one N atom in apical positions and in equatorial positions as well.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. All solvents were purified by distillation: THF and benzene were distilled from sodium/benzophenone, hexane and pentane were distilled from sodium metal, and CH_2Cl_2 was distilled from P_2O_5. Those were stored under an N_2 atmosphere. Other reagents employed in this research were used as received.

IR spectra were recorded on Shimadzu FTIR-4000 and FTIR-8100A spectrometers. ^1H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL EX-270, EX-400, and LA-300 spectrometers. ^1H NMR and ^{13}C NMR data were referenced to $Si(CH_3)_4$ as an internal standard. ^{31}P NMR data were referred to 85% H_3PO_4 as an external standard. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer.

Ruthenium complexes (**1**, **3**, and **6**) were prepared in accordance with the reported procedures.[15] Ruthenium complexes (**2**) can be prepared from **1** and also from **6**. Procedures for preparation of **2** from **6** were described below.

Preparation of $\{C_5H_4P(OC_6H_4NMe)_2\}(CO)_2RuCH_3$ (2a). A white suspension of **6** (219 mg, 0.38 mmol) in THF (2 mL) was treated with LDA (1.5 mL, 0.75 mmol) at −78 °C. After it had been stirred at −78 °C for 15 min, the reaction mixture was treated with MeI (0.030 mL, 0.48 mmol), warmed to room temperature, and then stirred for 2 h to complete the reaction. The solvent was removed under reduced pressure, and the residue was extracted with a small amount of benzene. The extract was loaded on a silica gel column and eluted with a mixture of hexane and benzene (2/3). The colorless band eluted first was collected, and the solvents were removed in vacuo to give **2a** as a white powder (88 mg, 0.17 mmol, 46%). Anal. Calcd for $C_{22}H_{21}N_2O_4PRu$: C, 51.87; H, 4.15; N, 5.50. Found: C, 52.08; H, 4.23; N, 5.51. Data: IR (cm^{-1}, THF) ν_{CO} 2020, 1959; ^1H NMR (δ, $CDCl_3$) 0.27 (s, 3H, $RuCH_3$), 3.23 (d, J_{PH} = 10.2 Hz, 6H, NCH_3), 5.16−5.20 (m, 2H, PC_5H_4), 5.67−5.70 (m, 1H, PC_5H_4), 5.76−5.79 (m, 1H, PC_5H_4), 6.67−6.70 (m, 2H, OC_6H_4N), 6.83−6.93 (m, 6H, OC_6H_4N); ^{13}C NMR (δ, $CDCl_3$) −31.64 (s, $RuCH_3$), 32.38 (d, J_{PC} = 2.5 Hz, NCH_3), 88.42 (d, J_{PC} = 15.9 Hz, PC_5H_4), 88.82 (d, J_{PC} = 15.9 Hz, PC_5H_4), 95.94 (d, J_{PC} = 251.4 Hz, PC_5H_4), 99.01 (d, J_{PC} = 17.1 Hz, PC_5H_4), 99.87 (d, J_{PC} = 15.8 Hz, PC_5H_4), 108.34 (d, J_{PC} = 7.3 Hz, OC_6H_4N), 109.00 (d, J_{PC} = 12.2 Hz, OC_6H_4N), 119.53 (s, OC_6H_4N), 120.43 (s, OC_6H_4N), 135.11 (d, J_{PC} = 22.0 Hz, OC_6H_4N), 146.13 (s, OC_6H_4N), 200.59 (s, CO), 200.72 (s, CO); ^{31}P NMR (δ, THF) −47.27 (s).

Preparation of $\{C_5H_4P(OC_6H_4NMe)_2\}(CO)_2RuCH_2Ph$ (2b). Treatment of **6** (252 mg, 0.43 mmol) with LDA (1.73 mL, 0.86 mmol) followed by $PhCH_2Cl$ (0.060 mL, 0.52 mmol) in a manner similar to that for **2a** gave a white powder of **2b** (130 mg, 0.22 mmol, 51%). Anal. Calcd for $C_{28}H_{25}N_2O_4PRu$: C, 57.43; H, 4.30; N, 4.78. Found: C, 57.13; H, 4.37; N, 4.67. Data: IR (cm^{-1}, THF) ν_{CO} 2019, 1961; ^1H NMR (δ, $CDCl_3$) 2.84 (d, J_{HH} = 8.6 Hz, 1H, $RuCH_2$), 2.92 (d, J_{HH} = 8.9 Hz, 1H, $RuCH_2$), 3.23 (d, J_{PH} = 10.2 Hz, 6H, NCH_3), 4.85−4.96 (m, 2H, PC_5H_4), 5.60−5.63 (m, 1H, PC_5H_4), 5.68−5.71 (m, 1H, PC_5H_4), 6.80−7.11 (m, 13H, OC_6H_4N, $CH_2C_6H_5$); ^{13}C NMR (δ, $CDCl_3$) 0.29 (s, $RuCH_2$), 32.40 (d, J_{PC} = 2.4 Hz, NCH_3), 89.96 (d, J_{PC} = 14.6 Hz, PC_5H_4), 91.42 (d, J_{PC} = 15.9 Hz, PC_5H_4), 95.61 (d, J_{PC} = 250.2 Hz, PC_5H_4), 98.81 (d, J_{PC} = 15.8 Hz, PC_5H_4), 101.09 (d, J_{PC} = 15.9 Hz, PC_5H_4), 108.41 (d, J_{PC} = 7.3 Hz, OC_6H_4N), 109.12 (d, J_{PC} = 11.0 Hz, OC_6H_4N), 119.64 (s, OC_6H_4N), 120.54 (s, OC_6H_4N), 122.86 (s, $CH_2C_6H_5$), 127.33 (s, $CH_2C_6H_5$), 127.96 (s, $CH_2C_6H_5$), 135.01 (d, J_{PC} = 22.0 Hz, OC_6H_4N), 146.11 (s, OC_6H_4N), 153.51 (s, $CH_2C_6H_5$), 200.11 (s, CO), 200.65 (s, CO); ^{31}P NMR (δ, THF) −47.46 (s).

Preparation of $\{C_5H_4P(OC_6H_4NMe)_2\}(CO)_2RuSnPh_3$ (2c). Treatment of **6** (108 mg, 0.19 mmol) with LDA (0.74 mL, 0.37 mmol) followed by Ph_3SnCl (73 mg, 0.19 mmol) in a manner similar to that for **2a** gave a white powder of **2c** (110 mg, 0.13 mmol, 70%). Anal. Calcd for $C_{39}H_{33}N_2O_4PRuSn$: C, 55.47; H, 3.94; N, 3.32. Found: C, 55.31; H, 4.03; N, 3.19. Data: IR (cm^{-1}, THF) ν_{CO} 2016, 1962; ^1H NMR (δ, $CDCl_3$) 3.15 (d, J_{PH} = 10.3 Hz, 6H, NCH_3), 4.73−4.77 (m, 1H, PC_5H_4), 4.82−4.86 (m, 1H, PC_5H_4), 5.43−5.46 (m, 1H, PC_5H_4), 5.59−5.61 (m, 1H, PC_5H_4), 6.59 (d, J_{HH} = 8.8 Hz, 2H, OC_6H_4N), 6.71−6.82 (m, 6H, OC_6H_4N), 7.18−7.22 (m, 9H, SnC_6H_5), 7.36−7.39 (m, 6H, SnC_6H_5); ^{13}C NMR (δ, $CDCl_3$) 32.34 (d, J_{PC} = 2.5 Hz, NCH_3), 86.52 (d, J_{PC} = 14.9 Hz, PC_5H_4), 87.36 (d, J_{PC} = 14.9 Hz, PC_5H_4), 92.11 (d, J_{PC} = 15.3 Hz, PC_5H_4), 93.86 (d, J_{PC} = 15.3 Hz, PC_5H_4), 98.37 (d, J_{PC} = 246.8 Hz, PC_5H_4), 104.48 (d, J_{PC} = 7.5 Hz, OC_6H_4N), 109.29 (d, J_{PC} = 12.4 Hz, OC_6H_4N), 119.75 (s, OC_6H_4N), 120.65 (s, OC_6H_4N), 128.02 (s, with Sn satellites, J_{SnC} = 9.9 Hz, SnC_6H_5), 128.13 (s, with Sn satellites, J_{SnC} = 45.4 Hz, SnC_6H_5), 134.87 (d, J_{PC} = 21.8 Hz, OC_6H_4N), 136.63 (s, with Sn satellites, J_{SnC} = 39.2 Hz, SnC_6H_5), 143.65 (s, SnC_6H_5), 146.19 (s, OC_6H_4N), 198.50 (s, CO), 200.14 (s, CO); ^{31}P NMR (δ, THF) −49.25 (s).

Preparation of $\{C_5H_4P(OC_6H_4NMe)_2\}(CO)_2RuH$ (2d). Treatment of **6** (154 mg, 0.26 mmol) with LDA (1.1 mL, 0.55 mmol) followed by CF_3COOH (0.020 mL, 0.26 mmol) in a manner similar to that for **2a** gave a pale yellow powder of **2d** (55 mg, 0.11 mmol, 42%). Anal. Calcd for $C_{21}H_{19}N_2O_4PRu$: C, 50.91; H, 3.87; N, 5.65. Found: C, 51.21; H, 3.94; N, 5.65. Data: IR (cm^{-1}, THF) ν_{CO} 2029, 1969; ^1H NMR (δ, C_6D_6) −10.80 (s, 1H, RuH), 2.87 (d, J_{PH} = 10.3 Hz, 6H, NCH_3), 4.47 (m, 2H, PC_5H_4), 5.39 (m, 1H, PC_5H_4), 5.52 (m, 1H, PC_5H_4), 6.36−7.28 (m, 8H, OC_6H_4N); ^{13}C NMR (δ, C_6D_6) 32.10 (s, NCH_3), 86.37 (d, J_{PC} = 14.6 Hz, PC_5H_4), 86.86 (d, J_{PC} = 15.9 Hz, PC_5H_4), 94.49 (d, J_{PC} = 17.1 Hz, PC_5H_4), 95.34 (d, J_{PC} = 15.9 Hz, PC_5H_4), 95.41 (d, J_{PC} = 247.8 Hz, PC_5H_4), 108.55 (d, J_{PC} = 5.9 Hz, OC_6H_4N), 109.69 (d, J_{PC} = 12.2 Hz, OC_6H_4N), 120.04 (s, OC_6H_4N), 120.97 (s, OC_6H_4N), 135.19 (d, J_{PC} = 21.9 Hz, OC_6H_4N), 146.76 (s, OC_6H_4N), 199.93 (s, CO), 200.16 (s, CO); ^{31}P NMR (δ, C_6D_6) −47.82 (s).

Preparation of $\{C_5H_4P(OC_6H_4NMe)_2\}(CO)_2RuCD_3$ (2a-d_3). Treatment of **6** (190 mg, 0.33 mmol) with LDA (1.3 mL, 0.65 mmol) followed by CD_3I (0.038 mL, 0.60 mmol) in a manner similar to that for **2a** gave a white powder of **2a-d$_3$** (92 mg, 0.18 mmol, 55%). Anal. Calcd for $C_{22}H_{18}D_3N_2O_4PRu$: C, 51.56; H, 3.56; D, 1.15; N, 5.47. Found: C, 51.60; H, 3.55; D, 1.15; N, 5.56. Data: IR (cm^{-1}, THF) ν_{CO} 2021, 1962; ^{1}H NMR (δ, $CDCl_3$) 3.23 (d, J_{PH} = 10.2 Hz, 6H, NCH_3), 5.17−5.21 (m, 2H, PC_5H_4), 5.67−5.70 (m, 1H, PC_5H_4), 5.77−5.79 (m, 1H, PC_5H_4), 6.67−6.70 (m, 2H, OC_6H_4N), 6.81−6.94 (m, 6H, OC_6H_4N); ^{13}C NMR (δ, $CDCl_3$) 32.37 (s, NCH_3), 88.38 (d, J_{PC} = 14.6 Hz, PC_5H_4), 88.75 (d, J_{PC} = 14.6 Hz, PC_5H_4), 95.86 (d, J_{PC} = 250.2 Hz, PC_5H_4), 98.99 (d, J_{PC} = 17.1 Hz, PC_5H_4), 99.82 (d, J_{PC} = 14.7 Hz, PC_5H_4), 108.30 (d, J_{PC} = 7.3 Hz, OC_6H_4N), 108.99 (d, J_{PC} = 12.2 Hz, OC_6H_4N), 119.50 (s, OC_6H_4N), 120.40 (s, OC_6H_4N), 135.08 (d, J_{PC} = 22.0 Hz, OC_6H_4N), 146.09 (s, OC_6H_4N), 200.61 (s, CO), 200.74 (s, CO), the CD_3 carbon could not be identified; ^{31}P NMR (δ, THF) −47.47 (s).

Preparation of $\{C_5H_4P(OC_6H_4O)_2\}(CO)_2RuCH_3$ (4). 3 (125 mg, 0.26 mmol) was dissolved in THF (4.0 mL), and LDA (0.53 mL, 0.27 mmol) was added to the solution at −78 °C. The mixture was stirred for 15 min. The solution was then treated with MeI (0.032 mL, 0.53 mmol) and warmed to room temperature. The solvent was removed under reduced pressure, and the residue was extracted with ether. The extract was dried in vacuo, and the resulting oily residue was extracted with pentane. The pentane extract was filtered, and the solvent was removed under reduced pressure to give a white powder of **4** (101 mg, 0.21 mmol, 79%). The complex was so hygroscopic that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained. Data: IR (cm^{-1}, THF) ν_{CO} 2016, 1959; ^{1}H NMR (δ, $CDCl_3$) 0.32 (s, 3H, $RuCH_3$), 5.27−5.31 (m, 2H, PC_5H_4), 5.85−5.87 (m, 2H, PC_5H_4), 6.93−7.08 (m, 8H, OC_6H_4O); ^{13}C NMR (δ, $CDCl_3$) −30.82 (s, $RuCH_3$), 84.73 (d, J_{PC} = 249.2 Hz, PC_5H_4), 90.63 (d, J_{PC} = 16.2 Hz, PC_5H_4), 99.76 (d, J_{PC} = 16.8 Hz, PC_5H_4), 110.98 (d, J_{PC} = 14.3 Hz, OC_6H_4O), 122.33 (s, OC_6H_4O), 143.72 (d, J_{PC} = 4.4 Hz, OC_6H_4O), 198.91 (s, CO); ^{31}P NMR (δ, THF) −14.41 (s).

X-ray Structure Determination for 2b. A single crystal of **2b** grown from pentane in a refrigerator was mounted on a Mac Science MXCκ diffractometer and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 32 carefully centered reflections in the range 29° < 2θ < 36°, corresponded to a monoclinic cell with dimensions of a = 10.753(3) Å, b = 29.180(7) Å, c = 8.015(3) Å, β = 94.32(3)°, Z = 4, and V = 2507.9(1) Å^3. $P2_1/c$ was selected as a space group which led to successful refinement. The data were collected at a temperature of 20 ± 1 °C using the ω scan technique. The intensities of three representative reflections were measured after 300 reflections. No decay correction was applied.

The structure was solved by direct methods with the SIR-92 program system.[22] The positions of all hydrogen atoms were calculated by assuming idealized geometries. Absorption and extinction corrections were then applied,[23,24] and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final R and R_w values of 0.034 and 0.037, respectively. All calculations were performed using Crystan-GM.[25]

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Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **2b** (6 pages). Ordering information is given on any current masthead page.

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