Reaction of Cyclopentadienyl Ruthenium Complexes with a Carborane Anion: Effect of the Spectator Ligands on the Substitution Site

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The reaction of cyclopentadienyl ruthenium complexes of the type $[RuCl(Cp)L_1L_2]$ (L_1, L_2 = PPh_3, PMe_2Ph, $PMePh_2$; L_1L_2 = dppe; L_1L_2 = COD; L_1 = CO, L_2 = PPh_3) with Licarb (Hcarb = 2-Me-1,2-dicarba-*closo*-dodecaborane) gives two types of complexes, $[Ru(H)(C_5H_4\text{-carb})L_1L_2]$ or $[Ru(carb)(Cp)L_1L_2]$, depending on the nature of the coordination set. The structures of $[Ru(carb)(Cp)(PMe_2Ph)_2]$ and $[RuCl(\eta^5\text{-}C_5Me_4H)(PMe_2Ph)_2]$ have been determined by single-crystal crystallography. The role played by the ligand set on the site of nucleophilic attack is discussed in light of the steric crowding and electronic density at the metal center.

Introduction

Cyclopentadienyl ruthenium(II) complexes are low spin d^6 coordinatively saturated octahedral systems and, as a consequence, rather inert toward substitution; for this reason, their use as catalysts has been generally very limited. However, rather recently, complexes of the type $[RuCl(Cp)(L)_2]$ (L = PPh_3, $PMePh_2$, PMe_2Ph, $^1/_2$dppe, CO, Ph_2PNHPh, $Ph_2PNHC_6H_{11}$, $^1/_2$-$Ph_2PN(Et)PPh_2$, $^1/_2Ph_2PN(^n Pr)PPh_2$, $^1/_2Ph_2PN(^i Pr)PPh_2$, and $^1/_2$-$Ph_2PN(^n Bu)PPh_2$) have been successfully employed as catalysts in a series of C−C bond forming reactions,[1−4] starting from a variety of diazo compounds. In all cases, preliminary dissociation of one neutral ligand (phosphine or CO) was needed to afford the effective catalytic species. We have an ongoing research project aimed at the improvement of the reactivity of this type of complexes by changing the steric and electronic character of the anionic ligand. For example, substitution of a chloride ligand with a bulky and poor electron-withdrawing anion, like the one of 2-Me-1,2-dicarba-*closo*-dodecaborane ($HCC(Me)B_{10}H_{10}$), should favor, both for steric and electronic reasons, the dissociation of a neutral ligand in the crucial catalytic step.

In this context, we were surprised by the preliminary results obtained in the reaction of $[RuCl(Cp)(PPh_3)_2]$ with an ethereal solution of Licarb (Hcarb = 2-Me-1,2-dicarba-*closo*-dodecaborane).[5] In fact, instead of a simple $Cl^-/carb^-$ exchange product, we isolated a hydrido Ru(II) complex, $[RuH(C_5H_4\text{-carb})(PPh_3)_2]$ (**1**), resulting from a formal nucleophilic attack of $carb^-$ on the cyclopentadienyl group. To our knowledge, this was the first example of a nucleophilic substitution reaction on a Cp ring coordinated to a fairly electron-rich metal center such as ruthenium(II). Indeed, very few examples are reported in the literature for this type of reaction. They involve electron-poor metal centers such as Os(IV),[6] W(IV),[7] and Mo(IV)[7a] in cyclopentadienyl complexes and carbanions (from lithium alkyls[6] or Grignard reagents[7b]) or rather exotic metallophosphide anions $Li[M(PPh_2)(CO)_5]$.[7a]

An article was published by Xie et al., almost at the same time of our preliminary communication, in which a similar ruthenium complex $[(\eta^5\text{-}Me_2C(C_5H_3)(C_2B_{10}H_{10}))RuH(PPh_3)_2]$ was obtained in good yield by the reaction of $[RuCl_2(PPh_3)_3]$ with $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]Li_2$, in which the Me_2C bridge joins a cyclopentadienyl and a carboranyl unit.[8] In an extension of this work, they reported later that the same reaction with complexes bearing phosphines with smaller cone angles yielded only the salt metathesis products $[(\eta^5\text{: }\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10}))RuL_2]$ (L_2 = $2PPh_2(OEt)$ or dppe).[9] The observed behavior with the PPh_3 ligands was justified with a sterically induced intramolecular coupling reaction between the *o*-carboranyl and the cyclopentadienyl functionality.

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We present here the results obtained in the reaction of the anion of 2-Me-1,2-dicarba-*closo*-dodecaborane with a number of ruthenium cyclopentadienyl complexes characterized by different sets of neutral ligands, $[RuCl(Cp)L_1L_2]$ (L_1, L_2 = PPh_3, PMe_2Ph, $PMePh_2$; L_1L_2 = dppe; L_1L_2 = COD; L_1 = CO, L_2 = PPh_3). The main purpose is to obtain information on how steric and electronic variations of the spectator ligands can direct this peculiar substitution reaction and, on the basis of this information, to propose a possible mechanism. The role of steric hindrance furthermore has been checked by replacing the Cp ring with the tetramethyl analogue C_5Me_4H.

Experimental Procedures

General Comments. The reagents (Aldrich-Chemie) were high purity products and generally used as received. All solvents were dried by standard procedures and distilled under nitrogen immediately prior to use. The reaction apparatus was carefully deoxygenated, the reactions were performed under argon, and all operations were carried out under an inert atmosphere. The complexes $[RuCl(Cp)(PPh_3)_2]$,[10] $[RuCl(Cp)(PMe_2Ph)_2]$,[11] $[RuCl(Cp)(PMePh_2)_2]$,[12] [RuCl(Cp)(dppe)],[13] [RuCl(Cp)(COD)],[14] $[RuCl(Cp)(CO)(PPh_3)]$,[15] and $[RuH(C_5H_4\text{-carb})(PPh_3)_2]$ (**1**)[5] and 1-methyl-1,2-dicarba-*closo*-dodecaborane (Hcarb)[16] were prepared according to published methods. The solution ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$-NMR spectra were acquired on a Bruker DRX-400 (400.13 MHz for ^1H, 100.62 MHz for ^{13}C, and 121.5 MHz for ^{31}P) at room temperature. The chemical shifts (δ) are reported in units of parts per million relative to the residual solvent signals, using tetramethylsilane as an internal standard, for proton and carbon chemical shifts and to external 85% H_3PO_4 (0.0 ppm) for phosphorus chemical shifts.

General Procedure for Reaction of Complexes $[RuCl(Cp)L_1L_2]$ with *n*-LiBu. Complexes **2**−**6** were obtained by reaction of $[RuCl(Cp)L_1L_2]$ with $carb^-$ in a 1:1.5 molar ratio, in anhydrous toluene, at room temperature for 3 days.

$[Ru(carb)(Cp)(PMe_2Ph)_2]$ (2). In this prototype reaction, *n*-BuLi (1 mL of a 1.6 M solution in hexane, 1.6 mmol) was added to Hcarb (0.126 g, 0.79 mmol, in 10 mL of diethyl ether). The resulting light yellow suspension was left under stirring for ca. 30 min and then added to a solution of $[RuCl(Cp)(PMe_2Ph)_2]$ (0.240 g, 0.50 mmol, in 25 mL of toluene). The suspension was stirred for 3 days at room temperature, after which LiCl was filtered off. The volatiles were removed under reduced pressure from the clear solution, and the residue was treated at 0 °C with hexane to give a yellow solid, which was filtered, washed with hexane, and dried (188 mg, yield 63%). ^1H NMR ($CDCl_3$): δ 1.59 (s, 3H, C*H*$_3$), 1.67 (t, 6H, C*H*$_3$ PMe_2Ph, $^2J_{PH}$ = 4.0 Hz), 1.89 (t, 6H, C*H*$_3$ PMe_2Ph, $^2J_{PH}$ = 4.0 Hz), 1.2−3.0 (br, 10H, B*H*), 4.37 (s, 5H, C_5H_5), 7.10−7.40 (m, 10H, Ph). ^{31}P NMR ($CDCl_3$): δ 8.3 (s, PMe_2Ph). ^{13}C NMR ($CDCl_3$): δ 21.5 (t, *C*H$_3$ PMe_2Ph, $^1J_{PC}$ = 13.0 Hz), 22.0 (t, *C*H$_3$ PMe_2Ph, $^1J_{PC}$ = 13.5 Hz), 28.4 (*C*H$_3$), 83.4 (t, C_5H_5, $^2J_{PC}$ = 2.0 Hz), 83.8 (CH_3-*C*), 87.2 (t (br), Ru-*C*, $^2J_{PC}$ = 12.3 Hz), 127.0−145 (Ph). FT IR (KBr, cm^{-1}): 3103−2853, 2527 (ν(B−H)), 1433, 1279, 908, 746. MS (ESI) *m/z*: 429 ($[Ru(Cp)(PMe_2Ph)(PMePh)]^+$, 30%), 305 ($[Ru(Cp)(PMe_2Ph)]^+$, 100%), 288 ($[Ru(Cp)(PMePh)]^+$, 35%). Anal. Calcd for $C_{24}H_{40}B_{10}P_2Ru$ (M = 599.7): C, 48.07; H, 6.72. Found: C, 48.31; H, 6.79.

$[Ru(carb)(Cp)(PMePh_2)_2]$ (3). The NMR data and elemental analysis indicate that the isolated solid is the substitution product $[Ru(carb)(Cp)(PMePh_2)_2]$ (**3**), together with small quantities of the starting materials Hcarb (ca. 5%) and $[RuCl(Cp)(PMePh_2)_2]$ (ca. 10%). Characterization of **3**: ^1H NMR ($CDCl_3$): δ 1.99 (s, 3H, C*H*$_3$), 1.83 (t, 6H, C*H*$_3$ $PMePh_2$, $^2J_{PH}$ = 3.6 Hz), 1.2−3.0 (br, 10H, B*H*), 4.57 (s, 5H, C_5H_5), 7.04−7.76 (m, 10H, Ph). ^{31}P NMR ($CDCl_3$): δ 24.9 (s, $PMePh_2$). ^{13}C NMR ($CDCl_3$): δ 16.1 (*C*H$_3$ $PMePh_2$), 17.1 (*C*H$_3$), 79.9 (t, C_5H_5, $^2J_{PC}$ = 2.1 Hz), 82.1 (CH_3-*C*), 86.1 (t (br), Ru-*C*), 128.6−133.4 (Ph). MS (ESI) *m/z*: 567 ($[Ru(Cp)(PMePh_2)_2]^+$, 15%), 367 ($[Ru(Cp)(PMePh_2)]^+$, 100%).

[Ru(carb)(Cp)(dppe)] (4). The NMR data indicate that the substitution product [Ru(carb)(Cp)(dppe)] (**4**) is contaminated by the starting materials Hcarb and [RuCl(Cp)(dppe)]. By repeated treatment of the solid with small portions of hexane (up to 159 mL) and of diethyl ether (up to 100 mL), **4** can be obtained pure in low yield (25 mg, 10%). ^1H NMR ($CDCl_3$): δ 1.32 (s, 3H, C*H*$_3$), 2.65 (m, 2H, C*H*$_2$), 3.16 (m, 2H, C*H*$_2$), 1.2−3.0 (br, 10H, B*H*), 4.79 (s, 5H, C_5H_5), 6.75−7.80 (m, 20H, Ph). ^{31}P NMR ($CDCl_3$): δ 77.2 (s, dppe). ^{13}C NMR ($CDCl_3$): δ 23.8 (m, *C*H$_2$), 27.6 (*C*H$_3$), 84.1 (t, C_5H_5, $^2J_{PC}$ = 2.1 Hz), 80.4 (CH_3-*C*), 85.5 (br, Ru-*C*), 126.1−137.1 (Ph). MS (ESI) *m/z*: 465 ($[Ru(Cp)(dppe)]^+$, 100%). Anal. Calcd for $C_{34}H_{42}B_{10}P_2Ru$ (M = 721.8): C, 56.57; H, 5.87. Found: C, 56.21; H, 5.62.

$[RuH(C_5H_4\text{-carb})(COD)]$ (5). Complex **5** obtained with the general procedure is contaminated by the presence of free Hcarb and can be obtained NMR pure in very low yield (3−5%) by careful washing with small quantities of cold diethyl ether. ^1H NMR (C_6D_6): δ −5.26 (s, 1H, Ru-*H*), 0.8−3.6 (br, 10H, B*H*), 1.21 (s, 3H, C*H*$_3$), 1.79 (m, 2H, C*H*$_2$), 1.86 (m, 2H, C*H*$_2$), 2.13 (m, 2H, C*H*$_2$), 2.30 (m, 2H, C*H*$_2$), 3.27 (m, 2H, C*H*), 3.67 (m, 2H, C*H*), 4.22 (m, 2H, C_5H_4), 5.12 (m, 2H, C_5H_4). ^{13}C NMR (C_6D_6): δ 22.4 (*C*H$_3$), 31.4 (*C*H$_2$), 32.5 (*C*H$_2$), 60.8 (*C*H), 61.4 (*C*H), 77.0 (CH_3-*C*), 79.3 (*C*-C_5H_4), 82.1 (C_5H_4), 88.9 (C_5H_4), 89.9 (C_5H_4). Complex **5** is unstable in $CDCl_3$ so that the initial NMR pattern [^1H NMR ($CDCl_3$): δ −5.44 (s, 1H, Ru-*H*), 1.2−3.1 (br, 10H, B*H*), 1.82 (s, 3H, C*H*$_3$), 2.15 (m, 6H, C*H*$_2$), 2.30 (m, 2H, C*H*$_2$), 3.15 (m, 2H, C*H*), 3.75 (m, 2H, C*H*), 4.78 (m, 2H, C_5H_4), 5.49 (m, 2H, C_5H_4)] evolves in a few days to that corresponding to the H/Cl exchange complex $[RuCl(C_5H_4\text{-carb})(COD)]$: ^1H NMR ($CDCl_3$): δ 0.96−3.5 (br, 10H, B*H*), 1.82 (s, 3H, C*H*$_3$), 2.18 (m, 6H, C*H*$_2$), 2.72 (m, 2H, C*H*$_2$), 4.51 (m, 2H, C*H*), 4.83 (m, 2H, C_5H_4), 5.29 (m, 2H, C_5H_4), 5.39 (m, 2H, C*H*). ^{13}C NMR ($CDCl_3$): δ 22.5 (*C*H$_3$), 26.7 (*C*H$_2$), 31.1 (*C*H$_2$), 76.6 (C_5H_4), 79.3 (*C*H), 89.6 (*C*H), 96.3 (C_5H_4); CH_3-*C*, *C*-C_5H_4, and C-C_5H_4 were not observed.

$[RuH(C_5H_4\text{-carb})(CO)(PPh_3)]$ (6). Complex **6** was obtained as a light maroon solid (215 mg, yield 65%). ^1H NMR (toluene-d_8): δ −11.05 (d, 1H, Ru-*H*, $^2J_{PH}$ = 30 Hz), 1.30 (s, 3H, C*H*$_3$), 1.20−3.00 (br, 10H, B*H*), 4.19 (m, 1H, C_5H_4), 4.25 (m, 1H, C_5H_4), 5.03 (m, 1H, C_5H_4,), 5.05 (m, 1H, C_5H_4), 7.50−7.60 (m, 15H, Ph). ^{31}P NMR (toluene-d_8): δ 66.72 (s, PPh_3).^{13}C NMR (toluene-d_8): δ 22.6 (s, *C*H$_3$), 75.3 (s, CH_3-*C*), 77.8 (s, *C*-C_5H_4), 83.4 (d, C_5H_4, $^2J_{PC}$ = 1.0 Hz), 86.5 (d, C_5H_4, $^2J_{PC}$ = 1.4 Hz), 87.4 (d, C_5H_4, $^2J_{PC}$ = 0.7 Hz), 90.4 (d, C_5H_4, $^2J_{PC}$ = 1.7 Hz), 98.1 (s, C_5H_4), 127.9−133.3 (Ph), 204.4 (d, *C*O, $^2J_{PC}$ = 14.85 Hz). FT IR (KBr, cm^{-1}): 3056−2857, 2569 (ν(B−H)), 1927, 1480, 1435, 1095, 745. Anal. Calcd for $C_{27}H_{33}B_{10}OPRu$ (M = 613.7): C, 52.70; H, 5.36. Found: C, 52.35; H, 5.25.

Synthesis of $[RuCl(\eta^5\text{-}C_5Me_4H)(PPh_3)_2]$ (7). This complex was prepared in two steps, employing the procedure already reported for the Cp* analogue.[17] A mixture of $RuCl_3 \cdot nH_2O$ (2.10 g, 9.3 mmol) and C_5Me_4H (2.7 mL, 1.85 g, 15.0 mmol), dissolved in ethanol (60 mL), was refluxed for 4 h; the resulting reddish brown

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Table 1. Crystallographic Data for [Ru(carb)(Cp)(PMe_2Ph)$_2$] (2) and [Ru(η^5-C_5Me_4H)Cl(PMe_2Ph)$_2$] (8)

	2	**8**
chemical formula	$C_{24}H_{40}B_{10}P_2Ru$	$C_{25}H_{35}ClP_2Ru$
fw (g mol^{-1})	599.67	533.99
T (K)	203(2)	293(2)
wavelength (Å)	1.5418	0.71073
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$Pna2_1$
a (Å)	14.519(5)	17.090(3)
b (Å)	13.791(3)	16.233(3)
c (Å)	14.581(5)	9.215(1)
β (deg)	94.09(5)	
volume (Å^3)	2912(2)	2556.4(7)
Z	4	4
D_{calc} (mg/m^3)	1.368	1.387
μ(cm^{-1})	54.75	8.52
F(000)	1232	1104
reflns collected	5727	3205
reflns unique	5511	3077
obsd reflns [$I > 2\sigma(I)$]	5077	3020
Params	494	271
final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0249$, $wR_2 = 0.0644$	$R_1 = 0.0362$, $wR_2 = 0.0872$
final R indices all data[a]	$R_1 = 0.0277$, $wR_2 = 0.0659$	$R_1 = 0.0376$, $wR_2 = 0.0887$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

suspension was filtered, giving a brown solid, which was washed with hexane (2 × 10 mL) and dried in vacuo (yield 63%). A solution of PPh_3 (2.10 g, 7.9 mmol) and the solid isolated in the previous step (1.0 g, 3.4 mmol) was refluxed for 12 h. The resulting suspension was filtered, and the isolated yellow solid was purified by recrystallization from a dichloromethane/hexane 1:1 mixture (yield 76%). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 6H, CH_3, $^4J_{PH}$ = 0.8 Hz), 1.11 (t, 6H, CH_3, $^4J_{PH}$ = 1.8 Hz), 3.76 (s, 1H, C_5Me_4H), 7.00−7.70 (m, 30H, Ph). ^{31}P NMR ($CDCl_3$): δ 40.4 (s, PPh_3). ^{13}C NMR ($CDCl_3$): δ 8.9 (*C*H$_3$), 9.5 (*C*H$_3$), 80.4 (s, *C*$_5$Me$_4$H), 85.3 (s, *C*$_5$Me$_4$H), 94.0 (s, *C*$_5$Me$_4$H), 127.0−142.0 (Ph). FT IR (KBr, cm^{-1}): 3052−2900, 1433, 1088, 698, 519. Anal. Calcd for $C_{45}H_{43}ClP_2Ru$ (M = 782.31): C, 69.09; H, 5.54. Found: C, 68.82; H, 5.48.

Synthesis of [RuCl(η^5-C_5Me_4H)(PMe_2Ph)$_2$] (8). The complex was prepared by displacement of the triphenylphosphine ligands from [RuCl(C_5Me_4H)(PPh_3)$_2$] (**7**) (0.25 g, 0.33 mmol) with a slight excess of PMe_2Ph (0.10 g, 0.70 mmol) in toluene (25 mL) under reflux for 8 h. The reaction mixture was then evaporated to small volume under reduce pressure; treatment with diethyl ether afforded a yellow solid, which was filtered and dried under vacuum (yield 63%). ^{1}H NMR ($CDCl_3$): δ 1.23 (br, 6H, CH_3), 1.32 (br, 6H, CH_3), 1.62 (m, 12H, CH_3 PMe_2Ph), 3.70 (s, 1H, C_5Me_4H), 7.25−7.65 (m, 10H, Ph). ^{31}P NMR ($CDCl_3$): δ 14.3 (s, PMe_2Ph). ^{13}C NMR ($CDCl_3$): δ 9.1 (*C*H$_3$), 18.2 (t, *C*H$_3$ PMe_2Ph), 18.9 (t, *C*H$_3$ PMe_2Ph), 81.3 (s, *C*$_5$Me$_4$H), 84.8 (m, *C*$_5$Me$_4$H), 93.2 (m, *C*$_5$Me$_4$H), 127.8−132.0 (Ph). FT IR (KBr, cm^{-1}): 3054−2902, 1433, 1101, 903, 700. Anal. Calcd for $C_{25}H_{35}ClP_2Ru$ (M = 534.02): C, 56.23; H, 6.61. Found: C, 55.83; H, 6.49.

Reactions of [RuCl(η^5-C_5Me_4H)L_2] (L = PPh_3, PMe_2Ph) with Licarb. The reactions were conducted using variable Licarb excesses (Ru/Hcarb/LiBu ratios 1:1.5:3 or 1:2:4) without any evidence of the formation of new products.

Crystal Structure Determination of 2 and 8. Crystals of **2** and **8** suitable for X-ray analysis were grown by slow crystallization at 0 °C of solutions in dichloromethane/hexane 1:1. Data of **2** were collected at 203 K on a Enraf Nonius CAD 4 single-crystal diffractometer (Cu− Kα radiation, λ = 1.5418 Å) and those of **8** at room temperature on a Philips PW1100 single-crystal diffractometer (FEBO system, Mo− Kα radiation, λ = 0.7107 Å). Details for the X-ray data are summarized in Table 1. The structures were solved by Patterson methods (**2**)[18] and by direct methods (**8**)[19] and refined against F^2 with SHELXL-97,[18] with anisotropic thermal parameters for all non-hydrogen atoms. Idealized geometries were assigned to the hydrogen atoms.

Results and Discussion

The cyclopentadienyl complexes [RuCl(Cp)L_1L_2] (L_1, L_2 = PPh_3, PMe_2Ph, $PMePh_2$; L_1L_2 = dppe; L_1L_2 = COD; L_1 = CO, L_2 = PPh_3) react with *o*-methyl carborane (Hcarb) in the presence of excess butyl lithium (Ru/Hcarb/LiBu 1:1.5:3) in toluene/diethyl ether to give substitution at the cyclopentadienyl ring or at the metal center depending on the nature of the coordination set (Scheme 1).

The resulting complexes are stable solids, which can be stored safely under an inert atmosphere. They are soluble in organic solvents, such as toluene, CH_2Cl_2, and $CHCl_3$, but mostly insoluble in *n*-hexane or diethyl ether. They have been fully characterized by elemental analysis and by standard spectroscopic techniques, and in the case of complexes [RuH(C_5H_4-carb)(PPh_3)$_2$] (**1**)[5] and [Ru(carb)(Cp)(PMe_2Ph)$_2$] (**2**), also by X-ray structure determination.

The ^{1}H NMR spectra of the hydrido complexes **1**, **5**, and **6** exhibit a characteristic hydride signal at negative fields (δ ca. −10 ppm), the multiplicity of which depends on the set of coordinated ligands: a triplet ($^2J_{PH}$ 34 Hz) for complex **1**, a doublet ($^2J_{PH}$ 30 Hz) for **6**, and a singlet for **5**. Furthermore, two pseudotriplets of signals for the cyclopentadienyl protons are present in the spectra of **1** and **5**, as expected for a C_5H_4X system;[20] the corresponding ^{13}C NMR spectra are consistent with the proton ones, and in particular, they show three signals for the Cp carbon atoms. The cyclopentadienyl region in the ^{1}H and ^{13}C spectra of **6** is more complex, due to the chirality at the ruthenium center; as a consequence, each CH group of the substituted Cp ligand resonates at different chemical shifts. The ^{31}P signals of **1** and **6** are observed at ca. 67 ppm, in the typical range of hydride phosphino complexes.[20,21]

The FTIR spectra of the hydrido compounds show, in particular, two bands: a narrow one with low intensity at 1970 cm^{-1} (stretching Ru−H) and a rather broad one centered at 2570 cm^{-1} (stretching B−H). The whole of these data, together with 2-D NMR spectra and NOE correlations, allows us to propose for **5** and **6** the same structure determined for **1**: a three-legged piano-stool structure with the hydride located under the carboranyl substituent and the neutral ligands positioned opposite to it.[5]

In the ESI-MS spectrum, **1** gives an ion at 585 *m*/*z* that corresponds to the loss of the hydride and of one triphenylphosphine ligand, to give [Ru(C_5H_4-carb)(PPh_3)]$^+$; further support is also given by the simulation of the isotopic pattern of the mass ion, which perfectly matches the experimental one.

The hydrido phosphine compounds slowly decompose in chlorinated solvents, to give phosphine oxides, whereas in toluene, they exhibit a very high stability, also at high temperatures (90−100 °C). The hydrido cyclooctadiene complex

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Scheme 1. Synthesis of Ruthenium Cyclopentadienyl Complexes 1−6

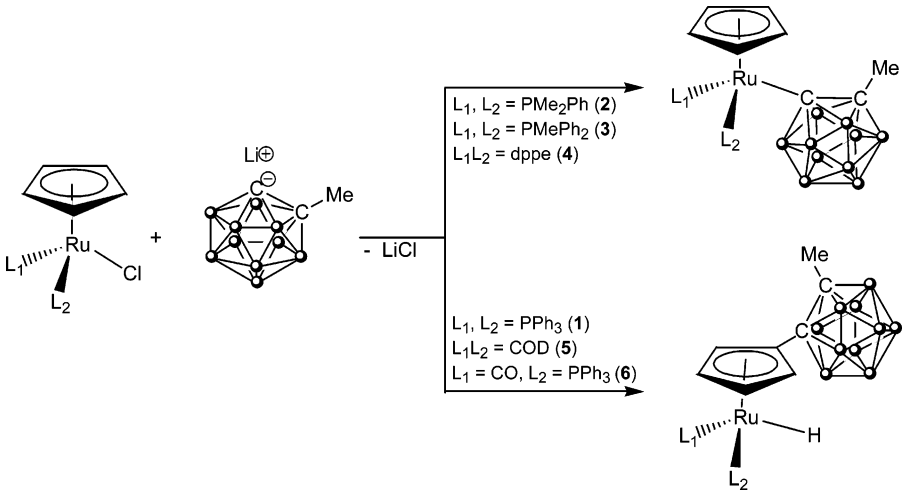


Table 2. Selected Bond Distances (Å) and Angles (deg) in Cyclopentadienyl Complexes 1, 2, and 8, [RuCl(Cp)(PMe$_2$Ph)$_2$], and [RuCl(Cp*)(PMe$_2$Ph)$_2$]

	1	**2**	**8**	[RuCl(Cp)(PMe$_2$Ph)$_2$][a]	[RuCl(Cp*)(PMe$_2$Ph)$_2$]
Ru−X[b]	1.55(2)	2.226(2)	2.458(2)	2.455(2)−2.436(2)	2.451(2)
Ru−P(1)	2.266(1)	2.312(1)	2.283(2)	2.292(2)−2.283(2)	2.297(1)
Ru−P(2)	2.274(1)	2.331(1)	2.293(2)	2.277(2)−2.288(2)	
Ru−Cp#[c]	1.907(2)	1.881(2)	1.871(2)	1.846−1.852	1.896(5)
P(1)−Ru−P(2)	97.38(2)	94.45(2)	95.49(7)	94.47(6)−96.14(6)	94.5(2)
X−Ru−P(1)	74.2(7)	94.40(6)	89.78(6)	90.83(6)−91.34(6)	89.62(5)
X−Ru−P(2)	87.3(7)	101.46(6)	88.95(6)	90.70(5)−86.40(5)	89.62(5)
Cp#−Ru−P(2)	126.3(3)	120.71(7)	122.9(2)	123.8−124.3	125.4(2)
Cp#−Ru−P(1)	129.9(3)	118.82(6)	128.5(2)	125.2−126.1	125.4(2)
Cp#−Ru−X	124.7(7)	121.11(8)	120.6(2)	122.4−121.9	

[a] Two independent molecules per unit cell. [b] X = D (**1**), C(6) (**2**), Cl (**8**), [RuCl(Cp)(PMe$_2$Ph)$_2$], and [RuCl(Cp*)(PMe$_2$Ph)$_2$]. [c] Cp# refers to the centroid of the cyclopentadienyl ring.

5 is unstable in $CDCl_3$ to give H/Cl exchange as already observed in the synthesis of the parent complex [RuCl(Cp)(COD)].[14]

The NMR features of **2**−**4** are markedly different. The ^{1}H, ^{13}C, ^{31}P, NMR spectra are consistent with coordination of the carboranyl anion to the metal center. A single signal is present in the ^{1}H and ^{13}C NMR spectra for the cyclopentadienyl proton and carbon nuclei, as expected for an unsubstituted ring. The ^{13}C NMR spectra show, in particular, the signal at δ 87.2 ppm, relative to the carboranyl carbon bonded to ruthenium, which appears as a triplet because of the virtual coupling with the two phosphines and is shifted well downfield with respect to the free ligand (δ 61.5 ppm).

The ^{31}P spectra show signals at higher fields with respect to the starting chloro complexes, as a consequence of the increased electron density on the metal center; the 1-methyl-1,2-dicarba-*closo*-dodecaborane exhibits in fact a lower electronegativity with respect to the chloride. In the ESI-MS spectra, complexes **2**−**4** exhibit a fragmentation path somewhat similar to **1**; in fact, their principal fragments correspond to [Ru(Cp)(L)]$^+$ (L = PMe$_2$Ph, PMePh$_2$, dppe), derived from a loss of a phosphine and the anionic carboranyl ligand.

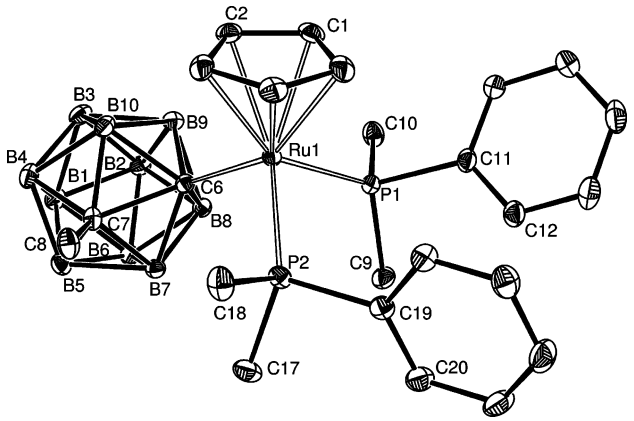


Figure 1. View of the structure of [Ru(carb)(Cp)(PMe$_2$Ph)$_2$] (**2**). Hydrogen atoms are omitted for clarity.

These data are in agreement with the structure of [Ru(carb)(Cp)(PMe$_2$Ph)$_2$] (**2**) determined by X-ray diffraction methods. A view of this complex is shown in Figure 1, and a selected list of bond distances and angles is given in Table 2. As expected, the complex assumes a three-legged piano-stool structure achieved as legs by the two P atoms of the phosphine molecules and by the C6 atom of the carboranyl ligand. By comparing the structure of **2** with that of **1**, it is possible to note that substitution of the hydride with the carboranyl ligand causes a slight lengthening of the Ru−P bond distances [2.3121(11) and 2.3312(7) Å in **2** vs 2.266(1) and 2.274(1) Å in **1**] and a slight narrowing of the P1−Ru1−P2 bond angle [94.45(2)° in **2** and 97.38(2)° in **1**] probably because of the steric hindrance of the carboranyl ligand.

The first investigated complex was [RuCl(Cp)(PPh$_3$)$_2$], and we justified the rather unexpected nucleophilic attack by the carboranyl anion at the Cp ring on the basis of the steric hindrance of the bulky triphenylphosphine ligands around the metal center.[5] The importance of steric factors in determining the site of nucleophilic attack has been confirmed by the behavior exhibited by the bis-phosphine complexes [RuCl(Cp)L$_1$L$_2$] (L$_1$, L$_2$ = PPh$_3$, PMe$_2$Ph, PMePh$_2$; L$_1$L$_2$ = dppe). In fact, in this series of cyclopentadienyl complexes, there is a smooth size variation of the two neutral ligands (cone angle values from

145 (PPh_3) to 136 ($PMePh_2$), 122 (PMe_2Ph), and 125 (dppe)),[22] and as expected, with the less hindering phosphine ligand set, the carboranyl anion coordinates the metal center via simple substitution of the chloride ligand. The molecular structure of **2** shows that this replacement has a very limited effect on the geometrical parameters of the coordination sphere around the metal. In other words, the carboranyl anion behaves like more common carbanions derived either from lithium alkyls or Grignard reagents, which are known to react with cyclopentadienyl halogen ruthenium complexes to give metal alkyl or aryl derivatives. However, the differences in cone angle values between PPh_3 and $PMePh_2$ seem too small to fully justify the observed different reaction pathways. In fact, the importance of electronic factors on determining the site attack is evidenced by the results obtained with the complex [RuCl(Cp)(CO)(PPh_3)], where one PPh_3 is replaced by one small CO ligand. Also in this case, rather unexpectedly, the reaction with Licarb gives substitution at the Cp ring (**6**). A similar result, attack at the Cp ring, is observed when the two phosphines are replaced by the non-hindering cyclooctadiene ligand (**5**). The evaluation of the role played by steric and electronic factors on determining the course of the reaction is not very easy; however, the whole of these data seems to indicate that electronic effects are predominant. In fact, the reactivity trend appears to be strictly related to the electron density on the metal, which is higher with the more basic phosphines (PMe_2Ph, $PMePh_2$, and dppe) and decreases in the presence of one CO ligand or of COD. This effect of the ligand set is quantified by electrochemical studies on a series of [RuCl(Cp)L_2] complexes, which clearly show that their oxidation potentials diminuish as the basicity of the ligands increases.[12,23] In this view, nucleophilic attack at the Cp ring is possible in the presence of poor electron-donor ligands, which lower the electron density on the metal and, as a consequence, on the coordinated Cp ring.

To gain further information on the role of steric factors on the reaction course and on its possible reaction mechanism, we have hindered the Cp ring with four methyl substituents and maintained a C−H group capable of undergoing a nucleophilic attack by carb$^-$. We have synthesized two new complexes with the tetramethyl cyclopentadienyl ligand (i.e., [RuCl(η^5-C_5Me_4H)(PPh_3)$_2$] (**7**) and [RuCl(η^5-C_5Me_4H)(PMe_2Ph)$_2$] (**8**)). The steric hindrance of the four methyl substituents does not introduce important modifications on the molecular structure of the complexes as shown by the structure determination of **8** by X-ray diffraction methods. In fact, the structural features of **8** are strictly comparable with those found in **2**, differing in the nature of the cyclopentadienyl ring (C_5Me_4H vs C_5H_5) and of the anionic ligand (Cl^- vs carb$^-$).

A view of the structure of **8** is given in Figure 2. A selected list of bond distances and angles is given in Table 2. The three-legged piano-stool structure shows as legs the two P atoms of the phosphine molecules and the Cl^- anion. The Ru−P bond distances, 2.283(2) and 2.293(2) Å, and the Ru−Cl one, 2.458(2) Å in **8**, are in good agreement with those of some comparable ruthenium complexes as [RuCl(Cp)(PMe_2Ph)$_2$][24] and [RuCl(Cp*)(PMe_2Ph)$_2$].[25] The repulsions between the phosphines and the Cp ring substituents are minimized, as a consequence of the reciprocal orientation of the ligands. In particular, the phenyl rings are oriented away from the plane defined by the carbons of the cyclopentadienyl ring; however, this conformation enhances the steric crowding around the chlorine ligand. Unexpectedly, the reactions of **7** and **8** with Licarb do not occur at all, and this gives indications as to a possible reaction mechanism.

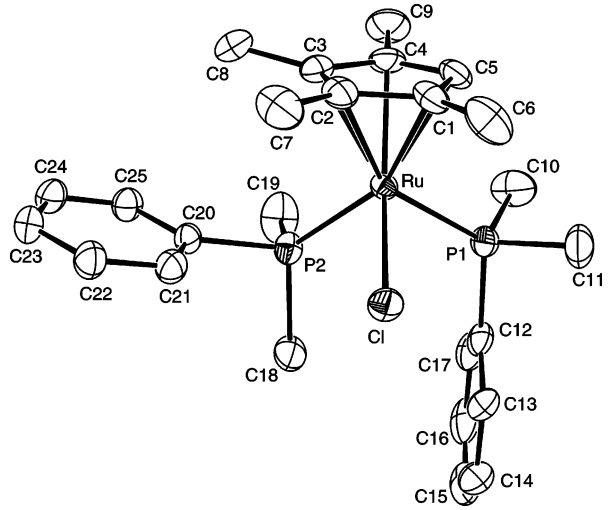
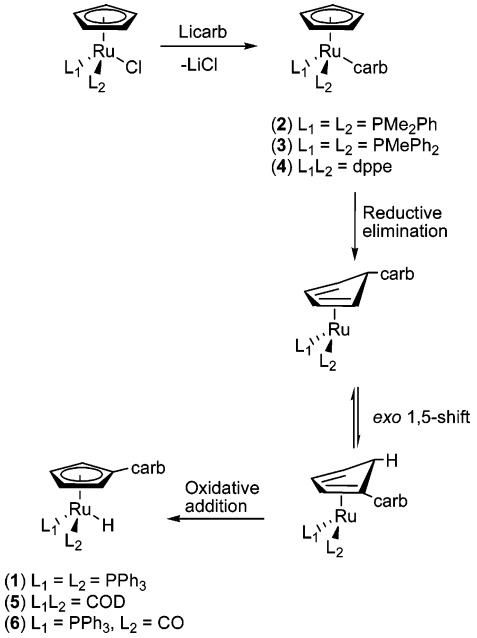


Figure 2. View of the structure of [RuCl(η^5-C_5Me_4H)(PMe_2Ph)$_2$] (**8**). Hydrogen atoms are omitted for clarity.

Scheme 2. Possible Reaction Mechanism for Synthesis of Complexes 1−6



The more likely mechanism for the observed reactivity is illustrated in Scheme 2.

The sequence of stages implies: (i) nucleophilic substitution of the chloride by the carboranyl anion and precipitation of LiCl, the resulting complex is the final product with strong electron-donor substituents (L_1, L_2 = 2 PMe_2Ph, dppe, 2 $PMePh_2$); (ii) reductive elimination process with formation of the C−C bond between the Cp and the carboranyl ligands favored by the poorer electron-donor ligand sets that reduce the electron density on the metal center; (iii) *exo*-1,5- shift to place a hydrogen in the endo position, followed by (iv) oxidative addition of this endo hydrogen to give the hydrido complexes **1**, **5**, and **6**. Considering in details the single stages: stage i is quite common, if we consider that Licarb can be seen as a particular type of lithium alkyl, which is known to give metathesis reactions with Ru−Cl bonds;[26] stage ii is very crucial and implies the migration of the carboranyl ligand from the ruthenium to the Cp carbon: this migration has been observed on an osmium cyclopentadienyl

complex for a coordinated EPh_3 (E = Ge, Si) anionic ligand and postulated for an alkyl group;[6] in stage iii, the *exo*-1,5 shift is also a well-known process operating in substituted and unsubstituted cyclopentadiene rings;[27] and in stage iv, intramolecular oxidative addition of a C−H bond to electron-rich metal centers is a fairly common reaction.[28] This mechanism is in agreement with the effect of the coordinated ligands and with the lack of reactivity exhibited by **7** and **8**, in which crowding around the Cl ligand should not allow its exchange by hindering the carboranyl ligand in step i.

An alternative mechanism involves in the first step direct attack of the carboranyl anion to the coordinated cyclopentadienyl ligand and successive oxidative addition by the C−H or C−carb bond to the ruthenium center giving the final complex. This mechanism, however, is more likely with an electron-poor or cationic Cp complex[29] and does not justify the behavior of **7** and **8**, which should, at least on steric grounds, easily react.

Supporting Information Available: Full listing of atomic coordinates, bond distances and angles, and summaries of the X-ray diffraction data for **2** and **8** and 1-D and 2-D NMR spectra for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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