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Synthesis of the half-sandwich ruthenium complexes $[Cp^*RuL_3]^+$ *via* naphthalene replacement in $[Cp^*Ru(C_{10}H_8)]^+$

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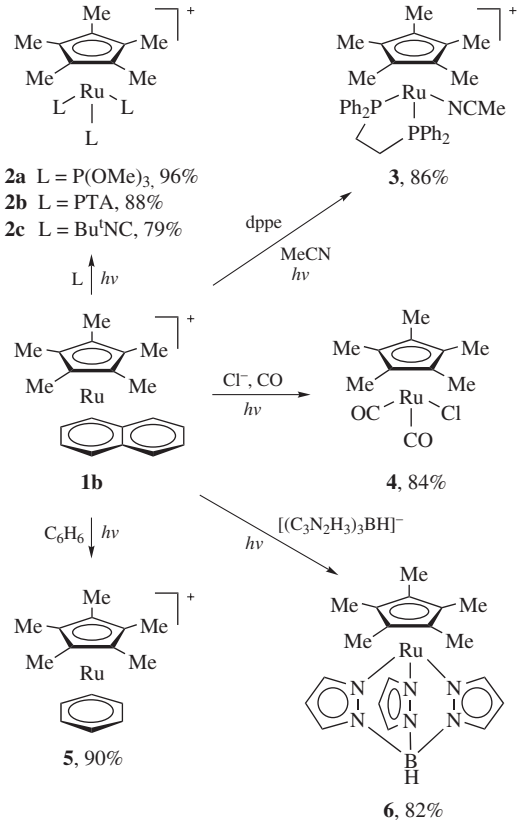
The cation $[Cp^*Ru(C_{10}H_8)]^+$ exchanges naphthalene for various ligands under near-UV (365 nm) or visible light irradiation giving the half-sandwich complexes $[Cp^*RuL_3]^+$ [L = $P(OMe)_3$, 1,3,5-triaza-7-phosphaadamantane, Bu^tNC], $[Cp^*Ru(dppe)(MeCN)]^+$, $Cp^*Ru(CO)_2Cl$, Cp*Ru[tris(pyrazolyl)borate] and $[Cp^*Ru(C_6H_6)]^+$ in 80–95% yields.

The half-sandwich cyclopentadienyl ruthenium complexes $[(C_5R_5)RuL_3]^+$ attract a considerable attention owing to their use in homogeneous catalysis.[1,2] They are commonly synthesized from the air-sensitive precursors $[(C_5R_5)Ru(MeCN)_3]^+$.[3] Recently, it was found that the cations $[CpRuL_3]^+$ (with the unsubstituted cyclopentadienyl ligand) are more conveniently prepared *via* the replacement of a naphthalene ligand in the air-stable complex $[CpRu(C_{10}H_8)]^+$ **1a**.[4] Here, we report the extension of this approach to the synthesis of the pentamethyl-substituted derivatives $[Cp^*RuL_3]^+$ from the air-stable and readily available[5] naphthalene complex $[Cp^*Ru(C_{10}H_8)]^+$ **1b**.

We found that heating **1b** with $P(OMe)_3$ in acetone at 60 °C for 5 h does not lead to naphthalene replacement. However, the same reaction under near-UV irradiation (365 nm) at room temperature gives the target half-sandwich complex $\{Cp^*Ru[P(OMe)_3]_3\}^+$ **2a** in 96% yield (Scheme 1).† Naphthalene



Scheme 1

† All reactions were carried out under argon, in anhydrous solvents, which were purified using standard procedures. The products were isolated in air. Complex $[\mathbf{1b}]PF_6$ was obtained using a published procedure.[5] Irradiation was performed by a household nail curing lamp (365 nm, 36 W). Column chromatography was performed on Acros silica gel (0.060–0.200 mm). The ^1H and ^{31}P NMR spectra were measured with a Bruker Avance 400 spectrometer at 20 °C in acetone-d_6 solutions unless otherwise stated. Chemical shifts are given in ppm relative to the residual signal of acetone-d_5 (^1H, δ 2.05 ppm) or an external standard of 85% H_3PO_4 (^{31}P).

*$[Cp^*RuL_3]PF_6$ [**2a–c**]PF_6 (general procedure)*. A solution of $[\mathbf{1b}]PF_6$ (25 mg, 0.05 mmol) and an excess of ligand L [$P(OMe)_3$, 59 μl, 0.5 mmol; 1,3,5-triaza-7-phosphaadamantane, 27 mg, 0.17 mmol; Bu^tNC, 37 μl, 0.5 mmol] in acetone (5 ml) was irradiated for 5 h. The solvent was evaporated; the residue was washed with Et_2O, dissolved in a minimal volume of CH_2Cl_2 ($MeNO_2$ in the case of **2b**), precipitated by an excess of a hexane–Et_2O mixture and dried *in vacuo*.

2a: yield 32 mg (96%). ^1H NMR, δ: 1.84 (q, 15H, Cp*, J_{HP} 2 Hz), 3.79 [m, 27H, $(MeO)_3P$]. ^{31}P NMR, δ: 148.2 (*cf.* ref. 12).

2b: yield 42 mg (88%). ^1H NMR, δ: 2.01 (m, 15H, Cp*), 4.13 (br. s, 18H, CH_2), 4.52 (d, 9H, CH_2, *J* 13 Hz), 4.60 (d, 9H, CH_2, *J* 13 Hz). ^{31}P NMR, δ: –37.2. Found (%): C, 36.92; H, 5.91. Calc. for $C_{28}H_{51}F_6N_9P_4Ru \cdot 2MeNO_2$ (%): C, 36.96; H, 5.89. Note that crystals submitted for X-ray diffraction correspond to the formula $[\mathbf{2b}]PF_6 \cdot 4MeNO_2$.

2c: yield 24 mg (79%). ^1H NMR, δ: 1.98 (s, 15H, Cp*), 1.56 (s, 27H, Me_3CNC). Found (%): C, 47.35; H, 7.00. Calc. for $C_{25}H_{42}F_6N_3PRu$ (%): C, 47.61; H, 6.71.

$[Cp^*Ru(dppe)(MeCN)]PF_6$ [**3**]PF_6. A solution of $[\mathbf{1b}]PF_6$ (50 mg, 0.1 mmol) and dppe (51 mg, 0.13 mmol) in acetonitrile (5 ml) was irradiated for 12 h. The solvent was evaporated, the residue was dissolved in a minimal volume of CH_2Cl_2 and precipitated by a mixture of hexane–Et_2O (1:1). The precipitate was dissolved in CH_2Cl_2 and eluted through a 5 cm silica gel column with a CH_2Cl_2–acetone mixture. The yellow band was collected and dried *in vacuo* to give [**3**]PF_6, 69 mg (86%). ^1H NMR, δ: 1.51 (s, 15H, Cp*), 1.83 (s, 3H, MeCN), 2.57 (br. s, 4H, CH_2), 7.63 (m, 20H, Ph). ^{31}P NMR, δ: 75.1 (*cf.* ref. 13).

$Cp^*Ru(CO)_2Cl$ **4**: Carbon monoxide was bubbled through an irradiated solution of $[\mathbf{1b}]PF_6$ (71 mg, 0.14 mmol), $[Et_3NCH_2Ph]Cl$ (37 mg, 0.16 mmol) in CH_2Cl_2 (5 ml) for 6 h. The solvent was evaporated, the residue was purified by elution through a 5 cm silica gel column first with hexane (to remove naphthalene) and then with a CH_2Cl_2–hexane (1:1) mixture. The yellow band was collected and dried *in vacuo* to give **4** (39 mg, 84%). ^1H NMR ($CDCl_3$) δ: 1.90 (s, 15H, Cp*) (*cf.* ref. 14).

$[Cp^*Ru(C_6H_6)]PF_6$ [**5**]PF_6. A solution of $[\mathbf{1b}]PF_6$ (57 mg, 0.11 mmol) and C_6H_6 (500 μl, 5.6 mmol) in acetone (5 ml) was irradiated for 18 h. The solvent was evaporated; the residue was washed with Et_2O, dissolved in a minimal volume of CH_2Cl_2, precipitated by Et_2O and dried *in vacuo* to give colorless [**5**]PF_6 (46 mg, 90%). ^1H NMR, δ: 2.09 (s, 15H, Cp*), 6.06 (s, 6H, C_6H_6) (*cf.* ref. 15).

replacement in **1b** also proceeds under visible light irradiation (>400 nm), although notably slower because the absorption of **1b** is maximal at 365 nm.[6]

Similar reactions of **1b** with Bu^{t}NC or 1,3,5-triaza-7-phosphaadamantane (PTA) produce tris-ligand complexes [Cp*Ru(Bu^{t}NC)$_3$]$^+$ **2c** or [Cp*Ru(PTA)$_3$]$^+$ **2b**, respectively. The reaction with 1,2-bis(diphenylphosphino)ethane (dppe) in acetonitrile affords the mixed-ligand complex [Cp*Ru(dppe)(MeCN)]$^+$ **3**. An attempt to prepare the tris-acetonitrile complex [Cp*Ru(MeCN)$_3$]$^+$ **2d** by the irradiation of **1b** in MeCN has failed, probably, because the strong absorption of formed product **2d** (λ_{max} = 370 nm, ε = 1287 dm^3 mol^{-1} cm^{-1}) prevents the absorption by starting complex **1b** (λ_{max} = 365 nm, ε = 760 dm^3 mol^{-1} cm^{-1}).[6] At the same time, refluxing **1b** in acetonitrile slowly produced **2d**. Unfortunately, we could not achieve 100% conversion in this reaction even after 20 h of reflux with the continuous extraction of released naphthalene by heptane. Note that an analogous reaction of unsubstituted naphthalene complex **1a** with MeCN reached 100% conversion within 35 h at room temperature.

In contrast to **1a**,[4(b)] complex **1b** does not react with carbon monoxide or chloride anion alone. The reaction with CO is presumably too slow, while naphthalene replacement by Cl$^-$ can be reversible.[8] However, **1b** readily reacts with Cl$^-$ and CO together giving Cp*Ru(CO)$_2$Cl **4** in 84% yield.

Complex **1b** also exchanges naphthalene for six-electron ligands. For example, the prolonged irradiation of **1b** with benzene leads to arene exchange resulting in thermodynamically more stable[9] complex [Cp*Ru(C$_6$H$_6$)]$^+$ **5** in 90% yield. The reaction with the tris(pyrazolyl)borate anion produces the neutral compound Cp*RuTp **6** [Tp = (C$_3$N$_2$H$_3$)$_3$BH] in 82% yield. However, a similar reaction with the substituted tris(3,5-dimethylpyrazolyl)-borate anion does not proceed, presumably, because of steric hindrances.

All of the compounds obtained were characterized by ^{1}H NMR spectroscopy. New complexes [**2b**]PF$_6$ and [**2c**]PF$_6$ were additionally characterized by elemental analysis. The structures of [**2b**]PF$_6$ and [**3**]PF$_6$ were established by X-ray diffraction (Figures 1 and 2).‡ The distance Ru···Cp* in cation **2b** (1.915 Å) is notably longer than that in **3** (1.870 Å), probably, because of steric effects imposed by large PTA ligands in **2b**. Interestingly, the Ru···Cp* distances in both **2b** and **3** are longer than that in the starting sandwich complex [Cp*Ru(C$_{10}$H$_8$)]$^+$ (1.803 Å),[5] which can be attributed to the strong *trans* influence of phosphorous ligands. The geometry of cation **3** is generally similar to that of the benzonitrile complex [Cp*Ru(dppe)(PhCN)]$^+$.[10]

In overall, we have developed a convenient method for the synthesis of Cp*Ru complexes *via* naphthalene replacement in [Cp*Ru(C$_{10}$H$_8$)]$^+$ **1b** under photochemical conditions. Compared to the unsubstituted complex [CpRu(C$_{10}$H$_8$)]$^+$, cation **1b** reacts less readily apparently because of steric hindrances. Nevertheless, we suggest that this general approach can be still applied to other ruthenium naphthalene complexes.[4(a),11]

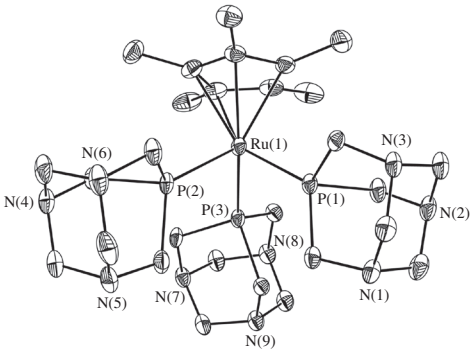


Figure 1 Structure of cation **2b** with ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)–P(1) 2.2997(11), Ru(1)–P(2) 2.2973(11), Ru(1)–P(3) 2.2926(11), Ru···C$_5$ 1.915.

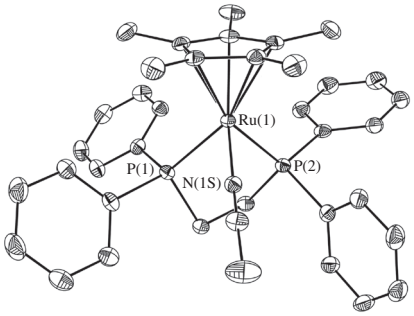


Figure 2 Structure of cation **3** with ellipsoids at a 50% probability level. All hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru(1)–N(1S) 2.0455(17), Ru(1)–P(1) 2.3013(5), Ru(1)–P(2) 2.3054(5), Ru···C$_5$ 1.870.

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*Cp*Ru(C$_3$N$_2$H$_3$)$_3$BH* **6**. A solution of [**1b**]PF$_6$ (50 mg, 0.1 mmol), K[(C$_3$N$_2$H$_3$)$_3$BH] (25 mg, 0.11 mmol) in acetone (5 ml) was irradiated for 18 h. The solvent was evaporated, the residue was dissolved in a minimal volume of light petroleum and eluted through a silica column by a mixture of light petroleum–acetone (5:1). The yellow band was collected, and the eluent was evaporated *in vacuo* to give **6** (36 mg, 82%). ^{1}H NMR, δ: 1.82 (s, 15H, Cp*), 6.19 (m, 3H, CH), 7.64 (m, 3H, CH), 7.86 (br. s, 3H, CH) (*cf*. ref. 16).

‡ *Crystallographic data*. Crystals of [**2b**]PF$_6$·4MeNO$_2$ (C$_{32}$H$_{63}$F$_6$N$_{13}$O$_8$P$_4$Ru, M = 1096.90) are monoclinic, space group $C2/c$, at 120 K: a = 23.1405(14), b = 18.2330(11) and c = 22.0670(13) Å, β = 90.0410(10)°, V = 9310.5(10) Å^3, Z = 8 (Z' = 1), d_{calc} = 1.565 g cm^{-3}, μ(MoKα) = 5.59 cm^{-1}, F(000) = 4544.

Crystals of [**3**]PF$_6$ (C$_{38}$H$_{42}$F$_6$NP$_3$Ru, M = 820.71) are monoclinic, space group $P2_1/c$, at 120 K: a = 11.4436(6), b = 17.3250(9) and c = 19.1253(9) Å, β = 104.4260(10)°, V = 3672.2(3) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.484 g cm^{-3}, μ(MoKα) = 6.17 cm^{-1}, F(000) = 1680.

Intensities of 54977 and 43783 reflections were measured with a Bruker APEX2 CCD diffractometer [λ(MoKα) = 0.71072Å, ω-scans, 2θ < 58°]; 12361 and 9766 independent reflections (R_{int} = 0.0983 and 0.0418) were used in the further refinement of [**2b**]PF$_6$·4MeNO$_2$ and [**3**]PF$_6$, respectively. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The H(C) atom positions were calculated, and they were refined in the isotropic approximation within a riding model. The refinement for [**2b**]PF$_6$·4MeNO$_2$ and [**3**]PF$_6$ converged, respectively, to wR_2 = 0.1713 and 0.0784, GOF = 0.995 and 1.052 for all the independent reflections [R_1 calculated against F for 7883 and 8190 observed reflections with $I > 2\sigma(I)$, is 0.0541 and 0.0343]. All calculations were performed using SHELXTL PLUS 5.0.

CCDC 994750 and 994751 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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