[Ru(η⁵-C₅Me₅)(Me₂NCH₂CH₂NMe₂)]⁺, a Stable 16-Electron Complex. Reaction with Dioxygen and Formation of a Monomeric Hydroxoruthenium Tetramethylfulvene Complex

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Summary: NaBAr'₄ (Ar' = 3,5-C₆H₃(CF₃)₂) abstracts chloride from $Ru(\eta^5$ -C₅Me₅)(Me₂NCH₂CH₂NMe₂)Cl (1) in Et₂O to give the stable cationic 16e complex [Ru(η^5 -C₅Me₅)(Me₂NCH₂CH₂NMe₂)]BAr'₄ (2). Exposure of a Et₂O solution of 2 to air at room temperature yields the novel monomeric hydroxotetramethylfulvene complex [Ru(η^6 -C₅Me₄CH₂)(Me₂NCH₂CH₂NMe₂)(OH)]BAr'₄ (4).

Coordinatively unsaturated half-sandwich ruthenium complexes that are not stabilized by heteroatomic anionic ligands through metal-ligand multiple bonds, e.g., alkoxides or halides,¹ appear to be very reactive and to date have not been isolated or structurally characterized. Thus, compounds of the type [Ru(η^5 -C₅- $Me_5)(P-P)]^+$ (P-P = tertiary bisphosphines) are prepared in situ and react readily with dioxygen to give stable peroxo Ru(IV) complexes [Ru(η^5 -C₅Me₅)(P-P)(η^2 - O_2]⁺.² The related complex [Ru(η^5 -C₅Me₅)(Ph₂PCH₂- (CH_2NMe_2)]⁺ smoothly undergoes *N*-methyl β -hydrogen elimination to give a cyclometallated complex.³ If the P-P or P-N coligand is replaced with a diamine, N-N, group, a remarkably stable unsaturated complex is obtained. Herein we report the first cationic 16e ruthenium complex $[Ru(\eta^5 \cdot \hat{C}_5 Me_5)(Me_2 NCH_2 CH_2 NMe_2)]^+$, adding to the recently described isostructural iron variants $[Fe(\eta^5-C_5Me_5)(Ph_2PCH_2CH_2PPh_2)]PF_6^{4a}$ and [Fe(η^5 -C₅Me₅)(Prⁱ₂PCH₂CH₂PPrⁱ₂)]BPh₄,^{4b} and also delineate some reactivities. It may be noted that the solid $Ru(\eta^{5}-C_{5}Me_{5})(acac)$ purported to be a 16e complex⁵ turned out to be a dimer.⁶

Halide abstraction from $Ru(\eta^5-C_5Me_5)(Me_2NCH_2CH_2-NMe_2)Cl$ (1)⁷ with NaBAr'₄ (Ar' = 3,5-C₆H₃(CF₃)₂)⁸ in



Figure 1. Structural view of $[Ru(\eta^5-C_5Me_5)(Me_2NCH_2CH_2-NMe_2)]BAr'_4$ (**2**). Selected bond lengths (Å) and angles (deg): $Ru-C(1-5)_{av}$, 2.124(7); Ru-N(1), 2.183(7); Ru-N(2), 2.180(6); N(1)-Ru-N(2), 80.3(3).

Et₂O affords the blue cationic 16e complex [Ru(η^5 -C₅-Me₅)(Me₂NCH₂CH₂NMe₂)]BAr'₄ (**2**) in 92% isolated yield.^{9,10,11} Characterization of **2** was achieved by elemental analysis, and ¹H and ¹³C{¹H} NMR spectroscopies.⁹ The complex is characterized by the presence of single resonances in the ¹H NMR spectrum for the NMe₂ and NCH₂CH₂N protons. The simplicity of the spectrum is indicative of a cationic complex that has $C_{2\nu}$ symmetry. This is also supported by the ¹³C{¹H} NMR data and unequivocally confirmed by X-ray crystallography (see Figure 1).¹² The angle between the planes defined by the C₅Me₅ ring and the atoms N(1), Ru, and N(2) is 89.3(3)°, indicating no pyramidalization

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⁽⁹⁾ Preparation and data for **2**: A solution of **1** (86 mg, 0.222 mmol) in Et₂O (4 mL) was treated with NaBAr'₄ (196 mg, 0.222 mmol) and stirred for 5 min at room temperature. After removal of the solvent, the residue was dissolved in Et₂O (0.5 mL), insoluble materials were removed by filtration, and the blue product was precipitated by addition of *n*-hexane. Yield: 248 mg (92%). Anal. calcd. for C₄₈H₄₃: BF₂₄N₂Ru: C, 47.42; H, 3.57; N, 2.30. Found: C, 47.77; H, 3.83; N, 2.04. ¹H NMR (δ , CD₂Cl₂, -40 °C): 7.76 (m, 8H), 7.61 (s, 4H), 2.88 (s, 12H, NMe₂), 1.80 (s, 4H, NCH₂CH₂N), 1.45 (s, 15H, C₅Me₅). ¹³C{¹H} NMR (δ , CD₂Cl₂, -40 °C): 160.3 (q, *J*_{BC} = 49.6 Hz), 133.3, 127.4 (q, *J*_{CF} = 31.5 Hz), 123.1 (q, *J*_{CF} = 272.3 Hz), 115.9, 69.3 (*C*₅Me₅).

⁽¹⁰⁾ If NaBPh₄ is used for halide abstraction, not **2** but the sandwich complex $Ru(\eta^5-C_5Me_5)(\eta^6-C_6H_5BPh_3)$ is quantitatively formed.

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⁽¹²⁾ Crystal data of **2**: monoclinic space group $P2_1/c$ (no. 14), a = 12.968(5) Å, b = 19.841(8) Å, c = 21.505(8) Å, $\beta = 104.91(1)^\circ$, V = 5347-(4) Å³, Z = 4, $R_I = 0.065$ ($I \ge 2\sigma(I)$), $R_I = 0.089$ (all data), $wR_2 = 0.192$ (all data), no. of reflections 6880, no. of refined parameters 677.



at the metal center. A planar ground-state structure has indeed been predicted on the basis of MO calculations for diamagetic d^6 complexes of the types CpML₂ and CpMLL' when L and L' are pure or predominant σ -donor ligands.^{1,13} The shortest distance between the ruthenium center and the carbon and hydrogen atoms of the NMe₂ groups is 2.97 and 3.05 Å, respectively, excluding agostic interactions. Compound 2 is remarkably stable for a 16e complex and does not react with H₂, HSiEt₃, or MeBr. However, treatment of **2** with Br₂ (0.5 equiv) affords the monobromo Ru(III) complex $[Ru(\eta^5-C_5Me_5)(Me_2NCH_2CH_2NMe_2)Br]^+$ (3) instead of the expected dibromo Ru(IV).^{2a}

Exposure of a Et_2O solution of **2** to air at room temperature yields the novel monomeric hydroxotetramethylfulvene complex $[Ru(\eta^6-C_5Me_4CH_2)(Me_2NCH_2-$ CH₂NMe₂)(OH)]BAr'₄ (4) in 86% yield (Scheme 1). This reaction involves methyl C-H bond cleavage of the C5-Me₅ ligand. ¹H and ¹³C{¹H} NMR spectra of **4** showed the characteristic resonances of the coligands.¹⁴ The X-ray analysis of crystals of 4 revealed¹⁵ its monomeric nature (see Figure 2). The coordination about the Ru-(II) is approximately octahedral, three sites being taken up by an η^6 -tetramethylfulvene, the remaining three by one terminal OH group and the Me₂NCH₂CH₂NMe₂ ligand. The methylenic =CH₂ is bent toward the metal by about 0.87 Å from the C₅ plane, corresponding to an angle of about 39.2°. Dioxygen-induced methyl C-H activations of transition metal coordinated C₅Me₅ and C₆Me₆ ligands, which may be related to this process, have been reported previously.¹⁶ The formation of a hydroxo species could involve prior dioxygen coordination at ruthenium. Indeed, if the reaction of $\mathbf{2}$ with O_2 is carried out at -50 °C in Et₂O, a diamagnetic complex, tentatively formulated as $[Ru(\eta^5-C_5Me_5)(Me_2NCH_2CH_2 NMe_2(O_2)^+$ (5), but contaminated with 4 (ca. 10%), is isolated and characterized by ${}^{1}H$ and ${}^{13}C{}^{1}H$ NMR



Figure 2. Structural view of $[Ru(\eta^6-C_5Me_4CH_2)(Me_2NCH_2 CH_2NMe_2)(OH)]BAr'_4$ (4). Selected bond lengths (Å) and angles (deg): Ru-N(1), 2.213(5); Ru-N(2), 2.238(5); Ru-O, 1.990(3); Ru-C(1), 2.074(6); Ru-C(2), 2.158(6); Ru-C(3), 2.184(7); Ru-C(4), 2.218(7); Ru-C(5), 2.186(6); Ru-C(6), 2.430(11); N(1)-Ru-N(2), 80.3(2).

spectroscopies.¹⁷ In the ¹³C{¹H} NMR spectrum, resonances of the ring carbon atoms of the C₅Me₅ ligand are low-field-shifted from 69.3 ppm in **2** to 106.2 ppm in **5**, indicative of an oxidation state of ruthenium >+II. On warming an anaerobic acetone- d_6 solution of 5 (contaminated with 4) from -50 to 0 °C, 4 is formed quantitatively as monitored by ¹H NMR spectroscopy.¹⁷ This conversion is also achieved even at low temperature upon addition of PPh_3 (1 equiv), giving 4 and $O=PPh_3$ in a ratio of 1:1. This result is evidence of 5 containing coordinated dioxygen. It is not clear at present whether a d⁵ Ru(III) superoxo or a d⁴ Ru(IV) peroxo complex is dealt with. The diamagnetic behavior of 5 would be consistent with both descriptions since in the first case magnetic coupling between the metal (S $= \frac{1}{2}$ and the superoxide ligand ($S = \frac{1}{2}$) may occur, resulting in a ground state with S = 0.18 Unfortunately, IR measurements are hampered due to the intensive bands of the BAr'_4^- anion overlapping with the O–O stretching frequencies of coordinated dioxygen (O2-1200-1070 cm⁻¹, O₂²⁻ 930-740 cm⁻¹).¹⁸ The formulation of a superoxo Ru(III) compound is conjectural but is in line with the finding that no $Ru(\eta^5-C_5Me_5)$ complex in conjunction with N-donor ligands in the oxidation state +IV is known. It should also be noted that 5 does not react with Me₂C=CMe₂ to give an epoxide.

In summary, we have shown that the $Ru(\eta^5-C_5Me_5)$ fragment bearing a hard σ -donor N–N coligand actually forms a remarkably stable 16e complex, while in the

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⁽¹⁴⁾ Preparation and data for 4: A solution of 2 (123 mg, 0.101 mmol) in Et₂O (4 mL) was stirred at room temperature in the presence of air for 3 min. After removal of the solvent, the residue was dissolved in Et₂O (0.5 mL), insoluble materials were removed by filtration, and the product was precipitated by adding *n*-hexane. Yield: 107 mg (86%). Anal. Calcd for C₄₈H₄₃BF₂₄N₂ORu: C, 46.81; H, 3.52; N, 2.27. Found: C, 46.72; H, 3.68; N, 2.14. ¹H NMR (δ , acetone-*d*₆, -50 °C): 7.80 (m, 8H), 7.69 (s, 4H), 4.47 (s, 2H, =CH₂), 3.07–2.96 (m, 2H), 2.89 (s, 6H), 62.0, 56.2, 51.0, 9.1, 8.9.

⁽¹⁵⁾ Crystal data of 4: triclinic space group $P\overline{1}$ (no. 2), a = 12.400-(4) Å, b = 13.176(4) Å, c = 17.276(5) Å, $\alpha = 96.63(1)^\circ$, $\beta = 96.52(1)^\circ$, $\gamma = 95.38(1)^\circ$, V = 2769(2) Å³, Z = 2, $R_I = 0.054$ ($I \ge 2\sigma(I)$), $R_I = 0.079$ (all data), $wR_2 = 0.163$ (all data), no. of reflections 9699, no. of refined parameters 919.

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case of the $Ph_2PCH_2CH_2NMe_2$ coligand oxidative addition of the methyl C–H bond takes place. For the Me₂-NCH₂CH₂NMe₂ ligand, not even any agostic interaction between the ruthenium center and the *N*-methyl C–H bond could be observed. Further, *in situ* prepared 16e complexes with a bisphosphine coligand are reactive toward H₂, Br₂, or O₂ undergoing oxidative addition to form Ru(IV) complexes. In contrast with the N–N coligand, such 2e changes do not appear to be realized, but instead a Ru(III) complex is favored. From this point of view, coordination of dioxygen should lead to a superoxo rather than a peroxo compound. This intermediate eventually activates a methyl C–H bond of the $C_5 M e_5$ ligand, giving rise to the hydroxoruthenium tetramethylfulvene complex.

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Supporting Information Available: Text giving full experimental details and analytical data for complex **3** and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **2** and **4** (32 pages). Ordering information is given on any current masthead page.

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