$[Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)]^+$, a Stable 16-Electron Complex. Reaction with Dioxygen and Formation of a Monomeric Hydroxoruthenium Tetramethylfulvene Complex

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*Summary: $NaBAr'_4$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) abstracts chloride from $Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)Cl$ (**1**) in Et_2O to give the stable cationic 16e complex $[Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)]BAr'_4$ (**2**). Exposure of a Et_2O solution of **2** to air at room temperature yields the novel monomeric hydroxotetramethylfulvene complex $[Ru(\eta^6\text{-}C_5Me_4CH_2)(Me_2NCH_2CH_2NMe_2)(OH)]BAr'_4$ (**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 $[Ru(\eta^5\text{-}C_5Me_5)(P{-}P)]^+$ (P−P = tertiary bisphosphines) are prepared *in situ* and react readily with dioxygen to give stable peroxo Ru(IV) complexes $[Ru(\eta^5\text{-}C_5Me_5)(P{-}P)(\eta^2\text{-}O_2)]^+$.[2] The related complex $[Ru(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CH_2NMe_2)]^+$ 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 $[Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)]^+$, adding to the recently described isostructural iron variants $[Fe(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CH_2PPh_2)]PF_6$[4a] and $[Fe(\eta^5\text{-}C_5Me_5)(Pr^i_2PCH_2CH_2PPr^i_2)]BPh_4$,[4b] and also delineate some reactivities. It may be noted that the solid $Ru(\eta^5\text{-}C_5Me_5)(acac)$ purported to be a 16e complex[5] turned out to be a dimer.[6]

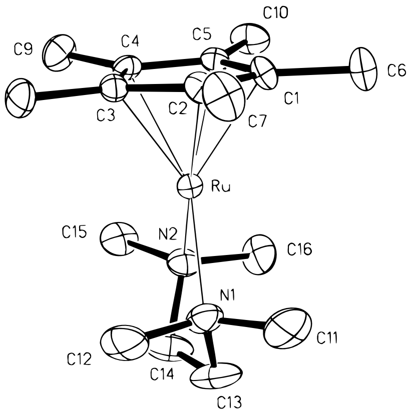

Figure 1. Structural view of $[Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)]BAr'_4$ (**2**). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$, 2.124(7); Ru−N(1), 2.183(7); Ru−N(2), 2.180(6); N(1)−Ru−N(2), 80.3(3).

Halide abstraction from $Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)Cl$ (**1**)[7] with $NaBAr'_4$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$)[8] in Et_2O affords the blue cationic 16e complex $[Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)]BAr'_4$ (**2**) in 92% isolated yield.[9,10,11] Characterization of **2** was achieved by elemental analysis, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies.[9] The complex is characterized by the presence of single resonances in the ^1H NMR spectrum for the NMe_2 and NCH_2CH_2N protons. The simplicity of the spectrum is indicative of a cationic complex that has C_{2v} symmetry. This is also supported by the $^{13}C\{^1H\}$ NMR data and unequivocally confirmed by X-ray crystallography (see Figure 1).[12] The angle between the planes defined by the C_5Me_5 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 Et_2O (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 Et_2O (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 $C_{48}H_{43}BF_{24}N_2Ru$: C, 47.42; H, 3.57; N, 2.30. Found: C, 47.77; H, 3.83; N, 2.04. ^1H NMR (δ, CD_2Cl_2, −40 °C): 7.76 (m, 8H), 7.61 (s, 4H), 2.88 (s, 12H, NMe_2), 1.80 (s, 4H, NCH_2CH_2N), 1.45 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, −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_5Me_5), 57.1, 48.3, 8.5 (C_5Me_5).

(10) If $NaBPh_4$ is used for halide abstraction, not **2** but the sandwich complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5BPh_3)$ is quantitatively formed.

(11) For related 16e ruthenium complexes, see: Campion, B. K.; Heyn, R. H.; Tilley, D. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278. Lindner, E.; Haustein, M.; Mayer, H. A.; Gierling, K.; Fawzi, R.; Steinmann, M. *Organometallics* **1995**, *14*, 2246. Sutter, J.-P.; James, S. L.; Steenwinkel, P.; Karlen, T.; Grove, D. M.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 941. Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Mikami, A. Tani, K.; Nakamura, A. *Organometallics* **1997**, *16*, 1016.

(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, $\beta = 104.91(1)°$, $V = 5347(4)$ Å^3, $Z = 4$, $R_1 = 0.065$ ($I \geq 2\sigma(I)$), $R_1 = 0.089$ (all data), $wR_2 = 0.192$ (all data), no. of reflections 6880, no. of refined parameters 677.

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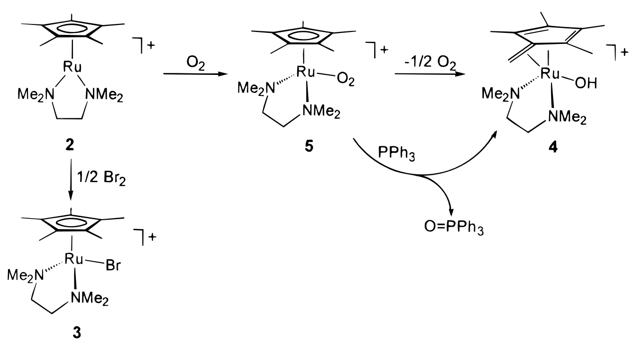
Scheme 1



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 $CpML_2$ 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 NMe_2 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 H_2, $HSiEt_3$, or MeBr. However, treatment of **2** with Br_2 (0.5 equiv) affords the monobromo Ru(III) complex $[Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)Br]^+$ (**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 $[Ru(\eta^6\text{-}C_5Me_4CH_2)(Me_2NCH_2CH_2NMe_2)(OH)]BAr'_4$ (**4**) in 86% yield (Scheme 1). This reaction involves methyl C−H bond cleavage of the C_5Me_5 ligand. ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** showed the characteristic resonances of the coligands.[14] The X-ray analysis of crystals of **4** revealed[15] 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 $Me_2NCH_2CH_2NMe_2$ ligand. The methylenic $=CH_2$ is bent toward the metal by about 0.87 Å from the C_5 plane, corresponding to an angle of about 39.2°. Dioxygen-induced methyl C−H activations of transition metal coordinated C_5Me_5 and C_6Me_6 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 **2** with O_2 is carried out at −50 °C in Et_2O, a diamagnetic complex, tentatively formulated as $[Ru(\eta^5\text{-}C_5Me_5)(Me_2NCH_2CH_2NMe_2)(O_2)]^+$ (**5**), but contaminated with **4** (ca. 10%), is isolated and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies.[17] In the $^{13}C\{^1H\}$ NMR spectrum, resonances of the ring carbon atoms of the C_5Me_5 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 d^5 Ru(III) superoxo or a d^4 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 ($S = {}^1/_2$) and the superoxide ligand ($S = {}^1/_2$) 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 (O_2^- 1200−1070 cm^{-1}, O_2^{2-} 930−740 cm^{-1}).[18] The formulation of a superoxo Ru(III) compound is conjectural but is in line with the finding that no $Ru(\eta^5\text{-}C_5Me_5)$ 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 $Me_2C{=}CMe_2$ to give an epoxide.

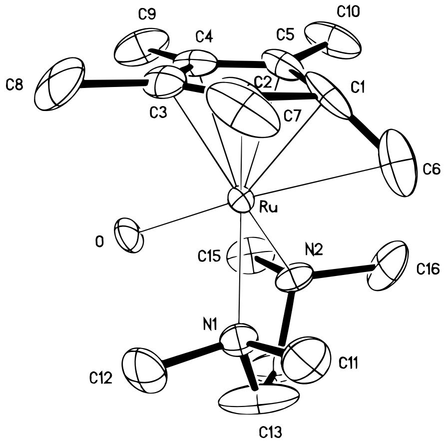


Figure 2. Structural view of $[Ru(\eta^6\text{-}C_5Me_4CH_2)(Me_2NCH_2CH_2NMe_2)(OH)]BAr'_4$ (**4**). Selected bond lengths (Å) and angles (deg): Ru−N(1), 2.213(5); Ru−N(2), 2.238(5); Ru−O, 1.990(3); Ru−C(1), 2.074(6); Ru−C(2), 2.158(6); Ru−C(3), 2.184(7); Ru−C(4), 2.218(7); Ru−C(5), 2.186(6); Ru−C(6), 2.430(11); N(1)−Ru−N(2), 80.3(2).

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

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[13] Ward, T. R.; Schafer, O.; Daul, C.; Hofmann, P. *Organometallics* **1997**, *16*, 3207.

[14] Preparation and data for **4**: A solution of **2** (123 mg, 0.101 mmol) in Et_2O (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 Et_2O (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 $C_{48}H_{43}BF_{24}N_2ORu$: 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, $=CH_2$), 3.07−2.96 (m, 2H), 2.89 (s, 6H), 2.74−2.62 (m, 2H), 2.55 (s, 6H), 1.74 (s, 6H), 1.72 (s, 6H). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, −50 °C): 163.0 (q, J_{BC} = 50.1 Hz), 135.9, 130.4 (q, J_{CF} = 32.0 Hz), 125.8 (q, J_{CF} = 271.8 Hz), 119.1, 103.2, 95.4, 70.3, 66.7, 62.0, 56.2, 51.0, 9.1, 8.9.

[15] Crystal data of **4**: triclinic space group $P\bar{1}$ (no. 2), $a = 12.400(4)$ Å, $b = 13.176(4)$ Å, $c = 17.276(5)$ Å, $\alpha = 96.63(1)°$, $\beta = 96.52(1)°$, $\gamma = 95.38(1)°$, $V = 2769(2)$ Å^3, $Z = 2$, $R_1 = 0.054$ ($I \geq 2\sigma(I)$), $R_1 = 0.079$ (all data), $wR_2 = 0.163$ (all data), no. of reflections 9699, no. of refined parameters 919.

[16] For related ruthenium fulvene complexes, see: Fan, L.; Turner, M. L.; Hursthouse, M. B.; Malik, K. M. A.; Gusev, O. V.; Maitlis, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 385. Fan, L.; Wei, C.; Aigbirhio, F. I.; Turner, M. L.; Gusev, O. V.; Morozova, L. N.; Knowles, D. R. T.; Maitlis, P. M. *Organometallics* **1996**, *15*, 98. Li, C.; Luo, L.; Nolan, S. P.; Marshall, W.; Fagan, P. J. *Organometallics* **1996**, *15*, 3456. Kölle, U.; Kang, B.-S. *J. Organomet. Chem.* **1990**, *386*, 267. For ruthenium−hydroxo systems, see: Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875.

[17] NMR data for **5**: ^1H NMR (δ, acetone-d_6, −50 °C): 7.80 (m, 8H), 7.68 (s, 4H), 3.12−2.70 (m, 4H), 2.87 (s, 6H), 2.70 (s, 6H), 1.56 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, −50 °C): 163.1 (q, J_{BC} = 49.6 Hz), 135.8, 130.3 (q, J_{CF} = 32.0 Hz), 125.6 (q, J_{CF} = 271.8 Hz), 119.1, 106.2 (C_5Me_5), 64.7, 56.5, 52.4, 9.7 (C_5Me_5).

[18] (a) Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828. (b) Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Am. Chem. Soc.* **1994**, *116*, 12079. (c) Egan, J. W.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445.

case of the $Ph_2PCH_2CH_2NMe_2$ coligand oxidative addition of the methyl C−H bond takes place. For the $Me_2NCH_2CH_2NMe_2$ 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 H_2, Br_2, or O_2 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_5Me_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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