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Synthesis, Structure, and Disproportionation of Labile (η^6-C_6H_6)Ru(CH_3CN)$_2$$Cl^+$ Salts

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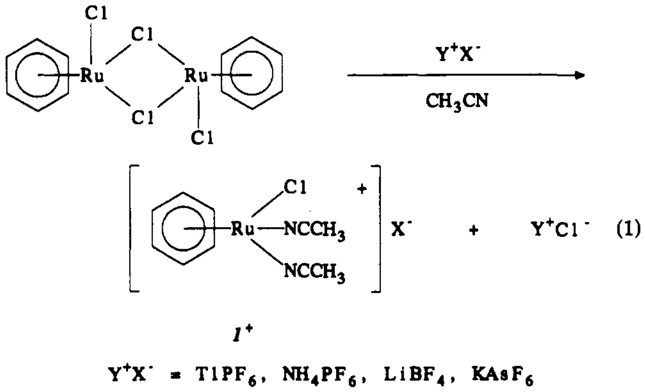
Summary: Chloride abstraction from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ *by a variety of reagents in acetonitrile leads to* $[(\eta^6\text{-}C_6H_6)RuCl(CH_3CN)_2]^+$ (1^+) *salts; the* BF_4^- *salt has been characterized by X-ray crystallography. In acetonitrile, both* CH_3CN *ligands are displaced by 1,2-bis(diphenylphosphino)benzene, 2,2′-bipyridine, or 1,10-phenanthroline to give* $[(\eta^6\text{-}C_6H_6)Ru(L{\sim}L)Cl]^+$ *chelates, while triphenylphosphine yields* $[(\eta^6\text{-}C_6H_6)Ru(PPh_3)(CH_3CN)Cl]^+BF_4^-$*. The lability of the Cl ligands is indicated by the disproportionation of* 1^+ *in nitromethane to yield* $\{[(\eta^6\text{-}C_6H_6)Ru]_2(\mu\text{-}Cl)_3\}^+$.

Organometallic complexes of ruthenium have been extensively studied due to their catalytic behavior in important reactions such as ring-opening metathesis polymerization.[1] During the development of routes to $[\eta^5\text{-}C_5(CH_3)_5]Ru(\eta^6\text{-arene})^+$ complexes,[2] we investigated a series of labile $[(\eta^6\text{-}C_6H_6)RuCl(CH_3CN)_2]^+$ (1^+) salts and found them to be versatile synthetic intermediates in organoruthenium chemistry. This report describes (a) the high-yield preparation of 1^+ salts from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (2), (b) ligand substitution reactions of 1^+, (c) the disproportionation of 1^+ to $\{[(\eta^6\text{-}C_6H_6)Ru]_2(\mu\text{-}Cl)_3\}^+$, and (d) the X-ray crystal structure of $1^+BF_4^-$.

Winkhaus and Singer first prepared 2 in 1967 and originally formulated it as a polymeric material due to its low solubility.[3] Subsequent reports[4,5] demonstrated the dimeric nature of the complex and delineated some of its reactivity patterns. Evidence was found for $[(\eta^6\text{-}C_6H_6)RuCl_2(\text{solvent})]$ species in solutions of 2 in coordinating solvents,[4] and $[(\eta^6\text{-}C_6H_6)Ru(CH_3CN)_3]^{2+}(BF_4)^-{}_2$ was synthesized from 2 and $Ag^+BF_4^-$.[4c] These results and the report[4b] of the intractable and poorly characterized $[(\eta^6\text{-}C_6H_6)RuCl(CH_3CN)_2]^+HgCl_3^-$ suggested the possibility of general and rational routes to 1^+ salts with conventional "innocent" counterions.[6]

To avoid the formation of $[(\eta^6\text{-}C_6H_6)Ru(CH_3CN)_3]^{2+}$, we sought chloride abstractors which would be less reactive than Ag^+. Reaction of 2 with 2 equiv of $TlPF_6$ in acetonitrile results in its clean conversion to $1^+PF_6^-$, while an excess of $TlPF_6$ leads to mixtures of 1^+ and $[(\eta^6\text{-}C_6H_6)Ru(CH_3CN)_3]^{2+}$. Surprisingly, reagents as innocuous as $LiBF_4$, NH_4PF_6, and $KAsF_6$ also convert 2 into 1^+ (eq 1). With these latter reagents, inert-atmosphere conditions are not required and yields in the 80–90% range are routinely obtained free of $[(\eta^6\text{-}C_6H_6)Ru(CH_3CN)_3]^{2+}$ contamination.[7] The salts of 1^+ with the above counterions are all yellow to orange crystalline materials. They appear to be indefinitely stable to air in the solid state and in acetonitrile solution. The lability of the acetonitrile ligands is apparent by the rapid CD_3CN/CH_3CN exchange in ^1H NMR spectra[7] of $1^+BF_4^-$.



As expected from this NMR behavior, the acetonitrile ligands of 1^+ may be displaced by other ligands. Reaction of $1^+BF_4^-$ in acetonitrile with 1,2-bis(diphenylphosphino)benzene, 2,2′-bipyridine, or 1,10-phenanthroline results in the clean formation of $[(\eta^6\text{-}C_6H_6)Ru(L{\sim}L)Cl]^+BF_4^-$ chelates, while the reaction of $1^+BF_4^-$ with 1 equiv of triphenylphosphine gives the monosubstituted product $[(\eta^6\text{-}C_6H_6)Ru(PPh_3)(CH_3CN)Cl]^+BF_4^-$ (Scheme I).[8] The Ru–Cl bonds in 1^+ also appear to be labile. Solutions of $1^+AsF_6^-$ in CH_3NO_2 show gradual color changes over the course of several days, and red prismatic crystals eventually precipitate.[9] Elemental analyses suggested the crystals

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[6] The $1^+BF_4^-$ salt was briefly mentioned as an intermediate generated in situ from 2 and $AgBF_4$, but it was not isolated or characterized: tom Dieck, H.; Kollvitz, W.; Kleinwächter, I. *Organometallics* **1986**, *5*, 1449.

[7] (a) Experimental details for $1^+BF_4^-$: Complex 2 (0.50 g, 1.00 mmol) and a 1.0 M CH_3CN solution of $LiBF_4$ (2.10 mL, 2.10 mmol) were placed in 25 mL of CH_3CN in an Erlenmeyer flask. No special precautions were taken to exclude air. The reddish suspension was stirred for 12 h and was then filtered to remove a colorless precipitate. The orange filtrate was evaporated to a solid, which was diffusion-crystallized from CH_3CN/Et_2O to give 0.63 g (82%) of $1^+BF_4^-$ as well-formed orange prisms. IR (cm^{-1}, $\nu_{C\equiv N}$, Nujol): 2324 w, 2298 w. ^1H NMR (400 MHz, CD_3CN, δ): 5.95 (s, C_6H_6). ^1H NMR (400 MHz, CD_3NO_2, δ): 6.02 (s, C_6H_6), 2.55 (s, CH_3CN). ^{13}C NMR (100 MHz, CD_3CN, ppm): 87.1 (s, C_6H_6). ^{13}C NMR (100 MHz, CD_3NO_2, ppm): 127.4 (s, $CH_3\mathit{C}N$), 87.6 (s, C_6H_6), 3.7 (s, $\mathit{CH_3}CN$). Dec pt: 273–278 °C (no melting). Anal. Calcd for $C_{10}H_{12}BClF_4N_2Ru$: C, 31.32; H, 3.15; N, 7.30. Found: C, 31.3; H, 3.2; N, 7.5. (b) Experimental details for $1^+PF_6^-$: Complex 2 (0.50 g, 1.00 mmol) and NH_4PF_6 (0.34 g, 2.10 mmol) were suspended in 25 mL of CH_3CN, and the mixture was stirred for 12 h. Reaction workup as above yielded 0.74 g (84%) of $1^+PF_6^-$ as orange crystals. Dec pt: 258–261 °C (no melting). Anal. Calcd for $C_{10}H_{12}ClF_6N_2PRu$: C, 27.19; H, 2.74; N, 6.34. Found: C, 27.5; H, 2.8; N, 6.8. (c) Experimental details for $1^+AsF_6^-$: Complex 2 (0.50 g, 1.00 mmol) and $KAsF_6$ (0.48 g, 2.10 mmol) were reacted as above to give 0.88 g (91%) of $1^+AsF_6^-$ as yellow-orange needles. Dec pt: 266–270 °C (no melting). Anal. Calcd for $C_{10}H_{12}AsClF_6N_2Ru$: C, 24.73; H, 2.49; N, 5.77. Found: C, 24.4; H, 2.5; N, 5.8.

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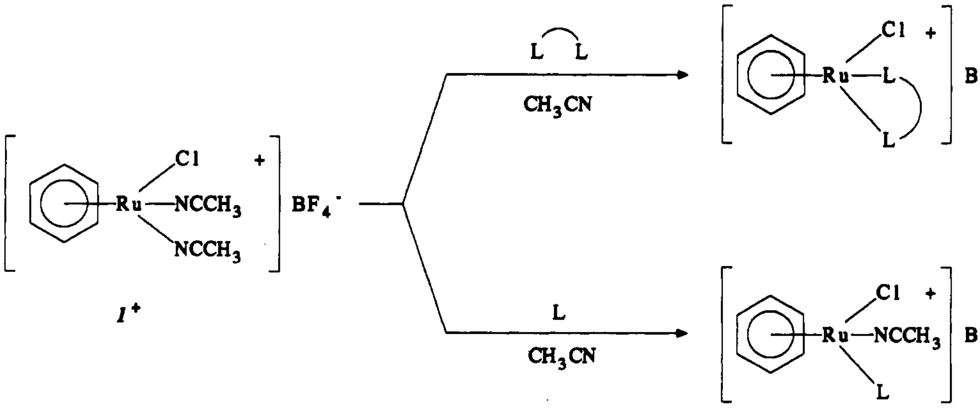
Scheme I



L⌒L = bis(diphenylphosphino)benzene, bipyridine, phenanthroline

L = triphenylphosphine

were $\{[(\eta^6\text{-}C_6H_6)Ru]_2(\mu\text{-}Cl)_3\}^+AsF_6^-$ ($3^+AsF_6^-$), and this has been confirmed by X-ray diffraction studies.[10] Complex 3^+ appears to result from the disproportionation of 1^+ into $(\eta^6\text{-}C_6H_6)Ru(Cl)_2$(solvent) and $[(\eta^6\text{-}C_6H_6)Ru(\text{solvent})_3]^{2+}$ (solvent = CH_3CN and/or CH_3NO_2) species. The $(\eta^6\text{-}C_6H_6)Ru(Cl)_2$(solvent) complex is then trapped by 1^+ to form the observed $3^+AsF_6^-$, which crystallizes from CH_3NO_2. Salts of 3^+ have been reported previously, and this disproportionation route to $3^+AsF_6^-$ is consistent with prior syntheses.[4c,11]

The unusual combination of high stability and high lability prompted us to explore the structure of 1^+ in more depth, and a single-crystal X-ray diffraction study was carried out on $1^+BF_4^-$.[12] The structure of the cation is shown in Figure 1. The ruthenium of 1^+ is formally in the +2 oxidation state, and the complex adopts the familiar "three-legged piano stool" geometry. A plane of symmetry passes through the Ru and Cl atoms and bisects the C3–C3′ and C5–C5′ bonds. The Ru–ring-plane distance of 1.655(1) Å is within the 1.622–1.717-Å range found for several other Ru^{II}(arene) complexes but is shorter than the average distance of 1.678 Å.[13] The Ru–Cl distance of 2.379(2) Å for $1^+BF_4^-$ also appears to be significantly shorter than the average bond length of 2.429 Å (range 2.396(7)–2.477(7) Å) in other $Ru^{II}Cl$ complexes.[14] The Ru–

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(8) (a) Experimental details for $[(\eta^6\text{-}C_6H_6)Ru(o\text{-}PPh_2C_6H_4PPh_2)Cl]^+BF_4^-$: A sample of $1^+BF_4^-$ (0.10 g, 0.26 mmol) and 1,2-bis(diphenylphosphino)benzene (0.125 g, 0.28 mmol) were stirred in 10 mL of acetonitrile for 8 h. The yellow reaction mixture was evaporated to a yellow tar, which crystallized upon addition of 2 mL of $CHCl_3$ to give yellow needles (0.207 g, 91%) of the product as a $CHCl_3$ solvate. ^1H NMR (400 MHz, CD_3CN, δ): 6.9–7.9 (m, $o\text{-}PPh_2C_6H_4PPh_2$), 7.58 (s, $CHCl_3$ solvate), 6.04 (s, C_6H_6). ^{13}C NMR (100 MHz, CD_3CN, ppm): 129–140 ($o\text{-}PPh_2C_6H_4PPh_2$), 96.3 (s, C_6H_6), 79.0 (s, $CHCl_3$ solvate). Dec pt: 242–244 °C. Anal. Calcd for $C_{36}H_{30}BClF_4P_2Ru\cdot CHCl_3$: C, 51.24; H, 3.60. Found: C, 51.0; H, 3.8. (b) Experimental details for $[(\eta^6\text{-}C_6H_6)Ru(2,2'\text{-bipyridine})Cl]^+BF_4^-$: A sample of $1^+BF_4^-$ (0.05 g, 0.13 mmol) and 2,2′-bipyridine (0.03 g, 0.19 mmol) were reacted as above. The gold-orange reaction mixture was evaporated to a yellow solid, which was diffusion-crystallized from CH_3CN/Et_2O to give 0.059 g (98%) of the product as opaque yellow crystals. ^1H NMR (400 MHz, CD_3CN, δ): 9.41 (d, J = 6 Hz), 8.32 (d, J = 8 Hz), 8.18 (t, J = 8 Hz), and 7.68 (t, J = 6 Hz, 2,2′-bipyridyl), 6.02 (s, C_6H_6). ^{13}C NMR (100 MHz, CD_3CN, ppm): 156.6, 155.8, 140.9, 126.8, and 124.7 (s, 2,2′-bipyridyl), 88.1 (s, C_6H_6). Dec pt: 233–234 °C. Anal. Calcd for $C_{16}H_{14}BClF_4N_2Ru$: C, 41.99; H, 3.08; N, 6.12. Found: C, 42.0; H, 3.2; N, 6.1. (c) Experimental details for $[(\eta^6\text{-}C_6H_6)Ru(1,10\text{-phenanthroline})Cl]^+BF_4^-$: A sample of $1^+BF_4^-$ (0.05 g, 0.13 mmol) and 1,10-phenanthroline (0.025 g, 0.14 mmol) were reacted as above to give orange crystals (0.062 g, 91%) of the product as a CH_3CN solvate. ^1H NMR (400 MHz, CD_3CN, δ): 9.74 (dd, J = 5, 1 Hz), 8.74 (dd, J = 8, 1 Hz), 8.14 (s), and 8.02 (dd, J = 8, 5 Hz, 1,10-phenanthroline), 6.10 (s, C_6H_6). ^{13}C NMR (100 MHz, CD_3CN, ppm): 156.6, 146.7, 139.8, 131.8, 128.4, and 127.1 (s, 1,10-phenanthroline), 87.7 (s, C_6H_6). Dec pt: 257–260 °C. Anal. Calcd for $C_{18}H_{14}BClF_4N_2Ru\cdot CH_3CN$: C, 45.96; H, 3.28; N, 8.04. Found: C, 45.8; H, 3.0; N, 7.9. (d) Experimental details for $[(\eta^6\text{-}C_6H_6)Ru(PPh_3)(CH_3CN)Cl]^+BF_4^-$: Triphenylphosphine (0.08 g, 0.31 mmol) and $1^+BF_4^-$ (0.10 g, 0.26 mmol) were stirred in 10 mL of CH_3CN for 3 h. The homogeneous reaction mixture was evaporated to an orange solid, which was diffusion-crystallized from CH_3CN/Et_2O to give 0.15 g (89%) of orange crystals of the product as a CH_3CN solvate. IR (cm^{-1}, $\nu_{C\equiv N}$, $CHCl_3$): 2325 w (CH_3CN solvate at 2292 w, 2255 w). ^1H NMR (400 MHz, CD_3CN, δ): 7.50–7.65 (m, PPh_3), 5.80 (s, C_6H_6). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.4–7.7 (m, PPh_3), 5.83 (s, C_6H_6), 2.02 (s, CH_3CN). ^{13}C NMR (100 MHz, CD_3CN, ppm): 129–135 (m, PPh_3), 92.4 (s, C_6H_6). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 128–134 (m, PPh_3), 127.4 (s, $CH_3\mathit{C}N$), 91.2 (s, C_6H_6), 3.7 (s, $\mathit{CH_3}CN$). Dec pt: 203–206 °C. Anal. Calcd for $C_{26}H_{24}BClF_4NPRu\cdot CH_3CN$: C, 52.07; H, 4.21; N, 4.34. Found: C, 51.9; H, 4.2; N, 4.3.

(9) Experimental details for $3^+AsF_6^-$: A sample of $1^+AsF_6^-$ (0.70 g, 1.44 mmol) was dissolved in 10 mL of hot CH_3NO_2, and the orange solution was filtered. The filtrate was allowed to stand in a sealed vial for 5 days. The solution gradually became red, and well-formed red crystals precipitated. The crystals were collected by filtration and washed with cold CH_3NO_2 and Et_2O to give 0.41 g (65%) of $3^+AsF_6^-$. Dec pt: >300 °C. ^1H NMR (400 MHz, CD_3NO_2, δ): 5.96 (s, C_6H_6). ^{13}C NMR (100 MHz, CD_3NO_2, ppm) 82.0 (s, C_6H_6). Anal. Calcd for $C_{12}H_{12}AsCl_3F_6Ru_2$: C, 22.05; H, 1.85. Found: C, 21.9; H, 1.7.

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(12) (a) Crystallographic data for $1^+BF_4^-$: $C_{10}H_{12}BClF_4N_2Ru$, mol wt 383.55, orthorhombic, space group *Pbcm* (No. 57), a = 7.661(4) Å, b = 10.394(1) Å, c = 17.753(1) Å, V = 1413.6 $Å^3$, Z = 4, d_{calcd} = 1.80 g cm^{-3}, $\lambda_{Mo\,K\alpha}$ = 0.710 73 Å, μ = 13.1 cm^{-1}. The data (1186 reflections, 1024 unique) were collected at 23 °C on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan mode (θ_{max} = 23°), and an empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least squares using 801 reflections with $I > 3.0\sigma(I)$ to R = 0.031, R_w = 0.047, and GOF = 2.31. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the arene ring were refined isotropically; hydrogens on the methyl groups could not be located and thus were not included in the calculations. The anion was disordered and modeled as two interpenetrating tetrahedra with eight F atoms of 0.5 occupancy. All calculations were performed on a PDP-11/34 computer using SDP-Plus.[12b] (b) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Konigsveld, H., Bassi, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

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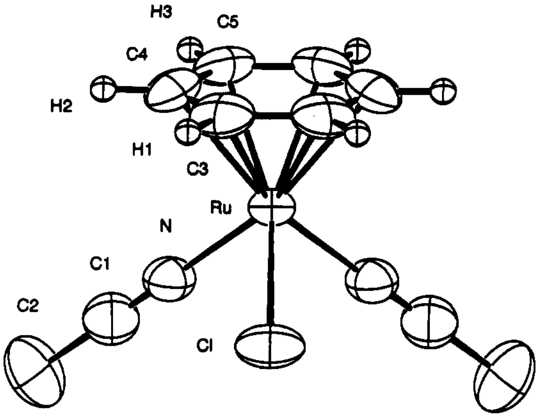

Figure 1. View of the cation of $1^+BF_4^-$. Important bond lengths (Å) and angles (deg): Ru–Cl = 2.379(2), Ru–N = 2.062(5), Ru–C3 = 2.166(5), Ru–C4 = 2.173(5), Ru–C5 = 2.188 (5), Ru–C_6H_6(plane) = 1.655(1), N–C1 = 1.135(7), C1–C2 = 1.482(9), C3–C3′ = 1.40(1), C3–C4 = 1.384(9), C4–C5 = 1.434 (8), C5–C5′ = 1.37(1); Cl–Ru–N = 85.3(1), N–Ru–N′ = 85.8 (3), Ru–N–C1 = 178.7(5), N–C1–C2 = 179.0(7), C3′–C3–C4 = 119.9(4), C3–C4–C5 = 120.4(6), C4–C5–C5′ = 119.6(3).

$NCCH_3$ linkage is linear, and the Ru–N distance of 2.062(5) Å is shorter than the 2.165(18) Å distance found in the related complex (1,5-COD)$RuCl_2(CO)(CH_3CN)$.[14d] The bond lengths and angles in $1^+BF_4^-$ are very similar to those found in the recently published $[(\eta^6\text{-}C_6H_6)Ru(CH_3CN)_3]^{2+}(PF_6)^-{}_2$ structure.[15]

In summary, a series of $[(\eta^6\text{-}C_6H_6)RuCl(CH_3CN)_2]^+$ salts, which are remarkably stable in the solid state and acetonitrile solution, have been synthesized in high yield. The salts are quite reactive, and both the acetonitrile and chloride ligands are labile. This combination of accessibility, stability, and lability makes the 1^+ salts potentially valuable synthetic reagents.

Supplementary Material Available: For $1^+BF_4^-$, text giving a structure determination discussion, figures giving stereoviews and the unit cell structure, and tables of crystal data, positional and thermal parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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