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Syntheses and Structures of Two Trifluoroacetate-Trapped Derivatives of a Ruthenium Butatrienylidene Complex

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Summary: The alkynyl ketone [$Ru(C{\equiv}CCOCHMe_2)(PPh_3)_2(Cp)$] *(1) reacts with trifluoroacetic anhydride at ambient temperature to give* [$Ru\{C{\equiv}CC(OCOCF_3)CMe_2\}(PPh_3)_2(Cp)$]$\cdot 0.5Et_2O$ *(2), an enynyl trifluoroacetate ester which structurally resembles a ruthenium butatrienylidene cation* ([$Ru{=}C{=}C{=}C{=}CR_2$]$^+$) *trapped by the attachment of a trifluoroacetate anion to* C_γ*. Compound 1 also reacts with 2 equiv of trifluoroacetic anhydride to form* [$Ru\{C{=}C(COCF_3)C(OCOCF_3)CMe_2\}(PPh_3)_2(Cp)$][$H(CF_3CO_2)_2$] *(3), in which* C_β *of compound 2 has been acylated by a trifluoroacetyl group. The structures of 2 and 3 have been determined by X-ray crystallography.*

Many stable transition-metal complexes of cumulated alkylidene ligands, i.e., vinylidene ($L_nM{=}C{=}CR_2$)[1-3] and allenylidene (propadienylidene, $L_nM{=}C{=}C{=}CR_2$)[1-7] complexes, have been isolated and characterized during the past 15 years. Dixneuf and co-workers have inferred the existence of pentatetraenylidene ($L_nM{=}C{=}C{=}C{=}C{=}CR_2$) complexes by trapping them with alcohols,[8-10] but no stable or transient metal butatrienylidene complexes ($L_nM{=}C{=}C{=}C{=}CR_2$) have yet been described. We report here an attempt to generate a cationic ruthenium butatrienylidene complex and the characterization of the resulting trifluoroacetate-trapped products.

The reaction of [$RuCl(PPh_3)_2(Cp)$] (Cp = η-C_5H_5),[11] $Me_3SiC{\equiv}CCOCMe_2H$,[12] and KF in refluxing methanol (Scheme I) results in the formation of [$Ru(C{\equiv}CCOCHMe_2)(PPh_3)_2(Cp)$] (1),[13] a crystalline, yellow solid which is stable in air indefinitely and in solution for several hours. The reaction between 1 and *1* equiv of trifluoroacetic anhydride (TFA) results in yellow, crystalline [$Ru\{C{\equiv}CC(OCOCF_3)CMe_2\}(PPh_3)_2(Cp)$]$\cdot 0.5Et_2O$ (2; 76% yield).[13] Compound 2 is air-stable as a solid and is stable in dichloromethane solution at −78 °C for many hours but quickly degrades in solution at room temperature. The reaction between 1 and 2 equiv of TFA leads to yellow, crystalline [$Ru\{C{=}C(COCF_3)C(OCOCF_3)CMe_2\}(PPh_3)_2(Cp)$][$H(CF_3CO_2)_2$] (3; 86% yield).[13]

The spectroscopic properties of 2, in particular alkynyl resonances in its ^{13}C NMR spectrum at δ_C 128.9 (C_α, triplet, $^2J_{PC}$ = 31.1 Hz) and 127.8 (C_β, triplet, $^3J_{PC}$ = 4.7 Hz) and a strong alkynyl infrared stretch at 2025 cm^{-1}, are consistent with the enynyl ester structure shown in Scheme I. The $^2J_{PC}$ value of 31.1 Hz for C_α is large in CD_2Cl_2, perhaps suggesting partial dissociation to the ion pair [$Ru(C{=}C{=}C{=}CMe_2)(PPh_3)_2(Cp)$]$^+$[$CF_3CO_2$]$^-$ (**2a**; Scheme I). Typically, $^2J_{PC}$ for [$Ru(C{\equiv}CR)(PPh_3)_2(Cp)$] ranges from 0 to ca. 25 Hz (e.g. $^2J_{PC}$ = 23.0 Hz for 1), and $^2J_{PC}$ for [$Ru(C{=}CR_2)(PPh_3)_2(Cp)$]$^+$ ranges from ca. 10 to 40 Hz.[1,14] However, the ionized form **2a** was not observable by ^1H NMR spectroscopy. Whereas an equilibrium between 2 and **2a** should lead to NMR coalescence of the two methyl groups, their resonances are sharp and distinct in CD_2Cl_2 at 25 °C and in THF-d_8 from 25 to 60 °C. Compound 2 reacts with the more polar solvents nitromethane, acetonitrile, and dimethyl sulfoxide. X-ray crystal structure analysis (Figure 1) shows 2 to have a linear Ru—C≡C—C chain, with typical Ru—C_α single-bond and $C_\alpha{\equiv}C_\beta$ triple-bond lengths. C_γ is bonded to a crystallographically disordered trifluoroacetate, satisfactorily refined as two rigid, overlapping CF_3CO_2 groups in 7:3 occupancies. The refined carbon–trifluoroacetate bond lengths (C3–O1, 1.43(2) Å; C3–O1A, 1.65(2) Å) are significantly longer than a typical C—O single bond in an enol ester (d_{av} = 1.35(2) Å in the Cambridge Crystallographic File[15]). The enynyl plane (Ru–C1–C2–C3–C4–C5–C6) makes a dihedral angle of 5.3° with the [$Ru(PPh_3)_2(Cp)$] pseudosymmetry plane (Cp0–Ru–C1), having the alkenyl group oriented anti to the Cp group (torsion angle Cp0–Ru–C3–C4 = 174.0°).

The spectroscopic properties of 3 are more complicated than those of 2. Its ^{13}C NMR spectrum indicates a vinylidene structure (δ_C 344.1, triplet, $^2J_{PC}$ = 14.5 Hz), but

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(13) Selected spectroscopic data are as follows (NMR spectra in CD_2Cl_2 except as noted; IR spectra in Nujol). 1: ^1H NMR δ_H 7.2 (m, 30 H, Ph), 4.38 (s, 5 H, Cp), 2.39 (sept, $^3J_{HH}$ = 6.94 Hz, 1 H, C*H*Me_2), 0.98 (d, $^3J_{HH}$ = 6.89 Hz, 6 H, Me); $^{13}C\{^1H\}$ NMR δ_C 189.0 (s, CO), 143.5 (t, $^2J_{PC}$ = 23.0 Hz, C_α), 139.5–128.1 (Ph), 121.3 (s, C_β), 86.7 (s, Cp), 42.7 (s, *C*HMe_2), 19.3 (s, Me); $^{13}P\{^1H\}$ NMR δ_P 50.32 (s, P); IR 2025 (vs, C≡C), 1602 (s, CO) cm^{-1}. 2: ^1H NMR δ_H 7.30 (m, 30 H, Ph), 4.33 (s, 5 H, Cp), 3.45 (q, $^3J_{HH}$ = 7.02 Hz, 2 H, OCH_2CH_3), 1.86 (s, 3 H, cis-Me), 1.67 (s, 3 H, trans-Me), 1.17 (t, $^3J_{HH}$ = 6.99 Hz, 3 H, OCH_2CH_3); $^{13}C\{^1H\}$ NMR δ_C 155.8 (q, $^2J_{FC}$ = 41.2 Hz, CO), 139.2–127.6 (Ph), 128.9 (t, $^2J_{PC}$ = 31.1 Hz, C_α), 127.8 (t, $^3J_{PC}$ = 4.7 Hz, C_β), 120.5 (s, C_δ), 115.4 (q, $^1J_{FC}$ = 286.6 Hz, CF_3), 105.1 (s, C_γ), 86.0 (s, Cp), 66.0 (s, OCH_2CH_3), 20.5 (s, cis-Me), 17.2 (s, OCH_2CH_3), 15.5 (s, trans-Me); $^{31}P\{^1H\}$ NMR δ_P 51.17 (s, P); IR 2049 (s, C≡C), 1782 (s, CO). 3: ^1H NMR ($CDCl_3$) δ_H 10.89 (br s, 1 H, O–H–O), 7.10 (m, 30 H, Ph), 5.22 (s, 5 H, Cp), 1.55 (s, 3 H, trans-Me), 1.30 (s, 3 H, cis-Me); $^{13}C\{^1H\}$ NMR δ_C 344.1 (t, $^2J_{PC}$ = 14.5 Hz, C_α), 177.6 (q, $^2J_{FC}$ = 34.3 Hz, F_3CCO), 159.0 (q, $^2J_{FC}$ = 39.4 Hz, F_3CCO), 154.1 (q, $^2J_{FC}$ = 43.0 Hz, F_3CCO), 134.6–128.9 (Ph), 132.9 (t, $^3J_{PC}$ = 5.3 Hz, C_β), 127.3 (s, C_γ), 125.8 (s, C_δ), 116.0 (q, $^1J_{FC}$ = 292.1 Hz, CF_3), 115.3 (q, $^1J_{FC}$ = 287.9 Hz, CF_3), 114.3 (q, $^1J_{FC}$ = 285.9 Hz, CF_3), 20.8 (s, trans-Me), 18.9 (s, cis-Me); $^{31}P\{^1H\}$ NMR δ_P 39.2, 36.4 (each d, $^2J_{PP}$ = 25 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ_F −74.29 (s), −75.37 (s), −76.59 (s, [$H(CF_3CO_2)_2$]$^-$); IR 1806 (vs, CO), 1785 (vs, CO), 1734 (vs, CO), 1685 (vs, C=C) cm^{-1}.

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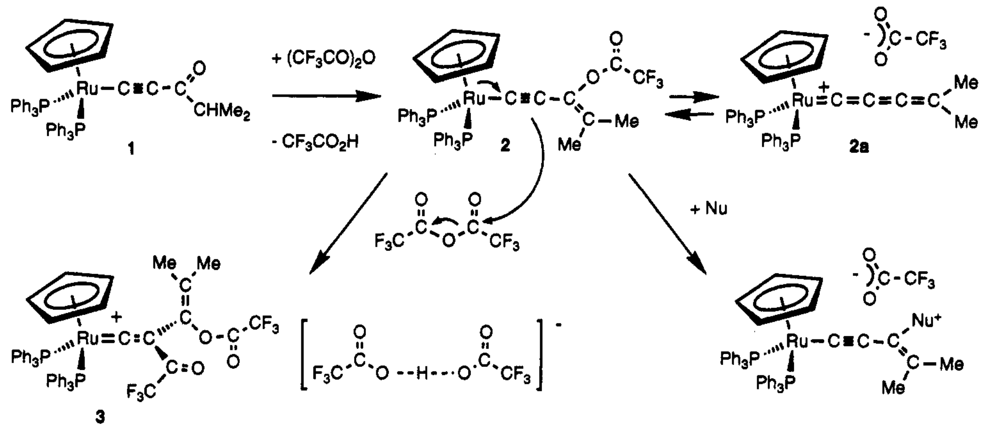
Scheme I



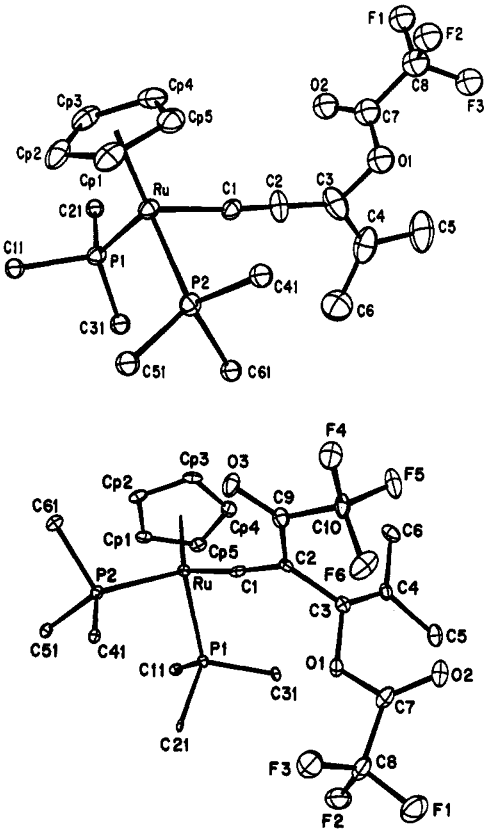


Figure 1. Perspective drawings of the central portions of compounds **2** (top) and **3** (bottom). Selected distances (Å) and angles (deg) are as follows. **2**: Ru–C1, 2.02(1); C1–C2, 1.20(1); C2–C3, 1.42(2); C3–C4, 1.37(2); C3–O1, 1.43(2); Ru–C1–C2, 175.1(11); C1–C2–C3, 175.2(14); C2–C3–C4, 131.5(15); C2–C3–O1, 118(2); C4–C3–O1, 106(2). **3**: Ru–C1, 1.812(9); C1–C2, 1.35(1); C2–C3, 1.50(1); C3–C4, 1.30(1); C3–O1, 1.44(1); C2–C9, 1.46(1).

the observation of two doublets in its ^{31}P NMR spectrum[13] indicates that the molecule does not have an effective plane of symmetry in solution. Further, there are three distinct trifluoroacetyl environments by ^{19}F NMR spectroscopy.[13] X-ray crystallographic data for **3** were collected at 95 K because of unresolvable disorder present in the crystal at room temperature. The structure of the cation of **3** confirms that it is a vinylidene complex, with the linear Ru=C1=C2 group displaying typical Ru=C$_\alpha$ and C$_\alpha$=C$_\beta$ double-bond lengths. Compound **3** is derived from **2** by attachment of a *trifluoroacetyl* group to C$_\beta$. C$_\gamma$ is bonded to a crystallographically well-ordered trifluoroacetate, with a long C3–O1 bond length (1.44(1) Å) as in **2**. The plane of the vinylidene ligand approximately bisects the pseudosymmetry plane of the [Ru(PPh$_3$)$_2$(Cp)] group (dihedral angle (Cp centroid–Ru–C1)–(C1–C2–C3–C9) = 76.9°). Steric crowding around the large vinylidene substituents is evidenced by several intramolecular contacts shorter than 3.5 Å. Restricted rotation of the vinylidene ligand accounts for the ^{31}P NMR inequivalence of the PPh$_3$ ligands. The hydrogen-bonded anion [H(CF$_3$CO$_2$)$_2$]$^-$ (O5–O6 distance 2.44(1) Å, H not located but confirmed by a ^{1}H NMR resonance at 10.89 ppm) and a molecule of CH$_2$Cl$_2$ complete the structure of **3**.

Scheme I summarizes the formation of compounds **1**–**3**. Alkynyl **1** is regioselectively acylated at oxygen by trifluoroacetic anhydride to form **2**. Acylation of **1** at oxygen rather than C$_\beta$ is probably favored by the crowded [Ru(PPh$_3$)$_2$(Cp)] environment and by the preference of trifluoroacetic anhydride for the harder oxygen site.[16] Compound **2** is acylated at C$_\beta$ to form **3** in a second, slower step.

Although compound **2** is not significantly ionized to **2a** in solution, trifluoroacetate is readily displaced from **2** by a variety of nucleophiles (Scheme I). In this system, both hard (methanol) and softer (phosphines, pyridine, etc.) nucleophiles attack at C$_\gamma$, unlike the isoelectronic [Mn(C=C=CR$_2$)(CO)$_2$(Cp)] system, in which hard nucleophiles attack the cumulene chain at C$_\alpha$ but soft nucleophiles attack at C$_\gamma$.[6] The lack of reactivity of C$_\alpha$ toward hard nucleophiles in the [Ru(PPh$_3$)$_2$(Cp)] system may be due to steric crowding by the bulky ancillary ligands. Further details of the nucleophilic and electrophilic reactivity of **2** are forthcoming.

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Supplementary Material Available: Text giving experimental procedures and spectroscopic data for **1**–**3** and listings of crystal structure data, positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes for **2** and **3** (29 pages). Ordering information is given on any current masthead page.

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