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Preliminary communication

Synthesis of alkene- and alkyne-pentamethylcyclopentadienyl dicarbonyliron complexes via the aquo derivative $[Fe(\eta\text{-}C_5Me_5)(CO)_2(OH_2)]^+BF_4^-$; crystal structure of the ruthenium analogue

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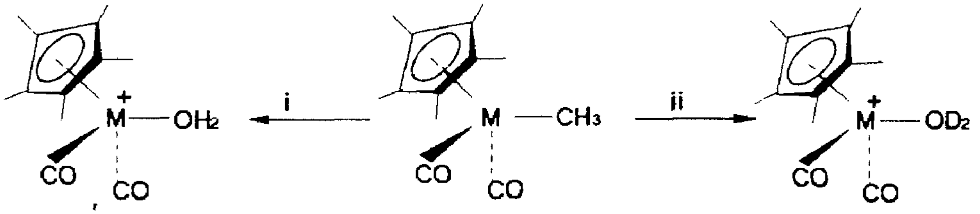
Abstract

$[Fe(\eta\text{-}C_5Me_5)(CO)_2(OH_2)]^+ BF_4^-$ (**2a**) reacts with alkenes and alkynes to give the new complexes $[Fe(\eta\text{-}C_5Me_5)(CO)_2(alkene)]^+ BF_4^-$ and $[Fe(\eta\text{-}C_5Me_5)(CO)_2(alkyne)]^+ BF_4^-$. The crystal structure of the ruthenium analogue $[Ru(\eta\text{-}C_5Me_5)(CO)_2(OH_2)]^+ CF_3SO_3^-$ (**2b**) is described.

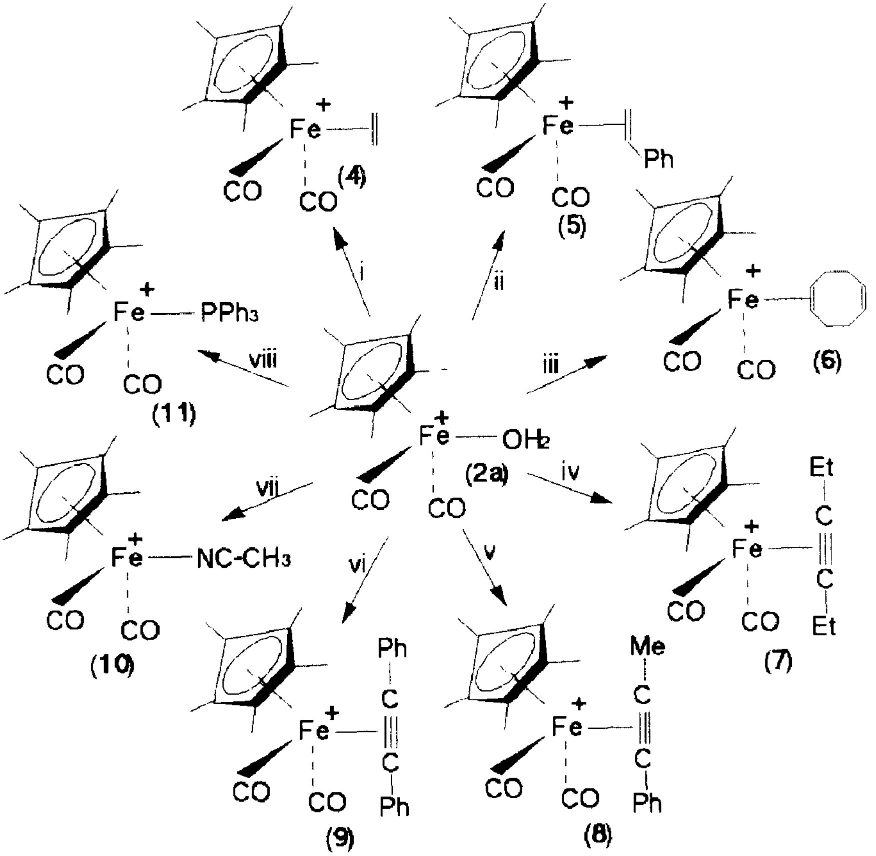
Complexes of the type $[Fp(alkene)]^+ X^-$ and $[Fp(alkyne)]^+ X^-$ $[Fp = Fe(\eta\text{-}C_5H_5)(CO)_2]$ are readily prepared by ligand exchange between unsaturated hydrocarbons and $[FpL]^+ X^-$, where L is a labile ligand (isobutene [1] or THF [2]), by hydride abstraction from Fp(alkyl) [3], by protonation of Fp(allyl) [4] or by dehalogenation of FpX with $AlCl_3$ or a silver salt in the presence of an alkene [5]. However, most of these routes do not afford the analogous $Fp^\star$ $[Fp^\star = Fe(\eta\text{-}C_5Me_5)(CO)_2]$ complexes [6], and we recently observed [7] that $[Fp^\star(alkene)]^+ X^-$ species may be obtained only in low purity by the reaction of $[Fp^\star(=CHOMe)]^+ X^-$ with silanes in the presence of ethene or styrene. We now report that both $[Fp^\star(alkene)]^+ X^-$ and $[Fp^\star(alkyne)]^+ X^-$ complexes may be conveniently prepared by ligand exchange with an aquo species $[Fp^\star(OH_2)]^+ X^-$ (**2a**), itself readily obtained by protonation of $[Fp^\star(CH_3)]$ in the presence of water. Organoiron aquo complexes were previously suggested to be putative reaction intermediates, but were not characterized [8,9]. Both **2a** and its ruthenium analogue $[Ru(\eta\text{-}C_5Me_5)(CO)_2(OH_2)]^+ X^-$ (**2b**) have now been fully characterized, and the crystal study of the latter determined.

The methyl $[Fp^\star(CH_3)]$ complex (**1a**) reacts cleanly at −80 °C with aqueous HBF_4 in methylene chloride to afford a red solution from which the air-stable aquo



(2a), M=Fe; **(2b)**, M=Ru **(1a)**, M=Fe; **(1b)**, M=Ru **(3a)**, M=Fe; **(3b)**, M=Ru

Scheme 1. Reagents and conditions. i, 1.2 equiv. aqueous HBF_4/CH_2Cl_2, −80 °C, 60 min 88% yield; ii, 1.1 equiv. HBF_4/OEt_2, 2 equiv. D_2O, −80 °C, 60 min.



Scheme 2. Reagents and conditions. i, C_2H_4 (1 atm), CH_2Cl_2, 30 °C, 16 h, 40% yield; ii, 3 equiv. $PhCH{=}CH_2$, CH_2ClCH_2Cl, 65 °C, 3 h, 60% yield; iii, 3 equiv. 1,5-cyclooctadiene, CH_2ClCH_2Cl, 65 °C, 3 h, 41% yield; iv, 3 equiv. C_2Et_2, CH_2ClCH_2Cl, 60 °C, 2.5 h, 70% yield; v, 3 equiv. C_2MePh, CH_2ClCH_2Cl, 60 °C, 1.5 h, 65% yield; vi, 3 equiv. C_2Ph_2, CH_2ClCH_2Cl, 70 °C, 2h, 75% yield; vii, CH_3CN, 20 °C, 1 h, 90% yield; viii, 2 equiv. PPh_3, CH_2Cl_2, 20 °C, 2h, 95% yield.

compound $[Fp^{\star}(OH_2)]^+ BF_4^-$ (**2a**) [12 *] is isolated in 88% yield by precipitation with diethyl ether (Scheme 1). A similar reaction between **1a** and $HBF_4 \cdot OEt_2$ in the presence of a small excess of D_2O gives $[Fp^{\star}(OD_2)]^+BF_4^-$ (**3a**) [12 *], the ^2H NMR

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* Reference number with asterisk indicates a note in the list of references.

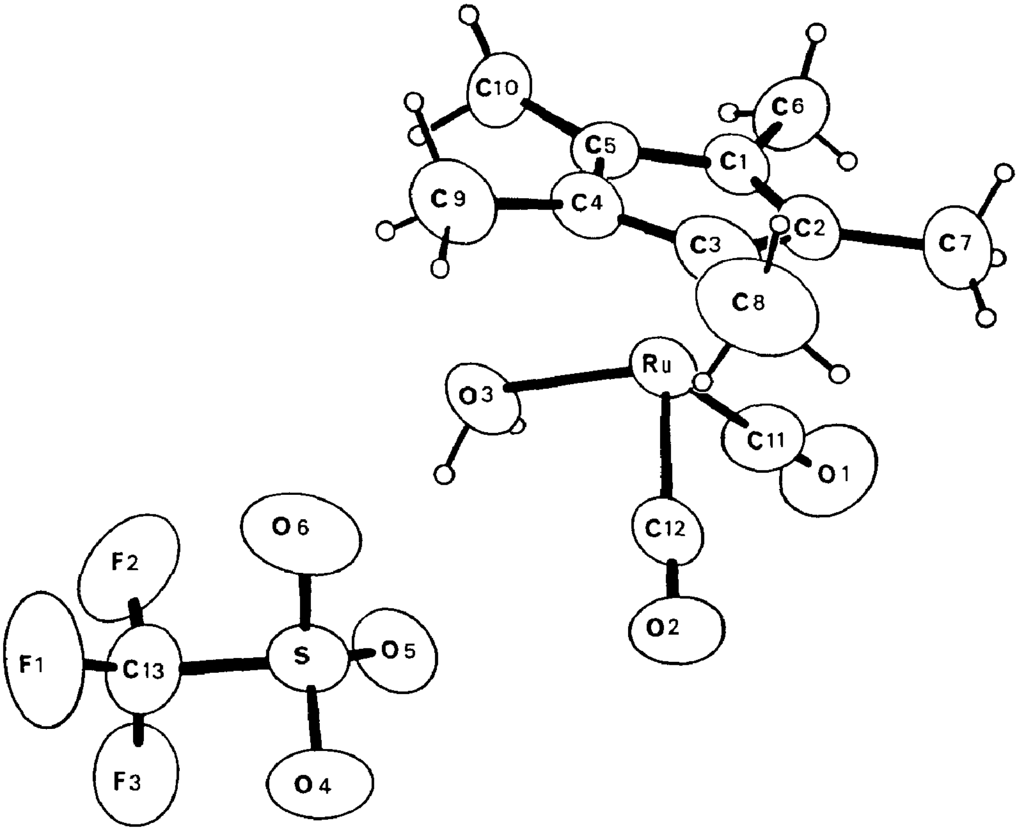

Fig. 1. Molecular structure of $[Ru(\eta\text{-}C_5Me_5)(CO)_2(OH_2)]CF_3SO_3$ (**2b**). Selected bond lengths (Å) and angles (°): Ru–C(1) 2.224(3); Ru–C(2) 2.117(4); Ru–C(3) 2.201(4); Ru–C(4) 2.217(4); Ru–C(5) 2.248(3); Ru–O(3) 2.171(3); Ru–C(11) 1.908(5); Ru–C(12) 1.899(4); C(11)–O(1) 1.128(5); C(12)–O(2) 1.130(4); O(3)–H_A(O3) 0.79(4); O(3)–H_B(O3) 0.77(4); H_A(O3)–O(3)–H_B(O3) 119.(4); O(3)–Ru–C(11) 94.8(2); O(3)–Ru–C(12) 94.8(1); C(11)–Ru–C(12) 92.4(2); Ru–C(11)–O(1) 174.0(4); Ru–C(12)–O(2) 172.7(4).

spectrum of which shows the presence of the coordinated water molecule (δ 2.27 ppm) readily distinguishable from free water (δ 4.69). Addition of an excess of D_2O to a methylene chloride solution of **2a** results in a fast exchange, shown in the ^1H NMR spectrum (CD_2Cl_2, 20 °C) by the disappearance of the signal at δ 2.41 ppm.

The ruthenium analogues **2b**, **3b** [12 *] were readily synthesized by the same procedure and isolated as tetrafluoroborate or triflate salts. The structure of **2b** was unambiguously established by a single crystal X-ray diffraction study, and is depicted in Fig. 1, the legend to which shows some bonding parameters [13 *]. The ruthenium displays the pseudooctahedral geometry invariably observed for such pianostool complexes [10]. Interest focuses on the structural features of the aquo ligand. The geometry of the latter is not modified by its coordination to the metal centre, and the long Ru–O(3) bond distance of 2.171(3) Å implies a relatively weak interaction between the metal and the water [11 *]. The distances H(O3)–O(5) (1.94(4) Å) and H(O3)–O(4) (2.04(4) Å) suggest that there may be hydrogen bonding between the triflate anion and the coordinated water molecule. This is consistent with the appearance of a ν(OH) band at 2720 cm^{-1} in the IR spectra of

2a and **2b**. This feature is observed for both the triflate and the tetrafluoroborate salts, indicating that an O–H · · · F interaction may also be present.

Treatment of **2a** with various two-electron ligands results in ready displacement of the water to give the compounds **4**–**11** [12 *] in good to excellent yield, as shown in Scheme 2. The aquo complex **2a** thus provides a highly convenient entry into the chemistry of $[Fp^{\star}(alkene)]^+$ and $[Fp^{\star}(alkyne)]^+$ cations, so making possible a study of the reactivity of the coordinated hydrocarbons in the new alkene complexes **4**–**6** and alkyne complexes **7**–**9**.

Supplementary material available. Tables of bond distances, bond angles and atomic coordinates will be deposited with the Cambridge Crystallographic Data centre, and additional Information is available from the author.

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12 The new complexes were characterized by elemental analyses, IR, and NMR spectroscopy. Selected spectroscopic data: **2a**: ^{1}H NMR (in CD_2Cl_2): δ 1.71 (s, 15H, Cp*) and 2.41 (s, 2H, OH_2), $^{13}C\{^1H\}$ NMR (in CD_2Cl_2): δ 9.3 ($C_5\mathit{Me}_5$), 98.1 (C_5Me_5), and 211.4 (CO), IR (nujol mull): 2025, 2087 (ν(CO)), and 2720 (ν(OH)) cm^{-1}. **2b**: ^{1}H NMR (in CD_2Cl_2): δ 1.48 (s, 2H, OH_2) and 1.80 (s, 15H, Cp*), $^{13}C\{^1H\}$ NMR (in CD_2Cl_2): δ 10.0 ($C_5\mathit{Me}_5$), 100.9 (C_5Me_5), and 198.3 (CO) IR (nujol mull): 2020, 2080 (ν(CO)) and 2720 (ν(OH)) cm^{-1}. **3a**; ^{2}H NMR (in CH_2Cl_2): δ 2.27 (s, OD_2). **6**; ^{1}H NMR (in $CDCl_3$): δ 1.90 (s, 15H, Cp*), 2.47 (m, 8H, $CH_{2\beta,\gamma}$), 3.96 (m, 2H, coordinated $=CH\alpha$), and 5.66 (m, 2H, uncoordinated $=CH\delta$), $^{13}C\{^1H\}$ NMR (in $CDCl_3$): δ 9.2 ($C_5\mathit{Me}_5$), 30.8 ($CH_{2\beta}$), 31.2 ($CH_{2\gamma}$), 83.7 (CH_α), 101.9 (C_5Me_5), 129.8 (CH_δ), and 212.7 (CO). 7; ^{1}H NMR (in $CDCl_3$): δ 1.43 (t, 6H, ^3J(H–H) 7.2 Hz, $CH_2\mathit{CH}_3$), 1.90 (s, 15H, Cp*), and 2.57 (q, 4H, ^3J(H–H) 7.2 Hz, CH_2), $^{13}C\{^1H\}$ NMR (in $CDCl_3$): δ 9.5 ($C_5\mathit{Me}_5$), 16.1 ($CH_2\mathit{C}H_3$), 18.9 ($\mathit{C}H_2CH_3$), 60.3 ($C\equiv C$), 102.4 (C_5Me_5), and 211.1 (CO). **8**: ^{1}H NMR (in $CDCl_3$): δ 1.80 (s, 15H, Cp*), 2.66 (s, 3H, CH_3), and 7.37 (m, 5H, C_6H_5), $^{13}C\{^1H\}$ NMR (in $CDCl_3$): δ 4.3 (CH_3), 9.6 ($C_5\mathit{Me}_5$), 79.8 ($\equiv\mathit{C}C_6H_5$), 85.8 ($\equiv\mathit{C}CH_3$), 104.9 (C_5Me_5), 126.4–133.4 (C_6H_5), and 211.4 (CO). **9**: ^{1}H NMR (in $CDCl_3$): δ 1.73 (s,

15H, Cp*) and 7.34–7.53 (2×m, 10H, C_6H_5), ^{13}C {^1H} NMR (in $CDCl_3$): δ 9.1 (C_5Me_5), 89.4 (C≡C), 97.3 (C_5Me_5), 123.4 (C_{ipso} Ph), 128.3 (C_{para} Ph), 128.4 (C_{ortho} Ph), 131.6 (C_{meta} Ph), and 210.5 (CO).

13 Crystal data for **2b**: $C_{13}H_{17}O_6F_3SRu$, $M = 459.4$, orthorhombic space group, *Pbca*, *a* 17.308 (4), *b* 15.117 (4), *c* 13.789 (3) Å, *Z* 8, μ 10.15 cm^{-1} (Mo-$K\alpha$) 0.71069 Å, θ_{max} 50 °, scan $\omega/2\theta = 1$, 3576 independent observed data of which 2194 with ($I > \sigma(I)$) were collected at 296 K on an Enraf–Nonius CAD-4 diffractometer. The structure was solved with a Patterson map and two Fourier differences. After isotropic and anisotropic refinements for Ru, F, O, S, C atoms, all the hydrogen atoms were found with a Fourier difference (between 0.50 and 0.26 eÅ^{-3}; 0.42 eÅ^{-3} for the two hydrogen atoms of the complexed water molecule).