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π/σ Equilibria in rhenium ketone complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CRR')]^+X^-$; a marked electronic effect upon the binding mode

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Abstract

The first series of metal ketone complexes for which both σ and π isomers can be isolated is reported. Electron-withdrawing substituents favor the π binding mode.

Although many examples of π and σ ketone complexes have been reported [1], there have been few systematic studies of the factors that influence the binding mode. In previous work, Taube and Harman have shown that the π isomer of the osmium acetone complex $[Os(NH_3)_5(O{=}C(CH_3)_2)]^{2+}$ is > 16 kcal/mol more stable than the σ isomer [2]. However, upon one-electron oxidation, which reduces metal π basicity, the σ isomer is favored by 5 kcal/mol. We wondered whether an analogous ligand-based electronic effect upon π/σ equilibria might be possible. For example, rhenium methyl ketone complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)R)]^+X^-$ ($R = CH_3$, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, C_6H_5) exist as σ isomers (> 97 : 3 σ/π) [3]. However, the corresponding aliphatic aldehyde complexes exhibit only π binding modes [4]. Hence, we sought to synthesize rhenium complexes of ketones with electron-withdrawing substituents [5*]. Such ligands should be stronger π acids, and thus more likely to exhibit a π binding mode.

Reaction of the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**1**) [3] and excess 1,3-dichloroacetone was monitored by ^1H and ^{31}P NMR at −36 °C (eq. i). A product formed in high yield ($\mathbf{2}^+BF_4^-$), but decomposed upon attempted workup. However, spectroscopic properties (^{31}P NMR 9.4 ppm, IR $\nu(NO)$ 1745–1740 cm^{-1}) resembled those found earlier for π aldehyde complexes [4,6], and differed from those of σ ketone complexes (^{31}P NMR 18–19

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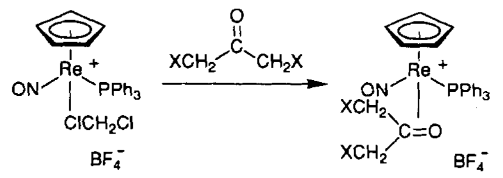
* Reference number with asterisk indicates a note in the list of references.



(i)

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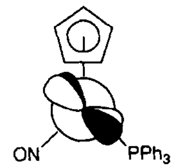
X = Cl, $2^+BF_4^-$

F, $3^+BF_4^-$



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ppm, IR ν(NO) 1697–1680 cm^{-1}) [3]. Thus, $2^+BF_4^-$ was tentatively assigned as the π ketone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}C(CH_2Cl)_2)]^+BF_4^-$.

Next, **1** and 1,3-difluoroacetone were similarly allowed to react in CH_2Cl_2 at −80 °C. Subsequent addition of ether (room temperature) precipitated the product $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}C(CH_2F)_2)]^+BF_4^-$ ($3^+BF_4^-$, 71%), which was assigned as a π ketone complex as described below. Alternatively, reaction of hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$, $Ph_3C^+PF_6^-$, and 1,3-difluoroacetone (CH_2Cl_2, −80 °C) gave analytically pure $3^+PF_6^-$ (66%) [7*]. This synthesis is analogous to one recently reported for the corresponding cationic alcohol complexes [8].

IR spectra of 3^+X^- (ν(NO) 1762–1749 cm^{-1}) showed no traces of any absorptions in regions characteristic of σ complexes [3,6]. The ^{13}C NMR spectrum of $3^+PF_6^-$ exhibited an upfield CO resonance (83.5 ppm) that was coupled to both fluorines (σ ketone complexes [3]: 216–240 ppm), and two CH_2F resonances. Two CH_2F ^{19}F NMR resonances were also observed ($\Delta\nu$ 2536 Hz, 282.7 MHz). These did not coalesce at 50 °C, which sets a lower limit of 13.4 kcal/mol on any dynamic process capable of exchanging the CH_2F groups (e.g., $\pi \rightarrow \sigma \rightarrow \pi'$ isomerization) [3].

Yellow plates of $3^+PF_6^-$ were grown from CH_2Cl/ether, and the structure was confirmed by X-ray crystallography (Fig. 1) [9*]. The 1,3-difluoroacetone ligand adopts a conformation that maximizes overlap of the C=O π^* acceptor orbital with the rhenium fragment HOMO I (angle between $\overline{Re{-}O{-}C}$ plane and Re–P bond: 10°). Similar solid state conformations are found with analogous π aldehyde complexes [4,6a]. The α carbons C25 and C26 are displaced 0.62 Å and 0.34 Å, respectively, from the nodal plane of the free ligand. Also, the C–O bond (1.35(1) Å) is much longer than that in the σ acetone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)_2)]^+PF_6^-$ (1.248(9) Å) [3].

Other halogenated ketones were briefly studied. An analogous reaction of **1** and pentafluoroacetophenone gave the analytically pure adduct $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)C_6F_5)]^+BF_4^-$ ($4^+BF_4^-$; 55%) [10*]. The NMR properties of $4^+BF_4^-$ in CD_3NO_2 at −30 °C were consistent with those expected for a π

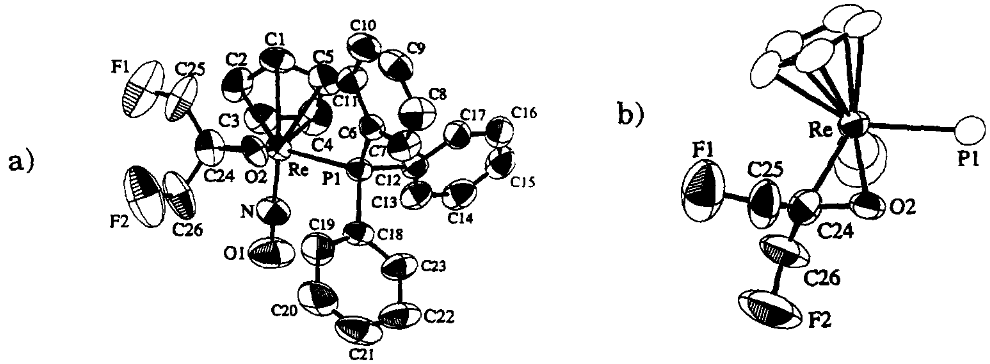

Fig. 1. Views of the cation of difluoroacetone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}C(CH_2F)_2)]^+PF_6^-$ ($3^+PF_6^-$): (a) numbering diagram; (b) view down rhenium-nitrogen bond with phenyl groups omitted. Selected bond lengths (Å) and angles (°): Re-C24 2.17(1), Re-O2 2.044(6), C24-O2 1.35(1), Re-N 1.737(9), Re-P 2.449(3), N-O1 1.19(1); O2-Re-C24 37.1(3), Re-O2-C24 76.5(5), Re-C24-O2 66.4(5), Re-N-O1 173(1), N-Re-P 90.5(3).

complex [10]. However, IR spectra at room temperature showed minor, medium-dependent amounts of a σ isomer (ν(NO), cm^{-1}: π 1745–1749, σ 1699–1695 cm^{-1}; CH_3NO_2 ca. 75:25, CH_2Cl_2 and KBr ca. 56:44). Similar solvent and temperature trends have been observed for related equilibria [6]. Fluoroacetone gave a less stable complex that appeared by ^{31}P NMR (CH_2Cl_2, −80 °C: 8.8, 18.0 ppm) to be a mixture of π and σ isomers.

In summary, this study has provided the first examples of π and σ ketone complexes of the same metal fragment, and established a marked ligand-based electronic effect upon the binding mode. Complementary trends have recently been documented with analogous aromatic aldehyde complexes [6]. Future efforts will be directed at quantifying π/σ isomer interconversion rates, and differences in chemical reactivity.

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7 Selected NMR data on **3**$^+$ PF_6^- (CD_3NO_2, $-27\,°C$): ^1H (δ) 6.29 (s, C_5H_5), 5.49 (dd, J(HF) 47.6 Hz, J(HH) 10.6 Hz, 1H), 4.92 (dd, J(HF) 47.2 Hz, J(HH) 11.7 Hz, 1H), 4.88 (dd, J(HF) 46.3 Hz, J(HH) 11.7 Hz, 1H), 4.64 (dd, J(HF) 47.8 Hz, J(HH) 10.6 Hz, 1H); $^{13}C\{^1H\}$ (ppm) 101.4 (s, C_5H_5), 87.7 (d, J(CF) 176.3 Hz, CH_2), 85.6 (d, J(CF) 172.0 Hz, $C'H_2$), 83.5 (dd, J(CF) 20.2, 19.8 Hz, CO); $^{31}P\{^1H\}$ (ppm) 10.0 (s); ^{19}F (ppm) -203.4 (t, J(FH) 47.2 Hz, F), -212.3 (t, J(FH) 46.2 Hz, F$'$). IR (cm^{-1}, KBr/CH_2Cl_2) ν(NO) 1762/1750 s. Anal. Found: C, 40.05; H, 3.05. $C_{26}H_{24}F_8NO_2P_2Re$ calc.: C, 39.90; H, 3.09%.

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9 *Crystal data* for **3**$^+$ PF_6^-: $C_{26}H_{24}F_8NO_2P_2Re$, $M = 782.6$, orthorhombic, space group P_{bca} (No. 61), $a = 12.163(2)$, $b = 16.583(2)$, $c = 27.851(2)$ Å, $Z = 8$, $V = 5617.58$ Å^3, $D_c = 1.85$ g cm^{-1}, $\mu = 99.76$ cm^{-1}. Final $R = 0.0437$ ($R_w = 0.0458$) for 3280 independent reflections with $I > 3\sigma(I)$, measured in the 2θ range 4–130° at 16 °C with Cu-K_α radiation on an Enraf–Nonius CAD-4 diffractometer. The structure was solved using standard heavy-atom techniques. Calculated hydrogen positions were used during refinement. Non-hydrogen atoms were refined with anisotropic thermal parameters.

10 Selected NMR data on **4**$^+$ BF_4^- (CD_3NO_2, $-30\,°C$): ^1H (δ) 6.33 (s, C_5H_5), 2.04 (s, CH_3); $^{13}C\{^1H\}$ (ppm) 103.3 (s, C_5H_5), 77.4 (s, CO), 20.6 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 11.4 (s). Anal. Found: C, 44.19; H, 2.79. $C_{31}H_{23}BF_9NO_2PRe$ calc.: C, 44.30; H, 2.76%.