

Synthesis and reactions of the rhenium fulvene complexes

$[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_4\text{R})]$ (R = F or CF₃): Products derived from initial C-F activation

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The UV irradiation of $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ in the presence of C₆F₆ effected intermolecular C-F and intramolecular C-H activation generating $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_5)]$ 1a in two isomeric forms. In the major isomer the CH₂ group lies trans to the C₆F₅ group both in solution and in the crystal. In the minor isomer the CH₂ lies cis to the C₆F₅ group. A similar reaction with C₆F₅CF₃ generates $[\text{Re}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\text{CO})_2(\text{C}_6\text{F}_4\text{CF}_3)]$ 1b in four isomeric forms. In the major form the CF₃ group is in the 4 position and the CH₂ group lies trans to the C₆F₄CF₃ group. The other three isomers are formed by rotation of the $\eta^6\text{-C}_5\text{Me}_4\text{CH}_2$ ligand as above, by placing the CF₃ at the 3 position, and by a combination of the two. Complex 1a reacted with PMe₃ to form the zwitterionic complex $[\text{Re}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{PMe}_3)(\text{CO})_2(\text{C}_6\text{F}_5)]$ and with MeO⁻ to form the anion $[\text{Re}(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{OMe})(\text{CO})_2(\text{C}_6\text{F}_5)]^-$, isolable as the NEt₄⁺ salt. The reaction of 1a with HX (X = Cl or Br) generated cis- $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{C}_6\text{F}_5)\text{X}]$ initially. Mor