

Synthesis and characterization of transition metal stabilized carbocations of the types $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{M}(\text{CO})_x\text{Cp}]\text{PF}_6$ ($x = 2$, $\text{M} = \text{Fe}$ or Ru ; $x = 3$, $\text{M} = \text{W}$, $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $n = 3\text{--}6$) and $[\text{Cp}(\text{CO})_2\text{Ru}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{W}(\text{CO})_3\text{Cp}]\text{PF}_6$ ($n = 3\text{--}5$) and the crystal structures of the complexes $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Ru}(\text{CO})_2\text{Cp}]$, $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_5\text{Ru}(\text{CO})_2\text{Cp}]$, $[\text{Cp}^*(\text{CO})_2\text{Fe}-(\text{CH}_2)_5\text{W}(\text{CO})_3\text{Cp}]$, and $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_5\text{W}(\text{CO})_3\text{Cp}]$

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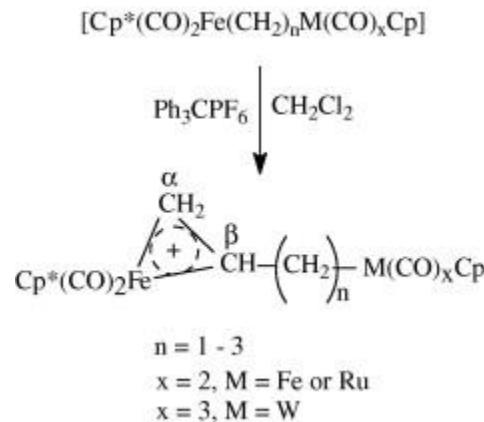
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Abstract

The mixed-ligand complexes $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{M}(\text{CO})_x\text{Cp}]$ ($x = 2$, $\text{M} = \text{Fe}$ or Ru ; $x = 3$, $\text{M} = \text{W}$, $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $n = 3\text{--}6$), type I, react with one equivalent of the hydride abstractor Ph_3CPF_6 to give the transition metal-stabilized carbocation complexes $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{M}(\text{CO})_x\text{Cp}]\text{PF}_6$. Similarly the new heterobimetallic complexes $[\text{Cp}(\text{CO})_2\text{Ru}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{W}(\text{CO})_3\text{Cp}]$, type II, react with Ph_3CPF_6 to give the carbocation complexes $[\text{Cp}(\text{CO})_2\text{Ru}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{W}(\text{CO})_3\text{Cp}]\text{PF}_6$. Spectroscopic data show that hydride abstraction selectively takes place from the methylene group β to the metal atom attached to the Cp^* ligand in type I complexes. In type II complexes, the reaction is totally metalloselective with hydride abstraction occurring at the CH_2 β to the ruthenium metal centre. All products have been characterized by IR, ^1H , ^{13}C NMR spectroscopy and elemental analysis. ^1H and ^{13}C NMR data clearly show that in the carbocation complexes one metal is σ -bonded to the alkanediyl carbocation while the other is bonded to the cationic end in a η^2 -fashion forming a chiral metallacyclopropane type structure. The molecular structures of the cationic metallacyclic complexes $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_3\text{H}_5)\}\text{Fe}(\text{CO})_2\text{Cp}]\text{PF}_6$ [E.O. Changamu, H.B. Friedrich, M. Rademeyer, *Acta Crystallogr., Sect. E* 62 (2006) m442.] and $[\text{Cp}^*(\text{CO})_2\text{Fe}(\mu-\text{C}_3\text{H}_5)\text{Ru}-(\text{CO})_2\text{Cp}]\text{PF}_6$ [H.B. Friedrich, E.O. Changamu, M. Rademeyer, *Acta Crystallogr., Sect. E* 62 (2006) m405.] have been confirmed by single crystal X-ray crystallography and reported elsewhere. The structures of the precursor complexes $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Ru}-(\text{CO})_2\text{Cp}]$ (1), $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_5\text{Ru}-(\text{CO})_2\text{Cp}]$ (2), $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_5\text{W}(\text{CO})_3\text{Cp}]$ (3), and $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_5\text{W}(\text{CO})_3\text{Cp}]$ (4), have been confirmed by single crystal X-ray crystallography. The structure of $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Ru}(\text{CO})_2\text{Cp}]$ is compared with that of its corresponding cationic complex, $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_3\text{H}_5)\}\text{Ru}(\text{CO})_2\text{Cp}]\text{PF}_6$.

Graphical abstract

The complexes $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{M}(\text{CO})_x\text{Cp}]$ ($n = 3-6$, $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $x = 2$, $\text{M} = \text{Fe}$ or Ru ; $x = 3$, $\text{M} = \text{W}$), undergo hydride abstraction selectively from the CH_2 β to $\text{Cp}^*(\text{CO})_2\text{Fe}$ to give the cationic metallocycles $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu\text{-}(\text{C}_n\text{H}_{2n-1})\}\text{M}(\text{CO})_x\text{Cp}]\text{PF}_6$ upon reaction with Ph_3CPF_6 . Similarly, $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_n\text{W}(\text{CO})_3\text{Cp}]$ ($n = 3-5$) undergo hydride abstraction from the CH_2 β to $\text{Cp}(\text{CO})_2\text{Ru}$ to give $[\text{Cp}(\text{CO})_2\text{Ru}\{\mu\text{-}(\text{C}_n\text{H}_{2n-1})\}\text{W}(\text{CO})_3\text{Cp}]\text{PF}_6$.



Keywords

- Alkanediyl carbocation, Mixed-ligand;
- Heterobimetallic;
- Metallacyclopropane;
- Hydride abstraction