Synthesis and characterization of transition metal stabilized carboxations of the types [Cp*(CO)2Fe{μ-(C5H2n−1)}M(CO)3Cp]PF6 (x = 2, M = Fe or Ru; x = 3, M = W, Cp* = η5-C5(CH3)5; Cp = η5-C5H5; n = 3–6) and [Cp(CO)2Ru{μ-(C5H2n−1)}W(CO)3Cp]PF6 (n = 3–5) and the crystal structures of the complexes [Cp*(CO)2Fe(CH2)3Ru(CO)2Cp], [Cp*(CO)2Fe(CH2)3Ru(CO)2Cp], [Cp*(CO)2Fe-(CH2)5W(CO)3Cp], and [Cp(CO)2Ru(CH2)5W(CO)3Cp]

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Abstract

The mixed-ligand complexes [Cp*(CO)2Fe(CH2)nM(CO)3Cp] (x = 2, M = Fe or Ru; x = 3, M = W, Cp* = η5-C5(CH3)5; Cp = η5-C5H5; n = 3–6), type I, react with one equivalent of the hydride abstractor Ph3CPF6 to give the transition metal-stabilized carboxation complexes [Cp*(CO)2Fe{μ-(C5H2n−1)}M(CO)3Cp]PF6. Similarly the new heterobimetallic complexes [Cp(CO)2Ru{μ-(C5H2n−1)}W(CO)3Cp], type II, react with Ph3CPF6 to give the carboxation complexes [Cp(CO)2Ru{μ-(C5H2n−1)}W(CO)3Cp]PF6. 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 CH2 β to the ruthenium metal centre. All products have been characterized by IR, 1H, 13C NMR spectroscopy and elemental analysis. 1H and 13C NMR data clearly show that in the carboxation complexes one metal is σ-bonded to the alkanediyl carboxcation while the other is bonded to the cationic end in a η2-fashion forming a chiral metallacyclopropane type structure. The molecular structures of the cationic metallacyclic complexes [Cp*(CO)2Fe{μ-(C5H5)}Fe(CO)2Cp]PF6 [E.O. Changamu, H.B. Friedrich, M. Rademeyer, Acta Crystallogr., Sect. E 62 (2006) m442.] and [Cp*(CO)2Fe{μ-C5H5}Ru-(CO)2Cp]PF6 [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 [Cp*(CO)2Fe(CH2)3Ru-(CO)2Cp] (1), [Cp*(CO)2Fe(CH2)3Ru-(CO)2Cp] (2), [Cp*(CO)2Fe(CH2)5W(CO)3Cp] (3), and [Cp(CO)2Ru(CH2)5W(CO)3Cp] (4), have been confirmed by single crystal X-ray crystallography. The structure of [Cp*(CO)2Fe(CH2)3Ru(CO)2Cp] is compared with that of its corresponding cationic complex, [Cp*(CO)2Fe{μ-(C5H5)}Ru(CO)2Cp]PF6.
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\(_2\) \(\beta\) to \(\text{Cp}^*(\text{CO})_2\text{Fe}\) to give the cationic metallocycles \([\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{M(\text{CO})_x\text{Cp}}]\) upon reaction with \(\text{Ph}_3\text{CPF}_6\). Similarly, \([\text{Cp(\text{CO})_2Ru(\text{CH}_2)_n\text{W(\text{CO})_x\text{Cp}}]} (n=3-5)\) undergo hydride abstraction from the CH\(_2\) \(\beta\) to \(\text{Cp(\text{CO})_2Ru}\) to give \([\text{Cp(\text{CO})_2Ru}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{W(\text{CO})_x\text{Cp}}]}\)PF\(_6\).

\(\text{Cp}^*(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{M(\text{CO})_x\text{Cp}}] \rightarrow \text{Cp}(\text{CO})_2\text{Fe}\{\mu-(\text{C}_n\text{H}_{2n-1})\}\text{M(\text{CO})_x\text{Cp}}]PF_6\)

**Keywords**

- Alkanediyl carbocation, Mixed-ligand;
- Heterobimetallic;
- Metallacyclop propane;
- Hydride abstraction