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Synthesis and characterization of transition metal stabilized carbocations of the types $[Cp^*(CO)_2Fe\{\mu\text{-}(C_nH_{2n-1}\}M(CO)_xCp]PF_6$ ($x = 2$, M = Fe or Ru; $x = 3$, M = W, $Cp^* = \eta^5\text{-}C_5(CH_3)_5$; $Cp = \eta^5\text{-}C_5H_5$; $n = 3$–6) and $[Cp(CO)_2Ru\{\mu\text{-}(C_nH_{2n-1})\}W(CO)_3Cp]PF_6$ ($n = 3$–5) and the crystal structures of the complexes $[Cp^*(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$, $[Cp^*(CO)_2Fe(CH_2)_5Ru(CO)_2Cp]$, $[Cp^*(CO)_2Fe\text{-}(CH_2)_5W(CO)_3Cp]$, and $[Cp(CO)_2Ru(CH_2)_5W(CO)_3Cp]$

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Abstract

The mixed-ligand complexes $[Cp^*(CO)_2Fe(CH_2)_nM(CO)_xCp]$ ($x = 2$, M = Fe or Ru; $x = 3$, M = W, $Cp^* = \eta^5\text{-}C_5(CH_3)_5$; $Cp = \eta^5\text{-}C_5H_5$; $n = 3$–6), type **I**, react with one equivalent of the hydride abstractor Ph_3CPF_6 to give the transition metal-stabilized carbocation complexes $[Cp^*(CO)_2Fe\{\mu\text{-}(C_nH_{2n-1})\}M(CO)_xCp]PF_6$. Similarly the new heterobimetallic complexes $[Cp(CO)_2Ru\{\mu\text{-}(C_nH_{2n-1})\}\text{-}W(CO)_3Cp]$, type **II**, react with Ph_3CPF_6 to give the carbocation complexes $[Cp(CO)_2Ru\{\mu\text{-}(C_nH_{2n-1})\}W(CO)_3Cp]PF_6$. 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 metallacylopropane type structure. The molecular structures of the cationic metallacyclic complexes $[Cp^*(CO)_2Fe\{\mu\text{-}(C_3H_5)\}Fe(CO)_2Cp]PF_6$ [E.O. Changamu, H.B. Friedrich, M. Rademeyer, Acta Crystallogr., Sect. E 62 (2006) m442.] and $[Cp^*(CO)_2Fe(\mu\text{-}C_3H_5)Ru\text{-}(CO)_2Cp]PF_6$ [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 $[Cp^*(CO)_2Fe(CH_2)_3Ru\text{-}(CO)_2Cp]$ (**1**), $[Cp^*(CO)_2Fe(CH_2)_5Ru\text{-}(CO)_2Cp]$ (**2**), $[Cp^*(CO)_2Fe(CH_2)_5W(CO)_3Cp]$ (**3**), and $[Cp(CO)_2Ru\ (CH_2)_5W(CO)_3Cp]$ (**4**), have been confirmed by single crystal X-ray crystallography. The structure of $[Cp^*(CO)_2\text{-}Fe(CH_2)_3Ru(CO)_2Cp]$ is compared with that of its corresponding cationic complex, $[Cp^*(CO)_2Fe\{\mu\text{-}(C_3H_5)\}Ru(CO)_2Cp]PF_6$.

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

1. Introduction

Whereas mononuclear complexes of the types $[Cp(CO)_2M(\eta^2\text{-}CH_2{=}CHR)]X$ (M = Fe or Ru) and $[Cp^*(CO)_2Fe(\eta^2\text{-}CH_2{=}CHR)]X$($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5(CH_3)_5$, R = alkyl or aryl group, X = BF_4 or PF_6) have

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been fairly well studied [3–11], there are very few reports of their bimetallic analogues in which both Cp and Cp* ligands are present in the same molecule. Furthermore, there are very few reports of heterodinuclear organometallic carbocations in the literature that have no metal–metal bonds [1,2,12].

Transition metal stabilized carbocations were believed to be cationic metal olefin complexes [6,7,10,12–15], which are strongly activated towards nucleophilic attack [16]. This phenomenon plays a key role in many important catalytic processes [17]. Transition metal olefin complexes are also considered to be models for catalytic intermediates in important industrial processes like metathesis, oligomerization and polymerization of alkenes and alkynes, hydration and oxidation of olefins and hydroformylation. Furthermore, there are reports that heterobimetallic catalysts are considered superior to their monometallic analogues in activity and selectivity [18]. A deeper understanding of the nature of the bonding in the reactive intermediates of these processes should give more insight into the mechanisms of the catalytic reactions.

The bonding between unsaturated hydrocarbons and transition metals is usually treated as donor–acceptor in nature and is mostly described in terms of the Dewar–Chatt–Duncanson (DCD) model [19,20]. The validity of the DCD model has been supported by both experiment and theory [21–23], but more recent studies suggest that the model is not suited to quantify the distortion of the ligand in the complex or to predict the details of the bonding properties of different ligands [24]. For example, it does not distinguish between a π-bonded complex and a metallacycle as an alternative description of the three-membered cyclic structure. The latter is suggested to be prevalent in high oxidation state organometallic complexes [25]. Very recent experimental and theoretical studies by Scherer et al. on valence shell charge concentrations in olefin complexes of nickel also suggest that the nature of bonding between olefins and transition metals may be more complex than portrayed by the DCD model [26].

Our recent NMR studies on the complexes $[\{Cp(CO)_2Fe\}_2(\mu\text{-}C_nH_{2n-1})]PF_6$ ($n = 4$–10) and $[\{Cp(CO)_2Fe\}_2(\mu\text{-}C_nH_{2n-2})](PF_6)_2$ ($n = 5$–10) showed that the metals form metallacyclopropane type structures with the cationic end of the alkanediyl carbocation and that the positive charge is distributed mainly within the metallacycle [27]. These studies demonstrated that NMR spectroscopy may be used to distinguish between the traditional side-on bonding between unsaturated hydrocarbons and transition metals and the three-membered metallacycle. The metallacyclopropane complexes are chiral, with the β-CH carbon being the chiral centre. The chirality is observed in the ^1H NMR spectra in which the protons of the methylene groups attached to the chiral centre (γ-CH_2) are observed to be diastereotopic [1,2,6,27]. In some complexes this effect is also observed in the protons of the methylene group that is β to the chiral centre [6,27]. This effect is unlikely to be observed in side-on bonded ligands in which there is free rotation around the metal–ligand axis and the C_β–C_γ bond (see Fig. 1). Furthermore, X-ray diffraction studies have shown that the molecular geometries of the complexes $[Cp^*(CO)_2Fe\{\mu\text{-}(C_3H_5)\}Fe(CO)_2Cp]PF_6$ and $[Cp^*(CO)_2Fe\{\mu\text{-}(C_3H_5)\}Ru(CO)_2Cp]PF_6$ ($Cp^* = \eta^5\text{-}C_5Me_5$) are significantly distorted at the β-$CH^{\delta+}$ position to allow for greater interaction between the metal centre and the β-$CH^{\delta+}$ carbon resulting in the formation of chiral metallacyclopropane type structures [1,2].

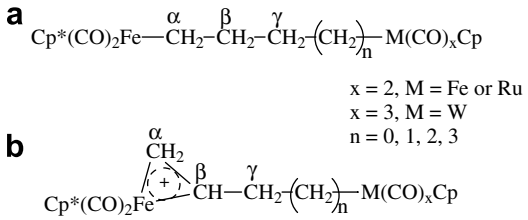

Fig. 1. Structural formula of (a) alkanediyl complex (b) transition metal-stabilized metallacyclic carbocation complex showing the labeling of carbon positions of the hydrocarbon ligand.

We now report on a series of the mixed-ligand transition metal alkanediyl complexes $[Cp^*(CO)_2Fe(CH_2)_nM(CO)_x\text{-}Cp]$ (where $n = 3$–6; $x = 2$, M = Fe, or Ru, $x = 3$, M = W) and $[Cp(CO)_2Ru(CH_2)_nW(CO)_3Cp]$ ($n = 3$–5) and their reactions with Ph_3CPF_6 to give the transition metal-stabilized carbocations $[Cp^*(CO)_2Fe\{\mu\text{-}(C_nH_{2n-1})\}M(CO)_x\text{-}Cp]PF_6$ (where $n = 3$–6; $x = 2$, M = Fe, or Ru, $x = 3$, M = W) and $[Cp(CO)_2Ru\{\mu\text{-}(C_nH_{2n-1})\}W(CO)_3Cp]PF_6$ ($n = 3$–5). The precursor complexes $[Cp^*(CO)_2Fe(CH_2)_nM\text{-}(CO)_xCp]$ (where $x = 2$, $n = 3$, M = Fe, $n = 3$–5, M = Ru) have been reported previously [28], but the rest are new.

2. Results and discussion

2.1. Preparation of the complexes $[Cp^*(CO)_2Fe\{\mu\text{-}(C_nH_{2n-1})\}M(CO)_xCp]PF_6$ (n = 3–6; x = 2, M = Fe or Ru; x = 3, M = W)

Reactions of the neutral complexes $[Cp^*(CO)_2Fe(CH_2)_n\text{-}M(CO)_xCp]$ (M = Fe, W or Ru, $n = 3$–6) with Ph_3CPF_6 in CH_2Cl_2 gave deep red solutions from which the carbocation complexes $[Cp^*(CO)_2Fe\{\mu\text{-}(C_nH_{2n-1})\}M(CO)_xCp]PF_6$ were obtained by precipitation with diethyl ether in good yields (32–89%). The solutions of tungsten containing complexes appeared bluish-green indicating partial decomposition. The complexes where $n = 3$ were precipitated as orange microcrystalline solids, while the rest of the complexes separated as red oils upon addition of diethyl ether to the CH_2Cl_2 solutions. The red oils swelled up into pale yellow, almost clear, spongy solids, which were found to be analytically pure after drying under reduced pressure. These have low melting points reminiscent of ionic liquids, as they consist of large cations, $[Cp^*(CO)_2Fe\{\mu\text{-}(C_nH_{2n-1})\}ML_y]^+$, associated with a relatively small counter anion PF_6^-.