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Electrospray ionization and tandem mass spectrometry characterization of novel heterotrimetallic $Ru(\eta^5-C_5H_5)(dppf)SnX_3$ complexes and their heterobimetallic $Ru(\eta^5-C_5H_5)(dppf)X$ precursors

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Abstract

Electrospray ionization and tandem mass spectrometry were used to characterize some novel heterotrimetallic complexes $Ru(\eta^5-C_5H_5)(dppf)SnX_3$ (1) (dppf = diphenylphosphine ferrocene; X = Cl, Br) and their heterobimetallic precursors $Ru(\eta^5-C_5H_5)(dppf)X$ (2) (X = Cl, Br, I, N₃). The positive-ion ESI mass spectra of 1 and 2 in acetonitrile solution showed the predominant presence of the $[Ru(\eta^5-C_5H_5)(dppf)]^+$ cation (3) of *m*/*z* 721. In the positive-ion ESI mass spectrum of the complex $Ru(\eta^5-C_5H_5)(dppf)N_3$ (2d), another prominent cation of *m*/*z* 735, i.e. $[Ru(\eta^5-C_5H_5)(dppf)N]^+$ (4), was also observed. Its formation was proposed to occur via the oxidation of the ruthenium atom $(Ru^{II} \rightarrow Ru^{III})$ followed by the loss of N₂. The positive-ion ESI tandem mass spectra of ions 3 and 4 showed mainly fragments formed by neutral losses of C_5H_5 , C_6H_5 and $P(C_6H_5)_2$. Finally, cation 3 was proposed to be the catalytic active species in the single-step conversion of methanol to acetic acid. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Ru-Sn complexes; Electrospray ionization; Ru-Sn-Fe complexes; Tandem mass spectrometry; Transient ionic species; Catalytic activity

1. Introduction

Electrospray ionization (ESI) is a soft ionization technique that has revolutionized the way molecules are ionized and transferred to the gas phase [1]. The ability to transfer an ion from solution to the gas phase makes ESI an ideal means to study ionic compounds. This was recognized in a very early stage of the development of ESI, when numerous inorganic salts were conveniently characterized [2–4]. Although electrospray mass spectrometry (ESI-MS) and tandem mass spectrometry (ESI-MS²) have been mainly and most successfully applied to the analysis of biomolecules [5–12], they have been increasingly used as a powerful structural characterization technique of transient intermediates [5–9], as well as in the study of intrinsic coordination catalysis [10,11]. Electrospray ionization can also be used to observe ionic species in solution, even in very low concentrations, which are difficult or impossible to detect by other techniques, such as electrochemistry and multi NMR (nuclear magnetic resonance) spectroscopy [2,12,13].

The purpose of synthesizing heteropolymetallic complexes bearing ferrocene backbones is that the coexistence of two or more metal atoms inside a coordination compound in principle would enable creating conditions for delicate and "tunable" mutual

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cooperative effects of the metal centers in their chemical interaction with external substrates. Furthermore, this kind of transition metal derivative possesses uncommon catalytic properties, as for instance in the cross-coupling of Grignard reagents of organic bromides and allylic alcohols [14].

Although ESI-MS and ESI-MS² have been increasingly used as powerful techniques for structural characterization of organometallic and coordination compounds [2,5,15–24], no similar studies on the characterization of heteropolymetallic complexes, especially those containing a Ru–Sn bond, have been reported. Therefore, the main purpose of this paper is to characterize the novel heterotrimetallic RuCp(dppf)SnX₃ complexes (1) as well as their heterobimetallic RuCp(dppf)X precursors (2) by ESI-MS and ESI-MS².

2. Experimental

Complexes 1 [25] and 2 [26] were synthesized following previously described procedures. Acetonitrile solutions of 1 and 2 were prepared in a concentration of 2×10^{-5} mol L⁻¹. All experiments were performed using a commercial LCQ Advantage ion trap mass spectrometer (ThermoElectron, San Jose, CA) equipped with an ESI source and operated in the positive ion mode. The spectra shown represent the average of about 50 scans (0.2 s/scan). Samples were infused into the ESI source with a syringe pump at a flow rate of $3-5 \,\mu L \,min^{-1}$. Typical ESI conditions were as follows: capillary temperature, 150 °C; sheath gas (N₂) flow rate, 20 units (roughly 0.50 Lmin^{-1}); spray voltage 4.5 kV; capillary voltage 25 V; tube lens offset voltage, 25 V. In the MS^n operation mode, the parent ion of interest was first isolated by applying an appropriate waveform across the end cap electrodes of the ion trap to eject all trapped ions by resonance, except those with the m/z ratio of interest. The isolated ions were then subjected to a supplementary ac signal for excitation by resonance and collision-induced dissociation (CID). The collision energy was set to a value at which product ions were produced in measurable amounts, i.e. ca. 10%. The isolation width used in the MS^n experiments was 2 units.

3. Results and discussion

Compounds 1 [25] and 2 [26] (Scheme 1) have already been fully characterized both in the solid state and in solution, which facilitates the comparison of their structural solution NMR patterns with ESI-MS and ESI- MS^2 .

Fig. 1 shows the ESI(+) mass spectrum of complex 2a in acetonitrile solution. Very similar ESI(+) mass spectra were obtained for the analogous complexes 2b and



Scheme 1.

2c (not shown). Through ESI, the cationic species $[Ru(C_5H_5)(dppf)]^+$ (3) (Scheme 1) is transferred from solution to the gas phase and detected by mass spectrometry. It is likely that the solution contains mainly neutral 2a, which is in equilibrium with 3 and Cl⁻. Because ruthenium displays seven abundant isotopes, $[^{104}$ Ru (18.6%), 102 Ru (31.6%), 101 Ru (17.1%), 100 Ru (12.6%), ⁹⁹Ru (12.7%), ⁹⁸Ru (1.86%)], ⁹⁶Ru (5.54%)] and iron possesses four isotopes [58Fe (0.28%), 57Fe (2.1%), ⁵⁶Fe (91.72%) ⁵⁴Fe (5.9%)] [27], cation **3** is detected by MS as an isotopomeric cluster of singly charged ions centered at m/z 721 (for ¹⁰²Ru and ⁵⁶Fe), and with an isotopic pattern that matches well to that calculated [28] for C₃₉H₃₃ P₂RuFe (Fig. 1). In solution, 3 associates with acetonitrile forming $[3 + CH_3CN]^+$, which is transferred to the gas phase by ESI and detected by MS as a solvent adduct ion centered at m/z762 (Fig. 1).

Fig. 2 shows the positive-ion ESI tandem mass spectrum at m/z 721, which is the highest abundance isotope of structure **3**. Upon CID, prominent fragments of m/z 657 ($[\mathbf{3} - C_5H_4]^+$), 644 ($[\mathbf{3} - C_6H_5]^+$), 580 ($[\mathbf{3} - C_6H_5^- C_5H_4]^+$), 536 ($[\mathbf{3} - P(C_6H_5)_2]^+$) and 305 ($[Fe(C_5H_4)P-(C_6H_5)_2]^+$) were observed, which is consistent with the structure proposed for **3** (Scheme 1).

The spectrum of **2d** (Fig. 3) obtained under the same electrospray conditions displays two major cations: **3** and $[Ru(C_5H_5)(dppf)N]^+$ (**4**). The latter was detected by MS as an isotopomeric cluster of singly charged ions centered at m/z 735 (for ¹⁰²Ru and ⁵⁶Fe), and with an



Fig. 1. Positive-ion ESI mass spectrum of the complex $[Ru(C_5H_5)(dppf)]Cl$ (2a) in acetonitrile solution. Insets show the ion intensities and the *m/z* distributions (experimental and calculated [28]) of cation 3 (C₃₉H₃₃P₂RuFe).



Fig. 2. Positive-ion ESI mass spectrum of mass-selected cation 3 (ionic cluster centered at m/z 721). For more details on the "empty and filled circle" notation, see [49].

isotopic pattern that fits well to that calculated for $C_{39}H_{33}P_2NRuFe$ [28]. In the positive-ion ESI tandem mass spectrum of the mass-selected ion 4 (not shown), the following most intense fragments are observed: [4 – C_5H_4] (*m*/*z* 671), [4 – C_6H_5] (*m*/*z* 658), [4 – FeC_5H_4] (*m*/*z* 615) and [4 – (C_6H_5)₃] (*m*/*z* 504).

The formation of ion 4 is suggested to occur in the electrospray ion source via an initial oxidation of the

ruthenium atom of **2d** (Ru^{II} \rightarrow Ru^{III}) followed by the release of a nitrogen molecule (Scheme 2). We assume that this initial oxidation contributes to the weakening of the N–N bond in the azide moiety, which ultimately causes the formation of cation **4**. In this cation, the remaining nitrogen stays connected to the ruthenium atom, likely via a double Ru–N bond (Scheme 1). This occurs because the filled ruthenium d_{yz} orbital is available to interact with the empty p_z nitrogen orbital, thus allowing the formation of a π Ru \rightarrow N bond. Moreover, the extra empty orbital in this N atom and its proximity with the Fe atom could suggest a Ru–N–Fe interaction, as represented in Scheme 2. However, additional studies are required to confirm this hypothesis.

Oxidation processes in electrospray ion sources are well known and can occur under certain experimental conditions [29–33]. Similar oxidation processes were also verified to take place for the analogous bimetallic ruthenocenyl ruthenium complex [Ru(C = CHPh)(η^5 -C₅H₅)(dppr)]Cl (dppr = [Ru(η^5 -C₅H₄PPh₂)₂]). In its positive-ion ESI mass spectrum, beside an intense fragment related to the singly charged cation [Ru(C = CHPh)(η^5 -C₅H₅)(dppr)]⁺, a doubly charged cation was also detected at low cone voltages. However, its formation was attributed to the oxidation of the dppr-ruthenium moiety, giving rise to a complex with Ru present in two different oxidation states (Ru^{II} and Ru^{III}) [19]. Based on this example, we can also consider the



Fig. 3. Positive-ion ESI mass spectrum of the acetonitrile solution of complex $[Ru(C_5H_5)(dppf)]N_3$ (2d). Insets show the ion intensities and the *m/z* distributions (experimental and calculated [28]) of cation 4 ($C_{39}H_{33}P_2NRuFe$).





alternative oxidation of the ferrocene centre in **2d** (Fe²⁺ \rightarrow Fe³⁺), a well known and facile process, to yield the cation of m/z 735 after the release of N₂. Although it is difficult to distinguish between both oxidation processes, i.e. Ru²⁺ \rightarrow Ru³⁺ or Fe²⁺ \rightarrow Fe³⁺, by using only mass spectrometry, electrochemical measurements could elucidate this issue. In fact, cyclic voltammetry experiments are underway in our laboratory and will be the subject of a future publication.

Fig. 4 shows the positive-ion ESI mass spectrum of complex 1a in acetonitrile solution (a similar mass spectrum was obtained for the analogous complex 1b). As previously verified for complex 2a, cation 3 (m/z 721) is by far the predominant species. Thus, it is likely that

in acetonitrile solution, **1a** is in equilibrium with **3** and its negative counterpart SnCl_3^- . This is an unexpected result since the presence of electronegative substituents (such as Cl, Br) connected to Sn, which promote the formation of a π RuSn bond and contribute to increase the order of this bond, should impede, or at least strongly inhibit, such a dissociation. Other minor clusters centered at m/z 756, $[\text{Ru}(\text{C}_5\text{H}_5)(\text{dppf})\text{Cl}]^+$ (**5**), m/z 911, $[\text{Ru}(\text{C}_5\text{H}_5)(\text{dppf})\text{SnCl}_2]^+$ (**6**) and m/z 946, $[\text{Ru}(\text{C}_5\text{H}_5)-$ (dppf)SnCl}_3]^+ (**7**) are also observed in this spectrum. The formation of these cations is tentatively explained in Scheme 3. For instance, cation **5** is likely formed via the previously described $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ oxidation followed by the loss of a neutral SnCl₂ molecule. On the



Fig. 4. Positive-ion ESI mass spectrum of the acetonitrile solution of complex $[Ru(C_5H_5)(dppf)]SnCl_3$ (1a). Insets show the ion intensities and the *m/z* distributions (experimental and calculated [28]) of cation 6 ($C_{39}H_{33}P_2Cl_2$ SnRuFe).

other hand, cation **6** is produced via a simple release of Cl⁻ from **1a**, whereas cation **7** corresponds to the singly charged intact complex **1a**, likely formed upon $Ru^{II} \rightarrow Ru^{III}$ oxidation. The experimental isotopic patterns of these cations fit well to those calculated for $C_{39}H_{33}P_2ClRuFe$ (**5**), $C_{39}H_{33}P_2Cl_2SnRuFe$ (**6**) (Fig. 4) and $C_{39}H_{33}P_2Cl_3SnRuFe$ (**7**) [28]. The mass-selection

and CID of **5** characteristically display the loss of a chlorine atom, giving rise to the fragment of m/z 721 as cation **3** (spectrum not shown). The positive-ion ESI tandem mass spectrum of the mass-selected ion **6** (not shown) furnishes exclusively cation **3** (m/z 721) via the release of a neutral SnCl₂ molecule. Finally, the mass selection and fragmentation of ion **7** also yields exclu-



Scheme 3.

sively the m/z 721 fragment via the SnCl₃ radical loss (spectrum not shown).

3.1. Detection of catalytically active species

It has been verified that complexes 2 and 1 [34] as well as similar heterotrimetallic Ru(II)-Sn(II) complexes [35,36] and RuCl₃-SnX₂ composite systems [37] are effective catalysts in the conversion of methanol to acetic acid [38]. The mechanism of this reaction has been studied [35,37,39,40] but is not yet fully understood. Thus, taking into account that ESI is able to transfer ions from solution to the gas phase [6,8,41-44], and most importantly, the composition of ESI-generated ions often closely reflects that of the solution [5,16,17,41,45,46], we hypothesize that cation 3, undoubtedly detected in acetonitrile solutions of complexes 2 and 1 (Scheme 1), could be the catalytically active species in this conversion. This hypothesis is based on several studies [47,48] describing the use of ESI-MS to detect cationic species likely to be involved in catalytic processes. For instance, Dyson and coworkers [48] verified that in the electrospray ionization mass spectrum of $[Ru_4 (\eta^6-C_6H_6)_4-(OH)_4]^{4+}$, the main species present in aqueous solution are the intact cubane tetramer and the dimer $[Ru_2-(\eta^6-C_6H_6)_2(OH)_2]^{2+}$ and proposed that the latter is an active benzene hydrogenation catalyst.

4. Conclusion

ESI proved to be a suitable and efficient technique for the characterization of heterotrimetallic $Ru(\eta^5-C_5H_5)(dppf)SnX_3$ (1) complexes, containing a Ru–Sn bond, and their heterobimetallic $Ru(\eta^5-C_5H_5)(dppf)X$ (2) precursors. The formation of cation 3, likely the catalytically active species in the single step conversion of methanol to acetic acid, from 2 and 1 seems to be a general tendency for these ruthenium complexes.

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