

Organometal clusters as models for corrosion inhibitors. The reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with benzotriazole

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Abstract

The products of the reaction between $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and benzotriazole, a widely used corrosion inhibitor, are discussed in the light of their spectroscopic data. The structural, chemical and electrochemical properties of these molecular clusters are considered, with the aim of providing new insights into the actual mechanism of protection of metallic surfaces from corrosion.

Introduction

The numerous studies of cluster chemistry during the past fifteen years were often stimulated by the expectation that a better understanding of the bonding and reactions of organometallic clusters would lead to benefits in the field of heterogeneous catalysis [1]. Unfortunately, up to now this target has only not often been reached probably because the remarkably stable derivatives containing a poly-metallic framework cannot provide satisfactory models for the labile chemisorbed species formed on the surface of a working catalyst.

On the other hand the suggestion that the reactions of metallic clusters may mimic those of a metal derivative in solution [2] is not only attractive from an academic point of view but may be of practical relevance for other processes that occur at metallic surfaces. One of the areas of interest may be that concerned with problems related to the chemical behaviour of corrosion inhibitors on metallic surfaces [3]. Since the chemicals commonly employed for this purpose are species which act as good ligands for transition metals through their nitrogen, oxygen, or sulfur donor atoms, it follows that a knowledge of structural, chemical and electrochemical properties of the molecular species obtained by reactions of such ligands with metal clusters might provide new insights into their action in protecting metallic surfaces.

Balezin and coworkers [4] have indeed suggested that the inhibiting action of

Table 1

Spectroscopic data for the complexes studied

Complex	IR ^a , $\bar{\nu}(\text{CO})$ (cm ⁻¹)	¹ H NMR ^b , δ (ppm)	ms. [M^+], m/e
I	2113m, 2076vs, 2064s, 2029vs, 2021vs, 2008s, 1995m, 1988m	7.25–7.90(m, 4H); –13.25(s, 1H)	975 ^c
II	3430w ^d , 2103m, 2063s, 2051vs, 2020vs, 2005s, 1992m, 1983w, 1973w	9.15(br, 1h, NH) ^e ; 7.22–7.83(m, 3H); –14.00(s, 1H)	975 ^c
III ^f	3409w ^d , 2102m, 2058s, 2052vs, 2018vs, 2005vs, 1990m, 1982w, 1973w	9.45(br, 1, NH), 8.14–6.99(m, 4H); –13.74(s, 1H)	

^a Cyclohexane. ^b CDCl₃. ^c [M^+] calculated on Os¹⁹² followed by stepwise loss of 10 CO's. ^d $\bar{\nu}(\text{NH})$ in CH₂Cl₂. ^e The chemical shift of this resonance is solvent, temperature and concentration-dependent. ^f Ref. 7.

such chemicals is due to the formation of insoluble organometallic complexes on the metallic surface. The resulting insoluble adherent layer can provide considerable protection.

In the light of these considerations we have made a preliminary study of the reaction between the labile derivative Os₃(CO)₁₀(NCCH₃)₂ [5] and benzotriazole (C₆H₅N₃), whose use as corrosion inhibitor for copper and its alloys and for cast iron is well established [6].

Results and discussion

Characterization of the clusters

Os₃(CO)₁₀(NCCH₃)₂ reacts promptly at room temperature with benzotriazole to afford mainly a yellow product (90% yield), whose spectral data suggest the molecular formula HOs₃(CO)₁₀(C₆H₄N₃) (I) (Table 1 and Fig. 1). On the basis of the available data two possible structures can be suggested for I (Fig. 2).

A choice between (Ia) and (Ib) was made possible by comparing the ¹⁵N NMR spectra of benzotriazole and I. The free ligand shows two absorptions at 374.4 (1N) and 364.4 (2N) ppm, respectively, as expected for the existence of a tautomeric equilibrium between the two limiting forms (Fig. 3). The existence of this equilibrium is also responsible for the appearance of only three signals in the ¹³C NMR spectrum.

Upon coordination, three signals of equal intensity are observed, at 346.7, 244.4 and 187.1 ppm, respectively. The large high-field shift shown by two ¹⁵N resonances unambiguously favours structure Ib. Although the assignment of the ¹³C resonances is straightforward for a rigid (Ib) structure (Fig. 1), it is interesting that the ²J(CH) coupling constants between the hydride and the carbonyls *trans* to it have the same value. This supports the view that there is the same electronic charge on both osmium atoms, and the differentiation within the carbonyl set has a structural origin, arising from the asymmetric disposition of the organic ligand. The minor product, HOs₃(CO)₁₀(C₆H₄N₃) (II) (5% yield), from the title reaction is an isomer of I corresponding to a product of oxidative addition of a C–H bond in a *peri*-position to the coordinated N atom (Fig. 4).

This assignment is made on the basis of the strong similarity of the IR spectrum

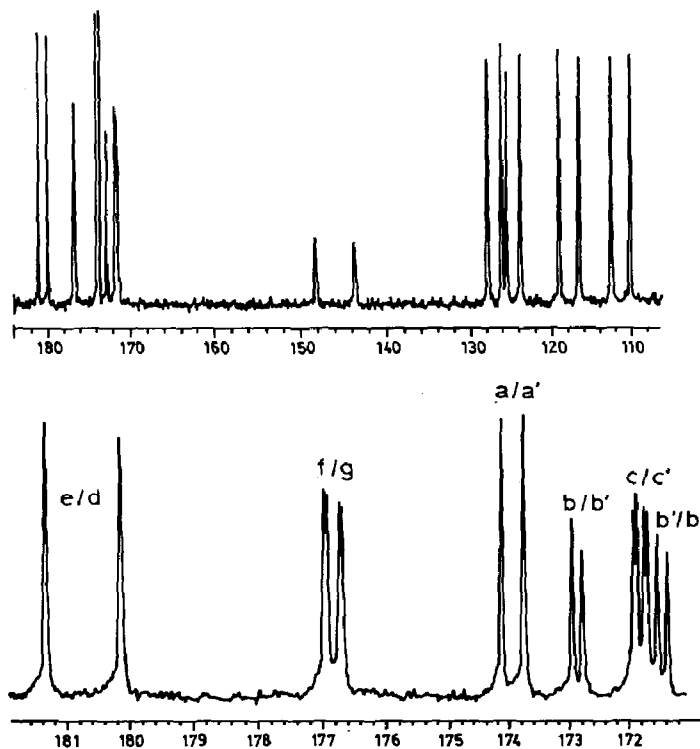


Fig. 1. Room temperature ^{13}C NMR spectrum of **1** in CDCl_3 at 67.9 MHz. Upper trace: overall spectrum; lower trace: expanded CO region with the assignment according to Fig. 2. The chemical shifts and integrated intensities are as follows: CO region: 183.3s (1), 180.1s (1), 176.9d (J 3.3 Hz) (1), 176.7d (J 2.2 Hz) (1), 174.1s (1), 173.7s (1), 172.9d (J 12.1 Hz) (1), 171.9d (J 2.2 Hz) (1), 171.7d (J 3.3 Hz) (1), 171.4d (J 12.1 Hz) (1); aromatic region: 126.8 dd ($^1J(\text{CH})$ 162 Hz, $^3J(\text{CH})$ 7.7 Hz) (1), 125.0 dd ($^1J(\text{CH})$ 162 Hz, $^3J(\text{CH})$ 7.7 Hz) (1), 117.9dd ($^1J(\text{CH})$ 165.2 Hz, $^3J(\text{CH})$ 7.7 Hz) (1), 111.4dd ($^1J(\text{CH})$ 165.3 Hz, $^3J(\text{CH})$ 7.7 Hz) (1).

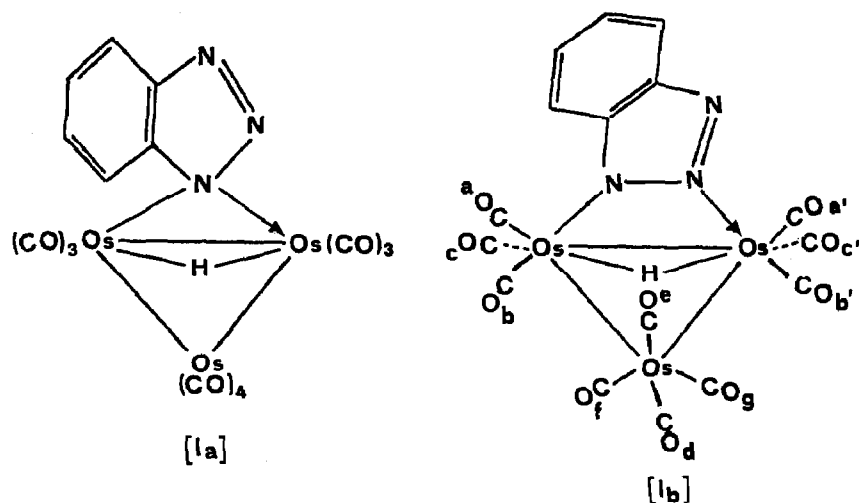


Fig. 2. Possible structures of $\text{HO}_3(\text{CO})_{10}(\text{C}_6\text{H}_4\text{N}_3)$ (**1**).

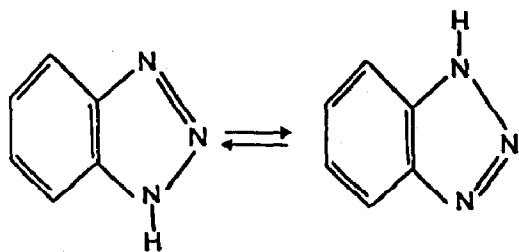


Fig. 3. The tautomeric equilibrium for $C_6H_5N_3$.

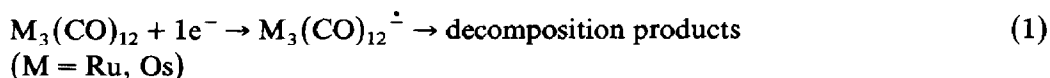
to that of the analogous derivative obtained from the reaction between $Os_3(CO)_{12}$ and benzimidazole, namely $HOs_3(CO)_{10}(C_7H_4N_2)$ (III) [7].

The 1H spectrum is also consistent with this proposal (Table 1).

Considerations of the mechanism of inhibition

It is generally accepted that the protection against oxidation is enhanced by an increase in the electron density on the metallic framework (in the benzotriazole case this is due to the good donor properties of the coordinated nitrogen atoms) which makes its oxidation more difficult. Donahue and coworkers [8] have tested this idea and obtained good correlations between the corrosion current densities of iron in the presence of several inhibitors and the Hammett σ - or the Taft σ^* -constants.

In order to evaluate the variation in electron density on the Os_3 skeleton caused by the coordination of benzotriazole, we have carried out cyclic voltammetric (CV) tests on the parent compound $Os_3(CO)_{12}$ and $HOs_3(CO)_{10}(C_6H_4N_3)$ (I). The electrochemistry of both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ has been investigated previously by polarographic and CV techniques, and is characterized by a chemically irreversible mono-reduction process [9] (eq. 1).



We repeated the CV experiments on $Os_3(CO)_{12}$ but using the relatively non-polar and inert solvent CH_2Cl_2 , a supporting electrolyte whose anion has low nucleophilicity, namely $[n-Bu_4N]BF_4$, and at a temperature as low as $-10^\circ C$. All

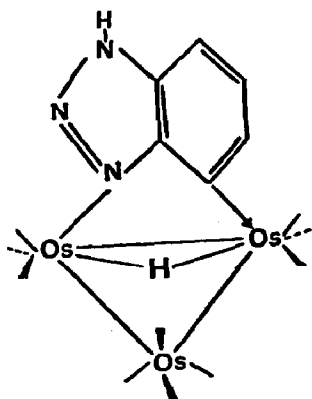


Fig. 4. Proposed structure of the isomer II.

these features should reduce the rate of decomposition of electrogenerated organometallic species [10]. Unfortunately, even under these conditions, $\text{Os}_3(\text{CO})_{12}$ still exhibits a chemically irreversible reduction step at a peak potential, E_p , of -1.43 V vs. SCE, followed on the return scan by a smaller broad oxidation peak at -0.23 V due to the reoxidation of an unidentified fragmentation product. Under the same conditions $\text{HOs}_3(\text{CO})_{10}(\text{C}_6\text{H}_4\text{N}_3)$ (I) exhibits similar behaviour: the CV response shows a chemically irreversible reduction process at E_p -1.52 V and a small oxidation peak at -0.36 V. In the potential range investigated (0 to -2.00 V) the free benzotriazole shows only a hump near to the solvent discharge. From this comparison (Fig. 5) we can conclude that the coordination of benzotriazole causes only a moderate increase in the electron density of the Os_3 frame (ΔE -90 mV). For example the progressive substitution of the moderately basic $\text{P}(\text{OPh})_3$ ligands for CO groups in $\text{Fe}_3(\text{CO})_{12}$ produces a decrease in the cathodic potentials of 198, (1 $\text{P}(\text{OPh})_3$), 384 (2 $\text{P}(\text{OPh})_3$) and 712 mV (3 $\text{P}(\text{OPh})_3$) respectively [9a]. This electronic effect seems to play only a minor role in the present case.

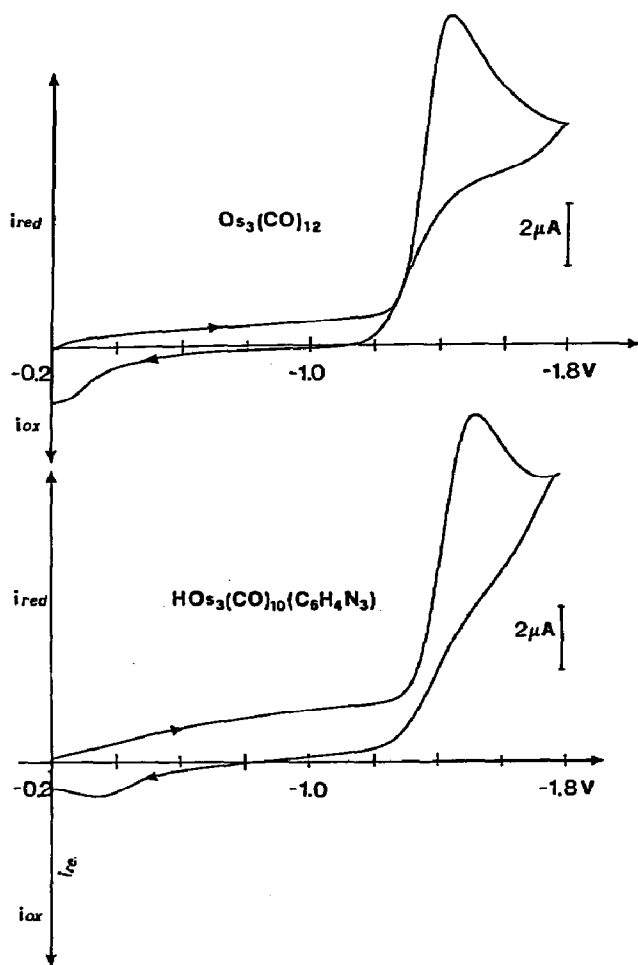


Fig. 5. Cyclic voltammograms for reduction of 5×10^{-4} M $\text{Os}_3(\text{CO})_{12}$ (a) or I (b) in CH_2Cl_2 with $[\text{Bu}_4\text{N}]\text{BF}_4$ 1×10^{-1} M. The working electrode was Pt, the scan rate 100 mV s^{-1} and the temperature 10°C .

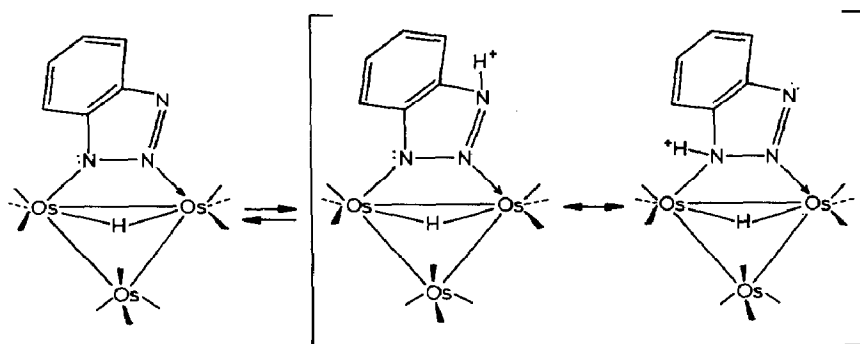


Fig. 6. Reaction scheme for the protonation of I.

From the stereochemical point of view, if benzotriazole adsorbed on to metallic surfaces adopts the same bonding mode as in I and II, its spatial disposition (almost normal to the trimetallic moiety) implies a hydrophobic role of the ligand in the protection of the metallic surface. In situ surface Raman spectroscopy studies have indeed suggested that at high surface coverage the benzotriazole molecules assume an end-on configuration, i.e. perpendicular to the metal (Cu) surface [11].

In order to gain more insight into this analogy we have undertaken a study of the protonation of I. When a solution of I was treated with an aliquot of CF_3COOH the ^1H NMR spectrum showed no change in the hydridic region and only minor differences in the aromatic region. The IR spectrum of the solution shows the appearance of a stretching N–H absorption at 3060 cm^{-1} but no significant shift was detected for the carbonyl stretching frequencies. This behaviour indicates that the nitrogen lone pair competes with basic sites on the metallic cluster which are not involved in the protonation, the opposite to what is normally observed with organoosmium clusters [8]. The acid–base interaction (shown in Fig. 6) seems to provide the most efficient inhibition by benzotriazole since it prevents the contact between protons and metallic surface and the subsequent electronation reaction.

Work in progress in our laboratory is aimed at a more detailed study of these ideas.

Experimental

Synthesis

$\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ was prepared by a published method [5]. In a Schlenk flask connected to a switchable nitrogen or vacuum supply, a solution of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (250 mg) and benzotriazole (35 mg) in 100 ml of CH_2Cl_2 was stirred at room temperature under nitrogen. The progress of the reaction was monitored by tlc and IR spectroscopy. After 2 h the solvent was removed under vacuum, and the residue was dissolved in a minimum amount of CHCl_3 and separated by tlc on Merck plates coated with a 0.25 mm layer of silica, with 9/1 v/v petroleum ether/diethyl ether as eluent. Two yellow bands correspond to the two $\text{HOs}_3(\text{CO})_{10}(\text{C}_6\text{H}_4\text{N}_3)$ isomers, 90% of I and 5% of II, respectively, were eluted; the complexes were extracted from silica and recrystallized from 9/1 v/v n-hexane- CH_2Cl_2 .

Instruments

The IR, ^1H and ^{13}C NMR spectra were recorded on Perkin-Elmer 580B, and JEOL GX 270/89 spectrometers (^1H at 270.0 MHz, ^{13}C at 67.9 MHz), and mass spectra on a AEI MS 12 (at 70 eV ionizing potential) instruments. For cyclic voltammetry an Amel Model 553 potentiostat modulated by an Amel Model 567 function generator was used. All experiments were performed with anhydrous deoxygenated CH_2Cl_2 solutions, $5 \times 10^{-4} \text{ M}$ with respect to the clusters under study and $1 \times 10^{-1} \text{ M}$ with respect to the supporting electrolyte $[\text{Bu}_4\text{N}]\text{BF}_4$; the working electrode was a platinum disk (area ca. 0.8 mm^2). The potential of the working electrode was determined relative to a Lugging capillary-SCE reference compartment. Compensation for the iR drop was not applied.

Protonation of (I)

To a 2 ml CDCl_3 solution of I (50 ml) in an NMR tube an aliquot (50 μl) of CF_3COOH was added dropwise under nitrogen. The progress of the reaction was monitored by ^1H NMR spectroscopy.

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