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Lead corrole complexes in solution: Powerful multielectron transfer reagents for redox catalysis

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ABSTRACT

The first observation of Pb(II)-complexes of corroles and their photoinduced oxidation to the corresponding Pb(IV)-derivatives is reported. These compounds display metal-centered redox chemistry in solution. Their potential for catalytic oxygen atom transfer processes is explored.

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Metallocorroles are attractive candidates for redox catalysis, since their specific electronic structure is very suitable to stabilize highvalent oxidation states of the coordinated central metals [1]. Compared to the closely related porphyrin-based systems, where the macrocyclic ring tends to be involved as a noninnocent ligand forming π -radical species,[2] this feature determines the extraordinary properties of oxygen atom transfer reagents such as manganese (V)-oxo corroles for the epoxidation of alkenes[3] or the O–O bond formation step in artificial photosynthetic water oxidation [4]. Quite unique reactivity patterns have furthermore been observed, when corrole complexes incorporate heavy-atom central ions [5].

In this context, the investigation of tetrapyrrole complexes with high-valent main group metals including Pb(IV), Sb(V) or Bi(V) is of considerable interest due to their intrinsic preference for multielectron reactivity and their potential to form catalytically active oxo species [6]. Especially, the reversible photochemical formation of very strong oxidants such as Pb(IV) compounds carrying hydroxo, oxo or carboxylato groups would be an extremely desirable reaction, since it is well established that high-valent lead compounds are useful reagents for mechanistically demanding substrate conversions such as carbon-carbon-bond formation [7] or electrocatalytic O₂-evolution [8].

We decided to explore this possibility and studied the metallation of triphenylcorrole[9] H_3 (TPC) **1** with various Pb(II) salts (Scheme 1)[10].

Interaction of an excess of the low-valent main group metal ions with the free base corrole ligand in solution resulted in gradual absorption spectral changes indicating the formation of a sitting-atop complex, which was allowed to further react under an inert atmosphere by stirring the mixture for several hours in the dark [10]. The occurrence of a diagnostic *p*-type hyper electronic spectrum [11] with band maxima at 310, 415, 450 and 680 nm including a "split" Soret band served as an indicator for the presence of a Pb(II) complex of triphenylcorrole. While at this stage the reaction product was very sensitive to demetallation and all attempts to completely remove excess salts initially failed, the obtained NMR- and high-resolution mass spectral data unambiguously displayed a set of signals and a characteristic isotope pattern consistent with a mononuclear TPC-compound (Fig. 1).

Interestingly, the positive ion ESI-signal at m/z = 731.01 corresponds to the cationic species (TPC)Pb⁺, which indicates the possibility



Scheme 1.

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Fig. 1. (a) ¹H-NMR spectrum of (TPC)Pb⁻ in CD₃OH at 25°C. (b) Electrospray mass spectrum of lead triphenylcorrole. Insert: calculated istope pattern for $C_{37}H_{23}N_4Pb(M^+)$: m/z = 731.176).

of a metal-centered redox reaction to reach the highly oxidizing Pb(IV)state within the intact macrocycle. Such a formation of cationic species from anionic complexes of divalent metals is an unusual but wellknown phenomenon in metallocorrole mass spectrometry, which was recently studied in some detail [12].

In addition to this reaction occuring in the mass spectrometer, the oxidation of the low-valent TPC-complex could also be induced photochemically. When solutions of Pb(II)-triphenylcorrole were

excited with monochromatic UV-light in the spectral region of the metal-centered *sp*-electronic transitions of the main-group central atom [14], the bright green colour of the complex caused by the prominent Q-band absorption at around 680 nm rapidly changed into a brownish-green. At the same time, within a few minutes of light-exposure, the irregular split Soret-band feature and the UV-maxima corresponding to the presence of divalent lead disappeared (Fig. 2). The photoproduct spectra in EtOH were characterized by a broadened Soret band around



Fig. 2. Spectral changes during the 313nm photolysis of (TPC)Pb⁻(**2**) in ethanol at (a) 0, 30, 90, 150, 180, 210, 240, 270, and (i) 300 s reaction times (1 cm cell, 298K, aerobic conditions).

410 nm, a flat Q-band pattern in the 550–750 nm region, and a conspicuous new absorption band with a maximum at 505 nm.

Progress of the light-driven reaction was simultaneously followed by means of mass spectroscopy, which allowed a tentative assignment of the photogenerated compound as a solvated (TCP)Pb(O) complex due to the occurrence of diagnostic Pb-signals and fragmentation peaks. Besides the fragment (TPC)Pb⁺ with m/z = 731.01, the species identified according to their characteristic isotope pattern include $M^+ \cdot EtOH$, $M^+ \cdot H_2O$ and M^+ , with M = (TPC)Pb(O) and m/z = 793.21, 765.17 and 747.16, respectively. When the synthesis and the photo-oxidation were alternatively carried out in MeOH solution, the corresponding (TPC)Pb(O) methanol adducts such as M^+ ·MeOH wit m/z = 779.12 were obtained instead. In all cases, the presence of sharp tetrapyrrole signals in the aromatic region of the ¹H-NMR spectra and the absence of any free base NH proton signals was consistent with the formation of diamagnetic metallocorrole species showing a singlet ground state. The occurrence of several isosbestic points in the initial phase of the photolysis together with the mass- and NMRspectroscopic data of the irradiated samples indicated the clean formation of the high-valent Pb(IV)-oxo complex of triphenylcorrole with obviously substitution-labile O-atom donor ligands such as additional solvent molecules in the axial coordination sphere. Interestingly, aqueous workup of the irradiated samples and extraction with diethyl ether always resulted in the occurrence of a novel main peak with m/z = 800.43 in the high resolution mass spectra, indicating the formation of a modified product with an additional OH-group attached to the molecule, which in analogy to other high-valent metallocorrole oxo complexes⁴ is tentatively assigned to a nucleophilic adduct such as (TPC)PbOOH · 2H₂O carrying an axial hydroperoxo ligand [14].

Although the spectrum of the oxidized compounds gradually changes within several days in methanol solution, thus indicating a currently unknown degradation process, the formation of the Pb(IV) triphenylcorrole species may also be driven as a reversible reaction. When the high-valent complex is allowed to react with typical oxygenatom transfer acceptors in solution, a gradual regeneration of the characteristic *hyper*-type electronic spectrum of the low-valent Pb(II) complex is observed in the course of a slow dark reaction. In the case of triphenylphosphine as a substrate, this process was followed by ³¹P-NMR spectroscopy, which clearly demonstrated the gradual formation of Ph₃P O as the corresponding reaction product. Within the scope of our present study, no attempts were made yet to accelerate this type of back-reactions by light, closing a photocatalytic redox cycle.

The spectroscopic features and reactivity patterns of the lead TPC complexes can be best rationalized by the following considerations.



Fig. 3. Qualitative MO-diagram for (a) low-valent and (b) high-valent lead corrole complexes. IL: Intraligand($\pi\pi^*$) transitions involving electrons localized at the macrocyclic ring; MC: Metal centered *sp*-excitation; MLCT: Metal-to-ligand charge transfer-, and LMCT: ligand-to-metal charge transfer transitions.

Upon complexation with divalent lead salts, an additional dipoleallowed metal-to-ligand charge transfer (MLCT) transition occurs (Fig. 3a), which shows substantial mixing with the intraligand (IL) bands of the corrole chromophore resulting in an irregular hyper-type spectrum [11,13]. The presence of a significantly Pb(6s)-localized HOMO in the frontier orbital region of the corrole ligand is also consistent with the results of supporting DFT-calculations. Due to the large ionic radius of Pb²⁺ (112 pm)[15] and the contracted tetrapyrrole core of the triphenylcorrole ligand, a considerable out-of-plane displacement of the main group metal is expected in the initial sittingatop complex, which may explain the tendency for demetallation at this stage of the reaction. Irradiation in the region of the metalcentered (MC) bands of the compound removes electron density from the stereochemically active 6 s lone-pair and leads to photo-metallation and oxidation. In the photoproduct, which is ascribed to a Pb(IV)species, the MLCT bands are no longer present, but a novel ligand-tometal charge transfer (LMCT) band is possible due to the availability of an empty Pb-centered orbital in the tetrapyrrole frontier orbital region (Fig. 3b). In agreement with the relative intensity and energetic position, the 505 nm band of the photoproduct (Fig. 2) is tentatively ascribed to such an allowed LMCT-transition in Pb(IV) triphenylcorrole, which shows some mixing with the four-orbital $\pi\pi^*$ -transitions of the tetrapyrrole macrocycle.

Interestingly, in the course of the Pb(II) to Pb(IV)-conversion, also a broad metal-to-metal charge transfer (MMCT) band occurs because of the intermediate presence of both reducing (TPC)Pb⁻ and oxidizing (TPC)Pb⁺ metal complexes in solution. Due to the stabilization of the Pb(IV) state within the corrole ligand, the maximum of this MMCTband at around 600 nm (Fig. 2) is red-shifted compared to the corresponding band in simple mixed-valent chloro complexes of Pb with a reported MMCT-maximum at 2.51 eV (494 nm) [16].

Oxidation of the central metal to the high-valent state Pb^{4+} should be accompanied by a significant contraction to 79 pm [15], thus reaching a similar size as high-spin Fe^{2+} , which still requires an out-of plane structure in tetrapyrroles, but readily accepts additional axial ligands. This is in good agreement with the observation of a quite stable (TPC)Pb⁺ core and the occurrence of several different lead(IV)-oxo species with attached solvent molecules in the coordination sphere. The large structural changes between low- and high-valent complexes may also serve to explain their rather slow thermal interconversion rate even in the presence of potential substrate molecules, since substantial reorganizational energy contributions are probably influencing the net two-electron transfer sequence.

In summary, the first examples of lead corroles are presented. Unlike all the closely related tetrapyrrole derivatives known so far, these compounds display metal-centered redox chemistry in solution. Their potential for photoredox catalysis and oxygen atom transfer processes seems very promising. Further investigations are currently underway which will focus on a more detailed characterization of the high-valent species and on the photocatalytic reactivity of these interesting multielectron transfer photosensitizers.

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Appendix A. Supplementary material

Electronic Supplementary Information (ESI) available: further experimental details, spectroscopic data and electronic structure calculations at the DFT-level. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.06.047.

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