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Complete List of Authors:	Zhou, Wen; Simon Fraser University, Chemistry Platel, Rachel; Simon Fraser University, Chemistry Teixeira Tasso, Thiago; Tohoku University, Department of Chemistry Furuyama, Taniyuki; Tohoku University, Department of Chemistry Kobayashi, Nagao; Tohoku University, Department of Chemistry, Graduate School of Science Leznoff, Daniel; Simon Fraser University, Department of Chemistry

Reducing Zirconium(IV) Phthalocyanines and the structure of a $Pc^{4-}Zr$ complex

Wen Zhou,[a] *Rachel H. Platel,*[a] *Thiago Teixeira Tasso,*[b] *Taniyuki Furuyama,*[b] *Nagao Kobayashi*[b] *and Daniel B. Leznoff*[a]

[a]Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A 1S6 Canada

[b]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Abstract

The synthesis and characterization of the ring-unsubstituted zirconium phthalocyanine $PcZrCl_2$ (**1**; Pc^{x-} = phthalocyaninato^{x-}) and its reduction products are described. X-ray analysis of **1** (crystallized from hot 1-chloronaphthalene) reveals that **1** is a chloride-bridged dimer $[PcZrCl]_2(\mu\text{-}Cl)_2$ in the solid-state; **1** was also characterized by UV-vis/MCD spectroscopy and cyclic voltammetry, which indicated reduction potentials at -0.55, -0.95 and -1.28 V. Although attempts to access these Pc-ring reduced species with KC_8 led to mixtures of reduced products due to the insolubility of both starting materials, one equivalent of the reducing agent KEt_3BH reacted with **1** to generate Pc^{3-}-containing species, as indicated by visible Q-band spectral changes (from λ_{max} = 686 for **1** to 589/611 nm), a single ESR peak (g=2.001) and paramagnetically shifted ^1H NMR resonances consistent with the presence of a Pc-radical anion. Addition of two equivalents of KEt_3BH to **1** generated Pc^{4-}-containing species, confirmed by a shift in λ_{max} to 522 nm and upfield-shifted ^1H NMR peaks relative to **1**. Reaction of **1** with one and two equivalents of LiCp* did not generate Cp*-substituted products but also effected reduction to analogous Pc^{3-} and Pc^{4-} species. This latter material, the air-sensitive ring di-reduced "ate"-complex $Pc^{4-}Zr(LiCl)_{1.5}(DME)_3$, of the form $[LiCl(DME)_4]_{0.5}[Pc^{4-}ZrClLi(DME)]$ was structurally characterized, illustrating partial bond localization in the Pc^{4-} ring, which also adopts a saddle-shape vs. the more typical dome-configuration found in **1**. This represents a rare example of an isolated and structurally characterized Pc^{4-} complex.

Introduction

Phthalocyanine ligands are highly redox-active, with extensive studies of metal-phthalocyanine (PcM) complexes in solution reported across the full range of oxidation states that the Pc ligand can access (0 to -6).[1-7] However, these Pc-ring reduced species are usually electrochemically generated and studied *in situ*;[8-12] very few reduced PcM complexes have been prepared in isolable amounts and only a handful of these extremely air- and moisture-sensitive materials have been structurally characterized.[13-20]

We have focused on this underdeveloped area of PcM-chemistry, with particular interest in early transition-metals and their broad organometallic chemistry and bond-activation catalysis.[21-22] For example, we reported the reduction of $PcNbCl_3$ and the X-ray crystal structure of the reduced product $K_2PcNbO \bullet 5DME$ in which both the redox-active Pc and the Nb were reduced, to Pc^{4-} and Nb(IV) respectively.[16] The reduction of PcMg in DME with trace H_2O present yielded $[K_2(DME)_4][PcMg(OH)]$, in which the Pc^{3-} anion was structurally characterized.[17] In both cases, KC_8 - a very convenient form of easily weighable potassium (but which is extremely pyrophoric) - was used as the reducing agent.[23]

As a comparison to the Nb-system, we targeted the synthesis of analogous PcZr(IV) systems[24-30] for reduction. Since zirconium(IV) is both diamagnetic and predominantly redox inactive, only reduction of the Pc ligand would be expected and thus the stoichiometric addition of reducing agents to prepare Pc^{3-} and Pc^{4-}Zr(IV) systems was examined. In the process, the use of several different reducing agents were explored in order to optimize the clean synthesis of these highly air-sensitive products and facilitate their structural characterization; the results are described herein.

Results and Discussion

$PcZrCl_2$ (**1**) was prepared by a modification of a literature procedure,[31] in which anhydrous $ZrCl_4$ and phthalonitrile were heated to 230 ˚C in chloronaphthalene for 15 minutes. Hot filtration and workup yielded insoluble **1** in moderate yield; a small amount of unreacted $ZrCl_4$ was also present in the crude product. X-ray quality crystals could not be obtained by recrystallization of this solid due to its insolubility. However, by stirring the reaction until it reached 230 ˚C and the $ZrCl_4$ was solublized, and then letting it stand without agitation while cooling slowly, crystals of **1** could be grown directly from the reaction mixture.

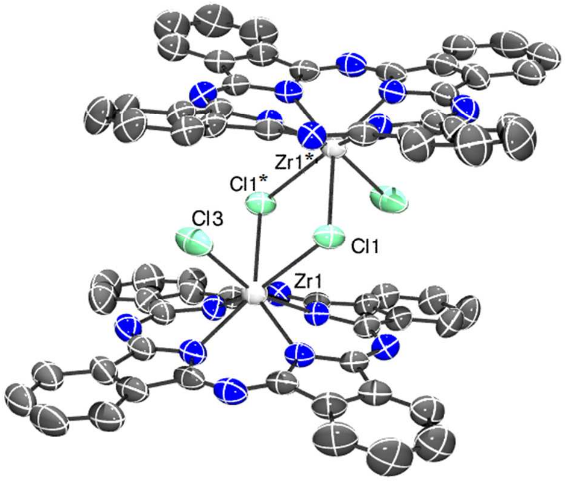

Figure 1: Molecular structure and numbering scheme of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50 % probability. Selected bond lengths (Å) and bond angles (°): Zr – Cl(1) 2.6422(14), Zr – Cl(3) 2.4268(16), Zr – Cl1* 2.6743(13) Zr – N(1) 2.221(4), Zr – N(3) 2.212(4), Zr – N(5) 2.231(4), Zr – N(7) 2.203(4), Zr···Zr 4.270, Zr – Cl(1) – Zr 106.88(5), Cl(1) – Zr – Cl(3) 81.16(6).

The crystal structure reveals a dinuclear complex with one bridging and one terminal chloride ligand per Zr(IV) centre (Figure 1), similar to previously reported structures of analogous Zr(IV) and Hf(IV) porphyrins[25-26] and nearly isostructural with the recently reported hafnium(IV) analogue.[32] The phthalocyanine core presents a bowl-shaped non-planar conformation with the Zr atom positioned 1.067 Å above the plane formed by the isoindole nitrogen atoms; this compares to 1.036 Å for the Hf(IV) analogue. The two non-coplanar PcZr moieties are connected by two nearly symmetrically bridging chlorides, with Zr-Cl1 and Zr-Cl1* bond lengths of 2.6422(14) and 2.6743(13) Å respectively; the terminal Zr-Cl bond length is substantially shorter, at 2.4268(16) Å. In the PcHf analogue, however, the terminal and bridging chlorides are much closer in length, with values of 2.6329(12) and 2.6589(12)/2.7476(11) Å respectively.[32] The Zr-N bond lengths (2.203 ~ 2.231 Å) are longer than in the PcHf analogue (2.190(4)-2.208(4) Å) but shorter than in monomeric PcZr structures (~2.34 Å), which generally have large axial ligands.[28, 33]

The absorption and MCD spectra of **1** in DMSO are characteristic of metallated Pcs with D_{4h} symmetry (Figure S1). The Q and Soret bands appear at 686 and 347 nm, with the associated Faraday *A* term in the corresponding MCD spectra. Figure 2 displays the cyclic voltammogram of **1** in DMSO with 0.1 M $^{n}Bu_4NClO_4$ as the supporting electrolyte. Complex **1** has three quasi-reversible reduction waves (at -0.55, -0.95 and -1.28 V) but no oxidation wave was detected within the window limit of the solvent (*ca.* 1.2 V). The first reduction potential is more positive than that of previously reported for the ring-chlorinated [Zr(Pc-Cl)(OH)$_2$] x 2H$_2$O (0.79 V),[34] while the reduction potential of **1** is close to that of cobalt and free-base Pcs, which were measured in DMSO.[35] The second reduction potential is still readily accessible by chemical reducing agents, indicating that both one- and two-electron reductions of **1** could be targeted. Since the gap between the first redox potentials ($E_{1ox} - E_{1red}$) correlate well with the positions of the Q bands,[36] the first oxidation potential can be calculated from the first reduction and the position of Q band. Applying this approach, the $E_{1ox} - E_{1red}$ of **1** should be 1.6-1.8 V, therefore, the first oxidation wave of **1** could not be observed.

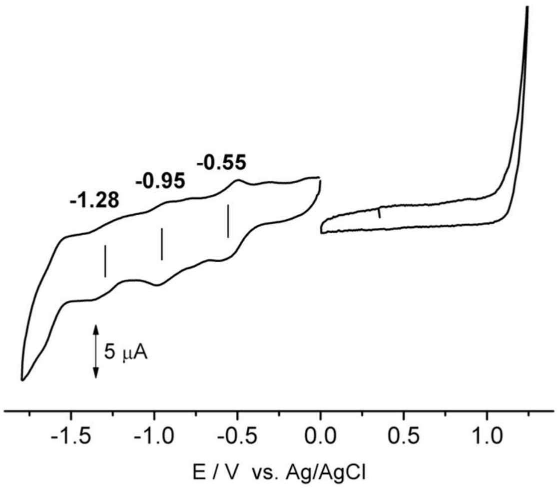

Figure 2. Cyclic voltammetry data for **1**, recorded in a 0.5 mM solution of **1** in 0.1 M $^{n}Bu_4NClO_4$/DMSO.

Thus, reduction of **1** was undertaken using various amounts of KC_8 (1-3 equivalents; see ESI) in either THF or DME (no reaction occurred in toluene or hexanes due to the complete insolubility of **1** therein). Upon addition of solid KC_8 to suspensions of **1** in THF, colour changes in the reaction mixtures as well as a dramatic increase in solubility of the Pc derivative were observed within a few seconds. With 1 equiv. of KC_8, a blue/purple reaction mixture was formed, while with 2 and 3 equiv. intense purple/pink solutions were formed. After reaction at ambient temperature for 24 hours, filtration through celite to remove graphite followed by solvent removal *in vacuo* gave gold/green powders.

Whereas axial substitution of a PcM complex induces minimal change to the UV-vis spectrum since the transitions due to the ligand have extremely large molar absorptivity coefficients, a change in the oxidation state of the Pc ligand causes significant changes to the absorption spectrum of a given Pc species.[6] Hence, the absorption spectra of the KC_8-reduced species were measured in DME (Figure S2). It is clear that when **1** is reduced with 1 eq. KC_8, a mixture of products in different Pc oxidation states is formed, as evidenced by the

UV-vis spectrum, which has maxima between 526 and 674 nm (Figure S2). This mixture likely arises from the fact that both **1** and KC_8 are almost completely insoluble in organic solvents, where as the product from the one-electron reduction of **1** becomes soluble in ethereal solvents, thus making the reaction between KC_8 and the initial product species more facile than that between KC_8 and **1**. The crude reaction mixtures did not yield any separable crystalline products, and only a small amount of homogeneous material was recovered by slow recrystallization over months.

The spectra of the products of the reaction with 2 and 3 equivalents of KC_8 show increasingly pure amounts of the product containing a Pc^{4-} unit, as indicated by the characteristic λ_{max} at 526 nm (Figure S2). This value is very similar to those published for other Pc^{4-} systems such as $[Pc^{4-}Zn]^{2-}$ (λ_{max} 522, 335 nm)[37] and $[Pc^{4-}Mg]^{2-}$ (λ_{max} 520, 335 nm)[38-39] as well as a $[Pc^{4-}NbO]^{2-}$ species (λ_{max} 521 nm)[16] supporting the conclusion that a $[Pc^{4-}Zr]$ species has been prepared in this case as well. Brief exposure of these solutions to air and re-measurement of the spectrum were consistent with the re-oxidized species containing a typical Pc^{2-} ligand; thus the Pc system remained intact during the reductions. The reduction products were also subjected to controlled oxidation by adding ferrocenium tetrafluoroborate in DME under an inert atmosphere; the oxidized materials showed MALDI-TOF mass spectra peaks corresponding primarily to $\{[PcZr][K]\}^+$ and a less intense signal consistent with $[PcZrOH_2]^+$.

In summary, unless used in excess, KC_8 is not a clean reducing agent for **1** (and for insoluble PcM complexes in general), as mixtures of products are formed that are not easily characterized or separated.

A soluble alternative to KC_8, albeit with a lower reduction potential, is sodium or potassium triethylborohydride. Borohydride-based reagents have been used as reducing agents in the isolation of other PcM complexes, such as in the preparation of $[^nBu_4N]PcCo$

from PcCo and [^{n}Bu$_4$N]BH$_4$.[40] Other reagents, including sodium fluorenone,[41] zinc dust[42] and potassium t-butylthiolate[13] have also been employed to chemically generate isolable reduced PcM complexes.

Thus, addition of one equivalent of KBEt$_3$H (as a 1M solution) to a suspension of **1** in THF rapidly generated a purple-blue coloured solution (and presumably H$_2$), with λ_{max} = 355, 589 and 611 nm in the UV-visible spectrum, consistent with a Pc^{3-} system (Figure 3).[37, 43] Notably, only small amounts of residual Pc^{2-} (or over-reduced Pc^{4-}-containing species) were observed by UV-vis spectroscopy, in contrast to the substantial mixtures obtained with one equivalent of KC$_8$. Slow addition of a second equivalent of KBEt$_3$H caused a further colour change to dark purple, and the resulting UV-visible spectrum was indicative of a Pc^{4-} unit, with λ_{max} = 522 nm (Figure 3). Removal of the THF solvent gave moderate yields of green/gold powders with Pc^{3-} (compound **2-K**) and Pc^{4-} (compound **3-K**) units respectively. The clean production of Pc^{3-} and Pc^{4-} species indicates that KBEt$_3$H is an efficient reagent for reduction of PcM complexes, even if the starting Pc-materials are insoluble.

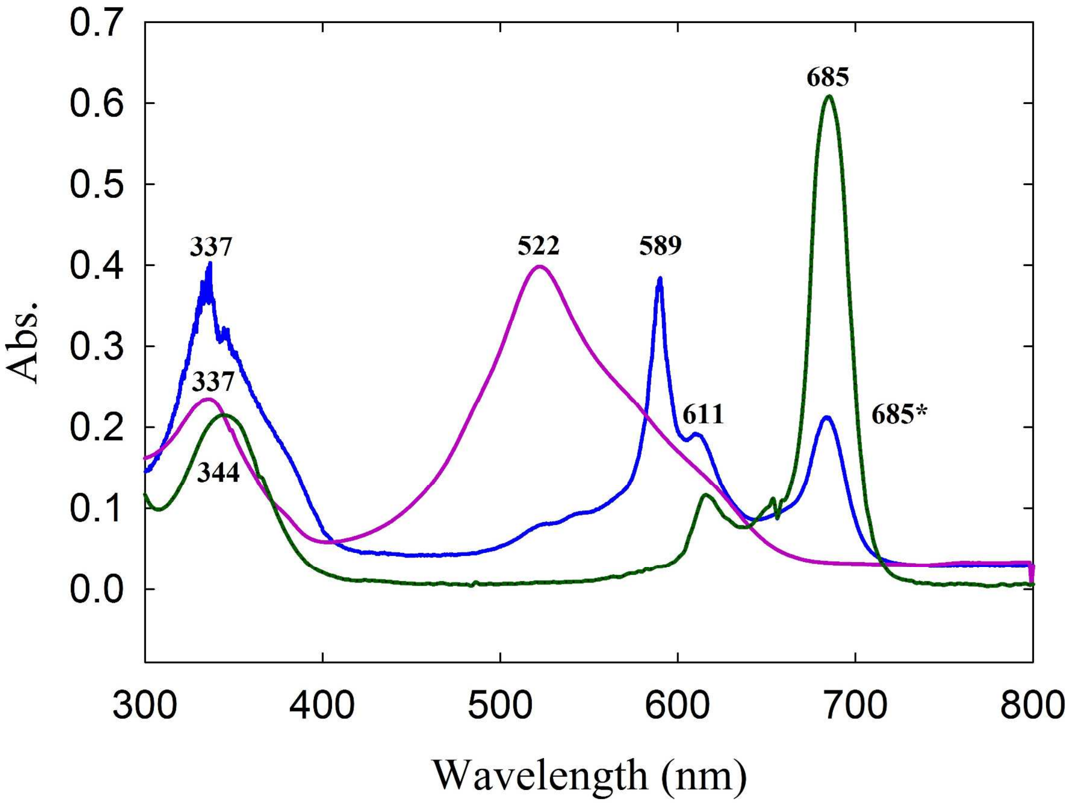

Figure 3: Electronic absorption spectra of **1** (green line) and its reduction products with one equiv. of $KBEt_3H$ (blue line, compound **2-K**, containing Pc^{3-}) and two equiv. of $KBEt_3H$ (purple line, compound **3-K**, containing Pc^{4-}). The * denotes an absorption peak attributable to partial re-oxidation of **2-K**.

Compound **2-K** crystallizes very rapidly from a DME/hexanes mixture at room temperature, forming blue/red dichroic fine, feathery needles that are extremely air and moisture sensitive; these crystals were both weakly diffracting and extensively twinned and a unit cell in which the structure could be solved was not found. Other solvent mixtures did not yield higher quality crystals. However, an EPR spectrum of **2-K** in THF at 77 K showed a single signal at g = 2.001 (lacking any resolved hyperfine coupling), consistent with the unpaired electron of a Pc^{3-} system (Figure S3).[19] The ^1H NMR spectrum of **2-K** is also consistent with the presence of a paramagnetic Pc^{3-} system, with the two Pc-ring protons at δ = -9.4 and –16.4.

Elemental analysis data suggests that **2-K** is likely best described as $Pc^{3-}ZrCl•KCl$ with some solvate.

On the other hand, **3-K** is diamagnetic and the ^1H NMR spectrum shows two sharp peaks at δ = 5.4 and 4.4. To the best of our knowledge, there is only one previous example where a di-reduced phthalocyanine species has been characterized by NMR spectroscopy: $PcGe(py)_2$, with ring-proton resonances at δ = 5.1 and 4.3.[15] Both sets of data are shifted significantly upfield from the region where Pc^{2-} ligand resonances would be expected - for example, the ^1H NMR spectrum of **1** has signals at δ = 9.06 and 8.03, and the ^1H NMR spectrum for a zirconium(IV) phthalocyanine with an axial dibenzoylmethane ligand shows ring proton signals at δ = 9.37 and 8.30.[29] This upfield shift for the Pc ring proton resonances in **3-K** reflects the reduction of aromaticity in the Pc ring as it is reduced from an 18 π-electron aromatic Pc^{2-} ligand to a 20 π-electron Pc^{4-} species. Characterization data, including a solid-state structure of the analogous **3-Li**-analogue (see below) suggests that **3-K** has the form $Pc^{4-}Zr•(KCl)_2$ with some solvate.

In order to target organometallic zirconium phthalocyanine derivatives, **1** was reacted with a range of alkylating agents. However, reaction of **1** with alkyl lithium salts, Grignard reagents, benzylpotassium or lithium phenylacetylide did not in any case lead to isolation of the desired $PcZrR_2$ derivative but rather a complex intractable mixture that included substitution and reduction products.

On the other hand, reaction of **1** in THF with one equivalent of LiCp* (Cp* = $C_5Me_5^-$) generated an immediate colour change to an intense, bright blue, suggesting the Pc ligand undergoes reduction; this was corroborated by the UV-vis spectrum of the product, with typical Pc^{3-} .λ_{max} values of 590 and 611, comparable to that for **2-K**. Additionally, the ^1H NMR spectrum contained signals corresponding to $C_{10}Me_{10}$ and the ESR spectrum contained a single resonance with identical metrical parameters to **2-K**, all consistent with the formation of a Pc^{3-} compound **2-Li**, analogous to **2-K**. Thus, the Cp* anion, rather than undergoing salt metathesis with **1**, acted as a reducing agent, generating a Pc^{3-} ligand and undergoing oxidative coupling itself (Equation 1).

$$Pc^{(2-)}ZrCl_2 + Li(C_5Me_5) \longrightarrow Pc^{(3-)}ZrCl + 1/2\ C_{10}Me_{10} + LiCl \quad \text{Eq. 1}$$

This reactivity can be contrasted with the analogous reaction of $PcScCl_2Li$ and LiCp*, which yields the substitution product PcScCp* rather than reduction of the Pc-ring;[44] this difference could be attributable to the more negative reduction potential of the PcSc-system, for which the first reduction wave in DMSO is found at -0.79 V (compared to -0.55 V for **1**).

The ^1H NMR spectrum of **2-Li** also indicates the presence of a paramagnetic species, showing two broad resonances, at $\delta =$ -11.8 and -22.0, of equal integration, comparable to that observed for **2-K**. Over the temperature range 298 – 358 K, the two peaks shift linearly towards the diamagnetic region as expected for a paramagnetic species, reaching -8 and -16.5 ppm at 358 K. Based on the characterization data, **2-Li** is likely best described as Pc^{3-}ZrCl•LiCl with some THF solvate.

Similarly, the reaction of **1** with 2 equiv. of LiCp* gave a material with the same spectroscopic signatures as **3-K** but in this case, X-ray quality crystals of this analogous **3-Li** system could be obtained from the layering of hexanes onto a purple DME solution of the product.

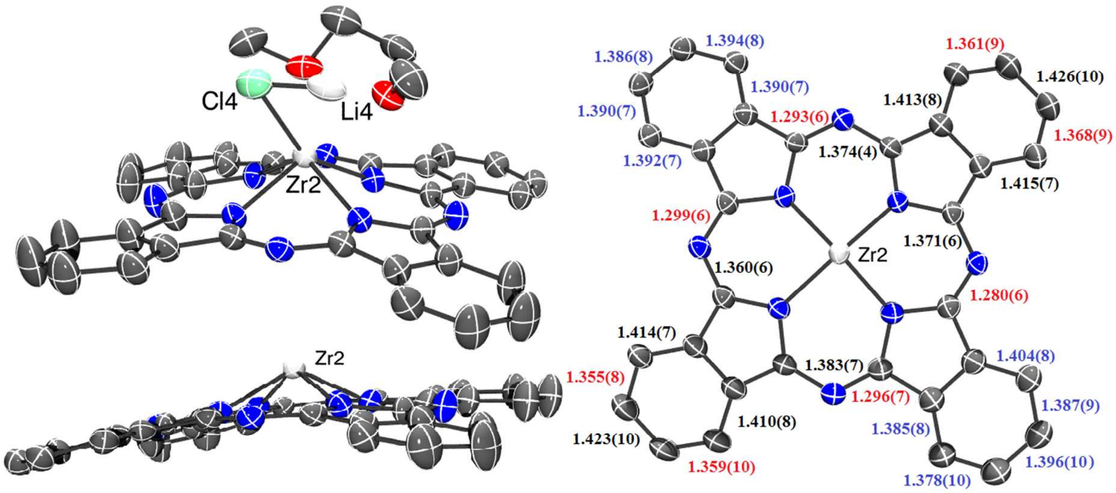

Figure 4. Left, top: Molecular structure and numbering scheme of **3-Li**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50 % probability. Left, bottom: Side-view of PcZr moiety, illustrating the non-planar arrangement of the Pc-quadrants. Right: Selected bond lengths in the Pc^{4-} ring, illustrating the partial bond localization (in long black and short red bond lengths; blue bond lengths remain delocalized).

The structure of **3-Li** (Figure 4, left top) confirmed the presence of a Pc^{4-}-based system (consistent with the spectroscopic signature) and a Zr(IV) centre that retained one equivalent of bound LiCl salt solvated by DME (as is common with Lewis-acidic Zr(IV) centres); an additional LiCl solvated by DME is present in the lattice. Thus, the structural formula from the X-ray crystal structure is $PcZr•(LiCl)_{1.5}(DME)_3$, similar to the formulae indicated by elemental analysis for the other reduced species reported herein. This represents the first structurally characterized example of a reduced PcZr moiety, joining only a handful of structures that show a Pc^{4-} ring.[15, 16] The quadrants of the Pc^{4-} ligand adopt a corrugated wave-type arrangement (Figure 4, bottom left) rather than the more symmetric dome-shape observed in **1**, as indicated by the dihedral angles between adjacent isoindolene planes: in **1** the angles are 9.6, 16.1, 11.7 and 13.0º while in **3-Li**, the angles are much larger, at 7.04, 20.30, 7.33 and 16.68º. In the Zr(IV) centre is positioned 0.965 Å above the Pc-plane vs. the

1.067 Å in **1**. The average Zr-N bond distance of 2.18 Å is shorter than in compound **1** (2.22 Å),

With respect to the bond lengths in the phthalocyanine core, as was previously observed in Pc^{4-}-containing $K_2PcNbO_3{\cdot}5DME$,[16] localized short/long bond length alternation is observed in two trans-quadrants of the Pc-ring (see Figure 4, right), with phenyl C-C bonds ranging from 1.355(8)-1.426(10) Å while being more delocalized and equivalent on the other two quadrants (1.385(8)-1.404(8) Å). Similarly, the core C-N bond lengths alternate between short 1.280(6)-1.299(6) Å and longer 1.360(6)-1.383(7) Å; this can be compared with 1.383(7)-1.400(9) Å in Pc^{2-}-containing **1**. This partial localization has been attributed to antiaromaticity in the 20π electron Pc^{4-} system.[15, 45]

Analogous reactions using NaCp also generated Pc^{3-} and Pc^{4-} containing complexes, but the reactions were much less clean, with several other (unidentified) products forming simultaneously (see ESI).

Preliminary attempts to harness the extra electrons in the reduced phthalocyanine ring to conduct oxidative addition-type reactions at Zr(IV) indicated that ligand-based oxidation chemistry could be accessed,[46] but in most cases clean products could not be isolated. For example, reaction of **3-Li** with diphenylacetylene resulted in a colour change from purple to green after stirring at room temperature, consistent with oxidation and election transfer from Pc^{4-} to Pc^{2-}, but an acetylene-bound PcZr complex could not be identified with certainty. The incorporation of LiCl, i.e., the "ate"-complex nature of **3-Li**, may hinder the ability of the Zr-centre to participate fully in further reactivity in this case; efforts to prepare salt-free analogues are in progress.

Conclusions

$PcZrCl_2$ (**1**) is a chloride-bridged, mostly insoluble dinuclear complex as crystallized from the initial reaction mixture. Reduction of **1** with KC_8 lead to mixtures of reduced species, illustrating that the insoluble reducing agent KC_8, while effective at attaining reduced products, is not an ideal reagent for reducing low-solubility PcM complexes unless used in excess. Alternatively, pure $Pc^{3-}Zr$ and $Pc^{4-}Zr$ complexes can be isolated by using appropriate equivalents of KEt_3BH as a reducing agent, and if the reduction potentials are not too negative (as in the PcSc-based system), LiCp* may also be harnessed as a clean reducing agent for PcM complexes. As an illustration of this, using two equivalents of LiCp*, $[Pc^{4-}Zr{\cdot}(LiCl)_{1.5}](DME)_3$, (**3-Li**) can be isolated, representing the first X-ray structure of a reduced PcZr-system and a rare example of a structurally characterized Pc^{4-} ring system, as confirmed by partial bond-localization in the Pc^{4-} macrocycle.

Experimental

General Procedures and Materials

All techniques and procedures were carried out under a nitrogen atmosphere either with an Mbraun Labmaster 130 glovebox or using standard Schlenk and vacuum-line techniques. All glassware was dried overnight at 160 °C prior to use. For reactions heated above 120 °C, a paraffin light oil bath was used (saybolt viscosity at 100 °F about 130 SUS). Toluene, tetrahydrofuran (THF), dimethoxyethane (DME) and diethyl ether (Et_2O) were distilled from sodium/benzophenone under nitrogen. Hexanes were distilled from sodium under nitrogen. 1-Chloronaphthalene was dried over CaH_2 and distilled under vacuum at 100 °C. KC_8 was prepared from a literature procedure.[23] All other reagents were purchased from commercial sources and used without further purification. NMR spectra were recorded at 294 K, unless otherwise stated, on a 400 MHz Bruker Avance III spectrometer, a 500 MHz Bruker Avance III spectrometer, or a 600 MHz Bruker Avance II spectrometer with a 5 mm QNP cryoprobe. All ^1H NMR shifts are reported relative to the impurity of internal solvent. X-band (9.3-9.4 GHz) EPR spectra were collected using a Bruker EMXplus spectrometer with a PremiumX microwave bridge and HS resonator. Elemental analyses (C, H, N) were performed at Simon Fraser University by Mr. Paul Mulyk on a Carlo Erba EA 1110 CHN elemental analyzer.

UV-vis were recorded on a Varian Cary 5000 spectrophotometer or a Hewlett-Packard 8453 diode array spectrophotometer in a 0.1 cm quartz cell or a 0.1 cm quartz cell equipped with a Kontes PTFE plug, HI-VAC value for air-sensitive samples.

Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic circular dichroism (MCD) spectra were obtained on a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet capable of producing magnetic fields of up to 1.03 T (1 T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla ($[\theta]_M$ / deg $dm^3mol^{-1}cm^{-1}T^{-1}$). CV measurements were recorded with a Hokuto Denko HZ5000 potentiostat under nitrogen atmosphere in DMSO solutions with 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Measurements were made with a glassy carbon electrode (area = 0.07 cm^2), an Ag/AgCl reference electrode, and a Pt wire counter electrode. The concentration of the solution was fixed at 0.5 mM and the sweep rates were set to 100 mV/s.

Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) experiments were determined with a Bruker Autoflex Speed spectrometer equipped with a 1 kHz smartbeam-II laser. Positive ion mass spectra were acquired typically within the 300- to 7000-m/z range. The mass spectrometer was operated in the reflection mode and the mass spectrum obtained for each image position corresponds to the averaged mass spectra of a minimum of 5000 consecutive laser shots. Flex Control 3.4 and flexAnalysis 3.4 software packages (Bruker Daltonics, Bremen, Germany) were used to control the mass spectrometer, set spectrum parameters and visualize spectral data. For sample preparation, approximately 15-20 mg of the sample was added to a 1 mL solution of the respective solvent under an inert atmosphere in a glovebox. A 2 μL solution was then pipetted on a ground steel plate, dried by evaporation, and irradiated without a matrix.

Synthesis of $PcZrCl_2$ (1)

This compound was prepared by a modification of a literature procedure.[31]

1-Chloronaphthalene (10 mL) was added to phthalonitrile (4.08 g, 24 mmol) and $ZrCl_4$ (0.932 g, 4.0 mmol) in a flask equipped with a stir bar and a reflux condenser. The reaction mixture was heated to 230 °C. During heating the colour of the solution changed from beige to yellow, red, purple and finally deep blue. The reaction mixture was maintained at 230 °C for 15 min before removing the flask from the oil bath, opening it to air and immediately filtering the mixture through a glass frit. After the dark blue powder had cooled, it was rinsed with dichloromethane (5 x 20 mL or until the filtrate ran clear). The product was transferred to a Schlenk flask equipped with a cold finger. Sublimation at 160 °C for 4 h removed traces of a colourless material and residual 1-chloronaphthalene to give $PcZrCl_2$ (**1**) as a dark blue powder. Yield: 1.29 g (48%). ^{1}H NMR: (500 MHz, DMSO-d_6) δ 9.06 (m, 8H, Ar*H*), 8.03 (m, 8H, Ar*H*) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ ppm; 154.4 (*C*N), 135.7 (*C*), 130.6 (*m*-*C*H), 122.3 (*o*-*C*H) ppm; UV-vis: (THF) λ_{max} 346, 608, 674 nm; MALDI-TOF MS: 675 (M^+); Anal. Calcd for $0.92(C_{32}H_{16}Cl_2N_8Zr) + 0.08(ZrCl_4)$ C, 55.31; H, 2.32; N, 16.12. Found C, 55.30; H, 2.32; N, 15.87.

Synthesis of 2-K

To a solution of **1** (67 mg, 0.100 mmol) in 15 mL THF, one equivalent of $KBEt_3H$ (0.11 mL of a 1.0 M solution in THF, 0.110 mmol) was added slowly, causing the solution to become dark purple/blue. After being stirred for 20 hours, the solvent was removed *in vacuo*, the residue was extracted first with 10 mL THF and then 2 mL hexanes, and then the extracts were filtered through Celite. A purple solid formulated as $Pc^{3-}ZrCl{\bullet}KCl(DME)_2$ (**2-K**) was isolated in two fractions (21 mg, 32.8%). UV-vis: (DME) λ_{max} 355, 589 and 611 nm; Anal. Calcd for $C_{32}H_{16}N_8ZrCl{\bullet}KCl{\bullet}2DME$: C, 53.74; H, 4.06; N, 12.53. Found C, 54.49; H, 4.38; N, 12.50. ^{1}H NMR: (500 MHz, THF-d_8/Toluene-d_8) -9.4 (br s, 8H, Ar*H*), and -16.4 (br s, 8H, Ar*H*) ppm. EPR (THF, 77 K): g = 2.001.

Synthesis of 3-K

To a solution of **1** (67 mg, 0.100 mmol) in 15 mL DME, two equivalents of $KBEt_3H$ (0.22 mL of a 1.0 M solution in THF, 0.220 mmol) was added slowly, causing the solution to become dark purple. After being stirred for 40 h, the solvent was removed *in vacuo*, the residue was extracted first with 4 mL DME and then 2 mL hexanes, and then the extracts were filtered through Celite. A purple solid of [PcZr(KCl)$_2$(DME)$_5$], **3-K** was isolated in three fractions (15 mg, 19.9%). UV-vis: (DME) λ_{max} 522 nm; Anal. Calcd for $C_{32}H_{16}N_8Zr$•2KCl•5DME: C, 51.90; H, 5.53; N, 9.31. Found C, 49.56; H, 5.29; N, 9.31. ^{1}H NMR: (500 MHz, THF-*d*$_8$/Toluene-*d*$_8$) 5.4 (br s, 8H, Ar*H*), and 4.4 (br s, 8H, Ar*H*) ppm;

Reaction of 1 with LiCp* to form 2-Li

A solution of LiCp* (35 mg, 0.250 mmol) in THF (3 mL) was added to a suspension of $PcZrCl_2$ (**1**, 169 mg, 0.250 mmol) in THF (7 mL). The reaction mixture was stirred at room temperature for 48 h, during which the colour of the mixture changed to a royal blue. The mixture was filtered through celite and the solvent removed *in vacuo* to leave a blue/red solid of PcZrCl•LiCl(THF)$_5$ (**2-Li**). UV/vis: (THF) λ_{max} 338, 590, and 611 nm Anal. Calcd for $C_{32}H_{16}N_8ZrCl$•LiCl•5THF: C, 59.93; H, 5.42; N, 10.75. Found C, 60.01; H, 5.61; N, 10.76. ^{1}H NMR: (500 MHz, THF-*d*$_8$/Toluene-*d*$_8$) δ -11.84 (br s, 8H, Ar*H*), -23.06 (br s, 8H, Ar*H*) ppm; EPR (THF, 77 K): g = 2.001.

Synthesis of 3-Li

A solution of LiCp* (28 mg, 0.200 mmol) in DME (3 mL) was added to a suspension of **1** (67 mg, 0.100 mmol) in DME (7 mL). The reaction mixture was stirred at room temperature for 40 h, during which the colour of the mixture changed to a royal blue and then bright purple. The solvent was removed *in vacuo* to leave a purple solid. The residue was extracted with 4 mL DME followed by 2 mL hexanes and then the extracts were filtered through Celite. Purple crystals of [LiCl(DME)$_4$]$_{0.5}$[PcZr•(LiCl)(DME)], **3-Li** were isolated in three fractions (12 mg, 17.4%). UV-vis: (DME) λ_{max} 338. 528 nm. The remaining powder was recrystallized from THF. Anal. Calcd for $C_{32}H_{16}N_8Zr$•2LiCl•6THF: C, 59.99; H, 5.75; N, 9.99. Found C, 60.47; H, 5.88; N, 9.40. ^{1}H NMR: (500 MHz, THF-d_8/Toluene-d_8) 5.1 (br s, 8H, Ar*H*), and 4.1 (br s, 8H, Ar*H*) ppm.

Single Crystal X-ray Diffraction

Suitable crystals of **1** and **3-Li** were coated in paratone oil, mounted on a MiTeGen Micro Mount, and transferred to the cold stream (150 K) of the X-ray diffractometer. Data was collected on a Bruker Smart instrument equipped with an APEX II CCD area detector fixed at a distance of 5.0 cm from the crystal and a Mo (for **1**) or Cu (for **3-Li**) Kα fine focus sealed tube (λ = 0.71073 and 1.54178 Å respectively) operated at 1.5 kW (50 kV, 30 mA), filtered with a graphite monochromator. Data was collected at 150 K; the temperature was regulated using an Oxford Cryosystems Cryostream. Additional crystallographic information can be found in Table S1.

All diffraction data were processed with the Bruker Apex II software suite. The structures were solved with direct methods (SIR92) and subsequent refinements were performed using ShelXle.[47] The DME solvent molecules in **3-Li** were disordered and subsequently modeled in two orientations. One phenyl ring on one of the phthalocyanine ligands and two LiCl were also disordered; the disorder were modelled in two orientation with restrains employed to maintain similar geometries.

Hydrogen atoms on carbon atoms were included at geometrically idealized positions (C-H bond distance 0.95) and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon atom. Diagrams were prepared using ORTEP-3 and POV-RAY.[48] Thermal ellipsoids are shown at the 30% probability level.

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Electronic Supplementary Information (ESI) available: Crystallographic data for **1** and **3-Li** in cif format (CCDC Deposition # 1060687-1060688), additional experimental synthetic and characterization details, UV-vis/MCD spectra for **1**, ESR spectrum of **2-K**, and UV-vis data for KC_8 reactions.

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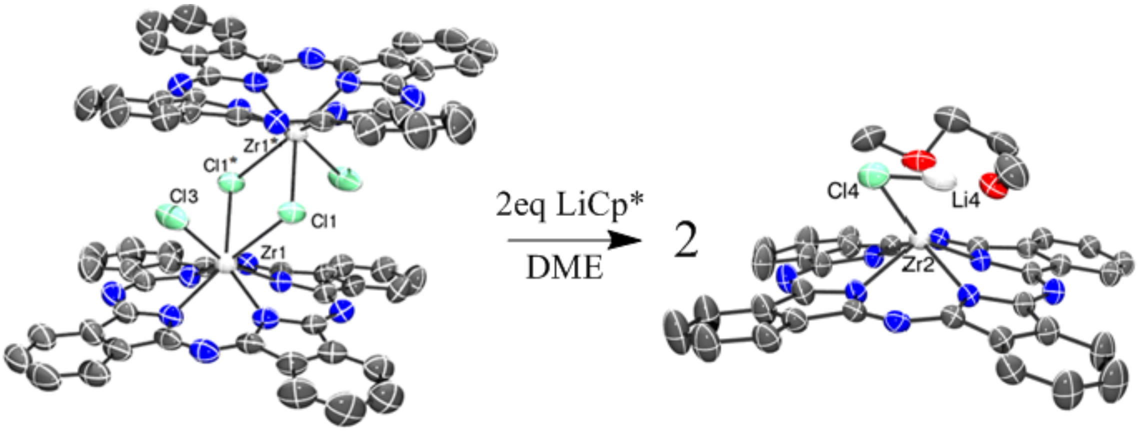
Reducing Zirconium(IV) Phthalocyanines and the structure of a Pc^{4-}Zr complex

Wen Zhou, Rachel H. Platel, Thiago Teixeira Tasso, Taniyuki Furuyama, Nagao Kobayashi and Daniel B. Leznoff



Reduced Zirconium(IV) phthalocyanines were prepared from a variety of reducing agents (KC_8, KEt_3BH or LiCp*) and a reduced Pc^{4-}Zr(IV) species was isolated and structurally characterized; it shows partial bond localization consistent with a reduction of the Pc ring.