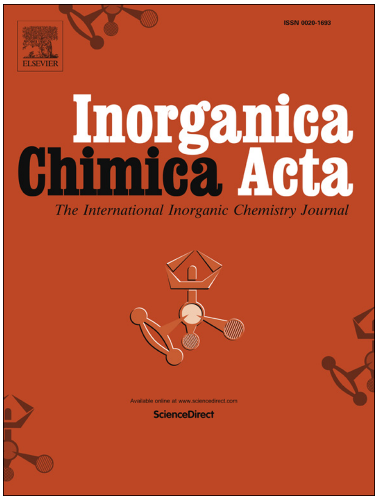

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Synthesis, Electrochemical and DFT study of octahedral bis(β-diketonato)-titanium(IV) complexes

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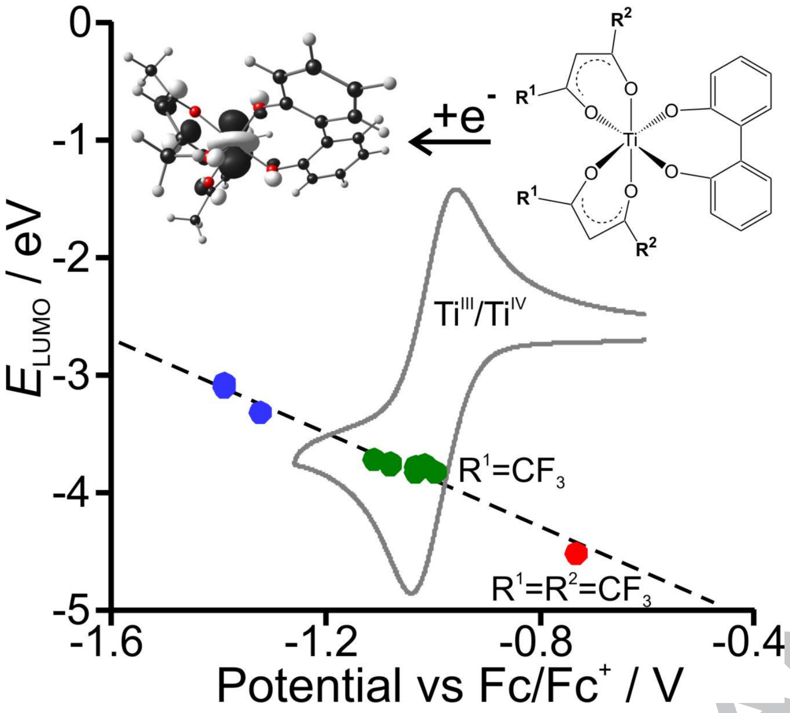
Abstract

The synthesis and electrochemistry of seven new and four known bis(β-diketonato)-titanium(IV) complexes are reported. Integrated electrochemical and quantum chemistry techniques have been used to show that the reduction potential of this series of eleven bis(β-diketonato)-titanium(IV) complexes, [Ti(R^1COCHCOR^2)$_2$biphen], are significantly influence by the electronic properties of the 1,3-β-diketonato-substituents (R^1, R^2), due to the efficient β-diketonato-metal π-conjugated character of the lowest unoccupied molecular orbital (LUMO) of the complexes. Electron density in the redox center is controlled by both inductive and resonance effects as seen by the spin density plots. Electron-withdrawing substituents make the reduction potentials more positive by stabilizing the reduced species. Both metal and ligand based redox processes are observed; the reversible metal Ti^{IV}/Ti^{III} reduction is followed by a considerably more negative, irreversible ligand reduction. The density functional theory calculated electronic structure of the first reduction is a Ti^{III} species while the second reduced species, is Ti^{III} coupled to a β-diketonato radical. A number of important relationships between the electronic properties of the substituents and the redox behavior have been developed. The experimentally measured reduction potentials gave excellent correlation in the linear relationship between experimental E_{pc} *vs* calculated E_{LUMO} ($R^2 = 0.98$).

Keywords

Electrochemistry; DFT; β-diketone; titanium(IV); electronegativity

TOC



Research highlights

- Cyclic voltammetry of 11 bis(1,3-disubstituted-β-diketonato)-titanium(IV) complexes
- Formal reduction potential relates to electronic parameters of substituents.
- Formal reduction potential relates to DFT calculated energies of the LUMO.
- Formal reduction potential relates to DFT calculated electron affinities.

1. Introduction

The β-diketonates are a flexible class of chelating ligands which have been used in transition metal chemistry for more than 100 years [1]. The well documented class of compounds, octahedral bis(β-diketonato)titanium(IV) complexes arose, partly due to their application in the field onocology, for example see **Figure 1** for tumour-inhibiting budotitane [2,3,4,5,6]. In the field of catalysis, research into post-metallocene catalysts for the polymerization of ethylene resulted in the development of a number of highly active structurally similar bidentate chelated titanium(IV) catalysts, see **Figure 1** [7,8,9,10,11]. Bis(β-diketonato)titanium-(IV) complexes may assist in the development of optically active enantioselective catalysts. It has been shown that the bis(β-diketonato)titanium-(IV) fragment due to its own dissymmetric (chiral) electronic structure, can discriminate between enantiomers of chiral *π*-donor ligands, for example, binding *O,O*'- bidentate 1,1-bi-2-naphtholate ligand (BINOL) in bis(β-diketonato)Ti(BINOL) resulted in an impressive, highly enantioselective process [12]. Applying this electronic stereochemical control to catalytic reactions has opened new research efforts in catalysis.

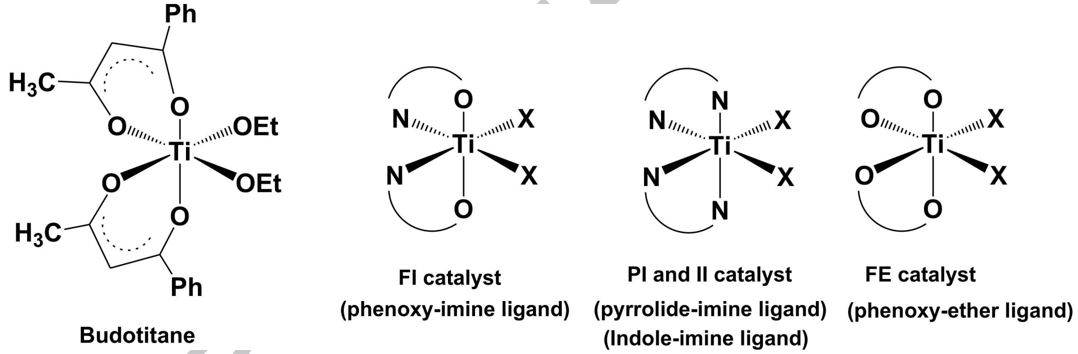
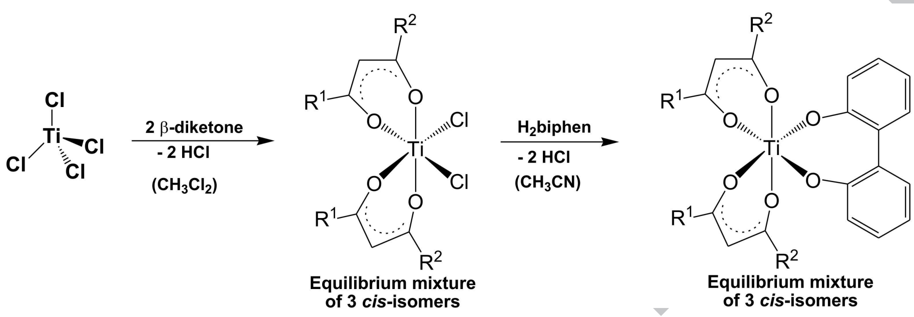


Figure 1. (a) Antitumour agent, Budotitane beloning to the bis(diketonato)titanium-(IV) complexes and structurally similar (b) highly active single-site ethylene polymerization titanium catalysts.

However, for these application the hydrolysis of titanium(IV) is a real and urgent problem [13], and therefore water resistance titanium (IV) complexes, are extremely valuable. The rate of hydrolysis can be significantly lowered by introducing electron-rich oxygen-based ligands. Here we have prepared 7 new bis(β-diketonato)-(2,2'-biphenyldiolato) titanium(IV) complexes containing three *O*,*O′*-chelated bidentate ligands with enhanced hydrolytic stability [14,15]. Knowledge of the chemical and electrochemical activity of these complexes towards reduction and oxidation, facilitates the study and understanding of their mechanistic action during different catalytic processes. Hence we are interested in how the electronic properties of the substituents (R^1, R^2 groups attached to the β-diketonate system) influences the reduction potential of the Ti^{IV}/Ti^{III} couple and in predicting redox potentials with the aim of designing organometallic molecules with specific redox potentials. We hereby present a combined electrochemical and computational chemistry (using DFT) study of a series of eleven [$Ti^{IV}(R^1COCHCOR^2)_2$biphen] complexes (seven are reported here for the first time) with substituents ranging from electron-withdrawing (*e.g.* CF_3) to electron-donating properties (*e.g.* CH_3), with R^1, R^2 = CF_3, CF_3 (**1**), CF_3, Ph (**2**) [15], CF_3, Fu (**3**), CF_3, Th (**4**), CF_3, CH_3 (**5**), CF_3, $CH_2(CH_3)$ (**6**), CF_3, $CH(CH_3)_2$ (**7**), CF_3, $C(CH_3)_3$ (**8**), Ph, Ph (**9**) [15] and Ph, CH_3 (**10**) [15] and CH_3, CH_3 (**11**) [14] where Ph = phenyl (C_6H_5), Fu = furyl (C_4H_3O) and Th = thienyl (C_4H_3S) and biphen = 2,2'-biphenyldiolato (**Figure 2**). Linear relationships were obtained by comparing experimentally measured reduction potentials E_{pc} of the [Ti(β-diketonato)$_2$biphen] series to calculated energies such as LUMO energy (E_{LUMO}), electron affinity (EA) and to a variety of electronic parameters describing the electron–withdrawing power of the R^1 and R^2 substituents on the β-diketonato ligand ($(R^1COCHCOR^2)^-$).



	R^1	R^2
(1)	CF_3	CF_3
(2)	CF_3	Ph
(3)	CF_3	C_4H_3O
(4)	CF_3	C_4H_3S
(5)	CF_3	CH_3
(6)	CF_3	$CH_2(CH_3)$
(7)	CF_3	$CH(CH_3)_2$
(8)	CF_3	$C(CH_3)_3$
(9)	Ph	Ph
(10)	Ph	CH_3
(11)	CH_3	CH_3

Figure 2. [$Ti(R^1COCHCOR^2)_2$biphen] complexes, with two strongly electron-withdrawing CF_3 substituents (red), one CF_3 substituent (green) and two non-CF_3 electron-donating substituents, Ph, CH_3 (blue). Abbreviations used for the β-diketonato ligand: $(R^1COCHCOR^2)^-$ = hfaa (R^1, R^2 = CF_3, CF_3), tfba = (CF_3, Ph), tffu = (CF_3, Fu), tfth = (CF_3, Th), tfaa = (CF_3, CH_3), tfma = (CF_3, CH_2CH_3), tfdma = (CF_3, $CH(CH_3)_2$), tftma = (CF_3, $C(CH_3)_3$), dbm = (Ph, Ph), ba = (Ph, CH_3) and acac = (CH_3, CH_3).

2. Experimental and Computational Methods

2.1 General

NMR measurements were recorded on a Bruker Avance DPX 300 NMR spectrometer at 298 K. Chemical shifts are reported as values relative to $SiMe_4$ (0 ppm). Cyclic voltammetry was performed utilizing a BAS 100 B/W Electrochemical Analyzer linked to a personal computer utilizing the BAS100W Version 2.3 software.

2.2 Synthesis of [Ti(β-diketonato)$_2$biphen] complexes (1) – (11)

The [Ti(β-diketonato)$_2$Cl$_2$] complexes used as starting material for the [Ti(β-diketonato)$_2$biphen] synthesis, were synthesised according to published methods [16,17] and the [Ti(β-diketonato)$_2$biphen] complexes were synthesized with slight changes as reported previously [14, 15]. To stirred solution of 2,2'-biphenyldiol (0.186g, 1 mmol in 15 ml CH_3CN) at RT, a solution of [Ti(β-diketonato)$_2$Cl$_2$] (1 mmol in 15 ml CH_3CN) was added dropwise at room temperature with an immediate colour change (clear/grey to orange/red). After refluxing for 4.6 h, the reaction mixture was cooled and solvent evaporated to dryness. The residue was washed in MeOH (non-fluorinated [Ti(β-diketonato)$_2$biphen] complexes) or CH_3CN (fluorinated [Ti(β)$_2$biphen] complexes) to dissolve unreacted biphenol. The pure product, obtained after recrystallization from dichloromethane/n-hexane, was stored under N_2 atmosphere. The characterization data of the complexes is provided in the Supporting Information.

2.3 Cyclic Voltammetry

Cyclic voltammetry measurements [18,19] were performed on 0.002 mol dm^{-3} compound solutions in dry acetonitrile (Aldrich, Biotech grade 99.93+% purity, anhydrous, kept under purified argon) containing 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate, (^{n}Bu$_4$N)(PF$_6$) (Fluka electrochemical grade), as supporting electrolyte and under a blanket of purified argon at 25 °C. A three-electrode cell, with a glassy carbon (surface area 7.07 x 10^{-6} m^2) working electrode, Pt auxiliary electrode and a Ag/Ag$^+$ (0.010 mol dm^{-3} $AgNO_3$ in CH_3CN) reference electrode [20] mounted on a Luggin capillary, was used [21,22]. All temperatures were kept constant to within 0.5 °C. Successive experiments under the same experimental conditions showed that all reduction and formal reduction potentials were reproducible within 0.005 V. All cited potentials were referenced against the Fc/Fc$^+$ couple as suggested by IUPAC [23]. Ferrocene exhibited a formal reduction potential $E°' = 0.072$ V *vs.* Ag/Ag$^+$, a peak separation $\Delta E_p = E_{pa} - E_{pc} = 0.070$ V and $i_{pc}/i_{pa} = 0.99$ under our experimental conditions. E_{pa} (E_{pc}) = anodic (cathodic) peak potential and i_{pa} (i_{pc}) = anodic (cathodic) peak current. $E°'$ (Fc/Fc$^+$) = 0.400 V *vs.* NHE [24] and SCE = 0.244 V *vs.* NHE.

2.4 Quantum Computational Methods and empirical parameters

Density functional theory (DFT) calculations were performed using the PW91/TZP (Triple ζ polarized) functional [25] and basis sets as implemented in the Amsterdam Density Functional (ADF2013) [26]. The functional, PW91, previously gave excellent results for geometry (good agreement between calculated and experimental) and for energies (good agreement between calculated and experimental isomer distribution) [15]. Geometry relaxed (adiabatic) energies of the neutral molecule (*N* electron system) and the N+1 (anion) and N+2 (dianion) electron systems, were calculated. These energies were used to obtain the electron affinity (EA) values of complexes, as calculated by: EA(complex) = $E(\text{complex})^{-} - E(\text{complex})$.

To determine the correct spin state of the dianion, namely S = 0 or S = 1, calculations with a selection of additional functionals were done, namely the GGA functionals OLYP (Handy-Cohen and Lee-Yang-Parr) [27,28,29,30], S12g [31], OPBE [32], the meta-GGA functionals M06-L [33], TPSS [34,35] as well as the hybrid functionals B3LYP (Becke 1993 and Lee-Yang-Parr) [36], B3LYP* [37] and S12h [31].

Solvent effects were taken into account for all optimized structures reported here. The COSMO (Conductor like Screening Model) model of solvation [**38**,**39**,**40**] was used as implemented [**41**] in ADF. The cavity type was Esurf [**42**] and the solvent used was CH_3CN.

Different empirical parameters can be used to quantify the electronic effect of the various substituents, R^1 and R^2, of the β-diketonato ligand, $(R^1COCHCOR^2)^-$, i.e., Gordy scale group electronegativities, $\chi_{R1} + \chi_{R2}$ [43,44], Hammett meta substituent constant, $\sigma_{R1} + \sigma_{R2}$ [45,46], and the Lever electronic parameter, E_L [47,48,49,50]. The pK_a of the free β-diketone [51,52,53], describing the acidic strength of the free β-diketone, can also be used to describe the influence of the β-diketonato ligand on the metal to which it is coordinated.

3. Results and Discussion

3.1 Preparation and solution behaviour of bis(β-diketonato)-(2,2'-biphenyldiolato) titanium(IV)

The reaction of 2,2'-biphenol in a 1:1 ratio with [Ti(β-diketonato)$_2$Cl$_2$] in CH_3CN yielded, [Ti(β-diketonato)$_2$biphen]. Using even higher ligand ratios of 2:1 or 3:1, yielded the same product instead of titanium products with more than one biphenolato ligand in the coordination sphere. This is similar to what was found for the reaction between Ti(acac)$_2$Cl$_2$ and 1,1'-methylene-di-2-naphthol.[54]. The biphenolato complexes exhibit high hydrolytic stability compared to the parent compounds; tested under the same conditions (0.01 % water/CH_3CN) as used by Keppler and Heim [55], it was found that the biphenolato complexes precipitate only slightly within 4 weeks compared to the dichloro complexes which precipitate within seconds. The solubility and hydrolytic stability of the CF_3-substituted bis(β-diketonato) biphen titanium(IV) complexes (soluble in DCM, chloroform, acetonitrile, acetone) differs from those of the non-CF_3 analogues; for example, where the former are soluble in acetonitrile but hydrolyze more easily, the latter are poorly soluble but more stable to hydrolysis.

The solution behavior of the parent compounds, bis(β-diketonato) dichloro titanium(IV) is well documented [16,17,56]. They exist as an equilibrium mixture of monomeric isomers which are fluxional and mutually transform each other on the time scale of nuclear magnetic resonance (NMR). Further, the CF_3 substituted analogues undergo a partial hydrolysis reaction, in which the hydrolyzed dinuclear {Ti(β-diketonato)$_2$Cl}$_2$(μ-O) is in equilibrium with the mononuclear [Ti(β-diketonato)$_2$Cl$_2$] [57,58].

Results obtained from variable temperature ^{1}H and ^{19}F NMR spectroscopy showed that bis(β-diketonato)biphenolato complexes (with asymmetric β-diketonate ligands) also exist as an equilibrium mixture of 3 *cis*-geometric isomers. However, there was no evidence for the formation of a partially hydrolyzed complex or the spontaneous equilibrium (hydrolysis) dimerization reaction in solution as is the case for the parent dichloro compound. The solid state, partially hydrolyzed, oxo- and biphenolato-bridged dinuclear, complex [59] (**Figure 3**) has been reported but its formation is through the chelation of H$_2$biphen with the parent dinuclear {Ti(β-diketonato)$_2$Cl}$_2$(μ-O) complex (in equilibrium with the mononuclear [Ti(β-diketonato)$_2$Cl$_2$] as indicated above) and not from the hydrolysis of [Ti(β-diketonato)$_2$biphen].

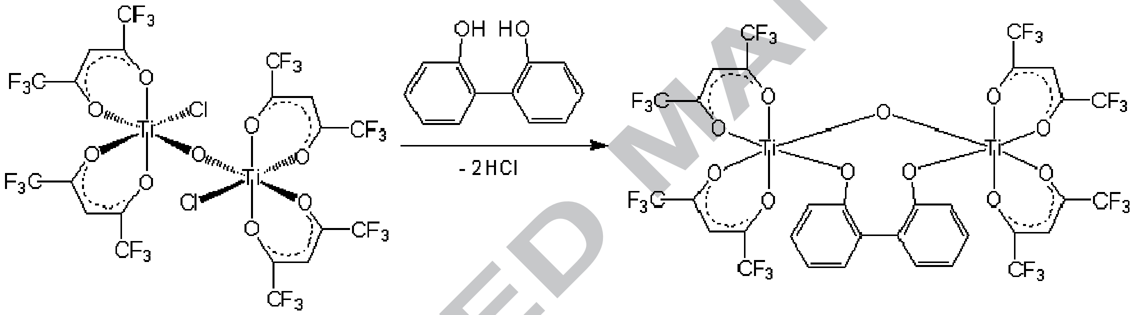


Figure 3. Structure of hydrolysed dimeric, {Ti(hfaa)$_2$}$_2$(μ-O)(μ-biphen) complex (right), with a bridging biphenolato ligand [59] that formed from {Ti(hfaa)$_2$Cl}$_2$(μ-O) (left).

3.2 Computational Chemistry Investigation

The neutral and reduced [Ti^{IV}(R^{1}COCHCOR^2)$_2$biphen] complexes (**1**) – (**11**) were optimized using DFT. The optimized coordinates are provided in the Electronic Supporting Information, the calculated energies of the LUMO (lowest unoccupied molecular orbitals) (E_{LUMO}) and calculated electron affinity (EA) are given in **Table 1**. The relative energies (eV), calculated by a selection of functionals for the dianion of complex (**11**), [Ti(acac)$_2$biphen]$^{-2}$, are given in **Table 2**. The results show that the dianion is paramagnetic with S = 1.

Insight into the electronic structure of the [Ti(β-diketonato)$_2$biphen] complexes allows one to understand and predict the electrochemical behavior. Frontier molecular orbitals, HOMOs (highest occupied molecular orbitals) and LUMOs, play an important role in redox reactions, for example, during reduction, an electron is transferred into the LUMO of the neutral species and this gained electron will be observed in the HOMO of the reduced species. Evaluation of the frontier molecular orbitals of the [Ti(β-diketonato)$_2$biphen] complexes, showed that the top three HOMOs are mainly biphenol-ligand based, the LUMO is mainly metal based, and the LUMO+1 is mainly β-diketonato-ligand based, with none of the first five LUMOs being biphenol-ligand based.

In most of cases reduction occur by adding an electron to the lowest unoccupied molecular orbital (LUMO) of a complex. However, sometimes molecular orbital reorganization occurs after the addition of an electron, leading to the use of a higher unoccupied orbital [60]. Therefore the frontier orbitals of the first reduced anion and the HOMO of the second reduced dianion of [Ti^{IV}(R^{1}COCHCOR^2)$_2$biphen] complexes (**1**) – (**11**) have been examined. **Figure 4** show the DFT calculated frontier orbitals of (a) neutral [Ti^{IV}(ba)$_2$biphen], HOMO which is ligand-biphenol based and LUMO which is mainly metal based; (b) HOMO of the first reduced anion, [Ti(ba)$_2$biphen]$^-$ which is mainly metal based (very similar to the LUMO of the neutral species) and (c) the HOMO of the second reduced dianion, [Ti(ba)$_2$biphen]$^{-2}$, which is mainly ligand-β-diketonato based. From these molecular orbitals, it can be deduced that a first reduction should be (Ti(IV)→Ti(III)) and a second reduction, β-diketonato→β-diketonato$^-$. The character of the top five LUMOs of the neutral complex supports that a biphenyldiolato ligand reduction would be unlikely.

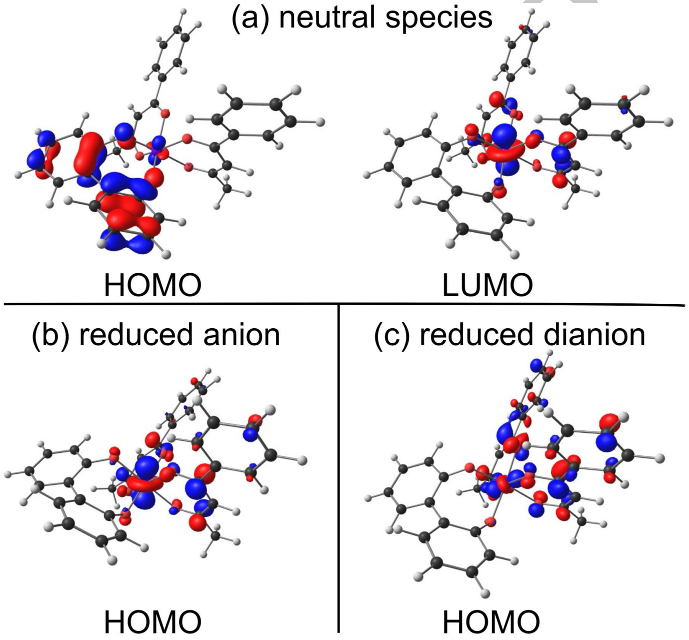


Figure 4. DFT presentation of frontier molecular orbitals of (a) neutral [Ti(ba)$_2$biphen], (b) first reduced anion (q = -1, S = ½) and (c) second reduced dianion (q = -2, S = 1)

The Mulliken spin density plots in **Figure 5** (a) – (c) portray the electron density of the added unpaired electron in the HOMO of the reduced complexes (**9**) – (**11**) and **Figure 5** (d), of the two added unpaired electrons of the dianionic species of (**10**). These spin density plots illustrates the efficient β-diketonato-metal π-conjugated character of the orbitals and show the effects of electron-withdrawing induction (as a result of substituent group electronegativities) and resonance (as a result of π-orbital overlap). Resonance stabilizes the complex by delocalizing charge from the β-diketonato backbone into an aromatic side group(s). As the number of phenyl groups attached to the β-diketonato ligand increases; the relative electron spin density on Ti^{III} decreases, i.e., the Mulliken spin populations are 0.635, 0.418 and 0.331 respectively for complexes with β-diketonato ligands, acac (CH_3, CH_3) (**11**), ba (CH_3, Ph) (**10**) and dbm (Ph, Ph) (**9**), with the remaining electron density distributed over the β-diketonato backbone and phenyl rings. Similarly, as the inductive electron–withdrawing CF_3 substituents increase, the relative electron density on Ti^{III} decreases i.e., 0.635, 0.492 and 0.381 respectively for complexes with β-diketonato ligands, acac (CH_3, CH_3) (**11**), tfaa (CF_3, CH_3) (**5**) and hfaa (CF_3, CF_3) (**1**) (See Figure S1 of the Supporting information).

Electron spin density on Ti for the dianionic species of (**11**), (**10**) and (**9**) are 0.857, 0.485 and 0.353 respectively, with the rest of the unpaired spin (*ca.* 1.1, 1.5 and 1.6 e^- respectively) distributed mainly over the β-diketonato ligands. Thus the dianionic species of [Ti(β-diketonato)$_2$(biphen)] can be described as titanium(III)-β-diketonato radical complexes, see the spin density plot of [Ti(ba)$_2$(biphen)]$^{2-}$, **Figure 5** (d).

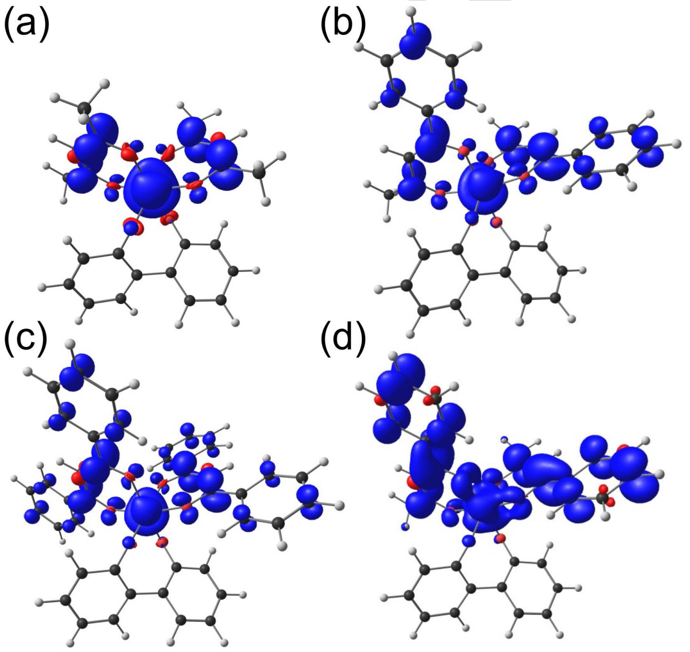


Figure 5. Mulliken spin density plots of the reduced complexes (a) [Ti(acac)$_2$biphen]$^-$ (**11**) (b) [Ti(ba)$_2$biphen]$^-$ (**10**), (c) [Ti(dbm)$_2$biphen]$^-$ (**9**) and dianion (d) [Ti(ba)$_2$biphen]$^{2-}$ (**10**) . The electron

density on $\mathrm{Ti^{III}}$ for the anions in (a) – (c) is 0.635, 0.418 and 0.331 respectively. The spin plots use an electron contour of 0.002 e/$\mathrm{Å^3}$. Colour code of atoms (online version): Ti (purple), C (black), O (red), H (white).

The electrochemical study presented below focuses on the first redox process. A linear relationship between the calculated energy of the LUMO (E_{LUMO}) of the neutral species and the experimental reduction potential (E_{pc}) can theoretically be derived [61]. The energy needed to reduce a complex (measured in volts as the reduction potential E_{pc}), is also closely related to electron affinity of a complex (EA, the amount of energy released when an electron is added to a molecule in the gaseous state) [62,63]. The DFT calculated energies, E_{LUMO} and EA are given in **Table 1** for complexes (**1**) – (**11**) and discussed further in section on Relationships.

3.3 Cyclic Voltammetry

The electrochemical data for the $\mathrm{Ti^{IV}/Ti^{III}}$ couple at 0.100 V s^{-1} is summarised in **Table 1** and the comparative cyclic voltammograms, shown in **Figure 7**. Data and CV graphs for scan rates 0.050 - 0.500 V s^{-1} are provided in the supporting information. Complexes (**2**) - (**11**) exhibit a distinctive one electron, electrochemically reversible $\mathrm{Ti^{IV}/Ti^{III}}$ couple according to **Scheme 1** with $0.062 \leq \Delta E_p \leq 0.091$ V which are similar to that of the ferrocene under the same conditions (ΔE_p = 0.070 V). The redox process is completely irreversible for (**1**). The redox process for (**2**) - (**11**) is chemically partially reversible, with $0.56 \leq i_{pa}/i_{pc} \leq 0.94$, at ν = 0.100 V s^{-1}, with relatively constant i_{pa}/i_{pc} ratios over the scanning rate of 0.100 – 0.500 V s^{-1}. **Figure 6** gives the CVs of [Ti(tfth)$_2$biphen], (**4**), at different scan rates. The linear plot of the difference in current intensity of the anodic and cathodic peaks (i_{pa} - i_{pc}) against the square root of the scan rate, also given in **Figure 6**, supports that the first reduction wave is reversible.

$$[\mathrm{Ti^{IV}}(\beta\text{-diketonato})_2\mathrm{biphen}] + e^- \rightleftharpoons [\mathrm{Ti^{III}}(\beta\text{-diketonato})_2\mathrm{biphen}]^- \longrightarrow [\mathrm{Ti^{III}}(\beta\text{-diketonato})_2\mathrm{biphen}]^{\bar{\bullet}}$$

Scheme 1. The reduction of [Ti(β-diketonato)$_2$biphen].

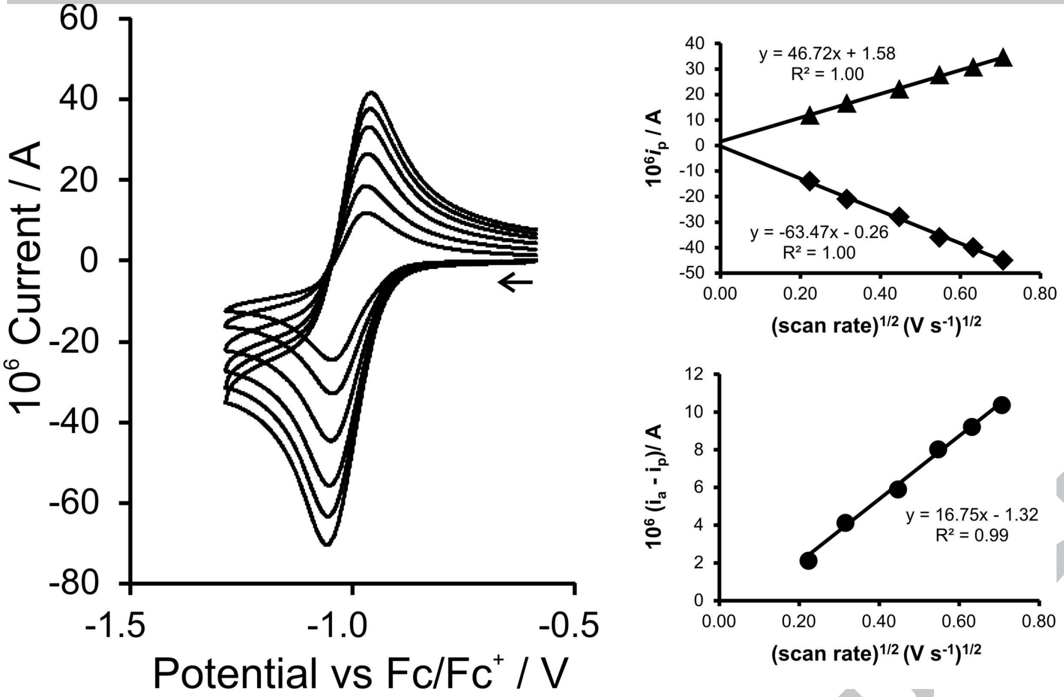


Figure 6. Cyclic voltammograms (*vs*. Fc/Fc$^+$) of [Ti(tfth)$_2$biphen] (0.002 mol dm^{-3}) at scan rates 0.050, 0.100, 0.200, 0.300, 0.400 and 0.500 V s^{-1}.

A comparison of the cyclic voltammograms of the [Ti(β-diketonato)$_2$biphen] series, listed in order of increasing reduction potentials, see **Figure 7**, show that the ease of reduction depends on the number of strongly electron-withdrawing CF$_3$ groups in the complex. Complex (**1**) containing β-diketonato ligands with two strongly electron-withdrawing CF$_3$ groups, is reduced most easily (has the most anodic (positive) potential, E_{pc} = -0.730 V) followed by complexes (**2**) – (**8**) containing β-diketonato ligands with one CF$_3$ groups (average E_{pc} = -1.050 V) and reduced least easily, are complexes (**9**) – (**11**) containing non-fluorinated β-diketonato ligands with weakly electron-donating CH$_3$ and Ph groups (average E_{pc} = -1.360 V). The difference in reduction potentials between the three groups is *ca*. 0.320 V and 0.310 V respectively. The significant influence of the electronic properties of substituent groups, R^1 and R^2, on reduction potentials, suggests that efficient electronic communication *via* conjugation between the electro-active metal centre and the substituent R groups exists (supported by DFT calculated electronic structures, see **Figure 4** and **Figure 5**). The electronic effect of the substituents other than CF$_3$, i.e., R = Ph, Fu, Th, CH$_3$, CH$_2$CH$_3$, CH(CH$_3$)$_2$ and C(CH$_3$)$_3$ is slighter, for example, the [Ti(**CF$_3$**COCHCO**R**)$_2$biphen] group has a difference in reduction potentials of *ca*. 0.100 V (see the CVs of complexes (**2**) – (**8**) in **Figure 7**). Electron density at the metal center is lowered by an interplay of inductive effects through the σ-system (if the substituent is electron-withdrawing) and resonance effects through the π-system (if direct resonance between the substituent group and the electro-active center in the reduced species exists) see **Figure 5**. For this reason, complexes containing ring-structures i.e., Ph = C_6H_5, Fu = C_4H_3O and Th = C_4H_3S (e.g. complexes (**2**) – (**4**)) tend to be reduced more easily than complexes containing chain or branched-structures, i.e., CH_3, CH_2CH_3, $CH(CH_3)_2$ and $C(CH_3)_3$ (e.g. complexes (**5**) – (**8**)). The ring-structures, Ph, Fu, Th, have lower group electronegativities (see **Table 1**), i.e., weaker σ-electron-withdrawing power but stronger π-electron-withdrawing power compared to the chain structures. This trend is observed clearly for the reduction of the free β-diketone [64].

The branched structures, complexes (**5**) – (**8**) show a small but meaningful shift towards more negative reduction potentials when increasing the branched size of the R^2 substituent from Me, Et, ^{i}Pr to ^{t}Bu, the potentials are -1.030 V (**5**), -1.075 V (**6**), -1.076 V (**7**) and -1.108 V (**8**) (see **Table 1**). This trend follows the σ-electron-donating order of Me < Et < ^{i}Pr < ^{t}Bu.

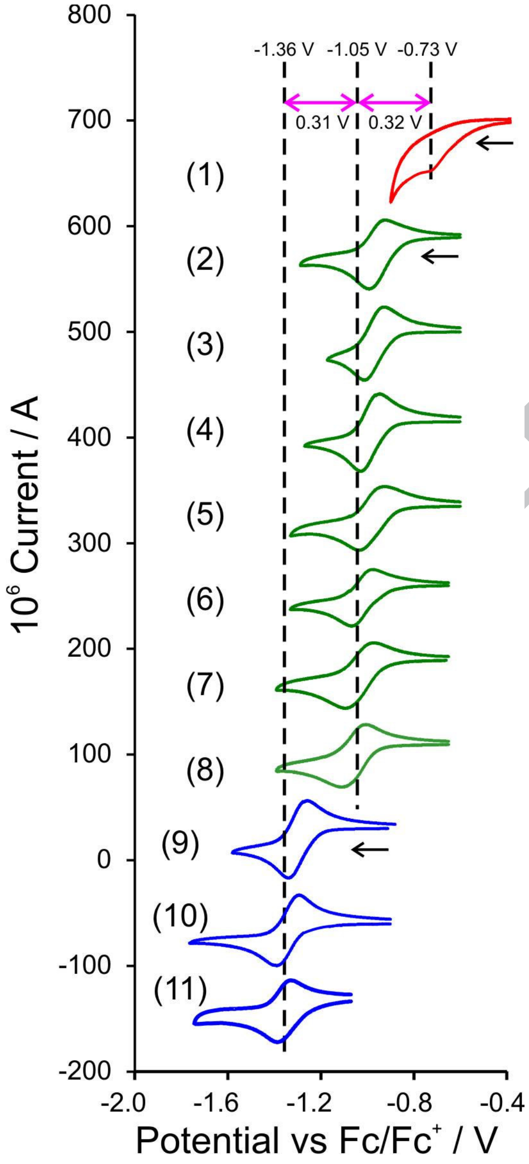


Figure 7. Comparative cyclic voltammograms (*vs*. Fc/Fc$^+$) at a scan rate of 0.100 V s^{-1} for [Ti(**R^1**COCHCO**R^2**)$_2$biphen] series (**1**) – (**11**) (0.002 mol dm^{-3}), showing the Ti^{IV}/Ti^{III} couple. The CVs shown in red represent the complex containing β-diketonato ligands with two strongly electron-withdrawing CF$_3$ substituents, those in green with one CF$_3$ substituent and those in blue contain, non-fluorinated electron-donating substituents, Ph, CH$_3$.

A wide potential scan of [Ti(ba)$_2$biphen] see **Figure 8**, shows two redox processes; the Ti$^{IV/III}$ redox couple (E_{pc} = -1.387 V *vs* Fc/Fc$^+$) and a more cathodic irreversible reduction at E_{pc} = -2.206 V *vs* Fc/Fc$^+$. Uncoordinated β-diketones are electrochemically active with reported reduction potentials ranging from -1.200 to -2.100 V for a similar series of β-diketones (E_{pc} = -1.243 V for Hhfaa and E_{pc} = -2.138 V for Hba) [64]. The reduction potential of a metal-chelated β-diketonato ligand, generally occurs at a more negative cathodic potential than for uncoordinated β-diketones [65], because the coordination of the β-diketone to a metal centre, forming a conjugated ring system, results in the coordinated β-diketonato ligand possessing higher electron density compared to the uncoordinated β-diketone. Therefore it can be inferred that the second redox process is a ligand reduction. This is further supported by the DFT investigation in which the frontier molecular orbitals of the optimized anion [Ti(ba)$_2$biphen]$^-$ indicates that the first reduction is metal based while the optimized dianion [Ti(ba)$_2$biphen]$^{2-}$ indicates that the second reduction is ligand based (see **Figure 4**). The CVs of uncoordinated β-diketone, Hba**,** and coordinated ligand ba in [Ti(ba)$_2$biphen] (**10**), are compared in **Figure 8**, showing a negative potential shift of 0.08 V. This is in the same order as the shift of 0.17 V for the coordinated ba ligand in tetrahedral [Cp$_2$Ti^{IV}(ba)]$^+$ClO$_4^-$ [65] (Cp = cyclopentadienyl).

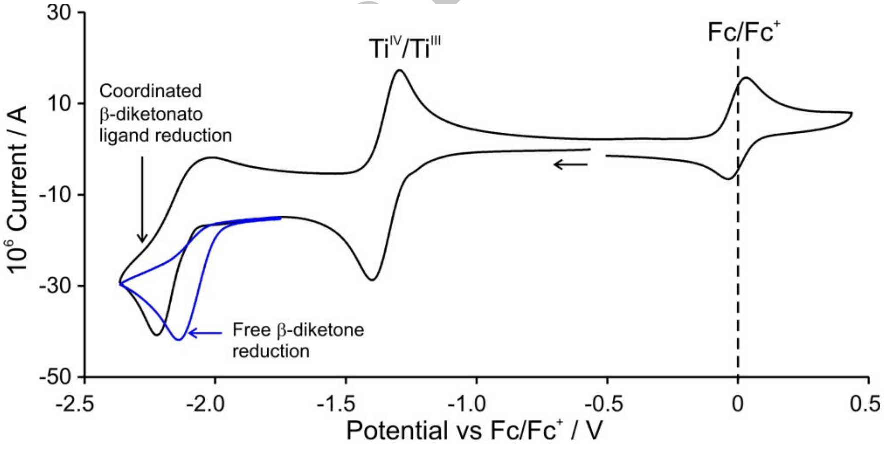


Figure 8. Wide potential scan (*vs*. Fc/Fc$^+$) of [Ti(ba)$_2$biphen] (0.002 mol dm^{-3}) at 200 mV s^{-1} with ferrocene used as an internal standard (Fc/Fc$^+$, $E^{0'}$ = 0 V). CV of uncoordinated ligand Hba reduction, (blue) is inserted for comparison.

Comparative cyclic voltammograms of [Ti^{IV}(β-diketonato)$_2$biphen] and the related parent compound, [Ti^{IV}(β-diketonato)$_2$Cl$_2$] [66] show an anodic shift of 0.600 V (see **Figure 9**). The chloro-ligands withdraw more electron density from metal centre compared to the electron donating *O*,*O′*-biphenyldiolato ligands, making titanium in [Ti(β-diketonato)$_2$Cl$_2$] easier to reduce (at less negative potentials) than the corresponding [Ti^{IV}(β-diketonato)$_2$biphen] complexes. This effect can also be seen from the DFT calculated Mulliken charge on titanium, i.e., 1.225 in [Ti^{IV}(acac)$_2$Cl$_2$], is lower than 1.794 in [Ti^{IV}(acac)$_2$biphen]. The substituents (R^1, R^2) of the β-diketonato ligand appear to have similar electronic influences on the titanium(IV) reduction for both [Ti^{IV}(β-diketonato)$_2$biphen] and [Ti(β-diketonato)$_2$Cl$_2$]; for example, a shift of 0.34 V for CF$_3$-β-diketonato (tfba and tfaa) complexes, compared to non-CF$_3$-β-diketonato (dbm and ba) complexes, is observed (see **Figure 9**) suggesting that the complexes might have similar conjugated LUMO systems. The spin density plots (see **Figure 10**) of these two (reduced) bis(β-diketonato)-titanium(IV) complexes, [Ti(acac)$_2$Cl$_2$]$^-$ and [Ti(acac)$_2$biphen]$^-$, showing the distribution of the added unpaired electron, illustrate the close resemblance of the orbitals involved in the reduction, as well as the effective β-diketonato-metal π-conjugated nature of the orbitals. The related behaviour is important because one can anticipate the reduction potentials of the dichloro complexes (based on the biphen complexes), which are otherwise difficult to observe due to complex instability (hydrolysis) [57,58], adsorption of the complex at the electrode surface and electrode passivation [66].

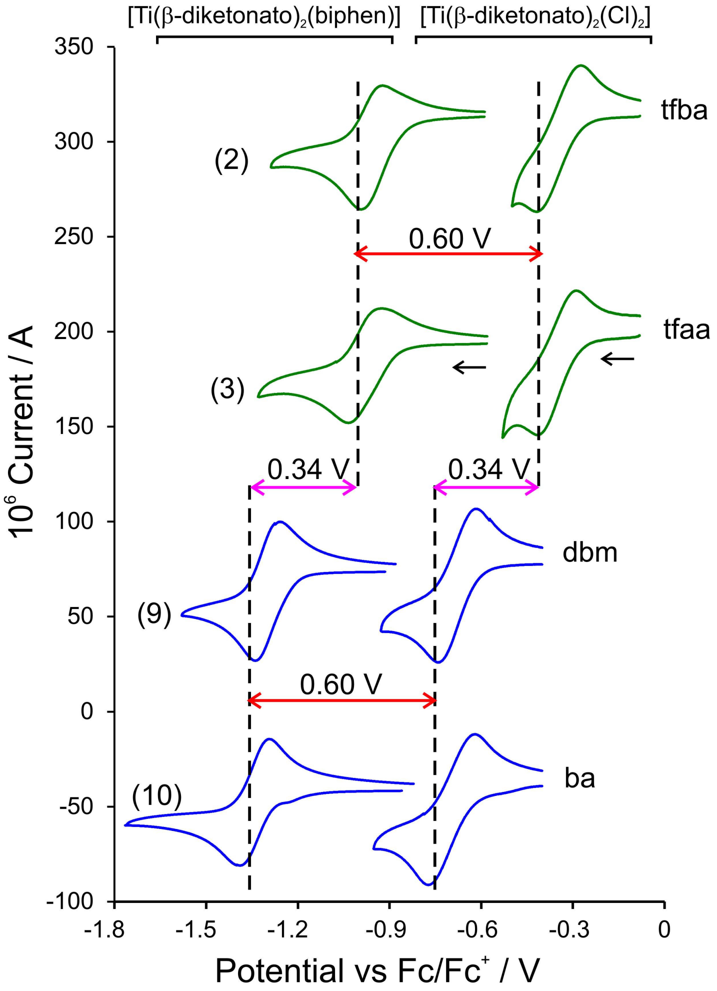


Figure 9. Comparative cyclic voltammograms (*vs*. Fc/Fc$^+$) at a scan rate of 0.100 V s^{-1} for [Ti($\mathbf{R}^{\mathbf{1}}$COCHCO$\mathbf{R}^{\mathbf{2}}$)$_2$biphen] and [Ti($\mathbf{R}^{\mathbf{1}}$COCHCO$\mathbf{R}^{\mathbf{2}}$)$_2$Cl$_2$] series (0.002 mol dm^{-3}), showing the Ti^{IV}/Ti^{III} couple. The CVs shown in green represent the complexes containing β-diketonato ligands with one strongly electron-withdrawing CF$_3$ substituents and those in blue contain, non-fluorinated electron-donating substituents, Ph, CH$_3$. Vertical dotted lines indicate average E_{pc} values.

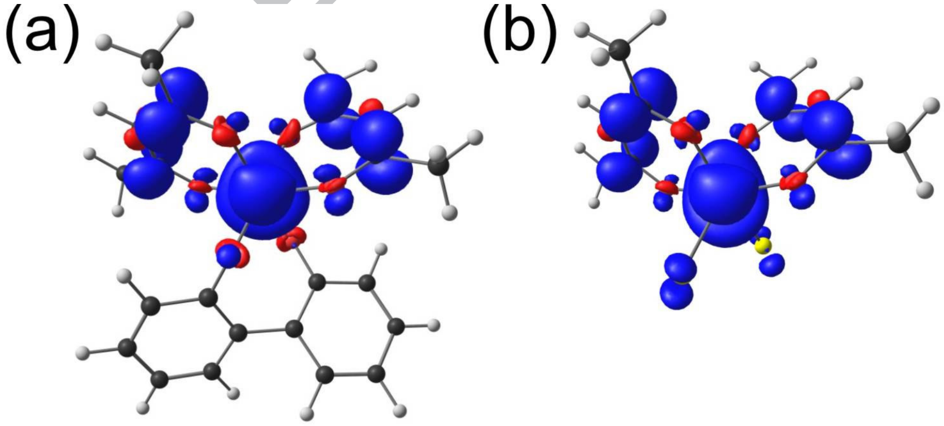


Figure 10. Mulliken spin density plots of the reduced complexes (a) [Ti(acac)$_2$biphen]$^-$ (**11**) and (b) [Ti(acac)$_2$Cl$_2$]$^-$.

Table 1. Empirical parameters, Gordy scale group electronegativities $\chi_{R1} + \chi_{R2}$, Hammett meta substituent constant, $\sigma_{R1} + \sigma_{R2}$, and the Lever electronic parameter, E_L and pK_a of the free β-diketone, Calculated LUMO energies (E_{LUMO}), electron affinities (EA), and experimental reduction potential (E_{pc} *vs*. Fc/Fc$^+$) of [Ti^{IV}(R^{1}COCHCOR^2)$_2$biphen] complexes (1) – (11).

β-diketonato	Complex no	R^1	R^2	pKa[a]	$\chi_R + \chi_{R'}$ [a,b]	$\sigma_R + \sigma_{R'}$ [a,c]	E_L[a]	EA (eV)	E_{LUMO} (eV)	E_{pc} *vs* Fc/Fc$^+$ (V)	$E^{\circ\prime}$ *vs* Fc/Fc$^+$ (V)
hfaa	1	CF_3	CF_3	4.71	6.02	0.86	0.17	3.055	-4.524	-0.730	
tfba	2	CF_3	Ph	6.30	5.22	0.49	0.05	2.559	-3.834	-0.991	-0.960
tffu	3	CF_3	Fu		5.24	0.49	0.05	2.491	-3.776	-1.012	-0.971
tfth	4	CF_3	Th	6.497	5.11	0.52	0.05	2.525	-3.790	-1.028	-0.990
tfaa	5	CF_3	CH_3	6.30	5.35	0.361	0.03	2.374	-3.832	-1.030	-0.985
tfma	6	CF_3	CH_2CH_3	6.64	5.32	0.36	-	2.354	-3.763	-1.075	-1.030
tfdma	7	CF_3	$CH(CH_3)_2$	6.80	5.30	-	-	2.371	-3.773	-1.076	-1.031
tftma	8	CF_3	$C(CH_3)_3$	7.13	5.28	0.33	-	2.370	-3.735	-1.108	-1.063
dbm	9	Ph	Ph	9.35	4.42	0.12	-0.04	2.209	-3.338	-1.358	-1.277
ba	10	CH_3	Ph	8.70	4.55	-0.009	-0.06	1.824	-3.086	-1.387	-1.344
acac	11	CH_3	CH_3	8.95	4.68	-0.138	-0.08	1.677	-2.571	-1.388	-1.348

[a] For a comprehensive list of pK_a values, Gordy scale group electronegativities, Hammett meta substituent constants and the Lever electronic parameter related to β-diketones, see reference [67] (Appendix).

[b] The group electronegativity ($\chi_R + \chi_{R'}$) on the Gordy scale: $\chi_{CF3} = 3.01$, $\chi_{Ph} = 2.21$, $\chi_{Fu} = 2.23$, $\chi_{Th} = 2.10$, $\chi_{CH3} = 2.34$, and $\chi_{CH2CH3} = 2.27$, $\chi_{CH(CH3)2} = 2.27$ and $\chi_{C(CH3)3} = 2.27$.

[c] The Hammett meta substituent σ constants: $\sigma_{CF3} = 0.43$, $\sigma_{Ph} = 0.06$, $\sigma_{Fu} = 0.06$, $\sigma_{Th} = 0.09$, $\sigma_{CH3} = -0.069$, $\sigma_{CH2CH3} = -0.07$, $\sigma_{C(CH3)3} = -0.10$,.

Table 2. Relative energies (eV) calculated by a selection of functionals for [Ti(acac)$_2$biphen]$^{-2}$.

S	**meta-GGA**		**hybrid**			**GGA**			
	M06-L	**TPSS**	**B3LYP**	**B3LYP***	**S12h**	**OLYP**	**OPBE**	**BP86**	**S12g**
0	0.06	0.06	0.20	0.14	0.25	0.08	0.10	0.03	0.01
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

3.4 Relationships

The reduction potential E_{pc} for the reversible Ti$^{IV/III}$ redox process of [Ti^{IV}(R^{1}COCHCOR^2)$_2$biphen] complexes (**1**) – (**11**) are compare to calculated energies of the LUMO (E_{LUMO}) and electron affinity (EA), as well as to empirical parameters that are related to the electron density on the β-diketone, i.e., pK_a of the β-diketone (R^{1}COCH$_2$COR^2), the sum of the group electronegativities χ_{R1} + χ_{R2} of the substituents, R^1 and R^2, the sum of the Hammett constants σ_{R1} + σ_{R2} and Lever electronic parameter, E$_L$. (tabulated in **Table 1**). The linear relationships between reduction potentials E_{pc} and these parameters are illustrated in **Figure 11** and **Figure 12**.

An excellent agreement between E_{pc} and the calculated E_{LUMO} (R^2 = 0.98 for gas phase calculations and 0.94 for calculations including CH$_3$CN as solvent) exits (see **Figure 11**), hence the nature of the LUMO dominates the redox chemistry. The LUMO, although located mainly on the metal, has a delocalized π-electron system, distributed over the conjugated β-diketone backbone and aryl substitutes (**Figure 4**), allowing for communication between the metal and substituents, R^1 and R^2, of the β-diketonato ligand. The Mulliken spin plots (**Figure 5**) clearly show that the unpaired electron density is distributed over the β-diketone backbone and aryl substitutes. The excellent correlation E_{pc} *vs* E_{LUMO} for gas phase calculations makes it possible to predict redox potentials based on the LUMO energies, with a high degree of accuracy. The correlation between E_{pc} *vs*. EA (R^2 = 0.92 for gas phase calculations and 0.96 for calculations using CH$_3$CN as solvent) can also be used. For E_{pc} *vs*. EA a better accuracy for calculations using the continuum model for solvent simulation than for gas phase calculations is obtained, while for E_{pc} *vs* E_{LUMO}, the gas phase calculations gave a better accuracy.

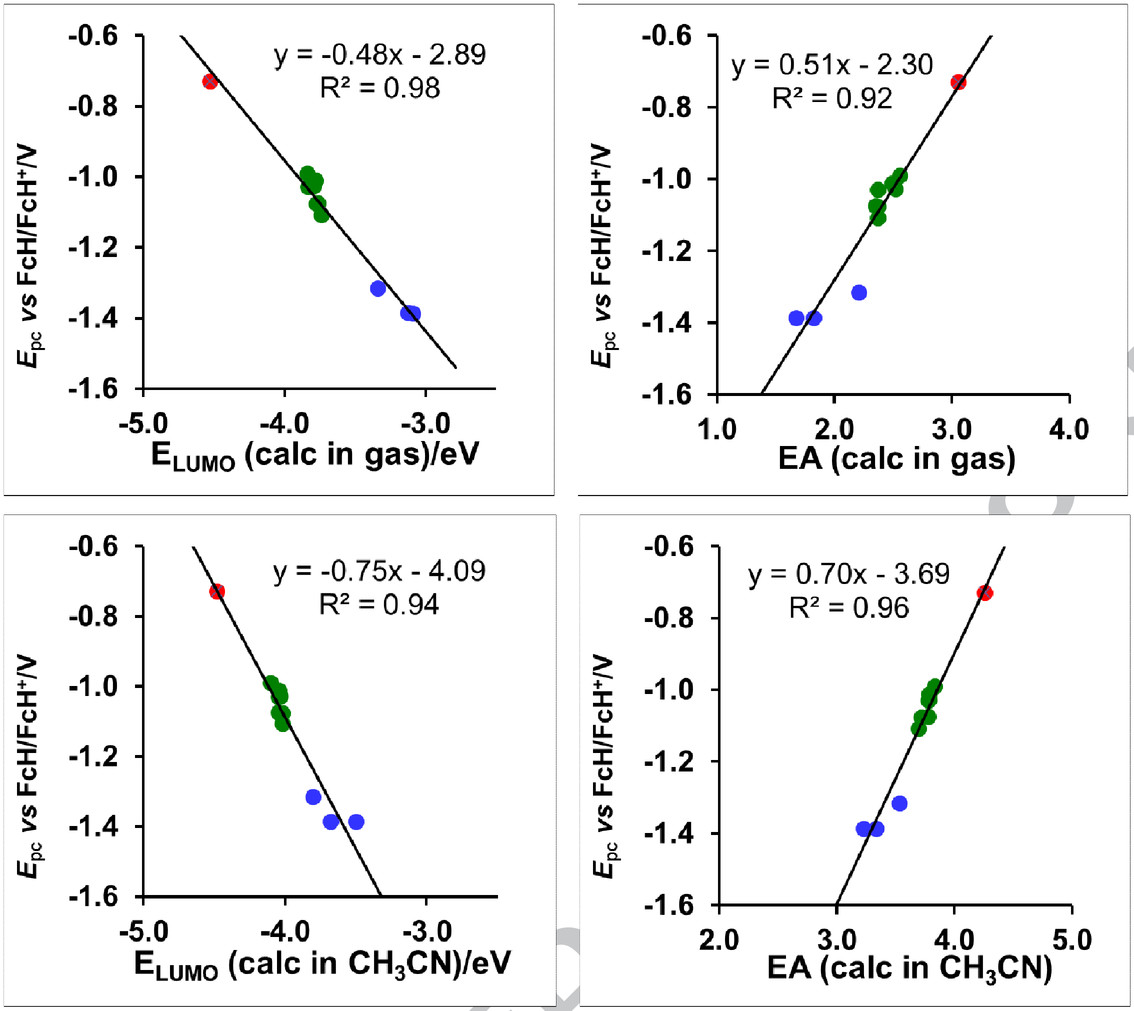


Figure 11. The linear relationships between reduction potential E_{pc} of [$Ti^{IV}(R^1COCHCOR^2)_2$biphen] and calculated energies of the LUMO (E_{LUMO}) and electron affinity (EA). The values shown in red represent the complex containing β-diketonato ligands with two strongly electron-withdrawing CF_3 substituents, those in green with one CF_3 substituent and those in blue contain, non-fluorinated electron-donating substituents, Ph, CH_3.

The correlation of E_{pc} of metal-β-diketonato complexes *vs* the selected empirical parameters (which quantify the electronic effect of the various substituents, R^1 and R^2, of the β-diketonato ligand, $(R^1COCHCOR^2)^-$, generally show good linear fits [65,66,67,68,69,70]. Results for the [$Ti^{IV}(R^1COCHCOR^2)_2$biphen] complexes are presented in **Figure 12**. In general as the electron withdrawing ability of the substituent groups increase, the electron density at the titanium metal center decreased and the complex is reduced more readily at a more positive (less negative) potential. This once again suggests that efficient electronic communication exists between the substituent R groups and the electro-active titanium metal center (supported by DFT calculate electronic structures). However, the (Gordy scale) group electronegativities, $\chi_{R1} + \chi_{R2}$ performed the worst as an indicator for reduction potentials (see **Figure 12**, $R^2 = 0.89$) because this parameter relies solely on inductive electron withdrawing effects of the substituents while the electron density at the metal center is reduced by an interplay of inductive effects through the σ-system (if the substituent is electron-withdrawing) and resonance effects through the π-system (if the complex contains aromatic groups R^1 and/or R^2). This results in the opposite trend for the following [Ti(β-diketonato)$_2$biphen] complexes which contain aromatic substituents; (dbm, $\chi_{R1} + \chi_{R2} = 4.42$, $E_{pc} = -1.317$ V) compared to (ba, $\chi_{R1} + \chi_{R2} = 4.55$, $E_{pc} = -1.387$ V) and (tfba, $\chi_{R1} + \chi_{R2} = 5.22$, $E_{pc} = -0.960$ V) compared to (tfaa, , $\chi_{R1} + \chi_{R2} = 5.35$, $E_{pc} = -1.030$ V), i.e. it appears as if the electron withdrawing ability of the substituent groups **increases** but the Ti reduces less readily. However this contradiction occurs because the phenyl group withdraws electron density from the metal center through resonance effects, (see this effect in the spin density plots, **Figure 5**).

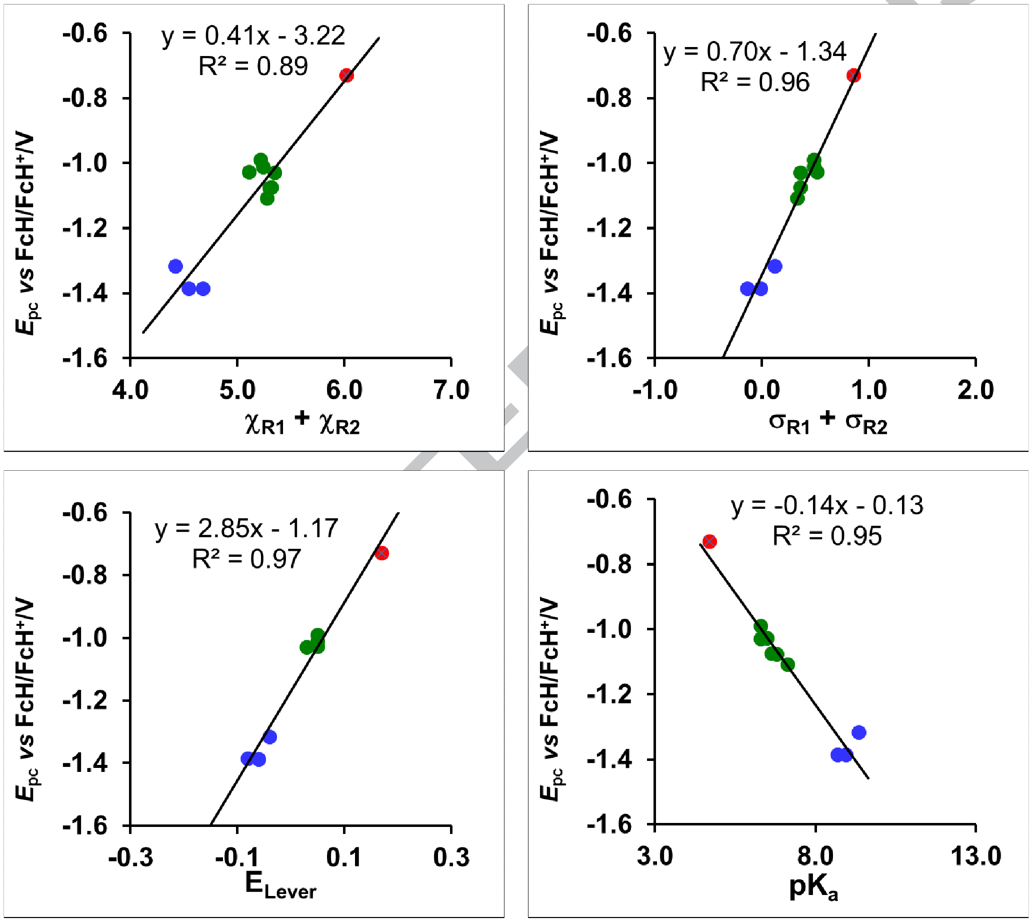


Figure 12. The linear relationships between reduction potential E_{pc} of [Ti^{IV}(R^{1}COCHCOR^2)$_2$biphen] and (a) pK_a of the β-diketone, (b) the group electronegativities $\chi_{R1} + \chi_{R2}$ of the substituents, R^1 and R^2, (c) the sum of Hammett constants $\sigma_{R1} + \sigma_{R2}$ of R^1 and R^2 and (d) Lever electronic parameter, E_L. The values shown in red represent the complex containing β-diketonato ligands with two strongly electron-withdrawing CF_3 substituents, those in green with one CF_3 substituent and those in blue contain, non-fluorinated electron-donating substituents, Ph, CH_3.

4 Conclusion

[Ti^{IV}(β-diketonato)$_2$biphen] complexes undergo two redox processes in acetonitrile; a reversible metal Ti^{IV}/Ti^{III} reduction followed by a considerably more negative, irreversible ligand reduction. The electronic properties of the 1,3-β-diketonate (R^{1}COCHCOR^2)$^-$ substituents significantly influenced the value of the Ti$^{IV/III}$ reduction potential indicating excellent electronic communication between the substituents R^1, R^2 and the electro-active titanium(IV) center. Electron withdrawing groups make reduction potentials more positive by stabilizing the reduced species, while electron-donating substituents have the opposite effect. Several important relationships between the substituents and redox behaviour were developed, i.e., linear trends between the reduction potentials E_{pc} of the Ti$^{IV/III}$ couple and DFT calculated parameters (LUMO energies, E_{LUMO} and electron affinity, EA), and between several electronic parameters used to describe the electron–withdrawing power of the R^1 and R^2 substituents. We have shown that redox-potentials give an excellent correlation in the linear relationship with calculated LUMO energies ($R^2 = 0.98$), and it is therefore possible to predict redox potentials with a high degree of accuracy. The poor correlation of E_{pc} *vs* group electonegativities of the R^1 and R^2 substituents on the β-diketonato ligand, is due aromatic substituents being more electron-withdrawing than predicted by the exclusively inductive group electonegativity parameter. The spin density plots of the reduced species clearly show the resonance electron–withdrawing effect of aromatic substituents.

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Supporting Information.

Tables, Figures, Characterization data, optimized coordinates. This information is available free of charge via the Internet.

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Graphical abstract

Table of content briefs

CV and DFT of bis(β-diketonato)-titanium(IV) complexes