Steric control in the metal–ligand electron transfer of iminopyridine–ytterbocene complexes

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A systematic study of reactions between Cp*2Yb(THF) (Cp* = η5-C8Me5) and iminopyridine ligands (IPy = 2,6-iPr2C6H3N-R, R = H (2a), 6-C6H4O (2b), 6-C6H3S (2c), 6-C6H5 (2d)) featuring similar electron accepting properties but variable denticity and steric demand, has provided a new example of steric control on the redox chemistry of ytterbocenes. The reaction of the unsubstituted IPy 2a with 1, either in THF or toluene, gives rise to the paramagnetic species Cp*2Yb(IPy)− (3a) as a result of a formal one-electron oxidation of the YbII ion along with IPy reduction to a radical-anionic state. The reactions of 1 with substituted iminopyridines 2b–d, bearing aryl or hetero-aryl dangling arms on the 6 position of the pyridine ring occur in a non-coordinating solvent (toluene) only and afford coordination compounds of a formally divalent ytterbium ion, coordinated by neutral IPy ligands Cp*2Yb[IPy]2 (3b–d). The X-ray diffraction studies revealed that 2a–c act as bidentate ligands; while the radical-anionic IPy in 3a chelates the YbII ion with both nitrogens, neutral IPy ligands in 3b and 3c participate in the metal coordination sphere through the pyridine nitrogen and O or S atoms from the furan or thiophene moieties, respectively. Finally, in complex 3d the neutral IPy ligand formally adopts a monodentate coordination mode. However, an agostic interaction between the YbII ion and an ortho C–H bond of the phenyl ring has been detected. Imino-nitrogens in 3b–d are not involved in the metal coordination. Variable temperature magnetic measurements on 3a are consistent with a multiconfigurational ground state of the Yb ion and suggest that the largest contribution arises from the 4f15-radical configuration. For complexes 3b and 3c the data of magnetic measurements are indicative of a YbII–closed shell ligand electronic distribution. Complex 3d is characterized by a complex magnetic behavior which does not allow for an unambiguous estimation of its electronic structure. The results are rationalized using DFT and CSSCF calculations. Unlike diazabutadiene analogues, 3a does not undergo a solvent mediated metal–ligand electron transfer and remains paramagnetic in THF solution. On the other hand, complexes 3b–d readily react with THF to afford 1 and free IPy 2b–d.

Introduction

Since the pioneering studies of Cloke and Edelmann in the early 1980s who introduced diimines in organolanthanide chemistry, this field of coordination chemistry has received a large boost due to the diversity of coordination modes offered by this class of ligands along with their intriguing redox properties. The idea to combine redox active diimine ligands and ytterbium ions possessing two stable oxidation states has proven to be particularly fruitful thus leading to the discovery of a series of challenging phenomena such as solvent mediated redox transformations, sterically induced reduction and redox isomerism. The course of the reactions between ytterbocenes and diimine ligands has been found to be affected by a number of factors. Depending on the nature of
6-(hetero)aryl substituted analogues \[2,6-\text{ iPr}_2(\text{C}_6\text{H}_3)\text{N} \] oxidative cleavage of the two presence of an excess of IPy, proceeds through the complete Cp-haptotropic rearrangements,9 and the steric demand of a steric factors and the inherent tendency of the bidentate IPy ligand \[2,6-\text{ iPr}_2\text{C}_6\text{H}_3\text{N} \] (indenyl) complex \((\text{Cp} = \text{indenyl})\) can lead to a dramatic rearrangement of the metal coordination sphere through unusual reactivity paths together with a permanent change of the ion oxidation state (Fig. 1).

The \(\text{Yb}^{\text{III}}\) bis(fluorenyl) complex \((\eta^5\text{C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_2\) in the presence of an excess of \(\text{IPy}\), proceeds through the complete oxidative cleavage of the two \(\eta^5\)-coordinated fragments, affording the paramagnetic \(\text{Yb}^{\text{III}}\) species coordinated by three iminopyridyl radical-anions \((\text{I})^{11b}\). Similarly, the \(\text{Yb}^{\text{II}}\) bis(indenyl) complex \((\eta^5\text{C}_9\text{H}_7)_2\text{Yb}(\text{THF})_2\) undergoes an unusual \(\text{N} = \text{C}\) bond insertion into a formal \(\eta^1\text{Yb} = \text{C}_9\text{H}_7\) bond thus leading to the half-sandwich and oxidized compound \((\text{II})^{11b}\). When bis(cyclopentadienyl) ytterbium complexes \(\text{Cp}_2\text{Yb}(\text{THF})_n\) \((\text{Cp} = \eta^5\text{C}_5\text{Me}_5, \eta^5\text{C}_9\text{H}_7\text{Me})\) are reacted with two equivalents of the same \(\text{IPy}\) a similar oxidative cleavage at one \(\text{Yb}-\text{Cp}\) bond takes place and \(\text{Yb}^{\text{III}}\) species \((\text{III})\) coordinated by two iminopyridyl radical-anions are formed.\(^{11a,15}\) For all these reactions, steric factors and the inherent tendency of the \(\eta^5\)-coordinated ligands to undergo haptotropic rearrangement are claimed to play a fundamental role in the whole transformation.

Despite the intriguing reactivity issues observed in the reaction of \((\eta^5\text{C}_9\text{H}_7)_2\text{Yb}(\text{THF})_2\) with the bidentate IPy ligand, \(6-\{\text{hetero} \text{aryl}\} \text{ substituted analogues} \ [2,6-\text{Pr}_2(\text{C}_6\text{H}_3)\text{N} = \text{CH}(\text{C}_9\text{H}_7\text{N})] \) behave unexpectedly as neutral \([\text{k}^2-\text{or} \text{k}^3-\text{coordinated}]\) systems by replacing THF molecules from the metal coordination sphere, without affecting the metal oxidation state of the targeted coordinative compounds \((\text{IV})\).\(^{16}\) The reason for the inhibition of metal-to-ligand electron transfer in the latter compounds is likely due to the lack of convergence between the ytterbium center and the bulkier substituted \(\text{IPy}\) ligands as a consequence of a metal ion size decrease in the case of a \(\text{Yb}^{\text{II}}/\text{Yb}^{\text{III}}\) oxidation.\(^{17}\) To gain additional insight into the steric regulation of these redox processes and to clarify the role of the steric and electronic properties of ligands bound to the ytterbium ion, hereafter we performed the study of the model ytterbocene complexes \(\text{Cp}^*_2\text{Yb}(\text{THF})\) \((\text{Cp}^* = \eta^5\text{C}_5\text{Me}_5)\) with unsubstituted and \(6-\{\text{hetero} \text{aryl}\} \text{ substituted iminopyridine ligands}\). A series of di- and trivalent ytterbium complexes coordinated by neutral or radical anionic ligands have been synthesized and fully characterized.

### Experimental section

#### General considerations and material characterization

All experiments were performed under an inert atmosphere, using standard Schlenk-tube and glove-box techniques. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl and hexane and toluene were dried by distillation from sodium/triglyme benzophenone ketyl prior to use. \((\eta^5\text{C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_2, \text{IPy 2a}\) and IPy \(2\text{b-d}\)\(^{13,16,20}\) were prepared according to literature procedures. Unless otherwise stated, all commercially available chemicals were used as provided from commercial supplies. \(^1\text{H}\) and \(^13\text{C}\) \((\text{H})\) NMR spectra were obtained on either a Bruker Avance-II 400 MHz NMR spectrometer or a Bruker DPX 200 MHz NMR spectrometer. Chemical shifts \((\delta)\) are reported in ppm relative to tetramethylsilane (TMS), referenced to the chemical shifts of residual solvent resonances \((\text{H} \text{ and } \text{C})\). IR spectra were recorded on a Bruker-Vertex 70 spectrophotometer. The N, C, and H elemental analyses were carried out in the microanalytical laboratory of the IOMC by means of a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of 0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Lanthanide metal analysis was carried out by complexometric titration.\(^{21}\)

#### General procedure for the synthesis of 3a-d

In a typical procedure, a toluene solution (20 mL) of \((\eta^5\text{C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_2\) \((0.50 \text{ g}, 0.97 \text{ mmol})\) was treated drop-
wise with a toluene solution (10 mL) of the appropriate ligand [2a–d] (0.97 mmol) and the reaction mixtures were maintained under stirring at 50 °C for the expected reaction times (24 h for 3a and 3c; 12 h for 3b; 28 h for 3d). For 3a, after removing volatiles under vacuum, the brownish-black solid was re-dissolved in 20 mL of nonane and the solution was cooled down to −20 °C to give brownish-black crystals of the complex in 76% yield. For 3b–d, brownish-black crystals were obtained directly from slow concentration of the toluene mixtures at room temperature in 70, 48 and 32% yield, respectively. Characterization data for [C5Me5]2Yb[κ2–κ3-Pr2(C6H3)NCH(C5H4N)]− (3a): elemental analysis calcd (%) for C44H42N2Yb: C, 63.36; H, 6.07; N, 3.95; Yb, 22.04. IR (Nujol, KBr), ν/cm−1: 1635 (s), 1560 (s), 1315 (m), 1270 (s), 1160 (m), 1020, 800 (s). 1H NMR (200 MHz, C6D6, 293 K): 1.31 (d, JHH = 7.0 Hz, 6H, CH3), 1.64 (br d, 12H, CH3), 1.74 (d, JHH = 7.5 Hz, 1H, CHAr), 2.02 (d, JHH = 7.5 Hz, 1H, CHAr), 3.41 (s, CH3 Cp*), 7.01; N, 4.17; Yb, 24.56. IR (Nujol, KBr), ν/cm−1: 3040 (br s, 30H, CH3 Cp*), 3.39 (m, 1H, CHiPr), 3.65 (m, 1H, CHiPr), 6.47 (br s, 1H, CH), 6.67 (br d, 3JHH = 7.0 Hz, 12H, CH3), 7.0 Hz, 12H, CH3.

Magnetic characterization
Magnetic measurements of crystalline samples of 3a–d were carried out by using an MPMS-XL SQUID magnetometer in the temperature range of 1.8–300 K with an applied magnetic field of 1000 Oe (up to 40 K) and 10 000 Oe (from 40 K to 350 K), to avoid saturation effects. Samples were prepared in a glove box by wrapping them in Teflon and then loaded in the SQUID magnetometer in less than 30°. The susceptibility is evaluated in the low field limit as \( \chi = M / H \). The raw data have been corrected for diamagnetic contribution of the sample holder, and the intrinsic diamagnetism of the sample, estimated by using Pascal’s constant to obtain the paramagnetic susceptibility.

X-ray crystallography
The X-ray data for 3a–d were collected on Bruker Smart Apex (3b,d), Bruker D8 Quest (3a) and Agilent Xcalibur E (3c) diffractometers (MoKα-radiation, ω-scans technique, \( \lambda = 0.71073 \) Å, \( T = 100(2) \) K) using SMART,28 APEX23 and CrystAlis PRO24 software packages. The structures were solved by direct and dual-space25 methods and were refined by full-matrix least squares on \( F^2 \) for all data using SHEXL.25 SADABS26 and CrystAlis PRO were used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. Hydrogen atoms H(10A) in 3b,c and H(3A) in 3d also were found from Fourier syntheses of electron density and were refined isotropically. Other hydrogen atoms in 3a–d were placed in calculated positions and were refined in the “riding” model with \( U(\text{iso}) = 1.2 \) Ueq of their parent atoms (U(\text{iso}) = 1.5 Ueq for methyl groups). 1552992 (3a), 1552993 (3b), 1552994 (3c), 1552995 (3d) contain the supplementary crystallographic data for this paper. The crystallographic data and structure refinement details are given in Table S1.†

Computational details
The calculations have been carried out with the Gaussian09 software27 at the DFT level using the hybrid functional B3PW91.28 Ytterbium atoms were treated with the small-core basis set. The geometry optimization has been performed without any symmetry constraints taking the geometry obtained from the X-ray diffraction measurement of the product. Analytical calculations of the vibrational frequencies of the optimized geometry were done to confirm that it’s a minimum. CASCF calculations were also carried out based on the SCF orbitals obtained for the triplet state and the active space choice is detailed in the manuscript.

Results and discussion
When a dark-red THF solution of Cp*Yb(THF) (1) is treated at room temperature with an equimolar amount of IPy ligand 2a,
the colour of the reaction mixture changed rapidly to deep brown thus indicating that a reaction takes place. Following the process by $^1$H NMR (THF-$d_8$, 293 K) spectroscopy proved the rapid oxidation of the metal ion to Yb$^{III}$ and the subsequent formation of a paramagnetic species. This result contrasts with earlier observations dealing with the reactivity of ytterbocenes in the presence of N,N-disubstituted diazabutadienes$^7$ where only non-coordinating aromatic and aliphatic hydrocarbons$^{5,6,16}$ allowed the reaction to take place, whereas no interaction occurred in the presence of coordinating solvents (i.e. THF, py). Hereby, 2a reacts with ytterbocene 1 in THF to give the paramagnetic complex \([\text{C}_5\text{Me}_5]_2\text{Yb}[^k_5,2,6-\text{Pr}_2(\text{C}_6\text{H}_3)\text{NCH}\{\text{C}_5\text{H}_4\text{N}\}][3a]^{–}\) as a result of a formal electron oxidation of the metal ion and IPy ligand reduction to the radical-anionic state (Scheme 1). In the present case, THF-to-IPy ligand displacement at the ytterbium center is likely facilitated by the reduced steric hindrance of IPy$^{16}$ compared to the more commonly used and sterically demanding N,N-disubstituted diazabutadiene systems.$^7$

3a was isolated in 76% yield as dark brown, air- and moisture-sensitive, microcrystals. Single crystals suitable for X-ray study were obtained from a concentrated toluene solution of the compound, cooled down to $–20$ °C for days. A perspective view of the 3a structure is given in Fig. 2 along with a selection of the main structural details [bond lengths (Å) and angles (°)]. The structure refinement data are given in Table S1 (see the ESf).

The ytterbium ion is $\eta^1$-coordinated by two Cp* ligands together with the two nitrogen atoms from the IPy framework that formally increase the final complex coordination number to eight (assuming CN 3 assigned for the Cp ligand). The Yb–C bond lengths in 3a \([\text{Yb}–\text{C}_\text{mean}]: 2.651(6)$ Å; \text{Yb}–\text{C}_\text{centre}: 2.345(2)$ Å\] are shorter than those measured on both the IPy-free ytterbocene 1 \([\text{Yb}–\text{C}_\text{mean}]: 2.69 Å; \text{Yb}–\text{C}_\text{centre}: 2.41 Å\]$ and the diamagnetic eight-coordinated pyridine adduct \(\{\text{Cp*}\}_2\text{Yb}(\text{Py})_2\) \([\text{Yb}–\text{C}_\text{mean}]: 2.74 Å\]. On the other hand, they are in good accord with Yb–C bond distances measured in related eight-coordinated Yb$^{III}$ complexes of the state-of-the-art \(\{\text{Yb}^{III}\}^{15,38,39}\). The 5-membered YbNCCN metallacycle in 3a is not planar and it forms a dihedral angle of 27.0(2)° between the planes defined by YbNN and NCCN atoms. Yb–N bond lengths \([2.325(2), 2.385(2)$ Å\] fall in a close range of those formerly reported for the related paramagnetic ytterbocene complexes coordinated by radical-anionic diazabutadiene ligands \(\{\text{IPy} \}^{16}$– \(\text{C}_5\text{Me}_5\}2\text{Yb}^{III}(\eta^5-\text{C}_5\text{Me}_4\text{H})\text{Yb}^{III}(\text{THF})\) \[\text{Yb}–\text{C}_\text{mean}: 2.604(6)$ Å\], \((\text{C}_5\text{Me}_5\}2\text{Yb}^{III}(\text{THF})\) \[\text{Yb}–\text{C}_\text{mean}: 2.628(5)$ Å\]$ and \((\text{C}_5\text{Me}_5\}2\text{Yb}^{III}(\text{THF})\) \[\text{Yb}–\text{C}_\text{mean}: 2.631(8)$ Å\]. Finally, bond distances within the NCCN fragment are markedly different from those typically measured for transition metal-coordinated$^{16}$ neutral IPy ligands \([\text{for } 3\text{a}: d(\text{C}=\text{N})=1.348(3)$ Å; \(d(\text{C}–\text{C})=1.408(3)$ Å\] . For model transition metal compounds containing neutral IPy ligands: \(\text{IPyM}^{II}\text{Cl}_2\) \(\{\text{M}^{II} = \text{Pd}^{39}, \text{Ni}^{36}, \text{IPy} = 2\text{a}\}: d(\text{C}=\text{N})=1.279(4)–1.278(3)$ Å; \(d(\text{C}–\text{C})=1.457(5)–1.463(4)$ Å\]. All these data taken together largely support the hypothesis of a trivalent oxidation state for the ytterbium ion in 3a as a result of one-electron metal oxidation along with a reduction of the coordinated IPy ligand to the state of a radical-anionic species.$^{11,15,37}$ However, all our attempts to detect the paramagnetic radical-anionic iminopyridine ligand in 3a (both in the solid state and in solution – hexane, toluene; 203–293 K) by the EPR technique failed. This outcome is in line with our previous studies where we demonstrated that Yb$^{III}$ complexes coordinated by paramagnetic radical-anionic diimino ligands are EPR-silent.$^6,10$ In addition, this behavior was not surprising at all given the fast electronic relaxation characterizing Yb$^{III}$ complexes and the even number of unpaired electrons of the resulting species.$^{38}$

The temperature dependence of the magnetic moment and of the molar susceptibility of 3a is reported in Fig. 3. A maximum in \(\chi_M\) vs. \(T\) data is observed, together with the presence of an unavoidable paramagnetic impurity of Yb$^{III}$ coordinated to diamagnetic ligands, which is responsible for the paramagnetic tail observed at \(T < 50$ K (Fig. 3A). By a fit of the corrected curves shown in Fig. 3B a maximum in \(\chi_M\) at 170 K along with a temperature independent paramagnetism
YbIII ions coordinated by radical-anionic bipyridine, phen-
shifts measured for related paramagnetic species containing
singlet at 3.41 ppm, in good agreement with the chemical
4f13-radical configuration (expected
at 350 K) suggests that the largest contribution is from the
ior; (B)
μ
and of the neutral Ipy
derivative [2,6-iPr2(C6H3)NCH(C5H4N)]
3a
broad interval from
anionic iminopyridine ligand give rise to a set of signals in a
trum of
3a
spins), in agreement with the results from the X-ray di
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Paper
Final contribution of 5.4 × 10−3 emu mol−1. Both these values are
consistent with a multiconfigurational ground state39 and the
observed μeff value at the highest measured temperature (4.19
at 350 K) suggests that the largest contribution is from the
4f13-radical configuration (expected μeff = 4.8 for uncoupled YbIII
and S = 1/2.

The 1H NMR spectroscopy is a sensitive tool that allows for
determining the magnetism of complexes in solution. The proton
NMR spectrum can qualitatively indicate whether the
complex is diamagnetic or paramagnetic. The 1H NMR spectrum
of 3a (benzene-d6, 293 K) shows a set of broadened
signals that are substantially shifted with respect to those of
related diamagnetic species (Fig. S1, ESI†) thus giving an
additional proof of its paramagnetic nature. The methyl
protons of the C5Me5 ring appear as a slightly broadened
singlet at 3.41 ppm, in good agreement with the chemical
shifts measured for related paramagnetic species containing
YbIII ions coordinated by radical-anionic bipyridine, phen-
anthrone or related ligands. The protons of the radical-
anionic iminopyridine ligand give rise to a set of signals in a
broad interval from −70 to 80 ppm.

Finally, the room-temperature electronic absorption spectra
of 3a (recorded in nonane), the radical-anionic potassium
derivative [2,6-Pr2(C6H3)NCH(C5H4N)]−K+ (recorded in THF)
and of the neutral Ipy 2a (recorded in hexane) were put at
comparison for the sake of completeness. The spectra are shown
in Fig. S3 (see the ESI†). The UV-Vis spectrum of 3a shows two
absorption bands at 355 and 455 nm, respectively. While the
neutral Ipy ligand 2a displays a single absorbance at 340 nm,
its potassium radical-anionic derivative [2,6-Pr2(C6H3)NCH
(C5H4N)]−K+ also displays two main absorbances at 355 and
525 nm, respectively. This comparative analysis is in line with
the presence of a radical-anionic iminopyridine ligand in solu-
tion and corroborates with the NMR data on the paramagnetic
nature of 3a.

With the aim of gaining additional insight into the role of
steric factors driving the metal-to-ligand electron transfer in
the above-mentioned coordinative compounds, we studied the
reaction of 1 in the presence of bulkier Ipy ligands (2b–d),
bearing coordinating or not-coordinating (hetero)aryl frag-
ments attached to the six-position of the pyridine core
(Scheme 2).

This systematic investigation takes advantage of the previous
outcomes of our study of the coordination modes and
electronic effects resulting from the reaction of the same class
of Ipy ligands with the bulkier bis(indenyl) ytterbium complex
(n5-C9H7)2Yb(THF)2.16 In that case, the coordination of
6-(hetero)aryl-substituted Ipy ligands occurred with the gene-
eration of diamagnetic species as a result of the simple replace-
ment of the two coordinated THF molecules.

Unlike the above-mentioned reaction with the bidentate Ipy
2a, Cp*2Yb(THF) (1) does not react in THF with the more steri-
dally demanding ligands 2b–d. This was preliminary con-
firmed by the absence of any appreciable color change in the
solutions of 1 upon treatment with an equimolecular amount of
2b–d. In addition, monitoring the reaction course over
several hours by 1H NMR (THF-d8, 293 K) spectroscopy has
showed only signals from unreacted starting materials. On the
contrary, the addition of 2a–d to a toluene solution of 1 at
room temperature (Scheme 2) resulted in the immediate
change of the solution colour from dark-red to brownish-
black. After slow concentration of each solution, brownish-
black microcrystals of complexes (C5Me5)2Yb[(C5Me5)2Yb
NCH(C5Me5)2–(C4H3O)] (3b), (C5Me5)2Yb[(C5Me5)2Yb
NCH(C5Me5)N–(C5Me5)H] (3c), (C5Me5)2Yb[(C5Me5)2Yb
NCH(C5Me5)N–(C5Me5)H–6-PH] (3d) were obtained in 70, 48 and 32% isolated
yields, respectively. Complexes 3b–d were isolated as highly
air- and moisture-sensitive solids showing moderate solubility
in aromatic and aliphatic hydrocarbons thus hampering their
full NMR characterization (13C[1H] NMR spectra).

Fig. 3 (A) μeff vs. T and χM vs. T curves of 3a before correction for the
paramagnetic impurity. The dotted line represents the fit to estimate the
amount of paramagnetic YbIII impurity assuming a Curie–Weiss behav-
or; (B) μeff vs. T and χM vs. T curves of 3a after correction for the para-
magnetic impurity. The horizontal dashed line represents the μeff value
expected at high temperature for a system formed by uncoupled YbIII
and S = 1/2.

Scheme 2 Reaction scheme for the generation of the coordination
compounds 3b–d.
Crystals suitable for single-crystal X-ray diffraction studies were grown by slow concentration of the respective toluene solutions at ambient temperature under a gentle stream of nitrogen. Complex 3b crystallizes as a solvate with one molecule of toluene while crystals of 3c and 3d do not contain any crystallization solvent. ORTEP representations of the three crystal structures are given in Fig. 4–6 along with a selection of the main structural details [bond lengths (Å) and angles (°)]; Table S1† lists their main crystal data and structural refinement details.

At odds with previously reported bis(indenyl)ytterbium/IPy coordination derivatives16 where ligands 2b and 2c–d behaved as tridentate and bidentate systems, respectively, the reaction of 1 with 2b–d leads to complexes 3b–d featuring different dent-
behavior. It presents a $\mu_{\text{eff}}$ value of 2.4 up to 280 K that is much lower than that expected for a single Yb$^{\text{III}}$-species and a radical anionic ligand, even assuming them to be antiferromagnetically coupled. Such a $\mu_{\text{eff}}$ value is also completely different from that presumed for a diamagnetic Yb$^{\text{III}}$-closed shell system. On the other hand, no maximum in $X_M$ vs. $T$, which would be indicative of a multiconfigurational ground state, is observed (see Fig. S17 of the ESI†). Notably, heating 3d from 270 K to 350 K gives rise to a clear-cut increase of the $\mu_{\text{eff}}$ value to 3.55. Such a variation is irreversible as witnessed by repeating the measurement after cooling down the sample. The value observed at high temperature is consistent with that expected for a strong antiferromagnetically coupled Yb$^{\text{III}}$-radical system, resulting in a $^1\text{F}_2$ state due to the combination of the $^2\text{F}_{7/2}$ term of Yb$^{\text{III}}$ and the $^2\text{S}_{1/2}$ term of a radical-anionic ligand.\textsuperscript{40}

It is noteworthy that the $\mu_{\text{eff}}$ vs. $T$ profile obtained after the first heating/cooling cycle can be perfectly rescaled, up to 270 K, on the pristine curve (see Fig. S18 of the ESI†). This result suggests that the species formed after heating above 270 K is also responsible for the intermediate $\mu_{\text{eff}}$ value measured before heating. Such a behavior can be reasonably explained by considering that the process leading to the increased $\mu_{\text{eff}}$ is already operative at room temperature (since the increase is visible above 270 K). Therefore, transformation already partially occurred when the sample is initially cooled down for measuring its magnetic properties. In other terms, the results of the magnetic investigation coupled with the outcomes of X-ray diffraction suggest that what we are actually measuring is not the structurally characterized form of 3d, but rather a product which evolves from 3d at $T > 270$ K. In this framework, it is tempting to attribute to 3d a diamagnetic character and to the evolution product a Yb$^{\text{III}}$-radical one. However, in the absence of definitive clues or clear-cut experimental evidence, this is a purely speculative hypothesis. Finally, we wish to stress here that a simple redox isomeric transition involving 3d cannot be invoked to explain the observed behaviour, since this should favour a closed shell configuration at high temperature.\textsuperscript{41} However, if a structural rearrangement takes place on heating, this might favour the Yb$^{\text{III}}$-radical charge distribution; such a coupled structural/electronic transition would be in analogy to what is often observed in the case of Co$^{\text{II}}$ complexes presenting similar temperature dependence of magnetic moment.\textsuperscript{19,42}

In contrast to 3a, the $^1\text{H}$ NMR spectra of 3b–d (benzene- $d_6$, 293 K) prove their diamagnetic nature in solution. The methyl protons of C$_5$Me$_5$ rings in 3b, 3c and 3d appear as singlets at 1.92, 2.11 and 2.24 ppm respectively, and they are in line with the chemical shifts earlier reported for diamagnetic complexes (C$_5$Me$_5$)$_2$Yb(L)$_n$ with coordinated O, N, and P-containing Lewis bases.\textsuperscript{43} At the same time, the signals of IPY ligands (2b–d) coordinated to the Yb ions in the $^1\text{H}$ NMR spectra give rise to the expected sets of signals with typical chemical shifts (see the ESI†). Finally, the UV-Vis spectra of 3b–d are consistent with the diamagnetic nature of these complexes in solution.

Calculations were carried out in order to determine the electronic nature of complexes 3a,b,d. The computational strategy is the same as that was developed by one of us (LM) to study multireference ground state complexes in bipyridine/phenanthroline Yb complexes.\textsuperscript{39,40,44} In summary, first DFT (B3PW91) geometry optimization using small core Relativistic Effective Core Potentials (RECP) was carried out and in a second step CASSCF calculations were performed. For complex 3a, within the precision of the DFT calculations, the displacement of a THF molecule from Cp$_2$Yb(THF) by the ligand 2a is expected to generate a Yb$^{\text{III}}$ complex through an exothermic process (3.8 kcal mol$^{-1}$) whereas the formation of a Yb$^{\text{III}}$ species is virtually thermoneutral (0.7 kcal mol$^{-1}$).\textsuperscript{45} Due to this very small energy difference between the Yb$^{\text{III}}$ and Yb$^{\text{III}}$ complexes, CASSCF calculations were carried out. As in previous CASSCF calculations on ytterbium, different active spaces were used. A first one distributing 14 electrons into the 8 orbitals (the 7 4f of the Yb and the $\pi^*$ one of the ligand) was used and leads to similar results to the 8 electrons/5 orbitals (4 4f + $\pi^*$) one. Finally, a reduced active space of 4 electrons/3 orbitals (2 4f + $\pi^*$) was tested and gave the same qualitative results as the two others. Therefore, only the results obtained with the last one are discussed here for the sake of simplicity. Two singlet states, a closed shell one ($f^{14}$) and an open-shell one (multiconfigurational state $f^{14} + f^{15}$), and a triplet state were computed. The open-shell singlet state was found to be the ground state with the triplet state only 4.1 kcal mol$^{-1}$ higher in energy and the closed-shell singlet is 5.3 kcal mol$^{-1}$ higher in energy than the ground-state. The open-shell singlet state is formed by 78% of Yb$^{\text{III}}$ and 22% of Yb$^{\text{II}}$. This is in line with the magnetic measurement that indicates that complex 3a is exhibiting a multiconfigurational character in the ground state with a major contribution from Yb$^{\text{III}}$.

In the same way, calculations were carried out on complex 3b. Unlike complex 3a, the coordination of the iminopyridine is not exothermic but rather slightly endothermic (5.8 kcal mol$^{-1}$). The formation of the Yb$^{\text{III}}$ complex from the Yb$^{\text{II}}$ one is also endothermic by up to 8.9 kcal mol$^{-1}$, making this highly unfavorable. To ensure this value, similar CASSCF calculations

![Fig. 7 \( \mu_{\text{eff}} \) vs. \( T \) curve for 3b (blue triangles), 3c (green rhombus) and 3d. For the latter, after the first heating cycle (red and white circles) the sample has been cooled down to 2 K and heated again up to 350 K (red squares).]
were carried out and the closed-shell singlet [Yb\(^{II}\)] turned out to be the lowest by up to 10.6 kcal mol\(^{-1}\) with respect to the triplet state (3b); the open-shell singlet being even higher in energy at 12.3 kcal mol\(^{-1}\). This is again in line with the magnetic measurement that indicates that the ground state of 3b is diamagnetic.

Finally, the calculations were conducted on the interesting 3d complex. At the DFT level, the coordination of the iminopyridine is found to be even more endothermic (14.6 kcal mol\(^{-1}\)) and the formation of the Yb\(^{III}\) complex is endothermic by 3.3 kcal mol\(^{-1}\) from the Yb\(^{II}\) one. Unlike the other cases, it is the coordination that appears to be complicated, it might not be the CASSCF calculations that would yield the answer. Indeed, at this level, the open-shell singlet is also found to be the ground state but with the triplet state almost degenerate (1.2 kcal mol\(^{-1}\)) and the closed-shell singlet only 5.3 kcal mol\(^{-1}\) higher in energy. With such low energy differences between the states, it is hard to conclude on the nature of the ground state.

For a family of metalloocene-type Yb\(^{III}\) complexes coordinated by radical-anionic diazabutadiene ligands, the existence of a reversible solvent mediated ligand-to-metal electron transfer has been formerly discovered.\(^5\)\(^c\)\(^6\) This phenomenon consists of the displacement of the radical-anionic diazabutadiene ligand by molecules of a coordinating solvent (THF, DME, Py) followed by electron transfer from the diazabutadiene radical anion to the ytterbium ion: as a whole, the process results in the oxidation of the ligand to the neutral diazabutadiene and the reduction of Yb\(^{III}\) to Yb\(^{II}\) (Scheme 3).

In order to check whether this behavior applies to related coordination compounds featuring IPy ligands, the reaction of 3a with THF was carried out. Unlike diazabutadiene congeners, 3a remains paramagnetic in THF-d\(_{6}\) solution and no redox replacement of the iminopyridine ligand by THF occurs (Scheme 4). In contrast to 3a, the addition of a stoichiometric amount of THF-d\(_{6}\) to benzene-d\(_{6}\) solutions of 3b–d resulted in the immediate replacement of the IPy ligands in the Yb coordination sphere by THF. The \(^1\)H NMR spectra of 3b–d recorded in THF-d\(_{6}\)/benzene-d\(_{6}\) mixtures have unambiguously demonstrated the generation of (C\(_5\)Me\(_5\))\(_2\)Yb(THF)\(_n\) and free IPy ligands 2b–d (Scheme 4). This result highlights the different reactivity of complexes 3b–d from 3a with respect to the replacement of IPy ligands by THF most likely caused by the different nature of metal–ligand interaction in these complexes. In addition, it demonstrates that metalloocene type Yb\(^{III}\) complexes coordinated by chelating radical-anionic diazabutadiene and IPy ligands behave differently in the presence of a coordinating solvent, despite their similar nature.

It can be inferred that such a different behavior between diazabutadienes and IPys is reasonably ascribed to the higher steric demand of the former class of ligands that is claimed to weaken the metal–ligand interaction. In 3a the energy of formation for Cp\(_*\)Yb\(^{III}\)-THF is not sufficient to compensate for the energy loss for the cleavage of Coulombic interaction between the Yb\(^{III}\) ion and the radical-anionic iminopyridine ligand. At the same time, the quick IPy displacement by stoichiometric amounts of THF in complexes 3b–d coordinated by a neutral IPy ligand is in line with the energies of coordination bonds in Yb\(^{III}\) complexes with N- and O-containing ligands.

**Conclusions**

In this paper we have described a new example of sterically controlled metal–ligand electron transfer by reacting (C\(_5\)Me\(_5\))\(_2\)Yb(THF) with IPy ligands featuring very similar electron accepting properties but variable denticity and steric
demand. The reactions of \( \text{C}_{2}\text{Me}_{3}\text{Yb} (\text{THF}) \) with ligands \( 2a-d \) proceed with the displacement of the coordinated THF molecule by means of an IPy framework. The observed outcomes highlight an important effect related to the steric demand of the iminopyridine systems on both their coordination mode and on their ability to foster metal-to-ligand electron transfer phenomena. Thus, the less sterically crowded \( 2a \) coordinates the metal ion as a bidentate system and a metal-to-ligand electron transfer takes place with the formation of a trivalent ytterbium species coordinated by a radical anionic IPy ligand. With the bulkier \( 2b \) and \( 2c \), potentially featuring as tridentate systems, the coordination to the metal ions takes place through the pyridine nitrogen and either O or S atoms of the heteroaryl substituents, only. For these neutral coordinative Yb\(^{III} \)-complexes \( 3b \) and \( 3c \) the imine nitrogen points away from the metal coordination sphere. For the bidentate \( 2d \) ligand, featuring steric hindrance similar to \( 2b-c \), a monodentate coordination to the Yb\(^{II} \) ion is accomplished through the pyridine nitrogen only. The reason which blocks metal-to-ligand electron transfer in compounds \( 2b-d \) is likely the impossibility of a close approach between the ytterbium center and the bulkier substituted IPy ligands as a consequence of a metal ion size decrease in the case of a Yb\(^{III} \)/Yb\(^{II} \) oxidation.

We note that while this trend is clearly defined in solution by NMR and in the solid state by X-ray data, magnetic analysis in the solid state confirms it only for \( 3a-c \). The former complex provides a magnetic response that is as expected for a multiconfigurational ground state with the largest contribution from the \( 4f^{13} \)-radical configuration, while \( 3b \) and \( 3c \) are diamagnetic and thus consistent with the closed-shell singlet ground state configuration. On the contrary, the magnetic behavior of \( 3d \) turned out to be extremely complex, suggesting the instability of its structure on heating above 270 K.

Unlike indenyl ligands cyclopentadienyl analogues are not prone to haptotropic rearrangements and the use of \( \text{Cp}^*\text{Yb} (\text{THF}) \) provided us with an opportunity to demonstrate clearly and unambiguously that bulkiness and the electronic properties of the aromatic carbocyclic ligands coordinated to the Yb\(^{II} \) ion are also decisive for the occurrence of intramolecular metal-to-ligand electron transfer and the type of coordination adopted by IPy ligands. The bidentate coordination of less sterically demanding Ipy \( 2a \) allows for a metal-to-ligand electron transfer resulting in a shortening of the Yb–Cp\(^* \) bonds and the formation of rather short Yb–N bonds \( (\text{Yb}(1)-(N(1) 2.325(2) \text{Å}) \). The introduction of bulky substituents into the Py ring excludes the possibility of such structural changes associated with oxidation and blocks the metal-to-ligand electron transfer. Indeed the resulting IPy complexes \( 2b-d \) feature Yb–Cp\(^* \) and Yb–N distances characteristic for Yb\(^{II} \) species.

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## Conflicts of interest

There are no conflicts to declare.
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