Bis(η-heteroarene) titanium complexes derived from 2,4,6-tri-*tert*-butylpyridine and 2,4,6-tri-*tert*-butylphosphorin: conformational preference in solution and redox activity [1]

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Abstract

The complexes $(Ti(NC_5H_2^tBu_3-2,4,6)_2]$ **1**, and $[Ti(PC_5H_2^tBu_3-2,4,6)_2]$ **2**, have been synthesised in moderate yields via the co-condensation reaction between titanium vapour and $[NC_5H_2^tBu_3-2,4,6]$ **3**, or $[PC_5H_2^tBu_3-2,4,6]$ **4** respectively. The conformation adopted by the molecules in solution has been investigated by NMR and is discussed in comparison with other first row transition metal bis(heteroarene) complexes. Both **1** and **2** are found to exist entirely in the synclinal conformation. The reaction of **1** and **2** with potassium results in formation of the potassium salts $K^+[\{Ti(NC_5H_2^tBu_3)_2\}^-]$ **5**, and $K^-[\{Ti(PC_5H_2^tBu_3)_2\}^-]$ **6** respectively.

Keywords: Titanium; Heteroarene; Metal vapour synthesis

1. Introduction

Over the last 10 years a considerable volume of compounds of the form $M(\eta\text{-heteroarene})_2$ have been synthesised and characterised. The range of compounds now present in the literature means that the susceptibility of the arene–metal bonding to both steric and electronic effects conferred by the heteroatom can be studied [1].

There is now precedent in the literature for the complete series of heteroarenes C_5H_5E (E = N, P, As, Sb, Bi); thus there is much to be learnt from systematic study of the properties of the homologous series, in which all compounds have the potential for both σ- and π-coordination [2]. The rings are aromatic according to spectroscopic data, and are capable of binding as such, but for the early members of the series, notably pyridine, the observed mode of ligation to a given metal is preferentially via the σ lone pair rather than in an η^6 fashion. Restriction of access to the lone pair for $\sigma(\eta^1)$

binding by *ortho*-H substitution is well documented, [3,4] and employment of symmetrically substituted heteroarenes also ensures that the electronic perturbation inflicted on the ring by the heteroatom is the predominant contribution to the observed synclinal:antiperiplanar product ratio observed in the sandwich complex, e.g. in $[V(PC_5H_2^tBu_3-2,4,6)_2]$ and $[Cr(PC_5H_2^tBu_3-2,4,6)_2]$ [5]. Measurement of these parameters by solution NMR techniques removes the possibility of packing forces dictating a particular conformation in the solid state. The rotation of the lutidine rings in $[Ti(NC_5H_2Me_2-2,6)_2]$ was found to be too rapid on the NMR timescale to correlate a favoured conformation with the observed anti conformation adopted in the crystalline state [6]. No conformational preference in solution or the solid state could be ascertained for the unsubstituted complexes $[Cr(\eta\text{-}NC_5H_5)_2]$ and $[Cr(\eta\text{-}AsC_5H_5)_2]$ due to rapid rotation of rings on the NMR timescale and disorder in the crystalline state [4].

We were interested in investigating the nature of the binding of highly sterically encumbered heteroarenes to early transition metals, as this area has been previously unexplored. The choice of the *tert*-butyl group to block ortho and para ring positions is well documented, and performs, inter alia, four functions [7]. The E lone pair donation possibility is blocked, so $\pi(\eta^6)$ binding be-

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[1] Dedicated to Malcolm Green on the occasion of his 60th birthday, with sincerest thanks for all his help and encouragement over the years.

comes favourable. The ring is rendered both highly soluble in hydrocarbon solvents, and volatile, making it suitable for metal-atom–ligand-vapour co-condensation experiments. The bulk confers a kinetic stability both upon the free ligand and on the derived metal complex; steric congestion of the ortho and para ring positions is also expected to slow the exchange processes allowing study of the distribution of conformational isomers. Finally the use of *tert*-butyl group substituents in the ortho positions removes the potential for C–H ortho-metallation reactions involving the α protons; this is potentially problematic because of their enhanced acidity due to the presence of the adjacent electronegative heteroatom [8].

We report herein the synthesis and characterisation of bis(η^6-2,4,6-tri-*tert*-butylpyridine)titanium and bis(η^6-2,4,6-tri-*tert*-butylphosphorin)titanium, their preferred conformation in solution, and redox activity.

2. Results and discussion

Co-condensation of titanium vapour with 2,4,6-tri-*tert*-butylpyridine 3, at 77 K affords, after work up, dark red crystalline [Ti(NC$_5$H$_2^t$Bu$_3$-2,4,6)$_2$] 1, in 31% yield. Analogous co-condensation between titanium and 2,4,6-tri-*tert*-butylphosphorin 4, followed by similar work up, affords [Ti(PC$_5$H$_2^t$Bu$_3$-2,4,6)$_2$] 2 in 20% yield based on titanium (Scheme 1).

Observation of unique environments in the ^{1}H NMR for resonances of the ortho arene *tert*-butyl groups at 293 K confirms that the rings in 1 and 2 exist in solution entirely in the synclinal conformation. The rings in 1 are static on the NMR timescale at ambient temperatures, but are freely rotating at 330 K. Calculation of an absolute value of $\Delta G^\ddagger$ for ring rotation from variable-temperature NMR studies is complicated due to the two site exchange involved in the coalescence process, but an upper limit of 68 kJ mol^{-1} may be deduced from the

Scheme 1.

coalescence temperature of 323 K for the ring protons. Similarly, the coalescence temperature for the ring protons in 2 is 353 K, giving an upper limit of 70 kJ mol^{-1} for $\Delta G^\ddagger$ for ring rotation. Cooling of both samples results in complete reversion to the syn conformation. The deviation from D_{6h} symmetry of the ring on replacement of CH by N or P involves an expansion of both the C–E–C bond angle and C–E lengths within the plane of the ring [2]. Thus the rotamer distribution will still display a slight preference towards the synclinal form if the covalent radius of the metal is small enough to enforce a close approach of the *tert*-butyl groups. Crystals of both 1 and 2 suitable for single-crystal X-ray structural analysis were isolated but disorder frustrated attempts to solve either structure.

Previous studies on the complexes [V(PC$_5$H$_2^t$Bu$_3$-2,4,6)$_2$], and [Cr(PC$_5$H$_2^t$Bu$_3$-2,4,6)$_2$], by Elschenbroich et al. [5] (using solution EPR and NMR methods respectively) yielded a synclinal:antiperiplanar ratio of 2:1 in [V(PC$_5$H$_2^t$Bu$_3$-2,4,6)$_2$], and 3:1 in the chromium sandwich. The EPR method is accepted as giving a less accurate measure of the product ratio. Conceivably, the greater radial extension of the Ti d-orbitals enhances the overlap of metal-d and ligand-p orbitals, resulting in production of the syn rotamer for both 1 and 2, presumably the electronically favoured conformation. In the chromium analogue, the reduced covalent radius of the central metal brings the rings into closer contact, and thus the formation of the synclinal rotamer as the major product is a result of the concomitant reduction in interligand repulsion. For vanadium, which falls between these two in size, the statistical rotamer ratio is found. No information is given as to whether this ratio is conserved as the thermodynamic ratio after equilibration of the rotamers of the two latter.

The electronic spectrum of 1 shows a single charge transfer band ($\varepsilon > 10^4$) at 385 nm. However, the charge transfer band in 2 is observed as two overlapping absorptions of equal intensity at 402 and 361 nm, both of similar magnitude to that in 1; this may be attributable to the presence of two rotamers which are not interconverting on the UV timescale.

The redox activities of 1 and 2 have been studied by cyclic voltammetry (CV). The voltammogram of 1, shown in Fig. 1(a), displays an irreversible oxidation at −0.45 V relative to ferrocene/ferricenium, a second irreversible oxidation at +0.605 V, and a quasi-reversible reduction at −2.855 V. The oxidation process at −0.45 V remains irreversible if the scan direction is reversed before the onset of the second wave at +0.605 V. The trace of 2, shown in Fig. 1(b), displays the same electron transfer processes; a quasi-reversible oxidation at −0.478 V, a second irreversible oxidation at +0.71 V, and a quasi-reversible reduction at −2.466 V. Hence, although the apparent similarity of the electrochemical response of 1 and 2 might be taken
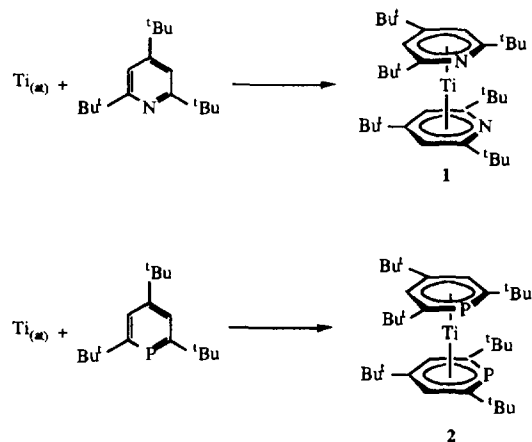
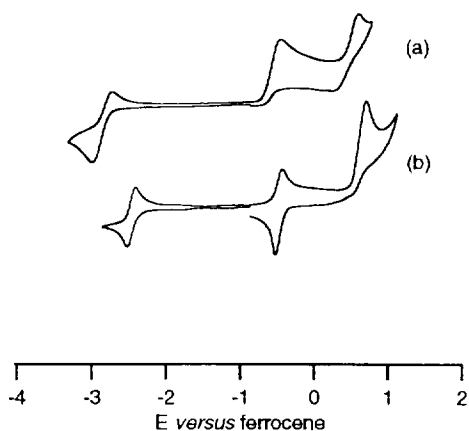Fig. 1. Cyclic voltammetric traces for **1** (a) and **2** (b) in THF/[(n-Bu)$_4$NPF$_6$] (0.2 M) at platinum vs. ferrocene; $T = 293$ K, $\nu = 200$ mVs^{-1}.

to reflect the similarity of the frontier molecular orbitals, the instability of **1**$^+$ on the CV timescale precludes detailed analysis. Comparison of the half-wave potentials for the reversible reduction waves **1/1**$^-$ and **2/2**$^-$, however, gives good indication of the increased

Fig. 2. EPR spectra of **1** (a) and **2** (b); dilute THF solution at 295 K.

electron donating properties of the phosphaarene compared with the pyridine-derived ring.

Introduction of a THF solution of **1** and **2** onto a potassium mirror resulted in an immediate reaction in each case to form the potassium salts: the dark brown solution of K$^+$[{Ti(NC$_5$H$_2^t$Bu$_3$)$_2$}$^-$] **5**, and the dark green solution of K$^+$[{Ti(PC$_5$H$_2^t$Bu$_3$)$_2$}$^-$] **6**. Both give well-resolved EPR spectra, represented in Fig. 2.

The spectrum of **5** consists of a single resonance centred around $g = 1.993$, with hyperfine structure arising from coupling to the ring protons, giving an apparent quintet. The assignment of the resonances is supported by a simulation (not including hyperfine coupling to titanium isotopes), Fig. 2(a), using A^1_H 0.22 mT and A^1_H 0.27 mT for coupling of the electron to protons in two distinct environments. The spectrum of **6** is more complex. The single resonance, $g_{av} = 1.992$, shows hyperfine structure due to coupling to two sets of ring protons, and to the ^{31}P nucleus, expected to give rise to a 27-line spectrum. This is successfully simulated using A^1_H 0.325 mT, A^1_H 0.352 mT, and A$^{31}_P$ 0.242 mT. Hyperfine coupling to titanium isotopes was observed for this case, but not included in the simulation. The isoelectronic species [V(PC$_5$H$_2^t$Bu$_3$-2,4,6)$_2$)] interestingly shows no visible hyperfine coupling to the ^{31}P nucleus in the arene [5]. The linewidth of the components of the hyperfine coupling to the ^{51}V nucleus is of a magnitude that could be ascribed to a coupling of less than 0.5 mT to the ^{31}P nucleus. These low values of A$^{31}_P$ are consistent with occupancy of the d$_{z^2}$ orbital by the unpaired electron giving rise to the resonance [9].

3. Experimental details

All experimental procedures were carried out using standard Schlenk line techniques under an atmosphere of dry dinitrogen or dry argon, or under dinitrogen in an MBraun or a Miller–Howe glove-box. Glassware and Celite 545 filter aid were flame-dried in vacuo prior to use. Solvents were refluxed over suitable drying agents, and distilled and degassed prior to use: THF was refluxed over potassium; hexane and pentane were refluxed over sodium–potassium alloy. NMR solvents were dried over potassium (d_{12}-cyclohexane) or sodium (d_8-toluene), transferred into ampoules, and stored under dinitrogen prior to use. The co-condensation experiments were performed using an apparatus of the type described by Cloke and Green [10].

NMR spectra were recorded on a Bruker WM360 spectrometer, an ACP250 spectrometer, and a Bruker Avance 300 DPX spectrometer. Chemical shifts are reported in ppm, relative to the residual proton chemical shifts of the deuterated solvent (^{1}H), internal solvent (^{13}C), and external H$_3$PO$_4$ (^{31}P). EPR spectra were recorded on a Bruker ESP 300 X-band spectrometer
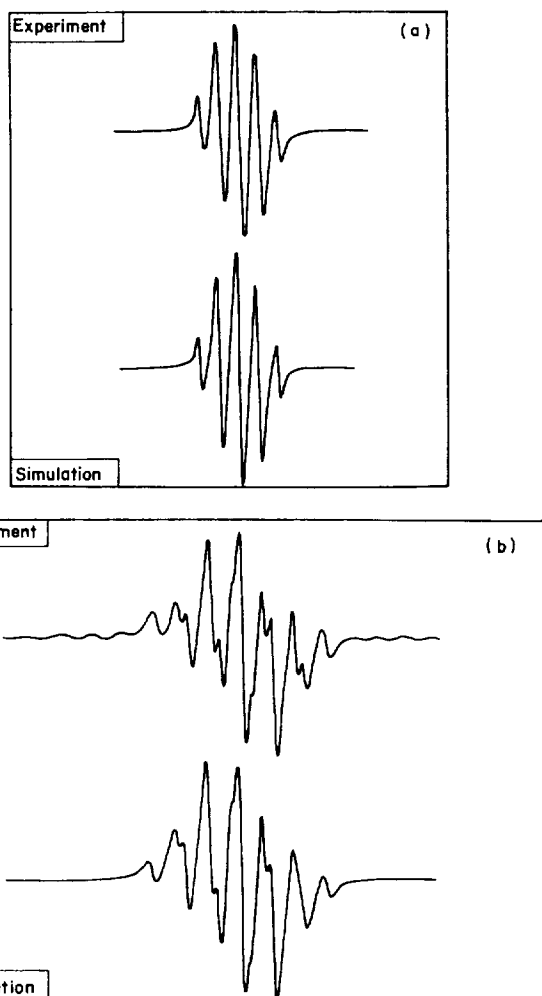
operating at a frequency of 9.4 GHz. UV–visible absorption spectra were recorded on a Phillips PU 8720 UV–vis spectrophotometer. Mass spectra were recorded on a Kratos MS80RF instrument. Cyclic voltammograms were recorded in THF/[(n-Bu)$_4$NPF$_6$] (0.2 M) with platinum electrodes vs. ferrocene internal standard, at 20°C, $\nu = 200$ mV s^{-1}. Data were processed using Echem Maclab software and IGOR. Elemental analyses were performed by Canadian Microanalytical.

The compounds 3 and 4 were synthesised using literature procedures [11,12].

3.1. Synthesis of bis(2,4,6-tri-tert-butylpyridine)titanium, 1

Titanium metal (1.25 g, 26 mmol) was evaporated using a positive hearth electron-beam gun, and co-condensed with 3 (24.2 g, 98 mmol) at 77 K. A dark brown matrix appeared over a period of 90 min, whose colour persisted on warm up to room temperature under an inert atmosphere. A brown solution was extracted with hexane (1 l), filtered through a bed of Celite and volatiles removed under reduced pressure. Excess free ligand was recovered by sublimation (55°C, 10^{-6} mbar). Extraction of the remnant dark solid in pentane (50 ml), filtration through Celite, followed by concentration of the solution, and slow cooling to −30°C afforded red-brown crystals of bis(2,4,6-tri-*tert*-butylpyridine)titanium in 31% yield (4.3 g). ^{1}H NMR (d_8-toluene): δ 5.7 (br s, 2H, ring CH), δ 5.6 (br s, 2H, ring CH), δ 1.4 (s, 18H, C(CH_3)-p), δ 1.3 (br s, 18H, C(CH_3)$_3$-o), δ 1.15 (s, 18H, C(CH_3)$_3$-o). ^{13}C{^{1}H} NMR: δ 137.72, 101.15 (s, ring C), 90.88, 86.55 (s, ring CH), 38.22, 37.47 (s, C(CH$_3$)$_3$-o), 35.37 (s, C(CH$_3$)$_3$-p), 32.57 (s, C(CH_3)$_3$-p), 31.62, 30.79 (s, C(CH_3)$_3$-o). UV–vis (pentane): λ_{max} 385 nm ($\varepsilon > 10^4$), 502 nm (weak). MS (EI): m/z 542 (30%) (M$^+$). Anal. Found: C, 75.18; H, 10.81; N, 4.99. [C$_{34}$H$_{58}$N$_2$Ti] requires C, 75.24; H, 10.77; N, 5.16%.

3.2. Synthesis of bis(2,4,6-tri-tert-butylphosphorin)titanium, 2

Titanium metal (0.49 g, 10 mmol) was evaporated using a positive hearth electron-beam gun, and co-condensed with 4 (21.0 g, 79 mmol) at 77 K. A dark brown matrix appeared over a period of 90 min, whose colour persisted on warm up to room temperature under an inert atmosphere. A brown solution was extracted with hexane (0.7 l), filtered through a bed of Celite and volatiles removed under reduced pressure. Excess free ligand was recovered by sublimation (60°C, 10^{-6} mbar). Extraction of the remnant dark solid in hexane (30 ml), filtration through Celite, followed by concentration of the solution, and slow cooling to −50°C afforded red-brown crystals of bis(2,4,6-tri-*tert*-

butylphosphorin)titanium in 20% yield (1.15 g). ^{1}H NMR (d_8-toluene): δ 6.19 (s, 2H, ring CH), δ 5.23 (s, 2H, ring CH), δ 1.50 (s, 18H, C(CH_3)-p), δ 1.27 (s, 18H, C(CH_3)$_3$-o), δ 1.26 (s, 18H, C(CH_3)$_3$-o). ^{31}P{^{1}H} NMR: δ −5.29. ^{13}C{^{1}H} NMR (d_{12}-cyclohexane): δ 128.96, 121.96 (d, ring C-o) ^{1}J$_{PC}$ 73 Hz, 108.57 (s, ring C-p), 98.29, 89.64, (d, ring CH) ^{1}J$_{CH}$ 158 Hz, 40.13, 39.95 (m, C(CH$_3$)$_3$-o) ^{2}J$_{CP}$ 11 Hz, 37.44 (s, C(CH$_3$)$_3$-p), 34.58, 34.10 (d, C(CH_3)$_3$-o) ^{3}J$_{CP}$ 4.6 Hz, 33.66 (s, C(CH_3)$_3$-p). UV–vis (pentane): λ_{max} 402 nm ($\varepsilon > 10^4$), 518 nm (weak). MS (EI): m/z 576 (56%) (M$^+$). Anal. Found: C, 69.39; H, 10.24. [C$_{34}$H$_{58}$P$_2$Ti] requires C, 70.81; H, 10.14%.

3.3. Reaction of 1 and 2 with potassium

A dilute brown solution of 1 (4 mg, 7 × 10^{-4} mmol) in THF (3 ml) was introduced onto a potassium mirror (3 mg, 0.1 mmol) in a one-piece silica EPR tube. The mirror dissolved rapidly, and the solution turned a dark brown. Analysis of the EPR of this solution, supported by a simulation, show this to be the radical anion salt K$^+$[{Ti(NC$_5$H$_2^t$Bu$_3$)$_2$}$^-$] 5.

The analogous reaction between a THF solution of 2 and a potassium mirror yielded a dark green solution. Analysis of the EPR of this solution, supported by a simulation, showed this to be the radical anion salt K$^+$[{Ti(PC$_5$H$_2^t$Bu$_3$)$_2$}$^-$] 6.

4. Conclusion

Use of the sterically demanding heteroarenes [NC$_5$H$_2^t$Bu$_3$] and [PC$_5$H$_2^t$Bu$_3$] in bis(arene)titanium complexes leads to exchange rates for rotation of the rings which are visible on the NMR timescale. Thus the preferred conformation of the molecules in the absence of possible crystal packing interactions is found to be 100% synclinal in each case. The reaction with potassium gives the monoanionic salts, with well-resolved EPR resonances showing hyperfine coupling to the aromatic ring protons, and to the ^{31}P nucleus in 2.

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