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Reference


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Synthesis and characterisation of a heterodinuclear ruthenium(II)–palladium(II) complex with two different cyclometallating sites

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Abstract

A bis-cyclometallating ligand bearing two different terdentate coordination sites (N–C–N: dipyridyl-benzene; P–C–P: diphosphaalkene-benzene moieties) has been synthesised. Selective reactions of appropriate metal complex precursors afforded a heterodinuclear ruthenium(II)–palladium(II) complex characterised by 1H, 31P NMR spectroscopy and FAB-MS techniques. We have compared its electrochemical and spectroscopic properties (absorption and emission) with the individual ruthenium(II) and palladium(II) subunits.

Keywords: Ruthenium complexes; Palladium complexes; Cyclometallated ligand complexes; Heterodinuclear complexes

1. Introduction

During recent years, the chemistry of coordination complexes containing cyclometallated terdentate ligands has received significant attention. Different sets of donor atoms (P–C–P, N–N–C, N–C–N, S–C–S etc.) have been used to prepare a wide range of metal complexes [1-14] (Ru, Os, Rh, Ni, Ta, Pd, Pt etc.). As a result of the strong metal–carbon σ bond, the ligand field and the electron density at the metal centre are increased by comparison with nitrogen or phosphorus donor atoms. Unusual reactivities [12,15-17] and new photophysical properties [10,18] have been evidenced in this type of complex. More recently, mixed-valence complexes (RuII–RuIII, OsII–OsIII) based on the N–C–N [19,20] or N–N–C [21] sets lead to an exceptional electronic coupling between the two metal centres. Similarly to this bis-terdentate ligand, we previously reported a dinuclear palladium complex containing two diphosphaalkene-benzene moieties [22]. We report here the synthesis and characterisation of a new bis-cyclometallating ligand 1 incorporating a dipyridyl-benzene and a disphosphalkene-benzene fragment. The different metal-binding sites of 1 permit the preparation of the heterodinuclear ruthenium(II)–palladium(II) complex 2 by selective reaction with the appropriate metal complex precursors (Scheme 1).

2. Experimental

2.1. Instrumentation

31P and 1H NMR spectra were acquired on a Bruker WP200SY spectrometer. Mass spectra were obtained by using VG mass lab TRIO-2 and VG ZAB-IIIF mass spectrometers. Electronic absorption and emission spectra were recorded with Kontron Uvikon 860 and Shimadzu RF 450 fluorimeters. Electrochemical measurements were carried out at room temperature by using a PAR model 362 potentiostat. Cyclic voltammeters, in THF containing 0.1 M n-Bu4NPF6 as supporting electrolyte, were performed using a three-electrode system with a platinum working electrode, a platinum-wire counter electrode and an SCE reference electrode.

2.2. Preparations

Most of the syntheses were performed under an argon atmosphere, in carefully dried glassware. All the reagents were purchased from Fluka and used as received. 4'-Tolyl-2,2':6'2"-terpyridine (terpy) [23], Ru(terpy)Cl3 [23], Ru(terpy)(dpb)PF6 (dpbh=1,3-dipyridyl-benzene) [19], [2,4,6-(ter-Bu)3]PH2 [24] and Pd[di(tri-t-butylphenylphospho-ethylene)]-1,3-benzene [11] were synthesised according to previously reported procedures.
2.2.1. 1-Bromo-3,5-dipyridyl-benzene (3)

A three-neck round-bottomed flask containing a magnetic stirring bar and fitted with a thermometer, a reflux condenser and a side arm capped with a rubber septum, was charged with 2-bromopyridine (2.18 g, 13.8 mmol) and freshly distilled THF (30 ml). The flask was cooled to -10 °C and the solution was degassed. It was then cooled to -78 °C and t-BuLi (20 ml, solution of t-BuLi 1.4 M in pentane) was slowly added via canula. Stirring was continued for 30 min. Anhydrous ZnCl₂ (1.9 g, 13.9 mmol) was added and the mixture was allowed to warm to room temperature. Pd(P(C₆H₄Br)₃)₄ (0.32 g, 0.28 mmol) and 1,3,5 tribromobenzene (2 g, 6.34 mmol) were added. The mixture was refluxed for 20 h. After cooling, the reaction mixture was quenched with an aqueous solution of NH₄Cl and extracted with CH₂Cl₂ (2 x 150 ml). The combined organic extracts were dried over MgSO₄ and the solvent was removed. Purification was accomplished by column chromatography using silica gel (eluent: CH₂Cl₂-MeOH). The pure product was isolated as a white solid; yield 0.83 g (42%). ¹H NMR (CD₂Cl₂): δ 8.70 (m, 2H); 8.63 (t, 2H, 1.6 Hz); 8.24 (d, 1H, 1.6 Hz); 7.83 (m, 4H); 7.29 (m, 2H). M.p. = 72 °C. MS: m/z = 310 (C₁₅H₁₁N₂Br requires 310.9).

2.2.2. 1,3-Dipropylene-acetal-3',5'-dipyridyl-biphenyl (5)

This compound was synthesised using the method described for 3. The bromo derivative 3 (0.94 g, 3.04 mmol) and the palladium catalyst (92 mg, 0.08 mmol) were added to the zinc derivative of 1-bromo-3,5-dipropylene-acetal-benzene (4) (25 g) (3.04 mmol). The reaction mixture was refluxed overnight. It was then hydrolysed and extracted twice with CH₂Cl₂. Chromatography (silica gel, 1% MeOH in CH₂Cl₂) yielded 0.9 g of pure compound (62%). ¹H NMR (CD₂Cl₂): δ 8.71 (ddd, 2H, 4.5, 1.8 and 1 Hz); 8.63 (t, 1H, 1.7 Hz); 8.29 (d, 2H, 1.7 Hz); 7.91 (dt, 2H, 7.5 and 1 Hz); 7.79 (td, 2H, 7.5 and 1.8 Hz); 7.78 (d, 2H, 1.7 Hz); 7.55 (t, 1H, 1.5 Hz); 7.28 (ddd, 2H, 7.5, 4.5 and 1 Hz); 5.56 (s, 2H); 4.24 (ddd, 4H, 12, 5 and 1.5 Hz); 3.98 (dt, 4H, 12 and 4.5 Hz); 2.18 (dt, 2H, 13.2 and 5 Hz); 1.42 (dt, 2H, 13, 2.5 and 1.5 Hz). M.p. = 192 °C. MS: m/z = 480 (C₉H₆N₂O₄ requires 480).

2.2.3. 1,3-Dialdehyde-3',5'-dipyridyl-biphenyl (6)

An aqueous solution of 4 M HCl (6 ml) was added dropwise to a solution of 5 (0.5 g, 1.04 mmol) in acetone (20 ml). The reaction mixture was stirred at room temperature for 6 h. Then, an aqueous solution of NaHCO₃ was added until pH 8 was reached. After extraction with CH₂Cl₂ (2 x 100 ml) and chromatography (silica, CH₂Cl₂-MeOH as eluent), 6 was obtained as a white solid (0.36 g, 96%). ¹H NMR (CDCl₃): δ 10.21 (s, 2H); 8.77 (m, 2H); 8.66 (t, 1H, 1.7 Hz); 8.57 (d, 2H, 1.5 Hz); 8.43 (d, 2H, 1.8 Hz); 8.40 (t, 1H, 1.5 Hz); 7.97 (br, d, 2H, 8 Hz); 7.86 (d, 2H, 7.5 and 1.8 Hz); 7.34 (ddd, 2H, 7, 5 and 1 Hz). M.p. = 207 °C. MS: m/z = 364 (C₂₀H₁₆N₄O₂ requires 364).

2.2.4. Ligand I

nBuLi (1.8 mmol) was added, under argon, to a solution of [(2,4,6-tri-t-butyl)-phenyl]-phosphine (0.5 g, 1.8 mmol) in THF (25 ml). Then, Cl₂SiMe₃-Bu (0.27 g, 1.8 mmol) and nBuLi (1.8 mmol) were successively added. After addition of the dialdehyde 6 (0.9 mmol), the mixture was stirred at room temperature for 22 h. The resulting products were purified by silica gel chromatography (CH₂Cl₂-ether mixture as eluent). The mixture of the two isomers E-E (86%) and E-Z (14%) obtained were recrystallized from a mixture of ether-EtOH (0.35 g, 51%). ³¹P [¹H] NMR (81 MHz, CDCl₃/H₂PO₄): δ 263.2 (isomer E-E); 261.5 and 244.4 (isomer E-Z). M.p. = 150-152 °C. MS: m/z = 885 (C₂₀H₁₆N₄P₂ requires 884.5).

2.2.5. Complex 2

A mixture of Ru(terpy)Cl₃ (20 mg, 0.037 mmol) and AgBF₄ (22 mg, 0.113 mmol) in acetone (10 ml) was refluxed for 2 h in air. After filtration, the solvent was evaporated and the residue was dissolved in ethanol (100 ml). To this solution was added the ligand 1 (33 mg, 0.037 mmol) and the solution was heated at reflux for 20 h. The solvent was then evaporated and the residue was dissolved in CH₂Cl₂ (10 ml). After addition of Pd(C₆H₄CN)₂Cl₂ (14 mg, 0.037 mmol) the reaction mixture was stirred, under argon, for 3 h. Chromatography (silica gel, CH₂Cl₂-MeOH as eluent) yielded 20 mg of pure 2 (80%). ³¹P [¹H] NMR (81 MHz, CDCl₃/H₂PO₄): δ 228. ¹H NMR (400 MHz, CDCl₃): δ 8.85 (s, 2H); 8.35 (d, 2H, 8 Hz); 8.34 (s, 2H); 8.12 (d, 2H, 8.2 Hz); 8.02 (d, 2H, 8.2 Hz); 7.78 (t, 2H, 7.7 Hz); 7.69 (t, 2H, 7.7 Hz); 7.66 (s, 4H); 7.56 (m, 4H); 7.46 (s, 2H); 7.20
(d, 2H, 4.8 Hz); 7.03 (d, 2H, 4.8 Hz); 6.91 (m, 2H); 6.64 (m, 2H); 2.54 (s, 3H); 1.78 (s, 36H); 1.42 (s, 18H). FAB-MS (nitrobenzyl alcohol matrix): m/z = 1450 (C82H89N5P3ClPdRu+ requires 1450).

3. Results and discussion

3.1. Synthesis of ligand 1 and complex 2

The synthetic scheme leading to 1 is summarized in Fig. 1. The key step is the cross coupling reaction between 1-bromo-3,5-dipyridyl-benzene (3) and the organozinc derivative of 4 bearing two protected aldehyde functions. This reaction, catalysed by the palladium tetrakis-triphenylphosphine complex, affords the intermediate 5 in moderate yield (62%). The synthesis of 3, previously reported [26], uses the Stille-type cross coupling [27]. It is little improved by substitution of 2-trimethylstannyl pyridine by the pyridylzinc reagent. After the deprotection of the precursor aldehyde, the two phosphaalkene substituents may be introduced following the method of Yoshifuji et al. [28] and previously described in the synthesis of 2,6-diphosphaalkene-pyridine [29]. As in this case, a mixture of two isomers (E-E and E-Z isomers) was obtained (see Fig. 1). Therefore, the aromatic region of the 1H NMR spectra shows a complicated pattern. On the other hand, the ratio of the isomers (86% for the E-E isomer) can be evaluated from the signal of the phosphorus atoms in the 31P{1H} NMR spectrum. The mass spectrum of 1 showed a molecular peak at m/z = 885, and the expected fragmentations also confirm the proposed structure.

The reaction (Fig. 2) of 1 with the transition metal precursors (Ru(tetapy)(acetone))2+ and Pd(C6H4CN)2Cl2 readily leads to the heterodinuclear complex 2 in high yield (80%). In view of the a priori numerous possibilities of reaction between the ditopic ligand 1 and the two inorganic fragments, the high preparative yield observed is indeed surprising.

The palladium precursor can react with the two different sites of coordination of 1 contrary to the ruthenium one. Actually, all attempts to introduce ruthenium into the diphosphaalkene-benzene moiety were unsuccessful. This difference of reactivity of the two terdentate sites towards ruthenium complexation can be exploited to prepare selectively some heterodinuclear complexes in two successive steps. The formulation of complex 2 was established by 1H, 31P{1H} NMR spectroscopy and by FAB-MS. The main peak at m/z = 1450 corresponds to the mass of the monocationic complex 2+ and has the appropriate isotopic pattern.

3.2. Electrochemical measurements

The electrochemical behaviour of 2 has been compared with those of the mononuclear palladium complex 7 and ruthenium complex 8 (Scheme 2).

The redox potentials of the complexes 2, 7 and 8 obtained by cyclic voltammetry in THF are reported in Table 1.
Each electrochemical reaction is consistent with single metal-based oxidation and ligand-based reduction. The redox couples show characteristic patterns for a reversible couple ($\Delta E_p$ close to 60 mV, $I_{pa} = I_{pc}$ and $I_p$ proportional to $E^{1/2}$). As previously reported [11], 7 shows a reversible reduction wave at $-1.23$ V. It is attributed to the addition of one electron in the $\pi$ antibonding orbital of the diphosphaalkene subunit, on the basis of the EPR spectrum of the reduced species. The redox couples of the ruthenium complex 8 indicate that the $\sigma$ donating properties of the deprotonated dipyridyl benzene strongly affects both the metal centre and the external terpyridine ligand. The stability of the Ru(III) state is illustrated by a drastic shift of potential (0.65 V) between 8 and the Ru(terpy)$_2^{2+}$ species. Otherwise, the terpyridine-centred reduction became more negative by at least 0.25 V as compared to the Ru(terpy)$_2^{2+}$ complex. The CV curve of the heterodinuclear complex 2 displays three redox couples directly attributable to Ru(II) oxidation (0.57 V), diphosphaalkene-benzene moiety reduction ($-1.22$ V) and terpyridine-centred reduction ($-1.48$ V) by comparison with the values of the isolated constituents 7 and 8. The main feature of this behaviour is the small effect of each of the organometallic parts on the other. This situation contrasts strongly with other homodinuclear complexes where a large influence is observed [19–21]. The neutral charge of the organo-palladium moiety is possibly one of the factors leading to a low interaction between the two subunits. Indeed, both electronic and electrostatic factors are much less predominant in this case. Another important parameter is the torsion angle around the interannular C–C bond. A torsion angle close to 90° leads to a negligible overlap between the $\pi$-electron clouds of the metallated rings.

3.3. Absorption and luminescence properties

In Table 2 are reported the $\lambda_{max}$ and $\epsilon_{max}$ values for the dinuclear complex 2 and related monomers 7 and 8.

The ruthenium complex 8 exhibits ligand-centred $\pi-\pi^*$ transitions in the UV region and broad metal-to-ligand charge transfer (MLCT) bands in the visible region. The palladium complex 7 shows also ligand-localised transitions at high energy. In the lower energy region ($\lambda > 330$ nm) a broad structureless absorption band can be assigned to a perturbed ligand-localised transition as already described in Pd(II) ortho-metallated complexes [30]. In addition, a broad band at 475 nm with a low extinction coefficient was assigned to a metal-centred transition. The spectrum of the heterodinuclear complex 2 is dominated by the $\pi-\pi^*$ transition and MLCT bands. In fact, the spectrum of 2 coincides almost with the sum of the spectra of the component subunits 7 and 8. On the basis of the spectroscopic and electrochemical data, we can again conclude that the ruthenium and palladium parts in 2 interact at most only slightly with each other.

The emission spectra of 2, 7 and 8 were recorded in degassed CH$_2$Cl$_2$ and CH$_3$CN solutions at room temperature. Generally, luminescence lifetimes of cyclometallated palladium complexes are very short in room-temperature fluid solution. We also did not observe any emission spectrum for complex 7. As previously reported, complex 8 displays a weak emission band centred at 785 nm ($\phi = 4.5 \times 10^{-5}$) due to the MLCT excited state [31]. This result can be interpreted as being caused by the $\sigma$-donating ability of the cyclometallating ligands. The emission spectrum of the heterodinuclear complex 2 exhibits a similar band to 8 ($\lambda_{max} = 800$ nm), but with a lower intensity (45% of the intensity of 8 in the same conditions). The decrease in intensity is slightly different in CH$_3$CN (30%). Considering the spectroscopic and redox properties of 2 in the frame of the localised orbital approach, an energy or electron transfer reaction cannot explain this phenomenon: (i) energy transfer is excluded by the lack of an accessible excited state of the palladium part; (ii) the electron transfer reaction towards the palladium subunit is
slightly endergonic (0.2 eV). More probably, we suppose that the palladium part acts as a tuner. Indeed, small perturbations of the energy levels of the ruthenium excited state may have important effects on the decay processes. Examples of this type of perturbation concerning Ru(II)–Pt(II) and Ru(II)–Pd(II) complexes have been already observed [32,33].

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