

Priority communication

Platinum bis-acetylide complexes with the 4,4'-dimethyl-2,2'-bipyridyl ligand

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Abstract

[Pt(Me₂bipy)Cl₂] (Me₂bipy = 4,4'-dimethyl-2,2'-bipyridine) and HC≡CC₆H₄-4-R react in the presence of diisopropylamine and CuI as catalyst to give the platinum bis-acetylides [Pt(Me₂bipy)(C≡CC₆H₄-4-R)₂] R = H, Me, NO₂. Initial spectroscopic, electrochemical and reactivity studies are presented. © 1997 Elsevier Science S.A.

1. Introduction

There is currently great interest in transition metal σ -acetylide complexes [1] and particularly in conjugated metal-containing polymers derived from them due to their non-linear optical properties [2], liquid crystallinity [3], electrical conductivity [4], photo-voltaic behaviour [5], and for the information which they may give about the photophysical processes occurring in light-emitting organic conjugated polymers [6]. The ancillary ligands in such metal-containing polymers are invariably phosphines, and this derives from the overwhelming proportion of mononuclear platinum group acetylides which are stabilised by phosphine ligands [1]. Alternatively, N-donor ligands are expected to impart strikingly different properties to both monomeric and polymeric systems, particularly with respect to their optical and redox behaviour [7] as well as their reactivity [8]. The need for more environmentally friendly materials also drives the search for alternative ligands to phosphines. We have therefore embarked upon the development of platinum group alkynyl chemistry with nitrogen donor ligands, and have found that stable complexes [Pt(Me₂bipy)(C≡CC₆H₄-4-R)₂] **1** (Me₂bipy = 4,4'-dimethyl-2,2'-bipyridine, R = Me (**a**), H (**b**), NO₂ (**c**)) may be readily prepared and isolated.

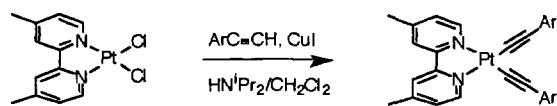
2. Results and discussion

Reaction of [Pt(Me₂bipy)Cl₂]¹ with three equivalents of HC≡CAr in CH₂Cl₂/HNⁱPr₂ in the presence of a copper iodide catalyst for 24 h gives the bis-alkynyl complexes [Pt(Me₂bipy)(C≡CAr)₂] (Ar = C₆H₄-4-Me

¹[Pt(Me₂bipy)Cl₂] was prepared by a procedure analogous to the literature preparation of [Pt(2,2'-bipyridine)Cl₂], see Ref. [9]. We employed Me₂bipy rather than the classical 2,2'-bipyridine (bipy) in order to increase the solubility of the complexes. Representative preparation and characterising data for **1a**: [Pt(Me₂bipy)Cl₂] (1.200 g, 2.67 mmol), *p*-tolylacetylene (928 mg, 8.00 mmol) and copper(I) iodide (25 mg, 0.13 mmol) were stirred together in a dry degassed mixture of CH₂Cl₂ (200 ml) and NHⁱPr₂ (30 ml) under a dinitrogen atmosphere for 24 h. The volatiles were removed in vacuo, the residue dissolved in the minimum amount of CH₂Cl₂ and passed through a 5 cm column of neutral alumina with CH₂Cl₂ as eluent. Evaporation of the solvent yielded **1a** as a bright yellow solid (1.255 g, 2.06 mmol, 77%). ¹H NMR (CD₂Cl₂, 250 MHz, δ ppm): 9.51 (d, ³J_{H⁶H⁵} = 5 Hz, ⁴J_{Pt-H⁶} = 40 Hz, 2H, H⁶), 7.91 (s, 2H, H³), 7.38 (d, ³J_{H⁵H⁶} = 5 Hz, 2H, H⁵), 7.29 and 7.09 (AA'BB', |J_{AB} + J_{AB'}| = 9 Hz, 8H, C₆H₄), 2.51 (s, 6H, (CH₃)₂bipy), 2.34 (s, 6H, C₆H₄). IR (CH₂Cl₂): ν (C≡C) = 2114, 2123 cm⁻¹. UV 396 nm (ϵ = 4863 mol⁻¹ cm⁻¹), 282 nm (ϵ = 23708 mol⁻¹ cm⁻¹). Positive ion FABMS shows a most intense cluster at *m/z* = 610 corresponding to [M+H]⁺. Anal. Found: C, 56.27; H, 4.09; N, 4.01. [C₃₀H₂₆N₂Pt]·1/2CH₂Cl₂ Calc.: C, 56.17; H, 4.14; N, 4.30%. The presence of half an equivalent of CH₂Cl₂ in the crystalline form was confirmed by ¹H NMR spectroscopy.

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1a, C₆H₅ **1b**, C₆H₄-4-NO₂ **1c**) which are isolated as bright yellow solids after flash column chromatography:

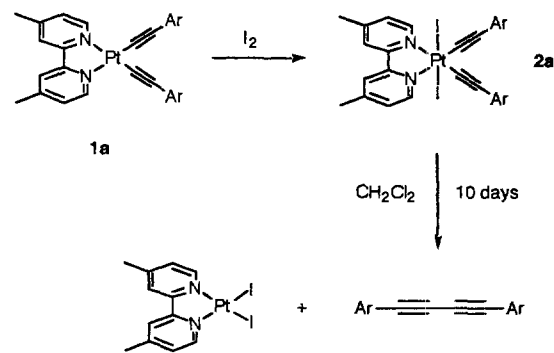


Ar = C₆H₄CH₃-4 **1a**, C₆H₅ **1b**, C₆H₄NO₂-4 **1c**

Complexes **1a–c** were characterised by a combination of ¹H NMR, IR, UV–vis and mass spectroscopy and elemental analysis. All data were in accord with the expected overall structure in which the platinum(II) centre is square planar with a bidentate Me₂bipy-*N,N'* ligand and two *cis* alkynyl ligands. ¹H NMR spectra suggest a mirror plane, which includes the platinum centre, orthogonal to the Me₂bipy ligand; IR spectra (CH₂Cl₂) show the expected symmetric and asymmetric stretches for the *cis* alkynyl triple bonds. ¹³C NMR spectra could not be obtained due to the low solubility of these complexes in common organic solvents.

The electronic spectrum of **1b** in dichloromethane solution is similar to that of [Pt(bipy)Cl₂] [10] and is dominated by two bands at λ_{max} = 396 nm (ε = 8200 mol⁻¹ cm⁻¹) and 287 nm (ε = 42500 mol⁻¹ cm⁻¹). We assign the absorption at 396 nm as a metal to ligand charge transfer (MLCT) band due to the Me₂bipy ligand and the band at 287 nm possibly to a second MLCT transition of the Me₂bipy ligand, as suggested for [Pt(bipy)Cl₂]. In complex **1b** both these bands undergo the expected solvatochromatic shifts for MLCT bands (i.e. to 386 and 282 nm respectively in acetonitrile). Two other bands which overlap with the 287 nm absorption are most likely due to π–π* transitions of the Me₂bipy and C≡CPh ligands (at 318 and 264 nm respectively). These absorptions do not undergo significant solvatochromic shifts. Any MLCT absorption due to the acetylide ligands (as observed in [Pt(L)₂(C≡CR)₂], L = phosphine) [11] is either absent or masked by absorptions due to the Me₂bipy ligand. Complex **1b** undergoes a fully reversible reduction at –1.84 V and a second irreversible reduction at –2.46 V vs. FeCp₂/FeCp₂⁺ as determined by cyclic voltammetry in dichloromethane solution. This behaviour is similar to that of [Pt(bipy)L₂]ⁿ⁺ (L = Ph, Cl, CN, n = 0; L = NH₃, pyridine, bipy, ethylenediamine, n = 2) [7] and is due to sequential one-electron reductions of the Me₂bipy ligand, i.e. the first reduction yields [Pt^{II}(Me₂bipy⁻)(C≡CPh)₂] rather than a d⁹ metal centre.

As a first investigation into the chemistry of these new complexes we have found that addition of diiodine to **1a** gives the oxidative addition product



Scheme 1. Ar = C₆H₄CH₃-4.

[Pt(Me₂bipy)(C≡CPh)₂(I)₂] **2a** in quantitative yield (see Scheme 1).²

There is an alternative geometry for **2a** to that in Scheme 1, in which the iodides are mutually *cis* and acetylides mutually *trans*, indeed the single IR C≡C stretching vibration supports this alternative geometry. However, the only previous platinum(IV) bis-acetylide complex that we are aware of possesses mutually *cis* acetylides and it too gives a single IR C≡C stretch [12]. We presume the actual geometry of **2a** is with mutually *cis* acetylides as this is consistent with the geometry of analogous dimethyl platinum(IV) complexes [Pt(NN')(Me)₂(I)₂] obtained on addition of I₂ to [Pt(NN')(Me)₂] [13]. Although stable for at least several weeks in the solid state, in solution complex **2a** slowly reductively eliminates 1,4-di-*p*-tolylbutadiyne CH₃C₆H₄C≡C–C≡CC₆H₄CH₃, with formation of the platinum diiodide [Pt(Me₂bipy)(I)₂]. The two products were identified by comparison of their ¹H NMR spectra with those of authentic samples. The reductive elimination takes 10 days to go to completion in CD₂Cl₂ solution at room temperature.

Despite their atypical nature (lack of phosphine ligands) the Me₂bipy platinum alkynyl complexes **1a–c** appear to be indefinitely stable at room temperature in air as solids. Aerated solutions in CD₂Cl₂ remain unchanged over seven days (as monitored by ¹H NMR spectroscopy). As mentioned above, alkynyl platinum complexes not containing phosphine ligands are unusual. To our knowledge the only previous examples

² Preparation and characterising data for **2a**: to a stirred solution of complex **1a** (120 mg, 0.197 mmol) in CH₂Cl₂ (10 ml) was added a solution of diiodine (50 mg, 0.197 mmol) in CH₂Cl₂ (3 ml) over 1 min. After 10 min the solvent was removed in vacuo to leave a brown solid **2a** in quantitative yield. ¹H NMR (CD₂Cl₂, 400 MHz, δ ppm): 9.45 (d, ³J_{H⁶H⁵} = 6 Hz, ⁴J_{Pt–H⁶} = 24 Hz, 2H, H⁶), 8.10 (s, 2H, H³), 7.58 (d, ³J_{H⁵H⁶} = 6 Hz, 2H, H⁵), 7.38 and 7.16 (AA'BB', |J_{AB} + J_{A'B'}| = 8 Hz, 8H, C₆H₄), 2.71 (s, 6H, (CH₃)₂bipy), 2.41 (s, 6H, C₆H₄). IR (CH₂Cl₂): ν(C≡C) = 2158 cm⁻¹. Anal. Found: C, 42.18; H, 3.09; N, 3.74. C₃₀H₂₆I₂N₂Pt Calc.: C, 41.73; H, 3.03; N, 3.24%.

which are not stabilised by phosphines are the complexes $[\text{Pt}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-CH}_3\text{C}_6\text{H}_4$) [14], platinates $[\text{Pt}(\text{X})_2(\text{C}\equiv\text{CR})_2]^{2-}$ ($\text{X} = \text{C}\equiv\text{CR}$, C_5F_5) [15] and complexes $[\text{Pt}(\text{COD})(\text{C}\equiv\text{CR})_2]$ ($\text{R} = \text{Ph}$, $\text{C}_6\text{H}_4\text{-4-}^t\text{Bu}$, $\text{C}_6\text{H}_4\text{-4-Me}$; $\text{COD} = 1,5\text{-cyclooctadiene}$) [16].

Acknowledgements

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