Note

Insertion reaction of dimethylacetylenedicarboxylate with the head-to-tail isomer of $Pt_2I_2(\mu\text{-}Ppy_3)_2$; Ppy_3 = tris(2-pyridyl)phosphine

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Abstract

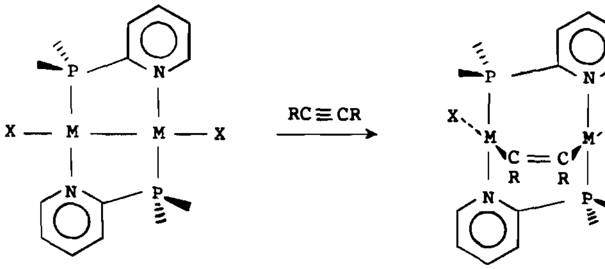
The head-to-tail (*HT*) isomer of $Pt_2I_2(\mu\text{-}Ppy_3)_2$ (**3**), where py = 2-pyridyl, is made by reaction of NaI with the chloro analogue (**2**), which it itself synthesized via a conproportionation reaction of a Pt(0) complex and *cis*-$PtCl_2(\mu\text{-}Ppy_3)_2$ (**1**). Complex **1** is formed by reacting appropriate Pt(II) precursors with Ppy_3. Dimethylacetylenedicarboxylate (DMAD) inserts into the Pt–Pt bond of **3** to give the A-frame species *HT*-$Pt_2I_2(\mu\text{-}Ppy_3)_2(\mu\text{-DMAD})$ (**4**); the reaction is kinetically first-order in both [**3**] and [DMAD], and the activation parameters ($\Delta H^{\neq} = 38$ kJ mol^{-1}, $\Delta S^{\neq} = -138$ J mol^{-1} K^{-1}) are consistent with a concerted process involving a four-centre transition state. Complexes **1–4** are characterized by elemental analyses and $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy.

Key words: Insertion reaction; Platinum complexes; Alkyne complexes; Dinuclear complexes

Introduction

As part of a general program investigating metal-complex catalyzed hydration of unsaturated organics, we have studied in detail the synthesis and characterization of square-planar complexes of the type $MX_2(PPh_{3-n}py_n)_2$ and the binuclear species $M_2X_2(\mu\text{-}PPh_{3-n}py_n)_2$ (M = Pd, Pt; X = halides; py = 2-pyridyl; n = 1–3) [1, 2]. All of the dinuclear species exist in the head-to-tail, *HT* form (implying the two phosphorus atoms are bound to different metals), while the $Pt_2I_2(\mu\text{-}PPh_{3-n}py_n)_2$ species have been isolated also as the head-to-head, *HH* form [1, 2].

We have previously reported on the reaction of *HT*-$Pd_2X_2(PPh_{3-n}py_n)_2$ species** with dimethylacetylenedicarboxylate (DMAD) to form the A-frame insertion product, a *cis*-dimetallated olefin species, eqn. (1); crystallographic and NMR data confirm the retention of the *HT* geometry for the M = Pd, X = Cl, n = 3 system [1].



(1)

We report here on the reaction of *HT*-$Pt_2I_2(Ppy_3)_2$ with DMAD, which is described by eqn. (1), including the kinetic aspects. There are relatively few kinetic data available generally on oxidative addition to binuclear metal complexes and, to our knowledge, none on DMAD reactions.

Experimental

The materials used, synthetic procedures for the ligands and complexes, and instrumentation used for $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra and UV–Vis spectra, have been largely described elsewhere [1, 3]. An external reference of 85% H_3PO_4 is used for reporting $^{31}P\{^1H\}$ shifts, while the $^{195}P\{^1H\}$ shifts are referenced to the absolute frequency of ^{195}Pt [3]. DMAD (Aldrich) used in the kinetic experiments was distilled under reduced pressure before use.

cis-$PtCl_2(Ppy_3)_2$ (**1**) was obtained by reacting a yellow CH_2Cl_2 solution (50 ml) of *cis*-$PtCl_2(PhCN)_2$ [4] (1.0 g, 3.76 mmol) with a colourless solution of 2.0 equiv. of Ppy_3 in CH_2Cl_2 (5 ml) at room temperature (r.t.) for 1 h; the resulting colourless solution was concentrated to 15 ml and Et_2O (20 ml) then added to precipitate **1** as a white solid (yield 90%). *Anal.* Calc. for $C_{30}H_{24}N_6Cl_6P_2Pt$: C, 45.23; H, 3.04; N, 10.55. Found:

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**Abbreviations used: py = 2-pyridyl; the $PPh_{3-n}py_n$ (n = 1–3) ligands in the dinuclear species are always bridging, but for convenience the μ-symbol is omitted; DMAD = dimethylacetylenedicarboxylate; dba = dibenzylideneacetone; COD = 1,5-cyclooctadiene; dpm = bis(diphenylphosphino)methane.

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C, 45.46; H, 2.94; N, 10.51%. $^{31}P\{^1H\}$NMR (CD_2Cl_2, −70 °C): δ 20.0, ^1J(PtP) 3910 Hz.

HT-$Pt_2Cl_2(Ppy_3)_2$ (**2**) was obtained by adding dropwise a purple $CHCl_3$ solution (60 ml) of $Pt(dba)_2$ [5] (0.25 g, 0.38 mmol) to a $CHCl_3$ solution (40 ml) of **1** (0.36 g, 0.38 mmol), and then refluxing the mixture under N_2 for 5 h. The solvent was removed completely on a Rotovap, and the crude product mixture redissolved in CH_2Cl_2; the solution was charged onto a silica gel column and eluted with 2% MeOH in CH_2Cl_2. The reddish-orange eluate following the yellow dba band was collected and evaporated to give an orange solid; the product was recrystallized from CH_2Cl_2/Et_2O (1:1) and dried *in vacuo* (yield 55%). *Anal.* Calc. for $C_{30}H_{24}N_6Cl_2P_2Pt_2$: C, 36.34; H, 2.44; N, 8.48. Found: C, 36.46; H, 2.50; N, 8.39%. $^{31}P\{^1H\}$ NMR($CDCl_3$, r.t.): δ 0.66, ^1J(PtP) 4074, ^2J(PtP)214, ^3J(PP) 18.2 Hz.

HT-$Pt_2I_2(PPy_3)_2$ (**3**) was made by reacting a CH_2Cl_2 solution (20 ml) of **2** (0.2 g, 0.2 mmol) with a five-fold excess of NaI dissolved in a minimum amount of water; MeOH (5 ml) was introduced to homogenize the mixture, which was stirred at r.t. for 1 h. The solution was concentrated to ~8 ml and the precipitated orange product was collected. washed extensively with H_2O and MeOH, and dried *in vacuo* (yield 95%). *Anal.* Calc. for $C_{30}H_{24}N_6I_2P_2Pt_2$: C, 30.67; H, 2.06; N, 7.15. Found: C, 30.69; H, 2.14; N, 6.96%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ −3.09, ^1J(PtP) 3936, ^2J(PtP) 205, ^3J(PP) 18.9 Hz. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, r.t.): δ −197.3, ^1J(PtP) 3901, ^2J(PtP) 207 Hz.

HT-$Pt_2I_2(\mu$-DMAD$)(Ppy_3)_2$ (**4**) was made by adding DMAD (0.2 ml, 1.6 mmol) to a 20 ml CH_2Cl_2 solution of **3** (0.1 g, 0.1 mmol) and stirring the solution for 15 min when the solution had turned from orange to yellow. The volume was reduced to ~3 ml; the orange solid that deposited was collected, and washed with Et_2O (3 × 10 ml) to remove excess DMAD. The product was dried at 80 °C *in vacuo* (yield 95%). *Anal.* Calc. for $C_{36}H_{30}N_6I_2O_4P_2Pt_2$: C, 32.84; H, 2.30; N, 6.38. Found: C, 32.80; H, 2.14; N, 6.16%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.); δ 8.37, ^1J(PtP) 4455, ^3J(PtP) 272 Hz. $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, r.t.): $\delta = 293.2$ doublet, ^1J(PtP) 4453 Hz.

Kinetic experiments for the conversion of $\mathbf{3} \rightarrow \mathbf{4}$ were conducted in an optical cell fitted with a side-flask [6]. In CH_2Cl_2, **3** exhibited absorption maxima at 403 nm ($\epsilon = 5.04 \times 10^3\ M^{-1}\ cm^{-1}$), while **4** showed a continuum (see Fig. 2 below). Absorbance readings at 518 nm or spectral changes from 360 to 600 nm were recorded as a function of time. Solutions of **3** were transferred from a stock solution and placed in the cell; neat DMAD was added via a syringe to the side-flask. Concentration ranges used were $(1.45\text{–}12.0) \times 10^{-4}$ M for **3** and $(0.81\text{–}4.54) \times 10^{-2}$ M for DMAD; thus, pseudo-first-order conditions were maintained for reactions, and standard log $(A_t - A_\infty)$ versus time plots gave excellent linearity from which the pseudo-first-order rate constants k_{obs} were evaluated (A_t and A_∞ are the absorbances at time t and 'infinity', respectively; the latter was known from the spectrum of **4**, and was also attained experimentally at the end of the kinetic run). Activation parameters were obtained from the Eyring plot of $\ln(k/T)$ versus $(T)^{-1}$.

Results and discussion

The *cis*-$PtCl_2(Ppy_3)_2$ complex (**1**) is readily made from *cis*-$PtCl_2(PhCN)_2$; *cis*-$PtCl_2$(COD) [7] can also be used as precursor [2, 8]. The magnitude of the ^{195}Pt–^{31}P coupling constant diagnoses the *cis*-geometry of **1**; the *cis*-^1J(PtP) values for $PtX_2(PR_3)_2$ complexes (typically 3600–4000 Hz) are ~1.5 larger than the corresponding *trans*-coupling [9]. Balch and co-workers [8] have reported previously on *cis*-$PtCl_2(PPh_2py)_2$ and *cis*- and *trans*-$PtI_2(PPh_2py)_2$. The Pt(I) chloro, dinuclear bridged complex **2** was synthesized via the conproportionation reaction of Pt(0) and the Pt(II) precursor **1**, a well established procedure for such species [2, 8] and the Pt(I) analogues [1]. The iodide analogue **3** was prepared by methathesis of **2** using NaI. That **2** and **3** are the *HT* isomers is demonstrated by the $^{31}P\{^1H\}$ data, which are exemplified in Fig. 1(a) for **3**: the major central peak A arises from the unlabelled isotopomer (Pt–Pt

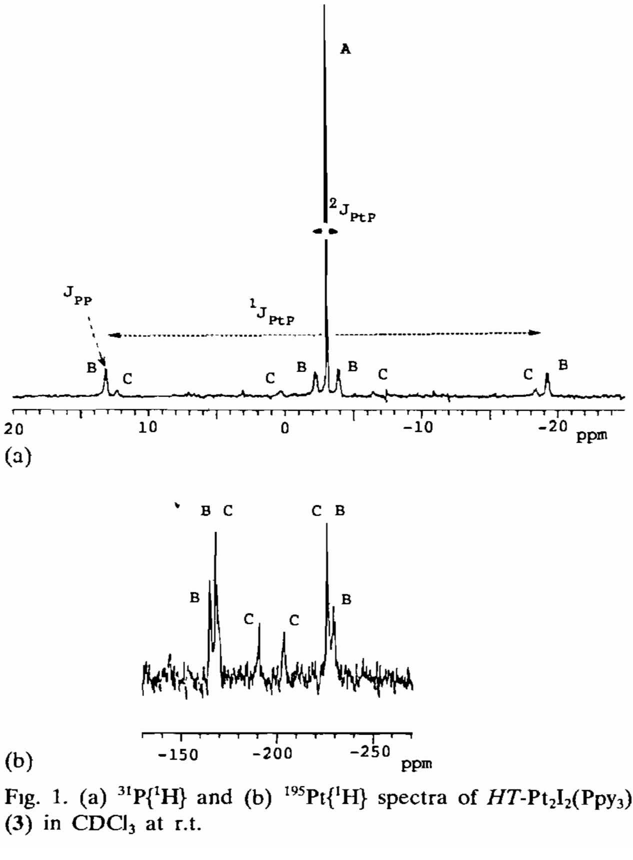

Fig. 1. (a) $^{31}P\{^1H\}$ and (b) $^{195}Pt\{^1H\}$ spectra of *HT*-$Pt_2I_2(Ppy_3)_2$ (**3**) in $CDCl_3$ at r.t.

species); the doublet of doublets (B) comes from the singly spin-labelled ^{195}Pt isotopomer (Pt*–Pt); and the signals labelled C arise from the doubly labelled isotopomer (Pt*–Pt*). The *HH* isomers show quite a different NMR pattern [2, 8]. Such assignments have been discussed in detail by Balch and co-workers [8]. The *HT* configuration for **3** is confirmed by the ^{195}Pt{^{1}H} NMR data (Fig. 1(b)), which show a 'doublet of doublets' arising from the B signals for the (Pt*–Pt) species and the C signals for the (Pt*–Pt*) species; the C lines actually arise from a second order AA'XX' spin system, but the poor signal/noise ratio obtained does not allow for such an analysis. Corresponding NMR data are obtained for a structurally characterized *HT*-$Pt_2Cl_2(PPhpy_2)_2$ complex, made via a similar route to that described for **2**, but using instead the $PPhpy_2$ ligand [2]. The distinction between *HT* and *HH* isomers is readily made via the multiplicity in the ^{195}Pt spectrum [2, 8].

An intuitively more obvious route to **3** might appear to be reaction of *cis*-$PtI_2(Ppy_3)_2$ species with $Pt(dba)_2$ in the conproportionation reaction. However, although the *cis*-diiodo complex has been made (via reaction of **1** with NaI [2]), the conproportionation reaction yields a mixture of the *HH* and *HT* isomers of $Pt_2I_2(Ppy_3)_2$, which requires a separation procedure to isolate **3** [2].

Complex **3** reacts readily with DMAD to give the expected, A-frame, insertion product **4**, which is isolated analytically pure. The NMR data are analogous to those shown in Fig. 1, although *J*(PP) was not resolved in the ^{31}P and only the main doublet was seen in the ^{195}Pt spectra**. Nevertheless, the data show that the *HT* configuration is maintained during the insertion reaction. Thus the reaction is a simple addition of an acetylene across the Pt–Pt bond, eqn. (1).

The reaction was monitored spectrophotometrically in CH_2Cl_2 (Fig. 2). The orange solution of **3** fades with time to generate a yellow solution of **4**, and the observed isosbestic point at 474 nm reveals a well-behaved system. Rates were followed by observing the decreasing absorption at 413 or 518 nm. The pseudo-first-order rate constants, k_{obs}, obtained from the linear semi-log plots (Fig. 3) were strictly first-order in [DMAD] (Fig. 3, inset); the bimolecular rate constant k (defined by rate $=k$[**3**][DMAD]) was readily determined over the temperature range 13–34 °C (at a specific temperature, k was obtained from the slope of a k_{obs} versus [DMAD] plot for a minimum of two values of [DMAD]). The k values at 13 °C (4.54×10^{-2} M^{-1} s^{-1}), 18 °C (6.19×10^{-2}), 21 °C (8.11×10^{-2}), 25 °C (9.00×10^{-2}), 29 °C (11.7×10^{-2}) and 34 °C (14.4×10^{-2}) yield a linear Eyring plot and the activation parameters $\Delta H^{\ne}=38\pm1$ kJ mol^{-1} and $\Delta S^{\ne}=-138\pm3$ J mol^{-1} K^{-1}.

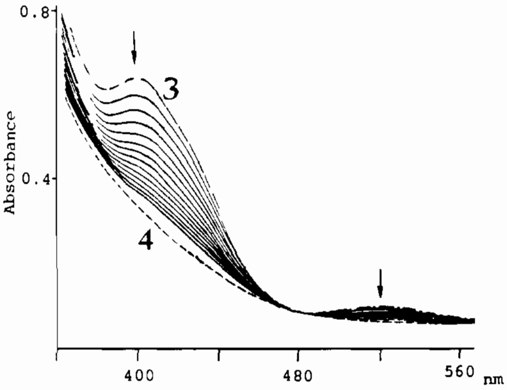

Fig. 2. Spectral changes for conversion of **3**→**4** at 21 °C in CH_2Cl_2, reaction (1). The spectrum labelled **3** was taken at $t=0$, and that labelled **4** is that of the product; the spectra in between were recorded every 3 min. [**3**] $=1.45\times10^{-4}$ M, [DMAD] $=0.81\times10^{-2}$ M.

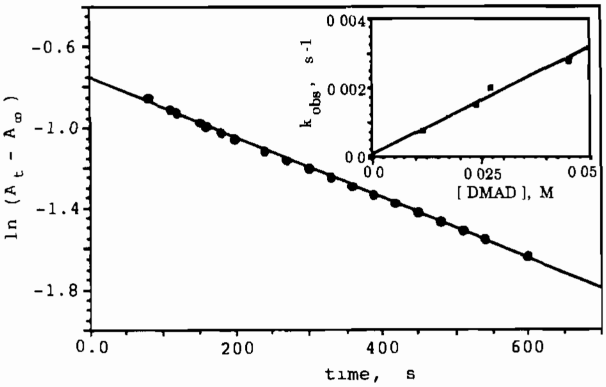

Fig. 3. Pseudo-first-order rate plot, $\ln(A_t-A_\infty)$ vs. t (data at 518 nm) for conversion of **3**→**4** at 18 °C in CH_2Cl_2; [**3**] $=1.18\times10^{-3}$ M, [DMAD] $=2.39\times10^{-2}$ M. Inset shows the observed first-order rate constants vs. [DMAD].

The activation parameters found for the net oxidative addition step are, in fact, typical of data for oxidative addition at a single metal centre, which has been reported upon extensively in the literature [10], but to our knowledge not for an acetylene substrate. The DMAD reaction involves formally a $Pt^{I}_{2}\rightarrow Pt^{II}_{2}$ system, in which the Pt–Pt bond is broken, but the electronic promotional energy [11] is now only for a single electron at each Pt centre and will be less than that required for 2e oxidative addition at one comparable metal centre; the other factors contributing to $\Delta H^{\ne}$, in what is pictured as a concerted addition within a four-centre transition state, are the incipient formation of two Pt–C bonds and incipient conversion of a carbon–carbon triple bond

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The methylpropiolate derivative of **3, formed *in situ*, contains two chemically inequivalent P atoms and these again are seen as two singlets (with Pt satellites) in the ^{31}P{^{1}H} (δ 12.24, ^1J(PtP) 4620, ^3J(PtP) 279 Hz; δ 10.12, ^1J(PtP) 4584, ^3J(PtP) 242 Hz) with unresolved PP coupling.

to a double bond. It may turn out that the activation parameters for the oxidative addition process for the same molecule at one or two metal centres are similar. Some data for oxidative addition of MeI to one or two iridium centres support such a generality [12]. The activation parameters for the DMAD reaction are quite similar to those for the analogous reaction of CO with $Pd_2Br_2(\mu\text{-dpm})_2$ to give, with cleavage of the metal–metal bond, the A-frame insertion product $Pd_2Br_2(\mu\text{-dpm})_2(\mu\text{-CO})$ ($\Delta H^{\neq} = 15$ kJ, $\Delta S^{\neq} = -121$ J K^{-1}, in dimethylacetamide solution [13]). The reaction of H_2S with the same Pd_2^I species in CH_2Cl_2 is again governed by comparable activation parameters ($\Delta H^{\neq} = 55$ kJ mol^{-1}, $\Delta S^{\neq} = -115$ J mol^{-1} K^{-1} [6]; the nature of the rate-determining step is not so well defined in this case, but the reaction involves oxidative addition of H_2S across the Pd–Pd bond. The significantly negative $\Delta S^{\neq}$ values for all three reactions are consistent with the pictured bimolecular processes, and the required 'lining-up' of the DMAD molecule parallel to the Pt–Pt bond might be expected to be less favourable entropically (more negative $\Delta S^{\neq}$) than the formation of the transition states involving the smaller gas molecules.

Further work on the reactions of DMAD with the *HT*- or *HH*-$Pt_2I_2(PPh_{3-n}py_n)$ species has been completed [2] and will appear in future publications; more complex systems result because the $PPhpy_2$ species exist as diastereomers [1], and some of the *HH* species form an *HH*-DMAD derivative that subsequently isomerizes to the *HT* form.

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