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AN UNUSUAL OXIDATION/METALLATION OF 2-VINYLPYRIDINE

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Summary

The vinyl group in *trans*-$[\text{PtBr}_4\{2\text{-}(\text{CH}_2{=}\text{CH})\text{py}\}(\text{PEt}_3)]$ undergoes oxidation/metallation in damp solvents to give $[\overline{\text{PtBr}_3\{2\text{-}(\text{CH}}_2\cdot\text{CO})\text{py}\}(\text{PEt}_3)]$; the mechanism of this reaction is discussed. Attempts to prepare this unusual complex from platinum(II) and platinum(IV) complexes containing 2-acetylpyridine were unsuccessful.

Introduction

We have previously shown that cleavage of the halogen-bridged compound $[\text{Rh}_2\text{X}_6(\text{PBu}_3)_4]$ (X = Cl, Br) with 2-vinylpyridine results in metallation of the alkenyl group with formation of $[\overline{\text{Rh}\{2\text{-}(\text{CH}}{=}\text{CH})\text{py}\}(\text{PBu}_3)_2\text{X}_2]$ in high yield [1]. A recent report [2] of an unusual oxidation/metallation promoted by ruthenium prompts us to report on products resulting from cleavage of $[\text{Pt}_2\text{Br}_8(\text{PEt}_3)_2]$ with 2-vinylpyridine.

Results and discussion

The halo-bridged complex $[\text{Pt}_2\text{Br}_8(\text{PEt}_3)_2]$ (I), which is obtained by bromination of $[\text{Pt}_2\text{Br}_4(\text{PEt}_3)_2]$ (II) [3], reacts with 2-vinylpyridine in sodium-dried benzene to give *trans*-$[\text{PtBr}_4\{2\text{-}(\text{CH}_2{=}\text{CH})\text{py}\}(\text{PEt}_3)]$ (III) together with a little *trans*-$[\text{PtBr}_2\{2\text{-}(\text{CH}_2{=}\text{CH})\text{py}\}(\text{PEt}_3)]$ (IV). The latter complex, IV, has been shown to be the same as that produced on cleavage of II with 2-vinylpyridine. Analytical and spectroscopic data on III and IV support these formulations (see Tables 1 and 2) and Raman spectra are consistent with a *trans*-configuration (ν(Pt—Br), (III) = 191, 206 cm^{-1}; (IV) = 208 cm^{-1}).

Recrystallation of III from damp solvents (benzene, acetone, methanol) gives $[\overline{\text{PtBr}_3\{2\text{-}(\text{CH}}_2\cdot\text{CO})\text{py}\}(\text{PEt}_3)]$ (V) as yellow crystals in high yield. The formulation of V is based on ^{1}H NMR spectra at 60 and 100 MHz which show, in addition to resonances due to the pyridine ring and triethylphosphine, 2 equivalent

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR Pt(II) and Pt(IV) complexes

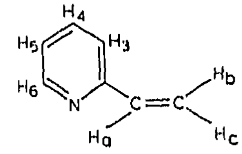
Complex	Analysis. Found (calcd.) (%)				Colour	M.p. (°C)
	C	H	N	Br		
trans-$[PtBr_2\{2\text{-}(CH_2{=}CH)py\}(PEt_3)]$	26.9(27.0)	4.0(3.8)	2.3(2.4)	27.3(27.65)	yellow	131
trans-$[PtBr_4\{2\text{-}(CH_2{=}CH)py\}(PEt_3)]$	21.2(21.2)	3.3(3.0)	1.5(1.9)		red	148–152
$[\overline{PtBr_3\{2\text{-}(C}H_2\cdot CO)py\}(PEt_3)]$	23.9(23.7)	3.2(3.2)	2.0(2.1)	36.0(36.5)	yellow	215–218
trans-$[PtBr_2\{2\text{-}(CH_3\cdot CO)py\}(PEt_3)]$	26.4(26.3)	3.8(3.7)	2.3(2.4)		yellow	207–208
trans-$[PtBr_4\{2\text{-}CH_3\cdot CO)py\}(PEt_3)]$	20.7(20.7)	2.6(2.9)	1.7(1.9)	42.3(42.4)	orange	133–136
trans-$[PtBr_4\{2\text{-}(CHMe{=}CH)py\}(PEt_3)]$	21.9(22.3)	3.0(3.2)	1.6(1.9)	42.9(42.5)	red	151–3

TABLE 2

SPECTROSCOPIC DATA

Complex	δ_P[a]	$^1J(Pt\text{-}P)$	δ_H[b] (ppm)					J (Hz)
			H_6	H_5	H_4	H_3	Others	
trans-$[PtBr_2\{2\text{-}(CH_2{=}CH)py\}(PEt_3)]$[c]	−3.4	3314	9.0	7.7	7.25	7.7	H_a 8.15, H_b 5.9, H_c 8.15	^3Jab 18.0, ^3Jac 10.4, ^2Jbc < 1
trans-$[PtBr_2\{2\text{-}(CH_3\cdot CO)py\}(PEt_3)]$[e]	−1.05	3405	9.1	7.9	7.5	7.8	Me 3.3(5), 2.7(1)[d]	
trans-$[PtBr_4(py)(PEt_3)]$	9.1	2060						
trans-$[PtBr_4\{2\text{-}(CH_2{=}CH)py\}(PEt_3)]$[c]	15.2	2125	9.2	7.9	8.55	8.1	H_a 7.4, H_b 6.6, H_c 6.1	^3Jab 0.0, ^2Jac 6.0, ^2Jbc < 1
trans-$[\overline{PtBr_3\{2\text{-}(C}H_2\cdot CO)py\}(PEt_3)]$[f]	6.55	2402	10.0	8.0	7.8	8.0	CH_2 4.3	$^2J(Pt\text{-}CH_2)$ 56.0

[a] In ppm from external H_3PO_4; positive values are downfield (higher frequency). [b] In ppm from internal TMS. [c]



[d] Figures in parentheses indicate relative concentrations. [e] $\nu(CO)$ 1968 cm^{-1}. [f] $\nu(CO)$ 1695 cm^{-1}.

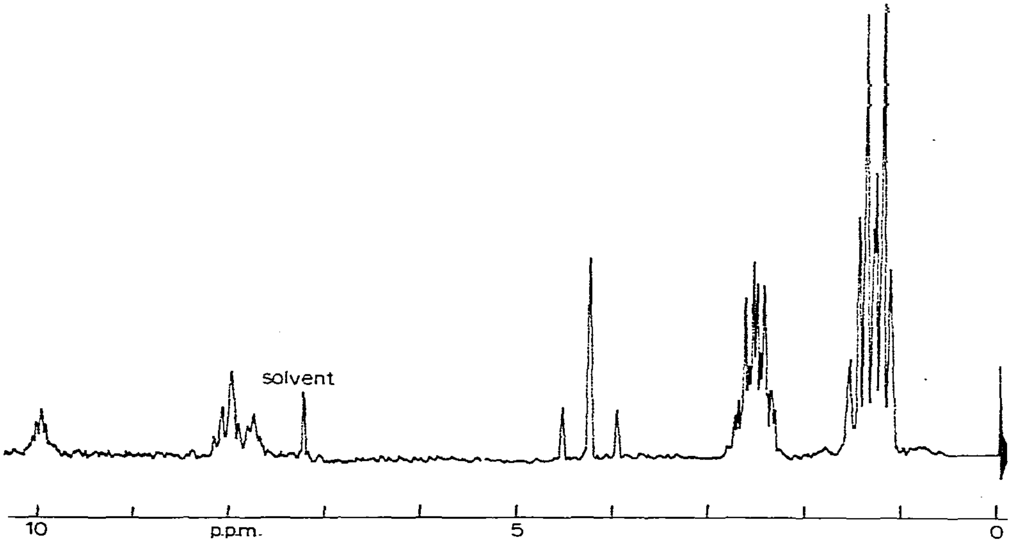
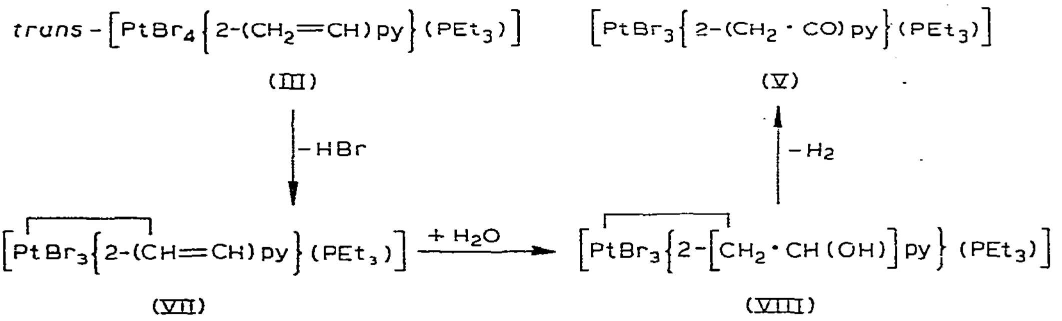


Fig. 1. 100 MHz ^{1}H NMR spectrum of $[\overline{\mathrm{PtBr_3\{2\text{-}(CH_2}}\cdot\mathrm{CO)py}\}(\mathrm{PEt_3})]$ in $CDCl_3$ solution.

protons (4.3 ppm) which are coupled to platinum only, see Fig. 1; ^{31}P NMR data are also consistent with a Pt(IV) oxidation state [4] and there is a strong band due to ν(CO) in the infrared spectrum at 1695 cm^{-1}. Furthermore the relative intensities of the observed peaks due to the parent ion in the mass spectrum agree very well with the simulated spectrum using the isotopic abundances of the constituent elements.

We have previously shown that neither *trans*-$[\mathrm{PtBr_2\{2\text{-}(CH_2Br\cdot CHBr)py\}(PEt_3)}]$ nor $[\overline{\mathrm{PtBr_3\{2\text{-}(CH_2}}\cdot\mathrm{CHBr)py}\}(\mathrm{PEt_3})]$ react with water [5] and thus can be discounted as possible intermediates in the formation of V. We have also shown that platinum(II) and platinum(IV) complexes containing 2-acetylpyridine do not give rise to V. Thus, *trans*-$[\mathrm{PtBr_4\{2\text{-}(CH_3\cdot CO)py\}(PEt_3)}]$ (VI) could be recovered unchanged after heating in toluene for 18 h and bromination of *trans*-$[\mathrm{PtBr_2\{2\text{-}(CH_3\cdot CO)py\}(PEt_3)}]$ in benzene gave VI. As a result, we propose that the following series of reactions occur during the conversion of III to V:



The formation of VII, which unfortunately has not yet been isolated, is analogous to the metallation of 2-vinylpyridine by rhodium(III) [1]: VII undergoes hydration via electrophilic addition to give VIII which then loses hydrogen to give V. It is difficult to predict whether or not Markownikov addition will occur in these and related systems [6] and the thermodynamic stability of V, in which the carbonyl group is conjugated with the pyridine, may well be the deciding factor. The novel elimination of hydrogen in the final step, which may occur for the same reason, will also relieve steric crowding.

Finally it should be noted that complexes containing 2-(CHMe=CH)py do not undergo oxidation/metallation. Thus *trans*-$[PtBr_4\{2\text{-}(CHMe{=}CH)py\}(PEt_3)]$, which contained an equal mixture of *cis*- and *trans*-alkenyl groups, could be recovered almost quantitatively on recrystallisation from damp acetone. The *trans*-alkene would be expected to undergo metallation more easily than the *cis*-isomer but obviously changes in steric and/or electronic effects, caused by introduction of a methyl group into the alkenyl grouping, are very important in controlling the above sequence of reactions.

Experimental

^1H NMR spectra were measured on Perkin—Elmer R10 and JEOL PS-100 spectrometers. ^{31}P NMR spectra were measured at 40.48 MHz using a JEOL PS-100 spectrometer and Fourier transform pulse methods with random noise decoupling of the protons. IR spectra (4000—400 cm^{-1}) were obtained using a Perkin—Elmer 457 instrument and Raman spectra were obtained on solid samples using a Coderg spectrometer with an OIP 181B Helium/Neon laser emitting 180 mW at 6328 Å. Mass spectra were recorded on an AEI MS 902 spectrometer at 70 eV and computer simulations of mass spectra were carried out as described previously [7]. Microanalyses were carried out by Mr. G. Powell in the University of Kent Microanalytical Laboratory.

2-Vinylpyridine was obtained from Rielly Tar and Chemical Corporation and was always fractionally distilled immediately prior to use. 2-(CHMe=CH)py was obtained via the Wittig reaction [8].

Preparation of $[Pt_2Br_8(PEt_3)_2]$

Slow addition of bromine (2 mol) in benzene to a solution of $[Pt_2Br_4(PEt_3)_2]$ (1 mol) in benzene resulted in the immediate precipitation of the desired complex as brown-red crystals. M.p. 164—5°C (Found: C, 11.4; H, 2.7; Br, 50.8. $C_{12}H_{30}Br_8P_2Pt_2$ calcd.: C, 11.4; H, 2.4; Br, 50.5%).

Preparation of trans-$[PtBr_4L(PEt_3)]$ ($L = 2\text{-}(CH_2{=}CH)py$, $2\text{-}(CHMe{=}CH)py$, $2\text{-}(CH_3 \cdot CO)py$)

The same procedure was used for the preparation of all these complexes and only the preparation when $L = 2\text{-}(CH_2{=}CH)py$ is described in detail. 2-Vinylpyridine (0.148 g) was added to a suspension of $[Pt_2Br_8(PEt_3)_2]$ (0.866 g) in sodium-dried benzene (250 ml). After shaking for 10 min all the solid had dissolved. The solution was set aside for 1 h. Concentrating the red solution gave red crystals of the product, which was recrystallised from dry benzene/pet. ether (B.p. 60—80°C). Further concentration of the original filtrate gave yellow crystals of *trans*-$[PtBr_2\{CH_2{=}CH)py\}(PEt_3)]$ which was more conveniently prepared by reaction of $2\text{-}(CH_2{=}CH)py$ with $[Pt_2Br_4(PEt_3)_2]$ in acetone solution.

Preparation of trans-$[PtBr_4(py)(PEt_3)]$

Addition of pyridine (0.053 g) in acetone (10 ml) to a solution of $[Pt_2Br_4(PEt_3)_2]$ (0.315 g) in acetone (50 ml) resulted in an immediate reaction. Concentrating the resulting pale yellow solution gave yellow crystals of *trans*-$[PtBr_2(py)(PEt_3)]$, m.p. 117°C. Dissolution of this complex (0.28 g) in benzene (50 ml) followed by addition of bromine (0.083 g) in benzene (25 ml) and standing overnight gave bright red crystals of the complex on concentration. Recrystallisation was effected from benzene/pet. ether (b.p. 60—80°C). M.p. 202°C, Raman ν(Pt—Br) 210, 193 cm^{-1} (Found: C, 18.0; H, 2.9; N, 1.9. $C_{11}H_{20}Br_4NPPt$ calcd.: C, 18.5; H, 2.8; N, 2.0%).

Preparation of $[\overline{PtBr_3\{2\text{-}(CH_2}\cdot CO)py\}(PEt_3)]$ *(V)*

Recrystallisation of *trans*-$[PtBr_4[2\text{-}(CH_2{=}CH)py\}(PEt_3)]$ from solvents (benzene, acetone, methanol), which had not previously been dried, gave almost quantitative conversion to yellow crystals of V which is a non-conductor in nitromethane solution.

Preparation of trans-$[PtBr_2\{2\text{-}(CH_3CO)py\}(PEt_3)]$

This preparation was carried out as described above for the preparation of *trans*-$[PtBr_2(py)(PEt_3)]$ and the two inequivalent Me resonances (Table 2) are probably due to conformational isomerism involving the acetyl group.

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