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Metal–Olefin Complexes.
Some Palladium(II) and Platinum(II) Complexes of Bis(3-dimethylarsinopropyl)but-3-enylarsine.
Four- and Five-coordinated Complexes Containing Coordinated and Uncoordinated Olefinic Groups

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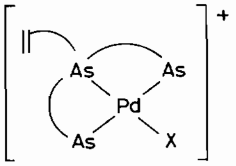
Abstract

The triarsine-olefin ligand, bis(3-dimethylarsinopropyl)but-3-enylarsine (tasol), reacts with palladium(II) and platinum(II) salts to form the complexes MX_2(tasol) (M = Pd, Pt; X = Cl, Br, I). The complexes are pentacoordinate in the solid state, the palladium(II) derivatives having an X_2As_3 donor set (X = Cl, Br, I) and the platinum(II) species having an XAs_3ol donor set (X = Cl, Br). The pentacoordinate [PtI_2(tasol)] has an I_2As_3 donor set. All the complexes are planar 1:1 electrolytes in solution, $[MX(tasol)]^+$, and have a XAs_3 donor set. The factors governing the structure of the complexes and the tendency for the olefinic group to be coordinated are discussed.

Introduction

There has been interest in mixed group 5B-olefin multidentate ligands for some time [1–6], and we have reported our studies of the reaction of tris(but-3-enyl)arsine with palladium(II) and platinum(II) salts. This potentially quadridentate ligand forms PdX_2L (X = Cl, I) and PtX_2L (X = Cl, Br, I, SCN) complexes [5]. The $PdCl_2L$ and PtX_2L (X = Cl, Br) are *cis*-planar and, as well as containing an arsine donor also contain a coordinated olefinic group in rapid equilibrium with uncoordinated olefins. The PdI_2L and PtX_2L (X = I, SCN) are halogeno- or pseudohalogeno-bridged dimers and contain only monodentate arsine-donor ligands [5].

We have also investigated the coordination chemistry of the structurally similar triarsine-olefin ligand bis(3-dimethylarsinopropyl)but-3-enylarsine, tasol. We have already reported that this ligand forms cationic trigonal bipyramidal $[NiX(tasol)]^+$ complexes which represent a rare example of nickel(II)–olefin coordination [6]. We here report the extension of these studies to the complexes formed between palladium(II) and platinum(II) with tasol.



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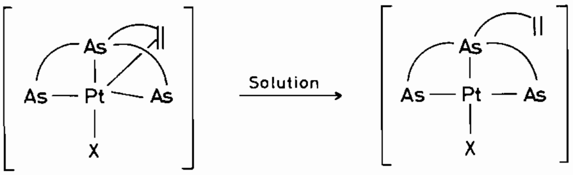

II III

Results and Discussion

Palladium(II) Complexes

Addition of tasol to an ethanolic solution of PdX_4^{2-} (X = Cl, Br, I) yielded the PdX_2(tasol) complexes, Table I. Only intractable red oils were formed in analogous attempts to prepare $Pd(NCS)_2$(tasol). The complexes are only slightly soluble in polar organic solvents. Fresh solutions in nitromethane and 1,2-dichloroethane indicate conductivities intermediate between non-electrolytes and 1:1 conductors, Table I.

The electronic spectra are reported in Table II, from which it can be seen that there are substantial

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TABLE I. Physical Properties and Analytical Data for the Complexes.

Complex	Colour	Analysis			Λ_M[b]
		%C[a]	%H[a]	%Hal[a]	
$PdCl_2$(tasol)	Orange	27.6(27.9)	4.7(5.2)	11.6(11.8)	8
$PdBr_2$(tasol)	Orange–red	23.9(24.4)	4.4(4.5)	23.5(23.2)	8
PdI_2(tasol)	Purple–brown	21.4(21.4)	4.5(4.1)		6
[PdCl(tasol)] BPh_4	Pale yellow	50.7(51.5)	6.2(5.8)		19
[Pd(SCN)(tasol)] BPh_4	Yellow–orange	50.7(51.3)	5.6(5.7)		19
$PtCl_2$(tasol)	Yellow–orange	24.1(24.4)	4.4(4.5)	10.5(10.3)	19
$PtBr_2$(tasol)	Orange	21.1(21.5)	3.9(4.0)		18
PtI_2(tasol)	Deep purple	19.8(19.3)	4.1(3.6)	28.6(29.1)	16

[a] Found (Calculated). [b] Conductivity of a 10^{-3} *M* solution in 1,2-dichloroethane.

TABLE II. Significant Infrared Absorptions/cm^{-1}.[a]

	Free tasol	$PdCl_2$-(tasol)	$PdBr_2$-(tasol)	PdI_2-(tasol)	[Pd(SCN)-(tasol)] BPh_4	$PtCl_2$-(tasol)	$PtBr_2$-(tasol)	PtI_2-(tasol)	$PtCl_2$-(tasol)[b]
$\nu(=CH_2)$	3075(m)				3080(sh)				
	3055(m)	3050(w)		3050(w)	3058(s)	3050(w)	3050(vw)	3060(w)	3050(m)
	3020(sh)		3010(sh)		3030(s)	3005(sh)	3005(w)		3020(sh)
$\nu(CN)$					2130(vs)				
$\omega(=CH_2)$ overtone	1820(w)					1950(w)	1950(w)		
$\nu(C=C) + \delta(C-H)$	1638(m)	1638(w)			1635(w)			1640(w)	1640(w)
$\omega(=CH_2)$	920(sh)	915(s)	905(s)	905(s)	905(s)	905(m)	905(s)	910(m)	920(s)
	910(w)								

[a] In Nujol mulls. [b] In 1,2-dichloroethane.

TABLE III. Electronic Spectral Data for the Metal Complexes.

Complex	E_{max} (ϵ_{max})/kK[a]	E_{max}/kK[b]
$PdCl_2$(tasol)		24.4
		27.35
	35.5(5800)	
	42.2(18500)	
$PdBr_2$(tasol)		23.75
		26.5
	28.8(1430)	
	37.7(sh)(8500)	
	42.0(18100)	
PdI_2(tasol)		20.0
		21.5(sh)
		23.6
		27.3
	27.7(sh)(5550)	
	36.1(sh)(12600)	
	41.2(22100)	
[PdCl(tasol)] BPh_4		c
	34.7(5700)	
	42.0(16500)	
[Pd(SCN)(tasol)] BPh_4		28.2
	28.6(2500)	
	37.5(sh)(12000)	
	41.8(15100)	
$PtCl_2$(tasol)		20.0(sh)
	34.6(1725)	23.8
	37.0(6700)	
	41.4(16300)	
$PtBr_2$(tasol)		19.5(sh)
		22.9
	32.4(1690)	
	38.5(18350)	
PtI_2(tasol)		16.0(sh)
		20.1
	28.1(1280)	
	33.7(1500)	
	39.8(17200)	

[a] In 1,2-dichloroethane. [b] Solid reflectance. [c] No absorption bands observed.

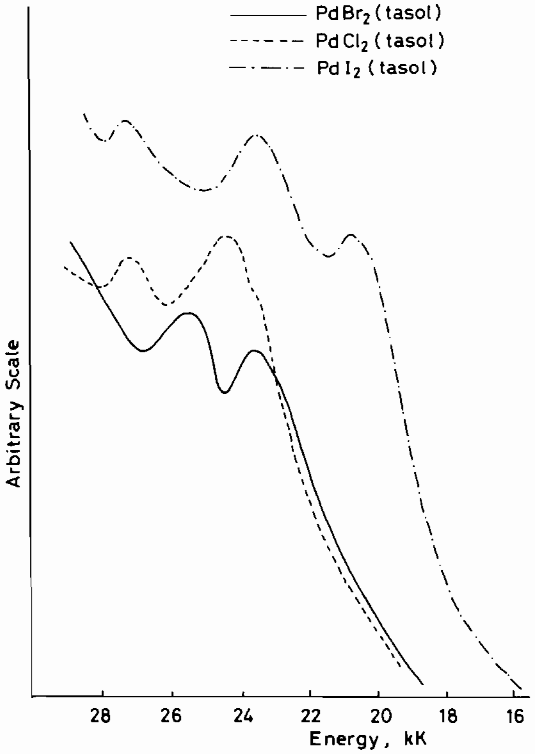

Fig. 1. Electronic spectra of the PdX$_2$(tasol) complexes.

differences between the solution spectra in dichloroethane and the solid reflectance spectra in the 22–30 kK region. The solution spectra are typical of planar palladium(II) species, but the presence of strong resolved bands below 26 kK in the solid state, Fig.1, is evidence of pentacoordination [7]. These results mirror the behavior of the triarsine, TAS, [TAS = PhAs(o-$C_6H_4AsPh_2)_2$], where, for example, PdI$_2$(TAS) is pentacoordinate, [PdI$_2$(TAS)], in the solid state, but is planar, [PdI(TAS)]I, in solution [8].

The mull infrared spectra are reported in Table III and, where solution spectra could be obtained, they were essentially similar. The spectra are consistent with free olefin groups. The failure of tasol to promote olefin coordination in palladium(II) reflects both the low affinity of olefins for palladium(II) in a cationic complex and the relatively low occurrence of pentacoordination in palladium(II) chemistry, *i.e.* both these factors militating against the formation of pentacoordinate [PdXAs$_3$ol]$^+$ and for planar [PdXAs$_3$]X in solution, (*I*). However, the situation of pentacoordination *versus* planar geometry is borderline since in the solid state [PdX$_2$As$_3$] complexes exist.

In an attempt to force olefin coordination the [PdX(tasol)]BPh$_4$ (X = Cl, SCN) complexes were synthesised. The molar conductance in 1,2-dichloroethane are consistent with the presence of 1:1 electrolytes.

The electronic spectra, Table II, are consistent with planar coordination in both the solid state and in dichloroethane solution. There is no evidence for palladium(II)–olefin coordination in the infrared spectra, Table III, and so these complexes are assigned the planar [PdXAs$_3$]$^+$ coordination environment, (*I*).

The mull infrared spectrum of [Pd(SCN)(tasol)]BPh$_4$ exhibits a single strong sharp ν(CN) absorption at 2130 cm^{-1}. This is good evidence for a Pd–SCN linkage [9], and is somewhat surprising in a complex which contains three soft arsenic donors. Both ligand and tetraphenylborate absorptions in the 700–850 cm^{-1} region precluded assignment of the ν(C–S) vibration.

Very low solubility precluded ^{1}H NMR studies on the PdX$_2$(tasol) and [PdX(tasol)]BPh$_4$ complexes.

Platinum(II) Complexes

The addition of tasol to a suspension of PtX$_4$$^{2-}$ in ethanol, followed by reflux and then by filtration led, after the addition of isopropanol, to the isolation of the PtX$_2$(tasol) (X = Cl, Br, I) complexes. As with the palladium(II) system, no solid Pt(SCN)$_2$(tasol) complex could be isolated. Although the complexes were generally insoluble, it was possible to obtain conductance measurements in 1,2-dichloroethane, in which the complexes exhibited behaviour indicative of 1:1 electrolytes, Table I.

The electronic spectra are reported in Table II, from which it will be seen that, like the PdX$_2$(tasol) species, the profiles of the solid state spectra are considerably changed upon dissolution in dichloroethane. The solution spectra are indicative of planar species and this, taken together with the conductivity data, suggest planar [PtX(tasol)]X species. The reflectance spectra exhibit absorption bands, Fig. 2, below 25 kK, suggesting pentacoordination.

Before discussing the infrared spectra it is worthwhile reviewing infrared criteria for metal–olefin bonding. In addition to the widely accepted shift to lower energy of the 'ν(C=C)' upon coordination, Nyholm has pointed to weak bands *ca.* 1500 cm^{-1} and at 1265–1280 cm^{-1} as evidence of metal-bonded olefinic groups [3], while Venanzi has observed that the weak overtone *ca.* 1850 cm^{-1} in free olefinic groups moves to higher frequency, 1900–2000 cm^{-1}, upon coordination [10].

The medium sharp ν(C=C) band in the spectrum of the free ligand at 1638 cm^{-1} is absent from the mull spectrum of [PtCl(tasol)]Cl, but is present in the solution spectrum in dichloroethane. Indeed the dichloromethane solution spectrum of [PtCl(tasol)]Cl is closely similar to that of free tasol, Table III. This suggests a [PtClAs$_3$]$^+$ coordination environment in solution. The presence of coordinated olefin in the solid state is suggested by a weak broad absorption at 1950 cm^{-1} and, in addition,

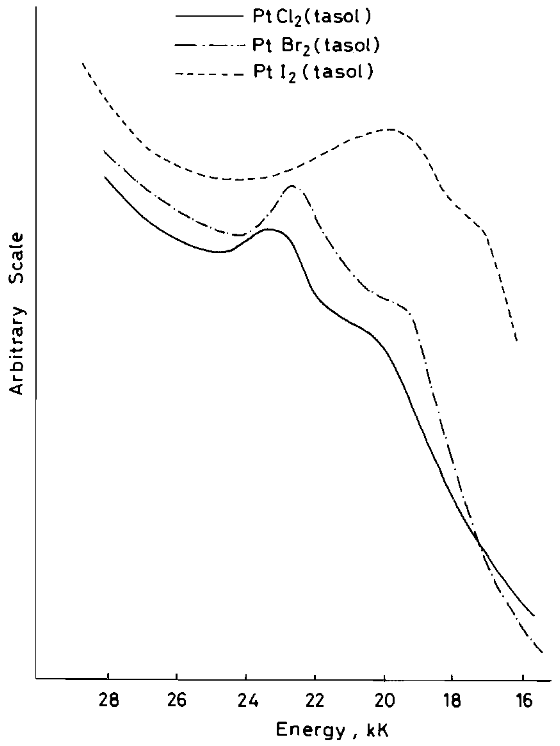

Fig. 2. Electronic spectra of the PtX_2(tasol) complexes.

a weak band at 388 cm^{-1}, assignable to $\nu(Pt-C_2)$. The presence of coordinated-$AsMe_2$ groups precludes the diagnostic use of the 1250–1280 cm^{-1} region. In addition bands at 300 and 265 cm^{-1} are assigned to ν(Pt–Cl) and ν(Pt–As), respectively. The solid state complex thus has a pentacoordinate $[PtClAs_3ol]^+$ coordination environment. The solid state electronic spectrum of [PtCl(tasol)] Cl is similar in profile to that of $[PtCl(QAS)]^+$ (QAS = $(o\text{-}C_6H_4\text{-}AsPh_2)_3As$) [11], which has a $[PtClAs_4]^+$ donor set. However, the bands in the latter complex are at slightly higher energy than those in [PtCl(tasol)] Cl, in keeping with the stronger donor strength expected for an arsine group in place of an olefinic group. The evidence thus points to $[PtCl(tasol)]^+$ having a trigonal bipyramidal structure, (*II*). The lability of the platinum olefin bond is indicated by the conversion to the planar complex (*III*) in solution.

The infrared and electronic spectra of $PtBr_2$(tasol) are broadly similar to that of $PtCl_2$(tasol) and this complex is thus assigned a trigonal bipyramidal $[PtBrAs_3ol]^+$ environment in the solid state and a planar $[PtBrAs_3]^+$ environment in solution.

The PtI_2(tasol) complex is extremely interesting. The mull infrared spectrum is very similar to that of the free ligand, yet the electronic reflectance spectrum strongly suggests pentacoordination. We thus assign a pentacoordinate $[Pt_2I_2As_3]$ environment in the solid state and a planar $[PtIAs_3]^+$ moiety in solution.

Conclusion

The triarsine-olefin ligand tasol reacts with d^8 metal ions as MX_2 to give (a) trigonal bipyramidal $[NiX(tasol)]^+$ (M = Ni, X = Cl, Br) complexes which contain coordinated olefin in the solid state and in solution and square pyramidal $[NiI_2(tasol)]$ which does not contain a nickel–olefin bond [6], (b) pentacoordinate $[PdX_2(tasol)]$, containing the X_2As_3 donor set, in the solid state, and planar $[PdX(tasol)]^+$, containing the XAs_3 donor set; the $[PdX(tasol)]BPh_4$ (X = Cl, SCN) contains the planar XAs_3 donor set in the solid state and in solution, and (c) the trigonal bipyramidal complexes $[PtX(tasol)]^+$ (X = Cl, Br) which contain the XAs_3ol donor set in the solid state but which form the planar $[PtX(tasol)]^+$ containing the XAs_3 donor set in solution, and the pentacoordinate $[PtI_2(tasol)]^+$, containing the IAs_3 donor set.

This study thus shows that there are several interplaying factors determining the structures and donor sets in the complexes, *viz.* (i) the trigonal symmetry of the tasol ligand, (ii) the tendency of these d^8 metal ions to adopt planar rather than pentacoordinate geometry Ni < Pd < Pt, (iii) the expected tendency of these metal ions to promote metal–olefin coordination, Ni < Pd < Pt, (iv) the competition between the halide ion and olefin for coordination to the metal.

We can thus conclude that the tendency for the ligand to promote a trigonal bipyramidal geometry and the known ease with which Ni^{2+} adopts this geometry overcomes the lack of affinity that a $3d^8$ metal ion in the +2 oxidation state might be expected to have for an olefin group; this is no doubt helped by the 'soft' arsine donors coordinated to the nickel(II) ion which will modify its relative 'hard' nature. However, since both $[NiI_2(tasol)]$ and $[PtI_2(tasol)]$ do not contain metal–olefin bonds, then the known tendency for halides to displace olefins coordinated to a metal, $I^- \gg Br^- > Cl^-$ [5, 12] is seen to exert a strong influence here.

The decreasing tendency for palladium(II) to either coordinate olefins or be pentacoordinate are mutually reinforced to produce planar Pd_2(tasol) which do not contain coordinated olefins. However, the stronger affinity for olefins expected of platinum(II) does produce trigonal bipyramidal pentacoordinate $[PtX(tasol)]^+$ (X = Cl, Br) in the solid state, but once again the olefin group is displaced by iodide in the $[PtI_2(tasol)]$ complex.

Experimental

Preparation of $PdCl_2$(tasol)

Sodium chloropalladite (0.5 g, 1.7 mmol) was dissolved in gently refluxing ethanol (20 cm^3) under nitrogen. The ligand tasol (0.72 g, 1.7 mmol) in ethanol (10 cm^3) was added to the stirred solution over five minutes. The solution rapidly changed colour from deep red to yellow and a colourless solid began to precipitate. The solution was refluxed for a further thirty minutes and then evaporated to dryness. The solid residue was leached with dichloromethane and the sodium salts removed by filtration. Concentration of the solution and the careful addition of isopropanol precipitated a yellow–orange solid in a yield of 0.72 g; 70%. The orange solid was recrystallised with difficulty from iso-propanol; the complex is rather hygroscopic and was stored in a dessicator.

Preparation of PdX_2 (tasol) (X = Br, I)

These complexes were prepared by the addition of a molar excess of the appropriate sodium halide to a solution of sodium chloropalladite in ethanol prior to the addition of the ligand. The complexes were isolated in a similar fashion to the chloride above. All attempts to isolate a thiocyanato-complex proved successful. Addition of the ligand to a solution of the $Pd(SCN)_4^{2-}$ ion gave a bright red solution. Work-up of this solution gave only red oils.

Preparation of $[PdX(tasol)]BPh_4$ (X = Cl and SCN)

These complexes were prepared by the addition of an ethanolic solution of sodium tetraphenylborate to a solution of the appropriate PdX_2(tasol) species in ethanol in a 1:1 molar ratio. The resulting solution was evaporated to dryness, leached with dichloromethane and the sodium salts removed by filtration. Evaporation to small bulk and careful addition of iso-propanol precipitated the complexes.

Preparation of PtX_2(tasol) (X = Cl, Br and I)

These complexes were prepared from sodium chloroplatinite in the same way as the analogous palladium complexes. The relevant physical data is given below:

Complex	*Solvent. recryst.*	*Yield*
$PtCl_2$(tasol)	CH_2Cl_2/iso-PrOH	55%
$PtBr_2$(tasol)	ethanol	60%
PtI_2(tasol)	insoluble	75%

The iodo-complex precipitated from the reaction mixture on cooling and no suitable solvent for recrystallisation could be found. As in the palladium series, no thiocyanato-complex could be isolated. *Physical measurements* were obtained as previously described [13].

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