

### Preliminary communication

## ALLYLPLATINUM COMPLEXES: SYNTHESIS FROM BIS(CYCLO-OCTA-1,5-DIENE)PLATINUM AND THEIR DYNAMIC BEHAVIOUR IN SOLUTION

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### Summary

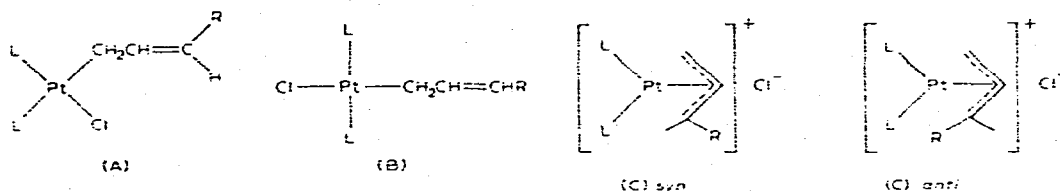
Allyl halides oxidatively add to  $[\text{Pt}(\text{cod})_2]$  to afford monomeric  $\eta^1$ -allyl complexes  $[\text{PtX}(\text{CH}_2\text{CR}^1=\text{CHR}^2)(\text{cod})]$  ( $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{H}$ , Me or Ph, X = Cl or Br;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{H}$ , X = Cl or Br;  $\text{R}^1 = \text{Cl}$ ,  $\text{R}^2 = \text{H}$ , X = Cl), which on treatment with  $\text{AgBF}_4$  yield  $\eta^3$ -allyl compounds  $[\text{Pt}(\text{CH}_2\text{CR}^1\text{CHR}^2)(\text{cod})]\text{BF}_4$ . The cyclo-octa-1,5-diene ligands are readily replaced by tertiary phosphines, phosphites, arsines, stibines, pyridine, or isocyanides. The dynamic behaviour of the  $\eta^1$ - and  $\eta^3$ -allyl species is discussed.

Whereas bis(cyclo-octa-1,5-diene)nickel reacts with allyl halides to give dimeric complexes  $[\text{Ni}(\mu\text{-X})(\eta^3\text{-allyl})_2]$  [1], we find that the platinum analogue  $[\text{Pt}(\text{cod})_2]$  [2] readily affords mononuclear  $\eta^1$ -allyl compounds  $[\text{PtX}(\text{CH}_2\text{CR}^1=\text{CHR}^2)(\text{cod})]$  ( $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{H}$ , Me or Ph, X = Cl or Br;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{H}$ , X = Cl or Br;  $\text{R}^1 = \text{Cl}$ ,  $\text{R}^2 = \text{H}$ , X = Cl). Treatment of these platinum species with silver tetrafluoroborate yields the corresponding tetrafluoroborate salts  $[\text{Pt}(\eta^3\text{-CH}_2\text{CR}^1\text{CHR}^2)(\text{cod})]\text{BF}_4$ . The cyclo-octa-1,5-diene ligand is readily replaced in both the neutral and ionic compounds by ligands L =  $\text{Ph}_3\text{P}$ ,  $\text{Cy}_3\text{P}$ ,  $(\text{MeO})_3\text{P}$ ,  $\text{Ph}_3\text{As}$ ,  $\text{Ph}_3\text{Sb}$ , py or t-BuNC. These new syntheses thus provide a general route to allylplatinum complexes via  $[\text{Pt}(\text{cod})_2]$ .

The dynamic behaviour of allylplatinum complexes [3, 4] has been of considerable interest in relation to the nature of the species present in solution. The presence of  $\eta^1$ -allyl groups in the compounds  $[\text{PtX}(\text{CH}_2\text{CR}^1=\text{CHR}^2)(\text{cod})]$  is indicated by the appearance in their infrared spectra of a band ( $\sim 1620 \text{ cm}^{-1}$ ) characteristic of a C=C group, while the chloro-species show Pt—Cl stretches at  $\sim 320 \text{ cm}^{-1}$ . The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of  $[\text{PtX}(\text{CH}_2\text{CH}=\text{CHR}^2)(\text{cod})]$  ( $\text{R}^2 = \text{Me}$  or Ph) are in accord with the presence of a non-fluxional  $\eta^1$ -allyl group. All the other  $\eta^1$ -allyl complexes, however, show dynamic behaviour at room temperature. The observed equivalence of the signals due to the cod group in both the  $^{13}\text{C}$  and  $^1\text{H}$  spectra of the fluxional complexes suggests that exchange of the ends

of the allyl moieties occurs via halide dissociation, formation of an  $\eta^3$ -allyl intermediate, followed by subsequent nucleophilic attack on the metal by halide from either side of the  $\pi$ -allyl group with concomitant re-formation of a  $\sigma$ -allyl species.

The allyl groups in the cations  $[\text{Pt}(\eta^3\text{-CH}_2\text{CR}^1\text{CHR}^2)(\text{cod})]^+$  ( $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{H}$ ,  $\text{Me}$  or  $\text{Ph}$ ,  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{H}$ ) are also fluxional, the protons undergoing *syn*, *anti* exchange at room temperature. This is in contrast to the species  $[\text{Pt}(\eta^3\text{-allyl})\text{L}_2]^+$  ( $\text{L} = \text{R}_3\text{P}$  or diars) which are non-fluxional when  $\text{X} = \text{BF}_4^-$ ,  $\text{ClO}_4^-$  or  $\text{PF}_6^-$ , but undergo a *syn*, *anti* exchange of the allyl substituents when  $\text{X} = \text{halide}$  [5]. This latter behaviour has been interpreted as involving a four co-ordinate square planar  $\eta^1$ -allyl non-ionic intermediate A of *cis*-stereochemistry [4].



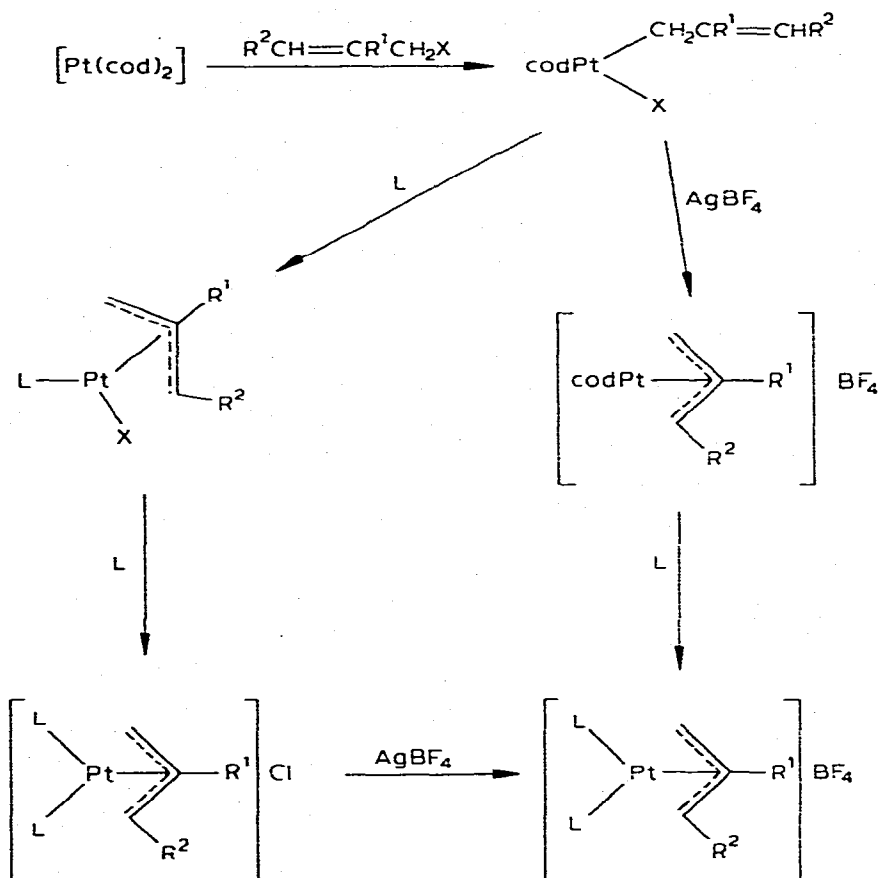
We have synthesised (see Scheme 1) complexes  $[\text{PtX}(\text{CH}_2\text{CHCHR}^2)\text{L}_2]$  ( $\text{L}_2 = \text{diphos}$ ,  $\text{R}^2 = \text{H}$  or  $\text{Me}$  and  $\text{X} = \text{Cl}$  or  $\text{BF}_4^-$ ;  $\text{L} = \text{PPh}_3$ ,  $\text{R}^2 = \text{H}$  or  $\text{Ph}$  and  $\text{X} = \text{Cl}$ ;  $\text{L} = \text{PPh}_3$ ,  $\text{R}^2 = \text{Me}$ ,  $\text{X} = \text{Cl}$  or  $\text{BF}_4^-$ ), and studied their  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra. The  $^{31}\text{P}$  spectra of the bis(diphenylphosphino)ethane chloro-complexes (Table 1) reveal, by comparison with the corresponding borofluoride salts, the presence of both cationic  $\eta^3$ -allyl species and neutral  $\eta^1$ -allyl complexes A. While the presence of the neutral complex  $[\text{PtCl}(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)(\text{diphos})]$  is only just detectable, the crotyl complex consists of  $\sim 75\%$  of the isomer  $[\text{PtCl}(\eta^1\text{-CH}_2\text{CH}=\text{CHMe})(\text{diphos})]$  at  $-80^\circ\text{C}$ , strongly indicative of exchange through this intermediate.

The  $^{31}\text{P}$  spectrum of  $[\text{PtCl}(\text{CH}_2\text{CHCHPh})(\text{Ph}_3\text{P})_2]$  shows the presence of two species. By comparison with the spectra of the diphos complexes, the weaker

TABLE 1  
 $^{31}\text{P}$  NMR DATA FOR  $[\text{PtCl}(\text{CH}_2\text{CHCHR}^2)\text{L}_2]$  COMPLEXES<sup>a</sup>

$\text{L}_2$	R	X	Isomer <sup>b</sup>	Chemical shifts and coupling constants
diphos	Me	$\text{BF}_4^-$	C( <i>syn</i> )	48.44 ( <i>J</i> (PtP), 3685; <i>J</i> (PP) 9), 46.53 ( <i>J</i> (PtP), 3781; <i>J</i> (PP), 9)
			C( <i>anti</i> )	47.03 ( <i>J</i> (PtP), 3655; <i>J</i> (PP), 6) <sup>c</sup>
diphos	Me	Cl	C( <i>syn</i> )	48.55 ( <i>J</i> (PtP), 3679), 46.74 ( <i>J</i> (PtP), 3784)
			A	44.30 ( <i>J</i> (PtP), 4398), 41.92 ( <i>J</i> (PtP), 1758)
diphos	H	Cl	C	47.46 ( <i>J</i> (PtP), 3696)
			A	43.54 ( <i>J</i> (PtP), 4341), 45.25 ( <i>J</i> (PtP), 1823)
diphos	H	$\text{BF}_4^-$	C	47.46 ( <i>J</i> (PtP), 3702)
2Ph <sub>3</sub> P	Ph	Cl	B	28.01 ( <i>J</i> (PtP), 3284)
			A	22.30 ( <i>J</i> (PtP), 2538; <i>J</i> (PP), 13), 18.86 ( <i>J</i> (PtP), 4490; <i>J</i> (PP), 13)
2Ph <sub>3</sub> P	H	Cl	C	15.92 ( <i>J</i> (PtP), 3933)
			B <sup>d</sup>	27.92 ( <i>J</i> (PtP), 3218)

<sup>a</sup> Measured at  $-80^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$  solution unless otherwise indicated. Shifts (ppm) are relative to  $\text{H}_2\text{PO}_4^-$ , with coupling constants in Hz. <sup>b</sup> See text. <sup>c</sup> Other  $^{31}\text{P}$  resonance not observed due to overlapping with signals of *syn* isomer. <sup>d</sup> Observed in toluene/benzene- $d_6$ .



SCHEME 1. Synthesis of allylplatinum complexes from  $[\text{Pt}(\text{cod})_2]$ .

signals at 22.30 and 18.86 ppm may be assigned to an isomer of type A. The remaining band cannot be due to an isomer C since it is a unique signal and because  $J(^{195}\text{Pt}-\text{P})$  is too small for an  $\eta^3$ -allyl system. This resonance must, therefore be due to a *trans* isomer B. Moreover,  $^{13}\text{C}$  studies ( $-80^\circ\text{C}$ ,  $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$  solutions) confirmed the presence of a second  $\eta^1$ -allyl species with  $J(\text{PtC})$  604 Hz for the carbon atom bonded to platinum. Studies on  $[\text{PtCl}(\text{CH}_2\text{CHCHMe})(\text{Ph}_3\text{P})_2]$  revealed that although the cationic complex (isomer C) is the dominant species in solution, comparison of the  $^{31}\text{P}$  spectrum with that of  $[\text{PtCl}(\text{CH}_2\text{CHCHPh})(\text{Ph}_3\text{P})_2]$  indicates that both isomers A and B may be present.

These results show that not only do *cis*-isomers A play a part in *syn-anti* exchange [4], but also that *trans* isomers B are involved in the equilibria. Indeed, in view of the increasing number of four co-ordinate platinum(II)  $\eta^1$ -allyl species known [6, 7] dynamic behaviour in solution may involve the two  $\eta^1$  neutral isomers with a cationic  $\eta^3$ -allyl species as intermediate. The latter may be the dominant isomer in certain solvents, in the solid state, or for steric reasons. This

is supported by the isolation of isomers B and C for  $[\text{Pt}(\text{CH}_2\text{CHCHR}^2)(\text{Ph}_3\text{P})_2\text{Cl}]$  ( $\text{R}^2 = \text{H}$  or  $\text{Me}$ ) [4, 8], and the isomerisation of  $[\text{Pt}(\text{CH}_2\text{CHCH}_2)(\text{Ph}_3\text{P})_2\text{Cl}]$  from structure C ( $\text{CH}_2\text{Cl}_2$  solution) to structure B ( $\text{C}_6\text{H}_5\text{Me}/\text{C}_6\text{D}_6$ ) (Table 1).

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