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Preliminary Communication

Organometallic phosphazenes: synthesis and characterization of Pt(II) and Pt(0) cinnammonitrile cyclophosphazene derivatives ☆

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Abstract

Hexakis(4-formylphenoxy)cyclophosphazene has been reacted with (cyanomethylene)triphenylphosphorane to yield the hexakis(4-cinnammonitrile phenoxy)cyclophosphazene compound. The cinnammonitrile moieties have been used to bind six $\{(PPh_3)_2Pt\}$ fragments on the olefin groups, six *trans*-$\{Pt(PPh_3)_2(CF_3)\}$ to the nitrile groups and both Pt(0) and Pt(II) groups to yield compounds **2**, **3** and **4**, respectively.

Keywords: Organometallic phosphazenes; Cinnammonitrile; Cyclophosphazene; Platinum derivatives

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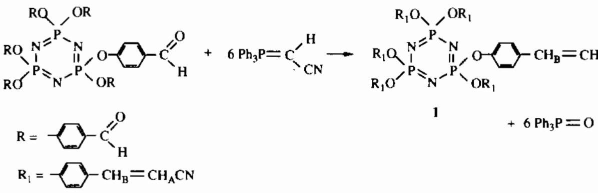
1. Introduction

Phosphazene chemistry, which lies at the interface between inorganic and organic chemistry, comprises of rings, short-chain linear phosphazenes and high molecular weight polymers. The synthesis of organometallic phosphazenes, i.e. macromolecule–metal complexes, connects polymer and metal-complex chemistries and represents an attractive field of research in order to obtain materials with potential catalytic activity, conductive and/or semiconductive properties, biochemical effects and so on [1].

The easy dissolution of phosphazenes in usual organic solvents transforms the 'microheterogeneous' regions formed by multifunctional metal–phosphazene complexes into homogeneous microreactors, which may exhibit new catalytic properties.

As for transition metals, they can be attached to cyclic or polymeric phosphazenes using four different strategies: (i) use of the electron–donor properties of the skeletal nitrogen atoms of phosphazenes [1,2]; (ii) through ionic linkages between protonated phosphazenes and metal anions [1,3]; (iii) direct covalent binding between a transition metal and a skeletal phosphorous atom [1,4]; (iv) binding through a side group attached to a skeletal phosphorous atom [1,5].

Recently, we have developed an innovative strategy for grafting vinyl-like polymers onto polyorganophosphazenes based on the introduction of olefinic moieties into phosphazene substrates by a Wittig reaction [6]. In particular, by reacting hexakis(4-formylphenoxy)cyclophosphazene with (cyanomethylene)triphenylphosphorane, the hexakis(4-cinnammonitrile phenoxy)cyclophosphazene compound **1** [1] has been obtained (Eq. (1)) as a mixture of *cis* and *trans* isomers with



(1)

☆ Dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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[1] **1**: IR (Nujol mull): $\nu(C{=}C)$ 1617; $\nu(C{\equiv}N)$ 2216 cm^{-1}. Selected NMR data ($CDCl_3$): ^1H NMR: δ 5.81 d ($^3J(HH) = 16.70$ Hz); 5.84 d ($^3J(HH) = 16.72$ Hz); 5.80 d ($^3J(HH) = 16.58$ Hz); 5.52 d ($^3J(HH) = 12.09$ Hz); 5.49 d ($^3J(HH) = 12.05$ Hz); ^{31}P NMR: 7.57–7.79 m.

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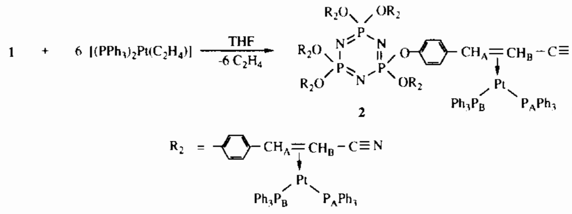
reference to the olefinic residues of the molecule. In fact, the ^{1}H NMR spectrum shows the H_A proton in the range 5.81–5.84 ppm as doublets for the *trans* conformation and in the range 5.49–5.52 ppm for the *cis* one, while the H_B proton is always masked by the phenyl group. The NMR pattern indicates that the cinnammonitrile moieties assume different conformations, forming atropisomers; this behaviour is in agreement with the presence of a multiplet in the narrow range 7.57–7.79 ppm in the ^{31}P NMR spectrum [5].

The cinnammonitrile moiety is a good binding group for metal centres [7] and the reactivity of **1** with Pt(0) and Pt(II) derivatives has been studied.

2. Syntheses and characterization

By reacting **1** with 6 equiv. of $[(PPh_3)_2Pt(C_2H_4)]$ in THF at room temperature the Pt(0) phosphazene derivative **2** [2] has been obtained according to Eq. (2),

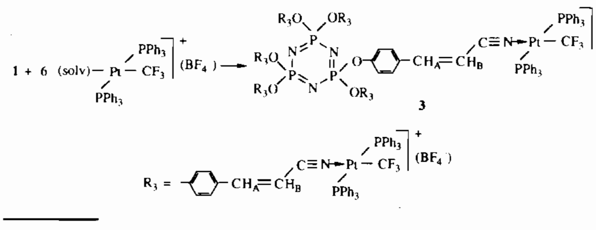


(2)

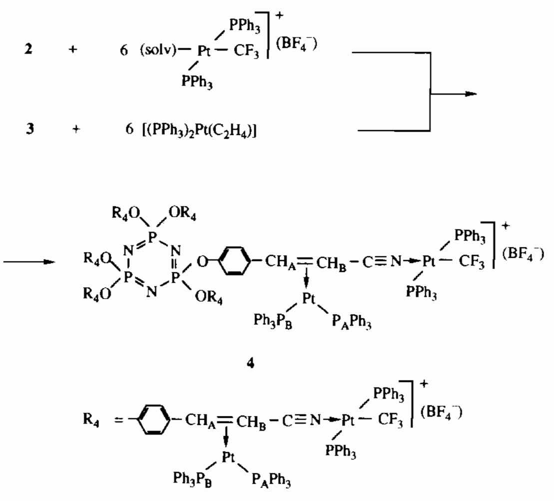
where the $\{(PPh_3)_2Pt\}$ fragment is selectively bonded to the double bond of cinnammonitrile.

The ^{31}P NMR spectrum of **2** clearly indicates the coordination of the Pt(0) moiety to a hindered system, thus making P_A and P_B magnetically different. Furthermore, the ^{1}H NMR spectrum shows a high-field shift of the olefinic protons due to the Pt(0) coordination.

When **1** is reacted with 6 equiv. of the coordinatively unsaturated Pt(II) cationic complex *trans*-$[(PPh_3)_2Pt(CF_3)(solv)]BF_4$ (solv = CH_2Cl_2) [8] in CH_2Cl_2 at room temperature, the Pt(II) phosphazene derivative **3** [3] has been obtained according to Eq. (3).



(3)



Scheme 1.

The selective coordination of the Pt(II) fragment to the nitrile function is clearly indicated by the increasing of the C≡N stretching, as observed in similar systems [8]. Furthermore, in the ^{31}P NMR spectrum the signals of the two equivalent *trans*-triphenylphosphines appear as a quartet (^3J(PF) = 20.1 Hz) at 21.69 ppm, flanked by ^{195}Pt satellites together with the signals of the phosphazene phosphorous atoms.

As illustrated in Eqs. (2) and (3), each of the compounds **2** and **3** contain six metal centres. An extension of this chemistry is represented by the formation of a phosphazene trimer containing twelve metal centres as reported in Scheme 1.

Thus, complex **4** [4] may be obtained by reacting either **2** with 6 equiv. of *trans*-$[(PPh_3)_2Pt(CF_3)(solv)]BF_4$ or **3** with 6 equiv. of $[Pt(PPh_3)_2(C_2H_4)]$. The IR data indicate that in **4** there is an interaction between the two metal centres through the cinnammonitrile moiety. The original C≡N stretching of **1** at 2216 cm^{-1} is shifted to 2263 cm^{-1} due to the coordination in **3** and to 2229 cm^{-1} in **4** because of the C=C coordination, which subtracts electrons to the conjugated system.

3. Conclusions

The reactions shown in Eqs. (2) and (3) and Scheme 1 appear of interest for three principal reasons. (i) Through the cinnammonitrile moiety it is possible to introduce into the phosphazene system metals in different oxidation states, the electrochemical behaviour of which is presently under investigation. Furthermore, the selectivity of the first attack by Pt(II) or Pt(0) indicates the possibility of introducing metal centres

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[2] **2**: yield 80%. IR (Nujol mull): ν(C≡N) 2199 cm^{-1}. Selected NMR data ($CDCl_3$): ^{1}H NMR: $\delta(H_A)$ 3.53 m ($^2J(H_APt) = 52.9$ Hz); $\delta(H_B)$ 2.51 m ($^2J(H_BPt) = 68.0$ Hz); ^{31}P NMR: $\delta(P_A)$ 26.96 (^1J(PPt) = 4037.6 Hz); $\delta(P_B)$ 26.08 ($^1J(P_BPt) = 3488.9$ Hz; $^2J(P_AP_B) = 33.4$ Hz); $\delta(P_{phosphazene})$ 7.51 m.

[3] **3**: yield 80%. IR (Nujol mull): ν(C≡N) 2263 cm^{-1}. Selected NMR data: ^{1}H NMR ($CDCl_3$): $\delta(H_A)$ 6.33 m; $\delta(H_B)$ 5.13 m; ^{31}P NMR: δ(P) 21.69 q (^1J(PPt) = 2873.8 Hz; ^3J(PF) = 20.1 Hz); $\delta(P_{phosphazene})$ 7.20 m.

[4] **4**: yield 70%. IR (Nujol mull): ν(C≡N) 2228 cm^{-1}. Selected NMR data: ^{1}H NMR: $\delta(H_A)$ 3.54 m; $\delta(H_B)$ 2.54 m; ^{31}P NMR: $\delta(P_A)$ 26.10 d ($^1J(P_APt) = 4772.2$ Hz; $^2J(P_AP_B) = 25.2$ Hz); $\delta(P_B)$ 22.21 d ($^1J(P_BPt) = 2813.5$ Hz; $^2J(P_AP_B) = 25.2$ Hz); δ(P) 22.25 q (^1J(PPt) = 2892.0 Hz; ^3J(PF) = 20.4 Hz); $\delta(P_{phosphazene})$ 7.10 m.

different from platinum into the phosphazene systems. (ii) The metal compound **4**, soluble in common organic solvent, appears a promising starting point for catalytic applications and multimetallic system preparation. (iii) The chemical and physical properties of phosphazene polymers and copolymers containing 4-formyl phenoxy groups may allow the extension of the above-reported reactions to a macromolecular level [9].

References

[1] (a) H.R. Allcock, J.L. Desorcie and G.H. Riding, *Polyhedron, 6* (1987) 119; (b) V. Chandrasekhar and K.R. Justin Thomas, *Appl. Organomet. Chem.*, *7* (1993) 1.

[2] H.R. Allcock, R.W. Allen and J.P. O'Brien, *J. Am. Chem. Soc., 99* (1977) 3984.

[3] J. Trotter, S.H. Whitlaw and N.L. Paddock, *J. Chem. Soc., Chem. Commun.*, (1969) 695.

[4] H.R. Allcock, M.N. Mang, G.H. Riding and R.R. Whittle, *Organometallics, 5* (1986) 1626.

[5] R. Bertani, G. Facchin and M. Gleria, *Inorg. Chim. Acta, 165* (1989) 73.

[6] G. Facchin, R. Bertani, A. Berton and M. Gleria, *Inorg. Chim. Acta, 147* (1988) 165.

[7] S.J. Bryan, P.G. Huggett, K. Wade, J.A. Daniels and J.R. Jennings, *Coord. Chem. Rev., 44* (1982) 149.

[8] R.A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri and R.J. Angelici, *Organometallics, 13* (1994) 1341.

[9] H.R. Allcock, *Acc. Chem. Res., 12* (1979) 351.