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# DICATIONIC ($\eta^5$-TRIPHENYLPHOSPHONIUM CYCLOPENTADIENYLIDE)($\eta^4$-DIENE)-PALLADIUM(II) AND -PLATINUM(II) COMPLEXES

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## Summary

The complexes $[M(Ph_3PC_5H_4)(Diene)][PF_6]_2$ (M = Pd, Diene = cycloocta-1,5-diene, norbornadiene; M = Pt, Diene = cycloocta-1,5-diene, norbornadiene, cyclooctatetraene) were prepared by treating the corresponding solvated species $[M(Diene)(Acetone)_2][PF_6]_2$, generated in situ, with triphenylphosphonium cyclopentadienylide. (The palladium(II) complex with cyclooctatetraene could not be obtained by this method.) The compounds are stable as solids for a long time, but decompose rapidly in solution. The palladium(II) complexes decompose more easily than the analogous platinum(II) species; the stability sequence for variation of the coordinated diene, is: cycloocta-1,5-diene > norbornadiene > cyclooctatetraene. In all the complexes the triphenylphosphonium cyclopentadienylide ligand is $\eta^5$-coordinated to the metal. In $[Pt(Ph_3PC_5H_4)(C_8H_8)][PF_6]_2$ the cyclooctatetraene has a rigid structure at 25°C. Attempts to isolate methoxy derivatives of the type $[M(Ph_3PC_5H_4)(Diene\text{-}OCH_3)]PF_6$ failed. The $^1H$ NMR spectra of the complexes are discussed.

## Introduction

The phosphorus ylides show a wide range of reactions which makes them very important tools for preparative organic chemistry [1]. Physical techniques and theoretical calculations indicate that a dominant feature of ylides is their dipolar zwitterionic nature, involving an onium center next to a carbanionic function [1,2]. There is also much potential for the use of ylides in organometallic chemistry [3], utilizing both the variety of reactions which they promote and their ability to function as ligands stabilizing the metal—carbon σ-bond.

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In the case of the triphenylphosphonium cyclopentadienylide (1), it has been shown that this ligand coordinates as the cyclopentadienyl ion, with the five-membered cyclopentadienylide ring behaving as a 6$\pi$-electrons donor [4—13]. It is therefore of interest to compare the properties of compounds containing 1 with those of the analogous $\eta^5$-cyclopentadienyl complexes.

Recently we reported the synthesis [13] and $^1$H and $^{13}$C NMR studies of $\eta^5$-triphenylphosphonium cyclopentadienylide-rhodium(I) and -rhodium(III) complexes containing, in some cases, a coordinated diene; we also described the crystal and molecular structure [14] of $[Rh(Ph_3PC_5H_4)(1,5\text{-}C_8H_{12})]BPh_4$. We have now extended our studies to the synthesis of $\eta^5$-triphenylphosphonium cyclopentadienylide-palladium(II) and -platinum(II) complexes containing coordinated dienes.

## Results and discussion

The poor nucleophile triphenylphosphonium cyclopentadienylide 1 does not react directly with $[M(Diene)Cl_2]$ complexes (M = Pd, Pt; Diene = cycloocta-1,5-diene, norbonadiene; cyclooctatetraene). We found that 1 reacts readily at room temperature with the solvated species generated in situ by treating $[M(Diene)Cl_2]$ with the stoichiometric amount of $Ag[PF_6]$ in acetone. From the reaction we isolated the dicationic five-coordinated complexes of palladium(II) and platinum(II) $[M(Ph_3PC_5H_4)(Diene)][PF_6]_2$ (M = Pd, Diene = $1,5\text{-}C_8H_{12}$ (2), $C_7H_8$ (3); M = Pt, Diene = $1,5\text{-}C_8H_{12}$ (4), $C_7H_8$ (5), $C_8H_8$ (6)). As solids they are stable for some weeks, but in solution they decompose in a few hours. Their stability [15] in solution depends on the nature of the coordinated diene, the metal and the solvent. The palladium(II) complexes are less stable than the analogous platinum(II) species, in keeping with the lower ability of palladium(II) to stabilize five-coordinated derivatives. The stability varies with the coordinated diene in the sequence cycloocta-1,5-diene > norbornadiene > cyclooctatetraene. The palladium(II) complex with cyclooctatetraene could not be obtained, and palladium metal was formed. In coordinating solvents such as dimethylsulfoxide and dimethylformamide, the compounds 2—6 decompose almost immediately, while in chlorinated solvents and in acetone, in which they are only sparingly soluble, they decompose in a few hours. Because of these properties we could not obtain satisfactory $^{13}$C NMR spectra and the formulation of the complexes 2—6 was based on the analytical, conductivity and $^1$H NMR data. The infrared spectra of the complexes are not informative but show the presence of uncoordinated anion along with the expected ligand modes.

Bearing in mind the strong affinity of palladium(II) and platinum(II) for allylic ligands, the main question about the nature of the isolated products concerns the way in which the $Ph_3PC_5H_4$ moiety is coordinated to the metal. Although the $^{13}$C NMR spectra give a more reliable guide to the effect of coordination on 1 [7,8,11,13], the literature shows that conclusive information can also be obtained from $^1$H NMR spectra. Thus when 1 is $\eta^5$-coordinated to a transition metal, the proton resonances of the cyclopentadienylide ring appear as two multiplets, assignable to the $\alpha$ and $\beta$ protons, shifted upfield compared with the signals from free 1. The chemical shift difference between $\alpha$ and $\beta$

protons is usually between 0 and $\simeq$0.40 ppm [12,13]. Anisotropy effects are thought to affect the value of $\Delta\delta$ between $\alpha$ and $\beta$ protons, greatly increasing its value [13,14].

When 1 is coordinated as a trihapto ligand (to the best of our knowledge there are only two examples in the literature [16,17]) the cyclopentadienylide ring proton resonances appear as two six-line multiplets (AA'BB'X pattern) and exhibit a chemical shift difference greater than that observed when $\eta^5$-coordination occurs (the reported values of $\Delta\delta$ are 0.57 ppm for $\{Pd(Ph_3PC_5H_4)[C_4(CO_2Me)_4]\}$ and 1.26 ppm for $[Pd(Ph_3PC_5H_4)Cl_2]$). Certainly each of the three possible dynamic modes for the $\eta^3$ or allylic coordination of 1 should exhibit two multiplets in the $^1$H NMR spectrum.

Thus for the complex 2 the proton resonances of the cyclopentadienylide ring appear as multiplets at $\delta$ 6.94 and 7.13 ppm, while for the analogous platinum(II) complex 4 they are not split and appear as a broad multiplet, at 6.90 ppm. For the norbornadiene-palladium(II) and -platinum(II) complexes 3 and 5 the proton resonances of the cyclopentadienylide ring are observed as broad multiplets at 6.90 and 6.88 ppm, respectively. The resonances associated with the diene ligands are shifted down field compared with those for neutral palladium(II) and platinum(II) complexes and they agree with literature data for cationic species. The coupling constants $J$(H—Pt) are in the range of those reported for platinum(II) diene complexes. In the cyclooctatetraene complex 6 the $\alpha$ and $\beta$ proton resonances of 1 are observed as multiplets at 6.96 and 7.10 ppm. As regards the cyclooctatetraene coordination the complex exhibit some interesting features. Thus its $^1$H NMR spectrum shows, in addition to the resonances of 1, two singlets with platinum satellites ($\delta$ 6.24 ppm, $J$(H—Pt) = 30 Hz; $\delta$ 6.02 ppm, $J$(H—Pt) = 38 Hz) which are assignable to the cyclooctatetraene proton resonances. The intensity ratio 4 : 4 : 4 between the cyclopentadienylide protons and the cyclooctatetraene protons (which give two singlets), together with a band at 1625 cm$^{-1}$ in the infrared spectrum due to the free double bonds [19], rule out the presence of a binuclear complex in which the cyclooctatetraene is coordinated to two platinum atoms. The $^1$H NMR data are consistent [18] with a rigid structure for the coordinated cyclooctatetraene and fluxional behaviour of the triphenylphosphonium cyclopentadienylide moiety. The latter is free to rotate [13] around its bond with the platinum, to make the complex symmetric, and so only two kinds of olefinic protons are observed. Thus we assign 1,2 : 5,6-$\eta^4$-bonding to cyclooctatetraene rather than the alternative 1,4-$\eta^4$-bonding. Decomposition of the sample above 35°C prevented $^1$H NMR study of the dynamic behaviour of the complex.

In conclusion, since the $^1$H NMR shows that the signals from the $\alpha$ and $\beta$ protons of the cyclopentadienylide ring are either not split (complexes 3—5), or, if split show only very small $\Delta\delta$ values (0.19 ppm for 2 and 0.15 ppm for 6) we suggest that 1 involves $\eta^5$-coordination. Thus, assuming that 1 occupies three coordination sites, the complexes 2—6 can be regarded as five-coordinated dicationic compounds of palladium(II) and platinum(II).

Several papers dealing with the synthesis and the reactivity of five-coordinated complexes of platinum(II) containing olefins have recently appeared [20]. On standing in solution these complexes generally lose the olefin to give four-coordinated species. In agreement with previous observations on the influence of $\pi$

TABLE 1

ANALYTICAL [a] AND PROTON NMR DATA

| Compound | Analysis: Found (calcd.) (%) | | $^1$H NMR [b] (ppm) | | |
|---|---|---|---|---|---|
| | C | H | $\delta(C_5H_4)$ [c, d] | $\delta$(Diene) [d] | Assignment [e] |
| 2, $[Pd(1,5\text{-}C_8H_{12})(Ph_3PC_5H_4)][PF_6]_2$ | 44.80(44.81) | 3.74(3.76) | 6.94(2), 7.13(2) | 6.05(4) | CH |
| | | | | 2.60(8) | $CH_2$ |
| 3, $[Pd(C_7H_8)(Ph_3PC_5H_4)][PF_6]_2$ | 44.17(44.21) | 3.30(3.34) | 6.90(4) | 5.94(4) | $CH_{olef.}$ |
| | | | | 3.95(2) | CH |
| | | | | 1.70(2) | $CH_2$ |
| 4, $[Pt(1,5\text{-}C_8H_{12})(Ph_3PC_5H_4)][PF_6]_2$ | 40.56(40.49) | 3.44(3.39) | 6.90(4) | 5.69(4) $J(H\text{—}Pt) = 42$ Hz | CH |
| | | | | 2.52(8) | $CH_2$ |
| 5, $[Pt(C_7H_8)(Ph_3PC_5H_4)][PF_6]_2$ | 39.83(39.87) | 3.05(3.01) | 6.88(4) | 5.00(4) $J(H\text{—}Pt) = 44$ Hz | $CH_{olef.}$ |
| | | | | 3.98(2) | CH |
| | | | | 1.32(2) | $CH_2$ |
| 6, $[Pt(C_8H_8)(Ph_3PC_5H_4)][PF_6]_2$ | 40.60(40.66) | 3.00(2.97) | 6.96(2), 7.10(2) | 6.24(4) $J(H\text{—}Pt) = 30$ Hz | CH |
| | | | | 6.02(4) $J(H\text{—}Pt) = 38$ Hz | CH |

[a] Conductivity data, in acetone solution, are in range expected for 1 : 2 electrolytes. [b] Acetone-$d_6$ solution. [c] $\alpha$ and $\beta$ protons are indistinguishable and are observed as multiplets. [d] Relative area ratios are in parentheses. [e] Of the diene protons.

back-bonding on the stability of five-coordinated complexes, electron-withdrawing groups on the coordinated double bond increase the stability (or lower the reactivity) of the complex. We think that the formation of the pentacoordinated compounds **2**—**6** can be explained by the presence in the molecule of both the dipolar, electron-withdrawing ligand $Ph_3PC_5H_4$ and the diene. Furthermore, the latter, being a chelate ligand, exercises a stabilizing effect. On the other hand formally five-coordinate palladium(II) and platinum(II) complexes containing the $\eta^5$-cyclopentadienyl ligand, whose electron withdrawing power is comparable to **1**, are known [21].

We failed to isolate a methoxy derivative of the type $[M(Ph_3PC_5H_4)(Diene\text{-}OCH_3)]PF_6$ either by treating the solvated complex $[M(Diene\text{-}OCH_3)(acetone)_2]^+$ with **1** or by treating the dicationic diene complexes **2**—**6** with methanol in the presence of base. From these reactions we obtained only inseparable mixtures of unstable compounds, and there was only doubtful spectroscopic evidence for the formation of the desired complexes.

## Experimental

Triphenylphosphonium cyclopentadienylide [22] and the complexes $[Pd(1,5\text{-}C_8H_{12})Cl_2]$ [23], $[Pd(C_7H_8)Cl_2]$ [24], $[Pd(C_8H_8)Cl_2]$ [25], $[Pt(1,5\text{-}C_8H_{12})Cl_2]$ [26], $[Pt(C_7H_8)Cl_2]$ [26] were prepared by literature methods.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in KBr pellets. Proton NMR spectra were recorded by using a Perkin-Elmer R 24B spectrometer with tetramethylsilane as internal reference. Conductivity measurements were made with a WTW LBR conductivity meter. Elemental analyses were performed by the microanalytical laboratory of the Organic Chemistry Institute of Milan.

All the reactions were carried out under oxygen-free nitrogen. Analytical and $^1H$ NMR data for the prepared compounds are reported in Table 1.

### *Preparation of (cycloocta-1,5-diene)(triphenylphosphonium cyclopentadienylide)palladium(II) bis-exafluorophosphate, $[Pd(Ph_3PC_5H_4)(1,5\text{-}C_8H_{12})][PF_6]_2$*

To an acetone solution (50 ml) containing 0.57 g (2 mmol) of $[Pd(1,5\text{-}C_8H_{12})Cl_2]$ was added 1.0 g (4 mmol) of $Ag[PF_6]$. The AgCl precipitate formed was removed by filtration and to the pale yellow filtrate was added 0.64 g of $Ph_3PC_5H_4$. The solution became brown, and after about 5 min reaction was complete. The solvent was evaporated off and the residual solid was rapidly dissolved in dichloromethane. Diethyl ether was added to precipitate the product as a yellow brown solid. The yield was 68%.

The complexes $[Pd(C_7H_8)(Ph_3PC_5H_4)][PF_6]_2$, $[Pt(1,5\text{-}C_8H_{12})(Ph_3PC_5H_4)][PF_6]_2$, $[Pt(C_7H_8)(Ph_3PC_5H_4)][PF_6]_2$ and $[Pt(C_8H_8)(Ph_3PC_5H_4)][PF_6]_2$ were prepared similarly. The yields were in the range 58—72%.

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