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PREPARATION AND REACTIONS OF PALLADIUM(II) AND PLATINUM(II) DIENYL COMPLEXES

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Summary

The preparation of M(diene · OCH_3)(L—L)Y complexes (M = Pd^{II}, diene = 1,5-cyclooctadiene, *endo*-dicyclopentadiene, L—L = 2,2'-bipyridyl, 1,10-phenanthroline, Y = hexafluorophosphate, diene = dicyclopentadiene, L—L = 1,2-bis(diphenylphosphino)ethane, Y = hexafluorophosphate; diene = 1,5-cyclooctadiene, L—L = ethylenediamine, Y = Cl; diene = norbornadiene, L—L = 2,2'- bipyridyl, phenanthroline, Y = Cl; M = Pt^{II}, diene = 1,5-cyclooctadiene, L—L = 2,2'-bipyridyl, 1,10-phenanthroline, Y = hexafluorophosphate) is reported. For M = Pd, treatment of the dienyl complexes with hydrochloric acid in methanol gives Pd(L—L)Cl_2, while for M = Pt the products are Pt(diene)Cl_2.

Introduction

The olefin-palladium(II) and platinum(II) complexes undergo many important reactions, especially five-coordination addition [1], nucleophilic attack on the coordinated olefin [2], and replacement of the olefin moiety [3] or of the ligand *trans* to it [4]. Additions of conjugate bases of alcohols [2], amines [5], carboxylic acids [6], keto esters [7], malonic esters [7] and β-diketones [8] to the coordinated double bond of a diene are also well known.

We now describe our studies of the preparation and reactions of [M(diene · OCH_3)(L—L)$]^+$ complexes (M = Pd^{II}, diene = 1,5-cyclooctadiene, *endo*-dicyclopentadiene, L—L = 2,2'-bipyridyl, 1,10-phenanthroline, diene = dicyclopentadiene, L—L = 1,2-bis(diphenylphosphino)ethane, diene = 1,5-cyclooctadiene, L—L = ethylenediamine, diene = norbornadiene, L—L = phenanthroline; M = Pt^{II}, diene = 1,5-cyclooctadiene, L—L = 2,2'-bipyridyl, 1,10-phenanthroline), some of which were known previously [9].

Experimental

The starting materials Pd(diene)Cl_2 [10], [Pd(diene · OCH_3)Cl$]_2$ [2a,11] and Pt(diene)Cl_2 [12] were made by published procedures. IR spectra were recorded as Nujol mulls (CsI discs) on a Perkin—Elmer 457 spectrophotometer, with a polystyrene film for calibration. ^1H NMR spectra were recorded on a Perkin—Elmer R 24B spectrometer. Conductivity measurements were carried out at 25° C over a complex concentration range of 2×10^{-4}—5×10^{-4} *M* using a LBR Conductivity Meter.

Preparation of [M(diene · OCH_3)(L—L)]PF_6 complexes. General procedure. M(diene)Cl_2 and $AgNO_3$ were mixed at room temperature in 1/2 ratio in methanol. After AgCl had been filtered off, L—L (1/1) and NH_4PF_6 were added. The solutions were set aside at —20° C, and the complexes [M(diene · OCH_3)(L—L)]PF_6 separated. The following were prepared in this way:

[Pd(C_8H_{12} · OCH_3)(Bipy)]PF_6 = (2,2'-Bipyridyl)(1-methoxycycloocta-4-ene-8σ,4π)palladium hexafluorophosphate, white needles (Yield 67%) (Found: C, 41.94; H, 4.31; N, 5.25. $PdC_{19}H_{23}ON_2PF_6$ calcd.: C, 41.72; H, 4.20; N, 5.12%).

[Pd(C_8H_{12} · OCH_3)(1,10-phenanthroline)]PF_6 = (1,10-phenanthroline)(1-methoxycycloocta-4-ene-8σ,4π)palladium hexafluorophosphate (Yield 75%) (Found: C, 44.20; H, 4.10; N, 4.92. $PdC_{21}H_{23}ON_2PF_6$ calcd.: C, 44.00; H, 4.00; N, 4.89%).

[Pd($C_{10}H_{12}$ · OCH_3)(Bipy)]PF_6 = (2,2'-Bipyridyl)(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)palladium hexafluorophosphate (Yield 60%) (Found: C, 43.90; H, 4.00; N, 5.00. $PdC_{21}H_{23}ON_2PF_6$ calcd.: C, 44.20; H, 4.03; N, 4.90%).

[Pd($C_{10}H_{12}$ · OCH_3)(1,10-phenanthroline)]PF_6 = (1,10-phenanthroline)(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)palladium hexafluorophosphate (Yield 55% after crystallization from CH_2Cl_2/ether) (Found: C, 46.90; H, 3.80; N, 4.72. $PdC_{23}H_{23}ON_2PF_6$ calcd.: C, 47.10; H, 3.86; N, 4.72%).

[Pt(C_8H_{12} · OCH_3)(Bipy)]PF_6 = (2,2'-bipyridyl)(1-methoxycyclocta-4-ene-8σ,4π)platinum hexafluorophosphate (Yield 65%) (Found: C, 35.70; H, 3.72; N, 4.30. $PtC_{19}H_{23}ON_2PF_6$ calcd.: C, 35.88; H, 3.62; N, 4.40%).

[Pt(C_8H_{12} · OCH_3)(1,10-phenanthroline)]PF_6 = (1,10-phenanthroline)(1-methoxycycloocta-4-ene-8σ,4π)platinum hexafluorophosphate (Yield 70%) (Found: C, 38.28; H, 3.60; N, 4.26. $PtC_{21}H_{23}ON_2PF_6$ calcd.: C, 38.23; H, 3.49; N, 4.24%).

Preparation of [Pd($C_{10}H_{12}$ · OCH_3)(P—P)]PF_6 = (1,2-bisdiphenylphosphinoethane)(3a,4,7,7a-tetrahydro-*exo*-6 methoxy-*endo*-4,7-methanoindene-*endo*-8σ,4π)palladium hexafluorophosphate.

[Pd($C_{10}H_{12}$ · OCH_3)Cl]$_2$ (0.2 mmol) was treated in methanol with 0.42 mmol of $AgNO_3$. AgCl was filtered off and then 1,2-bis(diphenylphosphino)ethane (0.4 mmol) and NH_4PF_6 were added to the solution. Evaporation of the solvent under vacuum and addition of water gave a yellow compound. (Yield 70%) (Found: C, 54.10; H, 4.60. $PdC_{37}H_{39}OP_3F_6$ calcd.: C, 54.60; H, 4.74%).

Preparation of [Pd(C_8H_{12} · OCH_3)(ethylenediamine)]Cl = (Ethylenediamine)-(1-methoxycycloocta-4-ene-8σ,4π)palladium chloride.

[Pd(C_8H_{12} · OCH_3)Cl]$_2$ (0.315 mmol) was treated with 0.75 mmol of ethylenediamine in CH_2Cl_2; a white compound precipitated, and more separated on addition of ether. Recrystallization was from methylene chloride/ether. (Yield 70%) (Found: C, 38.40; H, 6.64; N, 8.32. $PdC_{11}H_{23}ON_2Cl$ calcd.: C, 38.70; H, 6.74; N, 8.20%).

Preparation of Pd(C_7H_8 · OCH_3)(L—L)Cl (C_7H_8 = norbornadiene).

[Pd(C_7H_8 · OCH_3)Cl]$_2$ and L—L were mixed in a 1/2 ratio in methanol. The solutions were filtered and set aside at —20° C to give yellow solids. In this way we prepared:

$Pd(C_7H_8 \cdot OCH_3)$(2,2′-bipyridyl)Cl (Yield 85%) (Found: C, 51.16; H, 4.54; N, 6.59; Cl, 8.40; O, 3.88. $PdC_{18}H_{19}ON_2Cl$ calcd.: C, 51.28; H, 4.51; N, 6.64; O, 3.79; Cl, 8.42%).

$Pd(C_7H_8 \cdot OCH_3)$(1,10-phenanthroline)Cl (Yield 60%) (Found: C, 53.80; H, 4.31; N, 6.30. $PdC_{20}H_{19}ON_2Cl$ calcd.: C, 54.00; H, 4.27; N, 6.20%).

Preparation of $[Pd(C_7H_8 \cdot OCH_3)$(1,10-phenanthroline)$]PF_6$ = (1,10-phenanthroline)(*exo*-6-methoxy-2-norbornene-endo-5σ,2π)palladium hexafluophosphate.

$[Pd(C_7H_8 \cdot OCH_3)Cl]_2$ (0.188 mmol) was treated in CH_2Cl_2 with $AgPF_6$ in a 1/2 ratio. AgCl was filtered off and 1,10-phenanthroline (0.37 mmol) was added. The solutions were set aside at −20°C to give a yellow precipitate. (Yield 65%) (Found: C, 43.38; H, 3.35; N, 5.05. $PdC_{20}H_{19}ON_2PF_6$ calcd.: C, 43.20; H, 3.42; N, 5.00%).

Reaction of [Pd(diene · OCH_3)(L—L)]PF_6 complexes with HCl (diene = *endo*-dicyclopentadiene, 1,5-cyclooctadiene; L—L = 2,2′-bipyridyl, 1,10-phenanthroline, diene = *endo*-dicyclopentadiene, L—L = 1,2-bis(diphenylphosphino)ethane. A suspension of [Pd(diene · OCH_3)(L—L)]PF_6 in methanol was treated with a large excess of HCl. Pd(L—L)Cl_2 complexes were identified by comparison of their IR spectra with those of authentic samples. Reaction of $[Pt(C_8H_{12} \cdot OCH_3)$(L—L)]$PF_6$ and $[Pt(C_{10}H_{12} \cdot OCH_3)$(2,2′-bipyridyl)]Cl with HCl (C_8H_{12} = 1,5-cyclooctadiene; $C_{10}H_{12}$ = *endo*-dicyclopentadiene; L—L = 2,2′-bipyridyl, 1,10-phenanthroline). A suspension of the dienylplatinum complexes was treated in methanol with an excess of HCl. Pt(diene)Cl_2 complexes were formed and identified by comparison of their IR spectra with those of authentic samples. Addition of $FeSO_4$ to the filtrate gave an intense red colour, due to $[Fe(L—L)_3]^{2+}$.

Reaction of $Pd(C_7H_8 \cdot OCH_3)$(L—L)Cl with HCl (C_7H_8 = norbornadiene; L—L = 2,2′-bipyridyl, 1,10-phenanthroline, 1,2-bis(diphenylphosphine)ethane). A suspension of $Pd(C_7H_8 \cdot OCH_3)$(L—L)Cl in methanol was treated with an excess of HCl; Pd(L—L)Cl_2 complexes were formed and identified by comparison of their IR spectra with those of authentic samples.

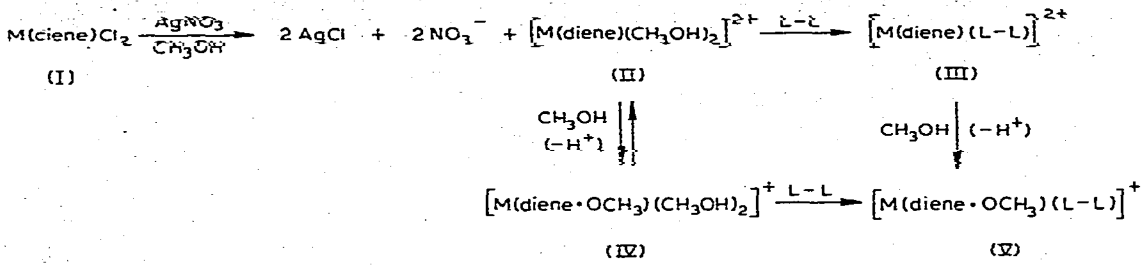
Reaction of [Pd(diene · OCH_3)(L—L)]ClO_4 complexes with $HClO_4$ (diene-1,5-cyclooctadiene, *endo*-dicyclopentadiene; L—L = 2,2′-bipyridyl). A suspension of [Pd(diene · OCH_3)(L—L)]ClO_4 was treated in CH_2Cl_2 with an excess of an aqueous solution of $HClO_4$. The *endo*-dicyclopentadienyl derivative decomposed, but $[Pd(C_8H_{12})$(2,2′-bipyridyl)$](ClO_4)_2$ was isolated. (Found: C, 38.53; H, 3.64; N, 5.05; O, 22.73. $PdC_{18}H_{20}N_2Cl_2O_8$ calcd.: C, 38.73; H, 3.58; N, 5.02; O, 22.95%).

Results and discussion

When a suspension of M(diene)Cl_2 in methanol is treated with $AgNO_3$ in a 1/2 ratio, AgCl is precipitated, and [M(diene · OCH_3)(L—L)]PF_6 compounds can be isolated after addition of L—L and NH_4PF_6. The formation of the dienyl complexes may be represented as in Scheme 1.

In neutral complexes, coordinated dienes usually undergo nucleophilic attack by conjugate bases of alcohols at the coordinated carbon atom [2]. In our case the reactivity towards methanol of the coordinated olefinic carbon should be enhanced by the bipositive charge of complexes II and III. It has also been reported that a *trans* attack of methanol or methoxide occurs on the olefinic

SCHEME 1. M = Pd^{II}, diene = 1,5-cyclooctadiene or dicyclopentadiene, L—L = 2,2′-bipyridyl or 1,10-phenanthroline; M = Pt^{II}, diene = 1,5-cyclooctadiene, L—L = bipyridyl or 1,10-phenanthroline.



carbon of [Pd(1,5-cyclooctadiene)(2,2′-bipyridyl)$]^{2+}$ [13].

All the [M(diene · OCH_3)(L—L)]PF_6 compounds (M = Pd^{II}, diene = 1,5-cyclooctadiene or dicyclopentadiene, L—L = 2,2′-bipyridyl or 1,10-phenanthroline; M = Pt^{II}, diene = 1,5-cyclooctadiene, L—L = 2,2′-bipyridyl or 1,10-phenanthroline) are 1/1 electrolytes in methanol. Their IR spectra show very strong absorptions in the region 1050—1100 cm^{-1}, due to stretching vibrations of the C—O—CH_3 group [9b], and characteristic bands of PF_6^- (835 cm^{-1} broad, vs and 560 cm^{-1} s, or vs). The bipyridyl complexes also show an absorption at about 1600 cm^{-1}, due to ring vibrations of the nitrogen-bonded ligand.

[Pd(C_8H_{12} · OCH_3)(ethylenediamine)]Cl and [Pd($C_{10}H_{12}$ · OCH_3)(P—P)]PF_6 (C_8H_{12} = 1,5-cyclooctadiene, $C_{10}H_{12}$ = dicyclopentadiene; P—P = 1,2-bis(diphenylphosphino)ethane) were better prepared by treating [Pd(diene · OCH_3)Cl$]_2$ with the appropriate chelated ligand. Both complexes are 1/1 electrolytes in methanol, and their IR spectra show characteristic bands of the C—O—CH_3 group; the ethylenediamine derivative also shows a series of absorptions in the region 3210—3090 cm^{-1} due to the coordinated diamine [9b].

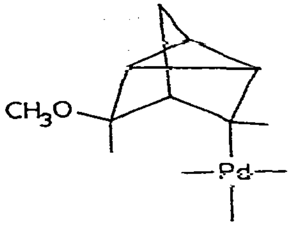
[Pd(C_8H_{12} · OCH_3)(2,2′-bipyridyl)$]^+$ reacts with $HClO_4$ in CH_2Cl_2, giving the dicationic [Pd(C_8H_{12})(2,2′-bipyridyl)]$(ClO_4)_2$ complex, and with HCl, in methanol, to give Pd(2,2′-bipyridyl)Cl_2. Details of the mechanism of the latter reaction have been published [14], the formation of the five-coordinated intermediate [Pd(C_8H_{12})(2,2′-bipyridyl)Cl$]^+$ being postulated.

Reactions of dienyl complexes with hydrochloric acid are affected by the nature of the central metal. [Pd(diene · OCH_3)(L—L)$]^+$ complexes react with HCl in methanol giving Pd(L—L)Cl_2 compounds, whereas the analogous reaction of the [Pt(diene · OCH_3)(L—L)$]^+$ (L—L = 2,2′-bipyridyl or 1,10-phenanthroline; diene = 1,5-cyclooctadiene or dicyclopentadiene) affords Pt(diene)Cl_2.

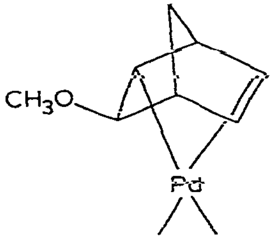
The difference in the nature of the reactions between palladium and platinum compounds may be directly related to the stability of the metal—olefin π bond. The course of the reaction reflects the known lower stability of this bond in palladium systems. Thus (C_8H_{12} · acac)Pt_2X_2 (acac = acetylacetonate, X = Cl, Br, I) reacts with triphenylphosphine or arsine (L) yielding (C_8H_{12}acac)PtXL, whereas the analogous palladium compounds give only PdL_2X_2 [15].

Enyl derivatives of norbornadiene may have both a nortricyclenyl (VI) or norbornenyl (VII) structure.

It has been suggested that the bonding in the norbornenylmetal system might be better represented by a π-homoallylic structure [16] although such a conclusion has been questioned [17]. The conversion of norbornenyl complexes into



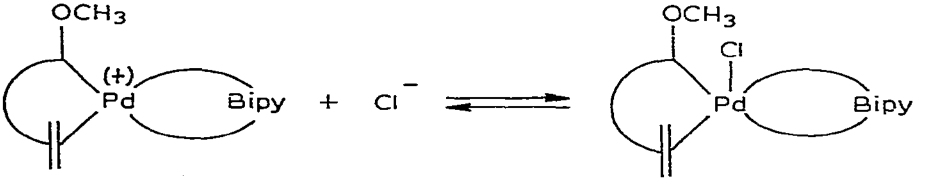
(VI)



(VII)

nortricyclenyl derivatives is promoted by Group V donor ligands, olefins or 1,3-dienes [18].

[Pd($C_7H_8 \cdot OCH_3$)(2,2′-bipyridyl)]PF_6 (C_7H_8 = norbornadiene) was previously prepared by treating [Pd($C_7H_8 \cdot OCH_3$)Cl]$_2$ with $AgPF_6$ and then with 2,2′-bipyridyl in tetrahydrofuran [9a]. When we carried out this reaction in CH_2Cl_2 with 1,10-phenanthroline we obtained [Pd($C_7H_8 \cdot OCH_3$)(1,10-phenanthroline)]-PF_6. This complex is a 1/1 electrolyte in methanol, and its IR spectrum shows characteristic bands of the C—O—CH_3 group and PF_6^- anion. Both [Pd($C_7H_8 \cdot OCH_3$)(L—L)]PF_6 (L—L = 2,2′-bipyridyl or phenanthroline) complexes can be considered norbornenyl derivatives. Treatment of [Pd($C_7H_8 \cdot OCH_3$)Cl]$_2$ with bipyridyl or 1,10-phenanthroline in methanol gave complexes formulated as Pd($C_7H_8 \cdot OCH_3$)(2,2′-bipyridyl)Cl (VIII) and Pd($C_7H_8 \cdot OCH_3$)(1,10-phenanthroline)Cl (IX). The ^1H NMR spectrum of VIII in $CDCl_3$ shows no resonance in the vinylic region. The most important signals were observed at ∂ 4.4(br, 1H) and 3.3(S, 3 H) ppm and in the range ∂ 2.24—1.2 ppm. These features support a nortricyclenyl structure for complex VIII in $CDCl_3$. Furthermore because of the low solubility in methanol of VIII, IX and of Pd($C_7H_8 \cdot OCH_3$)(P—P)Cl X [19] only their molar conductivity could be measured in this solvent. Values of $\Lambda_M(\Omega^{-1}\ cm^2\ mol^{-1})$ for methanol solutions of VIII increase as the concentration of the complex decreases and conductivity values for a 3.00×10^{-4} molar concentration of Pd($C_7H_8 \cdot OCH_3$)(P—P)Cl and for a 2.24×10^{-4} molar concentration of Pd($C_7H_8 \cdot OCH_3$)(1,10-phenanthroline)Cl are in the range of 1/1 electrolytes. On the basis of these findings it may be inferred that in a dissociating solvent, such as methanol, the norbornenyl structure is preferred by complexes VIII, IX and X, whereas less polar solvents, such as $CHCl_3$, favour a nortricyclenyl arrangement [19]. Conductometric data for methanol solutions of VIII may be consistent with the equilibrium 1, which was also reported to occur in nitromethane solutions of analogous platinum complexes [20].



(1)

Methanol suspensions of compounds VIII, IX and X react with HCl giving Pd(L—L)Cl_2 (L—L = 2,2′-bipyridyl, 1,10-phenanthroline, 1-bis(diphenylphosphino)ethane) complexes. Details of the mechanisms of this reaction will be presented in a forthcoming paper.

Acknowledgments

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