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Dinuclear organoplatinum(II)-methyldiphenylphosphine complexes of nicotinic acid

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Dedicated to Professor M.A. Bennett, FRS, on the occasion of his 65th birthday and in recognition of his outstanding contributions to organometallic chemistry.

Abstract

The preparation and characterisation of a series of novel, dinuclear organoplatinum(II) complexes of methyldiphenylphosphine, *trans*-[Pt$(PMePh_2)_2(C_5H_4N(CO_2H))$-μ-aryl-Pt$(PMePh_2)_2(C_5H_4N(CO_2H))](OTf)_2$ (aryl = phenyl, 4,4′-biphenyl, 4,4″-*p*-terphenyl, or 4,4′-benzophenone; OTf = triflate), in which nicotinic acid acts a nitrogen-donor ligand are described. The key structural feature of each complex is the presence of a carboxylic acid group at each end of the molecule. This allows for their association via intermolecular hydrogen-bonds in low polarity solvents. The complexes are potentially useful tectons (building blocks) for the construction of metal-containing supramolecular assemblies. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Dinuclear platinum complex; Hydrogen-bonding; Tecton; Nicotinic acid; Methyldiphenylphosphine

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1. Introduction

The hydrogen bond has long been known to play a pivotal role in controlling self-assembly processes in numerous biological and/or organic supramolecular systems [1]. In contrast, only more recently have major advances been made in the use of the coordinate-covalent bond for the construction of large molecular polygons and polyhedra by self-assembly [2]. Combining the coordinate-covalent and hydrogen-bonding motifs may greatly expand the utility of metal complexes as tectons (building blocks) in the construction of large molecular polygons and other types of supramolecular arrays [3]. In crystal engineering studies, for example, the hydrogen-bonding motif has been exploited in the synthesis of network solids that incorporate transition metal centres [3,4]. In contrast, there are few studies that provide evidence for the formation of discrete, metal-containing supramolecular aggregates in solution [5,6].

Herein we describe the preparation and characterisation of a series of novel, dinuclear organoplatinum(II) complexes of methyldiphenylphosphine which contain nicotinic acid as a nitrogen-donor ligand at each platinum center. Such complexes are potentially useful tectons that may allow one to construct discrete, supramolecular aggregates such as nanoscale cyclic entities in solution. The preparation and solution behaviour of related triphenylphosphine complexes has already been reported elsewhere [7], and the synthesis of the less sterically-demanding methyldiphenylphosphine complexes would allow for a study of the self-association properties of the tectons in non-aqueous solution as a function of phosphine steric bulk.

2. Results and discussion

The novel, linear bis(iodo) precursor complexes **1**–**3** were prepared by an oxidative-addition reaction employing the platinum(0) precursor $Pt(PMePh_2)_4$ and the diiodo derivatives of benzene, 4,4′-biphenyl, or 4,4″-*p*-terphenyl (Scheme 1). Alternatively, 4,4′-diiodobenzophenone was used to afford the bis(iodo) precursor **7**

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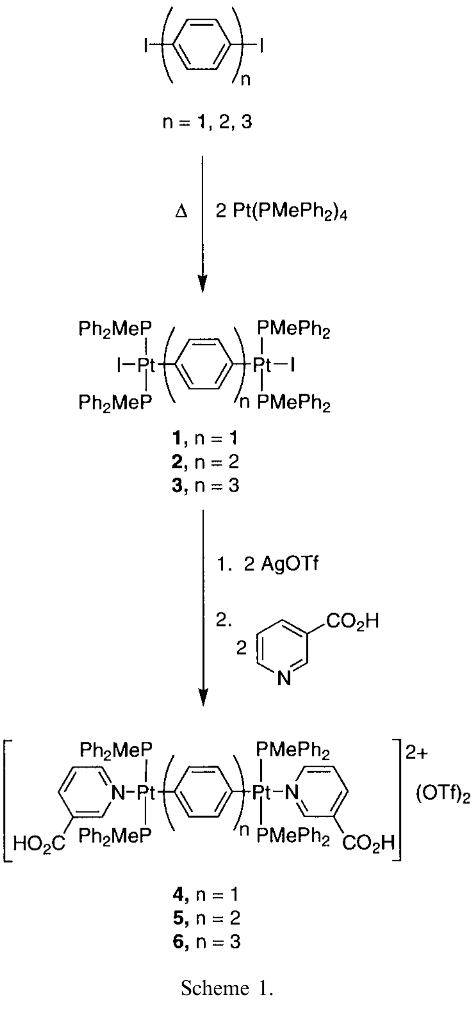
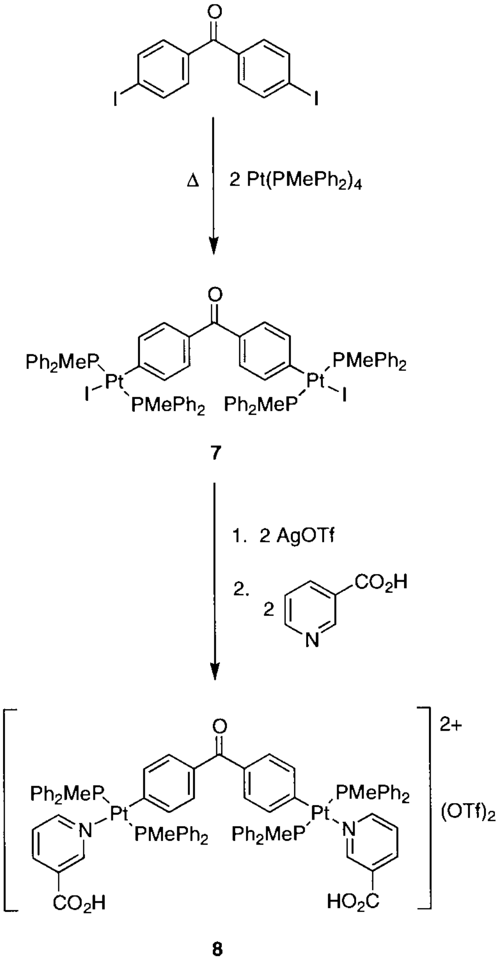
with a bridging 120° σ-aryl ligand (Scheme 2). The double oxidative-addition methodology that we employed in the preparation of the bis(iodo) species was previously reported for the synthesis of the analogous triphenylphosphine and triethylphosphine complexes [8]. The resulting bis(iodo) complexes **1**–**3** and **7** were then treated with two equivalents of AgOTf in CH_2Cl_2 solution, leading to the quantitative formation of the corresponding labile bis(triflato) species [9,10]. Although the triflato complexes could be isolated by careful evaporation of the solvent, it was more convenient to filter off the AgI precipitate and immediately proceed with the addition of two equivalents of nicotinic acid to afford the target complexes **4**–**6** and **8** as off-white solids in high yield and purity (Schemes 1 and 2).

The assignment of resonances in the ^1H-NMR spectra of the bis(iodo) complexes **1**–**3** and **7** was facilitated by means of 2D-NMR (COSY) experiments. In general, one can readily distinguish three sets of aromatic protons in the ^1H-NMR spectra of the bis(iodo) complexes. One set of signals, which appears as a complex multiplet, is attributed to the phenyl protons of the phosphine ligand. The bridging σ-phenyl ligand protons in **1** appear as a singlet owing to the symmetry of the complex, whereas for complexes **2**, **3** and **7**, the characteristic AA′XX′ resonances that appear upfield of the phenylphosphine multiplet are due to the *ortho* and *meta* protons of the bridging σ-aryl ligand. For complexes **1**, **2** and **7**, the *ortho* proton signals are flanked by ^{195}Pt satellites ($I = 1/2$; natural abundance = 33.8%) with $^3J_{PtH} = 48–55$ Hz, which is typical for σ-arylplatinum(II) complexes [8]. The platinum satellite signals of **3** were obscured by the *meta* proton resonances, hence the magnitude of $^3J_{PtH}$ could not be determined for this complex. In the ^1H-NMR spectra of complexes **1-3** and **7**, the P–Me protons appear as a multiplet centred at δ 1.4–2.1, which constitutes the X part of an $AMM'X_3X'_3$ spin system (where A = ^{195}Pt, M = ^{31}P, and X = ^1H). At this stage, we are unable to extract reasonable coupling data from the spectra, but related spin systems have been reported elsewhere [11], and a theoretical analysis of spin systems of the type $MM'X_nX'_n$ (where $n = 3$ and 6) has been described previously by Harris [12].



Scheme 1.



Scheme 2.

The ^1H-NMR assignments for the nicotinic acid complexes **4**–**6** and **8** were confirmed by means of

2D-NMR (COSY) spectroscopy. The assignments of the bridging aryl ligand and phosphine ligand protons correspond very closely to those described above for the bis(iodo) precursors. The pyridyl H^2 proton always appears as a singlet that is shifted downfield owing to its proximity to the electronegative nitrogen atom. The H^4 and H^6 protons appear as doublets (coupled to H^5), with H^6 being shifted downfield with respect to H^4 owing to its proximity to the nitrogen atom. The H^5 resonance was obscured by other aromatic signals. The CO_2H signal appears as a broad singlet and, as expected, its chemical shift is strongly dependent on temperature and concentration as a consequence of intermolecular hydrogen-bonding in low polarity solvents such as $CDCl_3$. At this stage, we cannot rule out hydrogen-bonding interactions of the complexes with the triflate ions, although comprehensive NMR titration studies with the related triphenylphosphine complexes do not support this notion [7]. The presence of small amounts of water also has a considerable influence on the chemical shift of the carboxyl proton. For example, a CD_2Cl_2 solution of **8** (0.05 mol dm^{-3}, 298 K) gives rise to a hydroxyl resonance at δ 5.7 when special precautions in the drying and handling of the complex (or solvent) are not observed. If the complex is dried by means of an azeotropic distillation using toluene, then the CO_2H signal moves to δ 9.3. When the same NMR experiment is performed under *strictly* anhydrous conditions, a chemical shift of δ 11.7–12.0 is observed for the carboxyl resonance and its linewidth narrows considerably.

The $^{31}P\{^1H\}$-NMR spectra of all complexes prepared in this work show the expected singlet flanked by ^{195}Pt satellite signals, consistent with mutually *trans* phosphine ligands. The magnitude of $^1J_{PtP}$ (ca. 3000 Hz) for all complexes falls in the range that is typical for *trans*-substituted σ-arylplatinum(II) complexes [11]. As expected, there are only minor differences observed in the magnitude of $^1J_{PtP}$ upon substitution of the iodo ligand with the pyridyl group, largely because the ^{195}Pt–^{31}P coupling is predominantly influenced by the nature of the *trans* ligand which, for the complexes prepared in this work, is always a tertiary phosphine. Despite the magnetic inequivalence of the methyldiphenylphosphine ligands in complexes **4**–**6** and **8**, which results in a complex multiplet for the P–Me group in the corresponding ^1H-NMR spectra (vide supra), there is no fine structure apparent in the ^{31}P resonance.

Positive-ion ESI-MS with **6** showed the expected molecular ion peak for the monomeric dinuclear species $[M-2OTf-2H]^+$ at *m*/*z* 1662. We were unable to identify peaks that corresponded to any type of non-covalent aggregate, even at high concentrations in low polarity solvents such as 1,2-dichloroethane. Complexes **4**, **5** and **8** failed to show any evidence of an intact species in their spectra and, instead, the pyridyl ligands in these complexes were readily lost and peaks corresponding to the resulting species $[M-2OTf-2C_5H_4N\text{-}(CO_2H)]^{2+}$ were identified. Similar behaviour has also been observed in the mass spectra of related triphenylphosphine systems [7].

3. Conclusions

In this work we have demonstrated that a variety of dinuclear organoplatinum(II) complexes of methyldiphenylphosphine with hydrogen-bonding functionality are readily prepared by a facile oxidative addition reaction utilising the platinum(0) precursor $Pt(PMePh_2)_4$ and diiodoaryl compounds, followed by exchange of the coordinated halide with nicotinic acid. The overall size of the tecton is governed by the nature of the bridging σ-aryl ligand, whilst the shape of the tecton is largely dependent on the σ-aryl bridging angle, i.e. ca. 120° for the 4,4′-benzophenone ligand, and ca. 180° for the mono-, bi- and ter-phenyl derivatives. These features allow for the construction of a variety of supramolecular aggregates by self-association in low polarity solvents. We are currently studying the effect of phosphine steric bulk on the self-association process in conjunction with other related species [7], and the results of this work will be reported elsewhere.

4. Experimental

4.1. General

All reactions were performed under a N_2 atmosphere using standard Schlenk techniques. All solvents were carefully dried and purified in the following manner: CH_2Cl_2 was distilled from CaH_2, and toluene was predried over $CaSO_4$ followed by distillation from sodium. Nicotinic acid and $Pt(PMePh_2)_4$ were stored in a desiccator over P_2O_5.

All 1D- and 2D-NMR spectra were recorded by means of a Varian Gemini 2000 (^1H at 300.10 MHz, ^{31}P at 121.50 MHz) spectrometer. Chemical shifts are reported in ppm with respect to TMS reference (^1H) or a sealed external standard of 85% H_3PO_4 (^{31}P). Electrospray Ionisation (ESI) Mass Spectra were obtained with a Finnegan LCQ mass spectrometer. HPLC grade methanol was used as the solvent. Elemental analyses were determined by Chemical and Microanalytical Services Pty Ltd, Melbourne (Australia).

Tetrakis(methyldiphenylphosphine)platinum(0) [13] and 4,4′-diiodobenzophenone [14] were prepared according to the literature procedures.

4.2. *Trans-1,4-phenyl-bis[(iodo)bis(methyldiphenylphosphine)]diplatinum(II)* (**1**)

1,4-Diiodobenzene (0.064 g, 0.194 mmol) and tetrakis(methyldiphenylphosphine)platinum(0) (0.388 g, 0.390 mmol) were placed in a Schlenk flask containing a magnetic stirring bar and fitted with a reflux condenser. Toluene (20 ml) was added to the flask, and the mixture was stirred at 85°C for 24 h. The solvent was removed in vacuo, and the residue was washed repeatedly with *n*-hexane to give **1** as an off-white solid (0.070 g, 24%). ^{1}H-NMR (CDCl$_3$): δ 7.61–7.26 (m, 40H, PPh$_2$), 6.53 (s, 4H, $^3J_{PtH} = 55$ Hz, Pt–Ph–Pt), 1.37 (m, 12H, P–CH$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 3.9 (s, $^1J_{PPt} = 2880$ Hz). Anal. Calc. for $C_{58}H_{56}I_2P_4Pt_2$: C, 45.80; H, 3.71. Found: C, 45.67; H, 3.70%.

4.3. *Trans-4,4′-biphenyl-bis[(iodo)-bis(methyldiphenylphosphine)]diplatinum(II)* (**2**)

Following a similar procedure to that described in Section 4.2, 4,4′-diiodobiphenyl and tetrakis(methyldiphenylphosphine)platinum(0) were reacted to give **2** as an off-white solid (yield 63%). ^{1}H-NMR (CDCl$_3$): δ 7.62–7.24 (m, 40H, PPh$_2$), 6.72 (d, 4H, $^3J_{HH} = 8.4$ Hz, $^3J_{HPt} = 48$ Hz, H^o), 6.49 (d, 4H, $^3J_{HH} = 8.4$ Hz, H^m), 1.91 (m, 12H, P–CH$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 4.3 (s, $^1J_{PPt} = 2929$ Hz). Anal. Calc. for $C_{64}H_{60}I_2P_4Pt_2$: C, 48.13; H, 3.79. Found: C, 48.22; H, 3.81%.

4.4. *Trans-4,4″-p-terphenyl-bis[(iodo)-bis(methyldiphenylphosphine)]diplatinum(II)* (**3**)

Following a similar procedure to that described in Section 4.2, 4,4″-diiodo-*p*-terphenyl and tetrakis(methyldiphenylphosphine)platinum(0) were reacted to give **3** as an off-white solid (yield 96%). ^{1}H-NMR (CDCl$_3$): δ 7.51–7.27 (m, 40H, PPh$_2$), 6.84 (d, 4H, $^3J_{HH} = 8.1$ Hz, H^o), 6.72 (d, 4H, $^3J_{HH} = 8.4$, H^m), 2.00 (m, 12H, P–CH$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 4.3 (s, $^1J_{PPt} = 2918$ Hz). Anal. Calc. for $C_{70}H_{64}I_2P_4Pt_2 \cdot 0.5CH_2Cl_2$: C, 49.36; H, 3.82. Found: C, 49.19; H, 3.71%.

4.5. *Trans-1,4-phenyl-bis[(nicotinic acid)bis(methyldiphenylphosphine)]diplatinum(II) bis(triflate)* (**4**)

Trans-1,4-phenyl-bis[(iodo)bis(methyldiphenylphosphine)]diplatinum(II) (0.065 g, 0.043 mmol) was suspended in CH$_2$Cl$_2$ (25 ml), and a suspension of AgOTf (0.021 g, 0.084 mmol) in CH$_2$Cl$_2$ (5 ml) was added to the flask. The mixture was stirred in the dark for 4 h, and AgI was removed by filtration through a short column of Celite filter-aid. A suspension of nicotinic acid (0.011 g, 0.086 mmol) in CH$_2$Cl$_2$ (5 ml) was added to the filtrate, and the mixture was stirred at room temperature for 1.5 h. A small quantity of unreacted nicotinic acid was removed by filtration through a pad of Celite. After evaporation of the filtrate to dryness, the residue was recrystallised from CH$_2$Cl$_2$–acetone to give **4** as a pale yellow solid (0.064 g, 99%). ^{1}H-NMR (CDCl$_3$): δ 9.88 (s, 2H, OH), 8.44 (s, 2H, H^2), 8.39 (d, 2H, $^3J_{HH} = 5.4$ Hz, H^6), 7.87 (d, 2H, $^3J_{HH} = 7.8$ Hz, H^4), 7.60–7.20 (m, 40H, PPh$_2$), 6.97 (m, 6H, H^5 and H^o), 1.70 (m, 12H, P–Me). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 8.6 (s, $^1J_{PtP} = 2855$ Hz). Anal. Calc. for $C_{72}H_{66}F_6N_2O_{10}P_4Pt_2S_2 \cdot 4CH_2Cl_2$: C, 42.43; H, 3.47; N, 1.30. Found: C, 42.13; H, 3.10; N, 1.62%.

4.6. *Trans-4,4′-biphenyl-bis[(nicotinic acid)bis(methyldiphenylphosphine)]diplatinum(II) bis(triflate)* (**5**)

The complex was prepared from **2** by a similar procedure to that described in Section 4.5, and it was isolated as a pale yellow solid (yield 64%). ^{1}H-NMR (CDCl$_3$): δ 9.29 (s, 2H, OH), 8.43 (s, 2H, H^2), 8.26 (d, 2H, $^3J_{HH} = 6.0$ Hz, H^6), 7.89 (d, 2H, $^3J_{HH} = 6.6$ Hz, H^4), 7.60–7.20 (m, 40H, PPh$_2$), 6.82 (d, 4H, $^3J_{HH} = 8.3$ Hz, H^o), 6.59 (d, 4H, $^3J_{HH} = 8.3$ Hz, H^m), 1.91 (m, 12H, P–CH$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 9.2 (s, $^1J_{PtP} = 2933$ Hz). Anal. Calc. for $C_{78}H_{70}F_6N_2O_{10}P_4Pt_2S_2$: C, 49.63; H, 3.74; N, 1.48. Found: C, 49.83; H, 4.01; N, 1.38%.

4.7. *Trans-4,4″-p-terphenyl-bis[(nicotinic acid)bis(methyldiphenylphosphine)]diplatinum(II) bis(triflate)* (**6**)

The complex was prepared from **3** by a similar procedure to that described in Section 4.5, and it was isolated as a pale yellow solid (yield 86%). ^{1}H-NMR (CDCl$_3$): δ 8.83 (s, 2H, OH), 8.46 (s, 2H, H^2), 8.29 (d, 2H, $^3J_{HH} = 4.8$, H^6), 7.91 (d, 2H, $^3J_{HH} = 7.5$ Hz, H^4), 7.57–7.24 (m, 40H, PPh$_2$), 1.64 (m, 12H, P–CH$_3$). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 9.2 (s, $^1J_{PPt} = 2882$ Hz). ESI-MS: m/z 1662 $[M - 2OTf - 2H]^+$. Anal. Calc. for $C_{84}H_{74}F_6N_2O_{10}P_4Pt_2S_2$: C, 51.38; H, 3.80; N, 1.43. Found: C, 51.22; H, 3.75; N, 1.50%.

4.8. *Trans-4,4′-benzophenone-bis[(iodo)-bis(methyldiphenylphosphine)]diplatinum(II)* (**7**)

Following a similar procedure to that described in Section 4.2, 4,4′-diiodobenzophenone and tetrakis(methyldiphenylphosphine)platinum(0) were reacted to give **7** as an off-white solid (yield 96%). ^{1}H-NMR (CDCl$_3$): δ 7.78–7.44 (m, 40H, PPh$_2$), 6.93 (d, 4H, $^3J_{HH} = 8.0$ Hz, $^3J_{PtH} = 54$ Hz, H^o), 6.78 (d, 4H, $^3J_{HH} =$

6.8 Hz, H^{m}), 2.10 (m, 12H, P–CH_3). $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): δ 3.9 ($^{1}J_{PtP} = 2886$ Hz). Anal. Calc. for $C_{65}H_{60}I_2OP_4Pt_2$: C, 48.04; H, 3.72. Found: C, 47.97; H, 3.61%.

4.9. *Trans-4,4′-benzophenone-bis[(nicotinic acid)bis(methyldiphenylphosphine)] diplatinum(II) bis(triflate)* (**8**)

The complex was prepared from **7** by a similar procedure to that described in Section 4.5, and it was isolated as a pale yellow solid (yield 97%). ^{1}H-NMR ($CDCl_3$): δ 9.29 (s, 2H, OH), 8.86 (d, 2H, $^{3}J_{HH} = 4.2$ Hz, H^{6}), 8.54 (s, 2H, H^{2}), 7.88 (d, 2H, $^{3}J_{HH} = 8.1$ Hz, H^{4}). $^{31}P\{^{1}H\}$-NMR ($CDCl_3$): δ 8.5 ($^{1}J_{PtP} = 2857$ Hz). Anal. Calc. for $C_{79}H_{70}F_6N_2O_{11}P_4Pt_2S_2 \cdot 0.5CH_2Cl_2$: C, 48.77; H, 3.65; N, 1.43. Found: C, 48.72; H, 3.51; N, 1.43%.

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