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Platinum and palladium bis(diphenylphosphino)ferrocene (dppf) complexes with heterocyclic N-acetamide ligands: Synthesis and molecular structures of [MCl(sac)(κ^2-dppf)] (M = Pt, Pd, sac = saccharinate), [PtCl(ata)(κ^2-dppf)] and [Pt(ata)$_2$(κ^2-dppf)] (ataH = N-(2-thiazolyl)acetamide)

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ABSTRACT

Room temperature addition of sodium saccharinate, Na(sac), to [MCl$_2$(κ^2-dppf)] (M = Pd, Pt; dppf = 1,1′-bis(diphenylphosphino)ferrocene) results in the formation of [MCl(sac)(κ^2-dppf)] in which the sac ligand is coordinated in a monodentate fashion through nitrogen. All attempts to coordinate a second saccharinate ligand were unsuccessful. In contrast, reaction of [PtCl$_2$(κ^2-dppf)] with N-(2-thiazolyl)acetamide (ataH) in the presence of KOH results in successive replacement of both chlorides affording [PtCl(ata)(κ^2-dppf)] and [Pt(ata)$_2$(κ^2-dppf)]. Crystal structures have determined for all four complexes. In both saccharinate complexes and [PtCl(ata)(κ^2-dppf)] the heterocyclic amide ligand is coordinated as expected through the amide-nitrogen. In contrast in Pt(ata)$_2$(κ^2-dppf) both ligands are bound through the nitrogen atom of the thiazole ring. In order to understand the adoption of these different ligand binding modes, geometry optimization calculations were carried out on different isomers of both ata complexes. For [PtCl(ata)(κ^2-dppf)] an energy difference of 10.5 kJ mol^{-1} was found between observed and unobserved isomers, while for [Pt(ata)$_2$(κ^2-dppf)] the difference was 9.3 kJ mol^{-1}. The reasons for the adoption of these different coordination modes are not clear but steric factors are likely to be a major contributory factor.

1. Introduction

There is considerable current interest in the coordination chemistry of the saccharinate (sac) ligand [1–5] primarily since the amide moiety is an important constituent of many biologically important compounds. Acid amide ligands in general have two potential coordination sites, the imine nitrogen and the carbonyl oxygen, while saccharinate also has two sulfonyl oxygen groups which can potentially coordinate to a metal [1–5]. As polyfunctional ligands, cyclic acetamides are able to form complexes with a wide range of metal ions. These generally take the form of mononuclear complexes, however, they are also known to form coordination polymers and in the case of bulky ligands such as sac they sometimes act as a simple counterion remaining outside of the coordination sphere [1,6].

Metal complexes of bidentate phosphanes have received significant attention as a result of their potential use as antitumor agents [7,8]. In this respect, platinum(II) complexes are of special interest due to the commercial use of *cis*-platin and related species in chemotherapy [9]. The metal-containing diphosphane bis(diphenylphosphino)ferrocene (dppf) and related derivatives are of particular interest, the high flexibility of the iron-cyclopentadienyl units allowing bite-angle changes to occur *via* low-energy pathways [10–12]. As part of our efforts to develop biologically active bifunctional compounds, we have studied the incorporation of two biologically active ligands in the same complex, for example phosphanes and thiones or amides [13–21]. As a continuation to this work we report herein the preparation of platinum(II) and palladium(II) bis(diphenylphosphino)ferrocene (dppf) complexes with heterocyclic N-acetamide co-ligands, the latter being derived from saccharine (sacH) and N-(2-thiazolyl)acetamide (ataH) (Scheme 1).

2. Experimental

2.1. General

NMR spectra were recorded on Varian Unity 500 or Gemini 200 spectrometers at the Institute for Anorganische Chemie,

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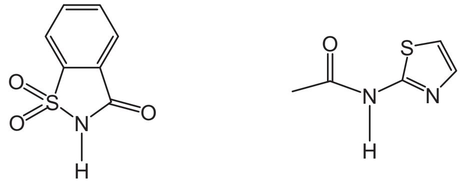

sacH ataH

Scheme 1.

Martin-Luther-Universitat, Halle, Germany or on a Bruker AMX400 spectrometer at University College London and referenced internally to the residual solvent peak (^{1}H and ^{13}C) or externally (^{31}P). All spectra were run in $CDCl_3$. IR spectra were recorded on a Shimadzu FT8400 spectrometer as CsI discs. Elemental analyses were carried out at University College London. Conductivity measurements were made on a conductivity meter type Philips PW9526. Melting points were measured on electro thermal 9300 melting point apparatus. $[PdCl_2(\kappa^2\text{-dppf})]$, $[PtCl_2(\kappa^2\text{-dppf})]$ and sodium saccharinate were purchased and used without further purification and N-(2-thiazolyl)acetamide [22] was prepared according to literature methods. All reactions were carried out in air using standard laboratory solvents.

2.2. *[PtCl(sac)(κ²-dppf)] (**1**)*

A warm ethanol (10 cm^3) solution of sodium saccharinate (0.096 g, 0.47 mmol) was added to a chloroform (20 cm^3) solution of $[PtCl_2(\kappa^2\text{-dppf})]$ (0.20 g, 0.23 mmol). The turbid yellow mixture was stirred at room temperature for 3 h then filtered. The filtrate was set aside to evaporate slowly at room temperature. The yellow crystals of $[PtCl(sac)(\kappa^2\text{-dppf})]$ (**1**) thus formed were filtered off and dried under vacuum (0.17 g, 72% yield). ^{1}H NMR: δ 8.13–6.93 (m, 24H, Ar), 5.35 (s, 1H, CH), 4.89 (s, 1H, CH), 4.67 (s, 1H, CH), 4.54 (s, 1H, CH), 4.45 (s, 1H, CH), 4.38 (s, 1H, CH), 4.19 (s, 1H, CH), 3.44 (s, 1H, CH), 3.38 (s, 1H, CH); ^{31}P{^{1}H} NMR: δ 15.30 (J_{PP} 14.5, J_{PtP} 3820 Hz), 6.01 (J_{PP} 14.5, J_{PtP} 3605 Hz). IR ν/cm^{-1}; IR(KBr) 3058w, 3016w, 2925w, 2860w, 1766s, 1587m, 1434m, 1299s, 1249s, 1161vs, 960m, 480s cm^{-1}; Elemental *Anal.* Calc. for $PtFeSNClP_2O_3C_{41}H_{32}$: C, 50.92; H, 3.34; N, 1.45. Found: C, 51.00; H, 3.50; N, 1.60%.

2.3. *[PdCl(sac)(κ²-dppf)] (**2**)*

A warm ethanol (10 cm^3) solution of sodium saccharinate (0.112 g, 0.55 mmol) was added to a chloroform (20 cm^3) solution of $[PdCl_2(\kappa^2\text{-dppf})]$ (0.20 g, 0.27 mmol). Following a similar procedure to above, $[PdCl(sac)(\kappa^2\text{-dppf})]$ (**2**) was isolated as a red-brown crystalline solid in 83% yield. ^{1}H NMR: δ 8.31–7.01 (m, 24H, Ar), 4.32 (br, 4H, CH), 3.42 (br, 4H, CH); ^{31}P{^{1}H} NMR: δ 37.20 (d, J_{PP} 12.7 Hz), 28.99 (d, J_{PP} 12.7 Hz). IR ν/cm^{-1}; IR(KBr) 3058w, 3051w, 2972w, 2918w, 1670s, 1586m, 1433m, 1294s, 1247s, 1155vs, 962m, 482s cm^{-1}; Elemental *Anal.* Calc. for $PdFeSNClP_2O_3C_{41}H_{32}$: C, 56.06; H, 3.67; N, 1.59. Found: C, 56.26; H, 3.40; N, 1.70%.

2.4. *[PtCl(ata)(κ²-dppf)] (**3**) and [Pt(ata)₂(κ²-dppf)] (**4**)*

A solution of ataH (0.027 g, 0.19 mmol) in ethanol (5 cm^3) and 1 cm^3 of KOH in ethanol (0.19 mmol, 0.5N) was added to a yellow solution of $[PtCl_2(\kappa^2\text{-dppf})]$ (0.08 g, 0.09 mmol) in chloroform (15 cm^3). The orange mixture thus formed was stirred at room temperature for 3 h then filtered. The filtrate was reduced in volume by half and methanol (5 cm^3) added. The mixture was set aside for few days. The orange solid thus formed was filtered off washed with hexane and dried under vacuum. Crystallization from a mixture of $CHCl_3$/MeOH/EtOH afforded 0.08 g (*ca.* 65%) of a highly crystalline orange solid consisting predominantly of orange rod-like crystals of $[Pt(ata)_2(\kappa^2\text{-dppf})]$ (**4**) but also containing a small number of small yellow blocks shown to be $[PtCl(ata)(\kappa^2\text{-dppf})]$ (**3**). Close inspection of crystals of **4** under a microscope showed that they consisted of a series of stacked thick plates. The crystals did extinguish under plane polarized light but attempts to get a good quality cell from preliminary X-ray data were not successful. Careful cleavage of one of these crystals gave a thin rod suitable for X-ray diffraction. (**3**) ^{1}H NMR: 328 K δ 8.5–6.9 (m, Ar + =CH), 6.50 (br, 1H, CH), 5.72 (vbr, 1H, CH), 4.68 (s, 1H, CH), 4.52 (s, 1H, CH), 4.18 (s, 2H, CH), 3.49 (s, 2H, CH), 2.49 (brs, 3H, Me); ^{31}P{^{1}H} NMR: 328 K δ 14.41 (d, J_{PP} 16.2 Hz, J_{PtP} 4048 Hz), 4.29 (d, J_{PP} 16.2 Hz, J_{PtP} 3290 Hz). (**4**) ^{1}H NMR: δ 7.74–6.98 (m, 20H, Ph), 6.65 (d, *J* 4.2 Hz, 1H, =CH), 6.03 (d, *J* 4.2 Hz, 1H, =CH), 4.83 (s, 2H, CH), 4.44 (s, 2H, CH), 4.32 (s, 2H, CH), 4.14 (s, 2H, CH), 2.34 (s, 3H, Me); ^{31}P{^{1}H} NMR: δ 3.38 (J_{PtP} 3519 Hz); IR ν/cm^{-1}; IR(KBr) 3086w, 2964w, 2921w, 1620s, 495s cm^{-1}; Elemental *Anal.* Calc. for $PtFeS_2N_4P_2O_2C_{44}H_{38}$: C, 51.22; H, 3.71; N, 5.43. Found: C, 51.20; H, 3.90; N, 5.70%.

2.5. *X-ray crystallography*

Single crystals were mounted on glass fibers and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction was carried out with SAINT PLUS and absorption correction applied using the program SADABS [23]. Structures were solved by direct-methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package [24].

Crystallographic data: $[PtCl(sac)(\kappa^2\text{-dppf})]$ (**1**): yellow block, size 0.28 mm × 0.16 mm × 0.14 mm, orthorhombic, space group $P2_12_12_1$, a = 10.4220(9) Å, b = 16.233(2) Å, c = 21.504(2) Å, V = 3638.0(6) Å^3, Z = 4, D_{calc} = 1.766 g/cm^3, μ = 4.450 mm^{-1}, $F(000)$ = 1904, final R indices [$F^2 > 2\sigma$] R_1 = 0.039, wR_2 = 0.062, R indices (all data) R_1 = 0.040, wR_2 = 0.064. $[PdCl(sac)(\kappa^2\text{-dppf})]$ (**2**): orange block, size 0.26 mm × 0.22 mm × 0.12 mm, orthorhombic, space group $P2_12_12_1$, a = 10.418(1) Å, b = 16.197(2) Å, c = 21.507(3) Å, V = 3629.0(8) Å^3, Z = 4, D_{calc} = 1.608 g/cm^3, μ = 1.156 mm^{-1}, $F(000)$ = 1776, final R indices [$F^2 > 2\sigma$] R_1 = 0.042, wR_2 = 0.087, R indices (all data) R_1 = 0.051, wR_2 = 0.090. $[PtCl(ata)(\kappa^2\text{-dppf})]$ (**3**): yellow block, size 0.08 mm × 0.08 mm × 0.07 mm, triclinic, space group $P\bar{1}$, a = 10.389(1) Å, b = 10.558(1) Å, c = 17.298(2) Å, α = 77.669(2)°, β = 85.180(2)°, γ = 69.840(2)°, V = 1739.9(4) Å^3, Z = 2, D_{calc} = 1.768 g/cm^3, μ = 4.697 mm^{-1}, $F(000)$ = 912, final R indices [$F^2 > 2\sigma$] R_1 = 0.041, wR_2 = 0.083, R indices (all data) R_1 = 0.051, wR_2 = 0.088. $[Pt(ata)_2(\kappa^2\text{-dppf})]$ (**4**): orange needle, size 0.22 mm × 0.08 mm × 0.06 mm, monoclinic, space group $P2_1$, a = 12.422(2) Å, b = 23.007(4) Å, c = 17.388(3) Å, β = 100.469(3)°, V = 4886.5(14) Å^3, Z = 2, D_{calc} = 1.402 g/cm^3, μ = 3.344 mm^{-1}, $F(000)$ = 2048, final R indices [$F^2 > 2\sigma$] R_1 = 0.097, wR_2 = 0.239, R indices (all data) R_1 = 0.140, wR_2 = 0.264.

2.6. *Computational details*

Calculations were performed with the GAUSSIAN 03 (G03) program package [25] employing the DFT method with Becke three parameter hybrid functional [26] and Lee–Yang–Parr's gradient corrected correlation functional (B3LYP) [27]. Geometry optimization was performed employing a two-layered ONIOM approach [28]. The LanL2DZ basis set [29] and effective core potential were