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Reactions of platinum(0) complexes with carbazole[1]

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Abstract

Reaction of carbazole with zerovalent [Pt(L)$_n$] gives oxidative insertion into the N–H rather than into a C–N bond; the product, *trans*-[HPt(L)$_2$(C$_{12}$H$_8$N)] (L = PMe$_3$; L = PEt$_3$) has been defined spectroscopically and by an X-ray determination. © 1998 Elsevier Science S.A. All rights reserved.

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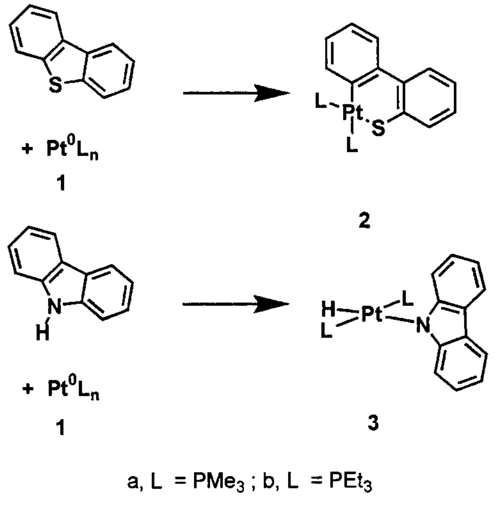
1. Introduction

We have reported extensive investigations of the chemistry of thiaplatinacycles. These complexes contain six-membered rings derived from the oxidative insertion of platinum(0), PtL$_n$, **1**, into the C–S bonds of a variety of thiophenes. Such complexes are likely to be intermediate in the platinum promoted hydrodesulfurization of thiophenes. These reactions have been shown to proceed with particular facility with dibenzothiophene giving **2** [1], as well as with benzothiophene and thiophene and methylthiophenes [2,3].

Another undesirable pollutant from the burning of fuel oil is NO$_x$, and while much of the nitrogen comes from the air, a significant portion arises from the combustion of N-containing heterocycles [4]. This is similar to the formation of SO$_x$ from the combustion of fuels containing sulfur heterocycles such as thiophenes. Thus the removal of nitrogen heterocycles is also highly desirable. It was therefore of considerable interest to compare the oxidative insertions of platinum(0) into thiophenes with the reactions of Pt(0) with the nitrogen counterparts, the pyrroles and their annelated analogues, the indoles and carbazoles.



a, L = PMe$_3$; b, L = PEt$_3$

2. Results and discussion

In view of the facility with which dibenzothiophene reacts, we commenced our studies by reacting PtL$_n$, **1**, with *N*-methylcarbazole. In fact under the conditions

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[1] With best wishes to Professor Pascual Royo on his 60th birthday.

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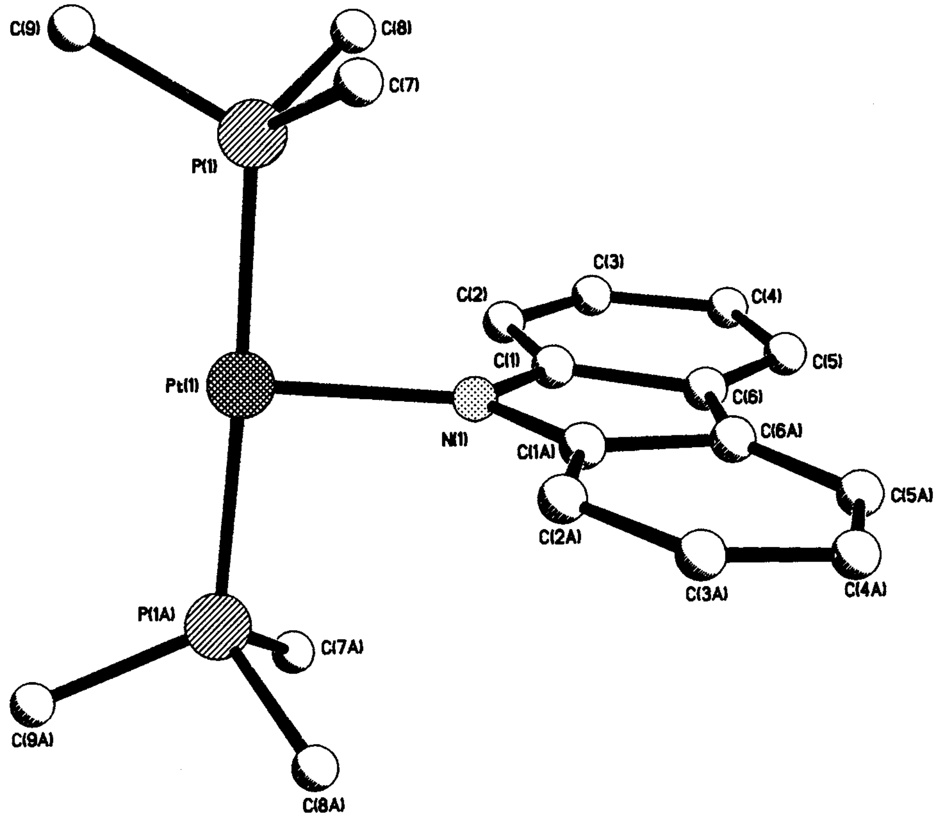

Fig. 1. A view of the molecular structure of $[HPt(PMe_3)_2(C_{12}H_8N)]$, complex **3a**, hydrogens omitted for clarity. Significant bond lengths (Pt–P(1) = Pt–P(1A) = 2.259(6); Pt–N, 2.09(2) Å) and angles (P(1)–Pt–P(1A) 177.4(2)°, N–Pt–P(1) = N–Pt–P(1A) = 91.29(10)°).

which had been successful for dibenzothiophene, (100°C in toluene and removing the volatiles in vacuo) no reaction at all could be detected. However, carbazole itself underwent ready reaction with both $[Pt(PMe_3)_4]$ (**1a**) and $[Pt(PEt_3)_3]$ (**1b**) to give *trans*-$[HPt(L)_2(C_{12}H_8N)]$ (**3a**, L = PMe_3; **3b**, L = PEt_3) by insertion of PtL_2 into the carbazole N–H bond. Complex **3a** was also prepared in 87% isolated yield in a one-pot reaction directly from $K_2[PtCl_4]$, carbazole, trimethylphosphine, and sodium hydroxide.

The NMR spectra of **3a** and **3b** delineated the structures. They each showed the platinum hydride resonance at high field, coupled to two *cis*-^{31}P nuclei and to the ^{195}Pt; this defined the *trans* disposition of the H and the carbazolyl moiety. As expected, the two *trans*-phosphines were equivalent and showed a single resonance, coupled to ^{195}Pt.

To check the identity of the complex a crystal was grown for X-ray analysis. This determination (Fig. 1) confirmed the basic structure showing the *trans* phosphines (Pt–P 2.259(6) Å) and the carbazolyl *cis*- to them (Pt–N 2.09 Å). The Pt, the two P atoms and the N were all coplanar and the molecule had a plane of symmetry through the nitrogen and the platinum, perpendicular to the Pt–P(1)–P(2)–N plane. The hydride was not located but its position, *trans* to the carbazolyl N, was evident from inspection of the molecule. One interesting feature was the near linearity of the P–Pt–P axis (angle P(1)–Pt–P(2) 177.4(2)°); this arose because the carbazolyl was not in the coordination plane but very nearly perpendicular to it, at an angle of 96.4° to the Pt–P(1)–P(2)–N plane.

Thus the carbazole gives the platinum some protection from attack along the axial directions. Presumably as a consequence of this, the complexes **3** are stable, even in solution, to air. However they slowly decompose in chloroform (containing HCl) to give $[PtL_2(H)Cl)]$.

Although oxidative addition reactions of the N–H of carbazole appear not to have been reported previously, Jonas and Wilke [5] and Stone and coworkers [6] noted that pyrrole underwent oxidative addition at the N–H to the tricyclohexylphosphine complexes of nickel(0) and platinum(0) to give *trans*-$[HM\{P(C_6H_{11})_3\}_2(C_4H_4N)]$, where M = Ni or Pt and C_4H_4N = 1-pyrrolyl.

3. Experimental

3.1. 'One-pot' preparation of [HPt(PMe$_3$)$_2$(C$_{12}$H$_8$N)] **3a**

PMe$_3$ (6.7 ml of a commercial 1 M solution in toluene), and K$_2$[PtCl$_4$] (500 mg, 1.20 mmol, dissolved in 3 ml of water) were added to a solution of NaOH (211 mg, 1.26 mmol) dissolved in EtOH (10 ml) under N$_2$. The mixture was stirred until colourless (30 min at 20°C), and then at 60°C (2 h). The solution was vacuum-evaporated giving a brown-yellow solid residue, containing **1a**. It was extracted with hot toluene (4×5 ml), and the red-brown solution filtered into a Schlenk tube containing carbazole (211 mg, 1.26 mmol). The mixture was stirred (110°C, 17 h), and vacuum-evaporated to dryness. ^{1}H NMR analysis of the crude solid revealed the formation of **3a** ($>90\%$), with small amounts of unreacted carbazole and OPMe$_3$. The impurities were removed by washing with acetone (2×5 ml). The tan solid **3a** was finally air-dried. Yield 547 mg (87%). Pure samples for elemental analysis and X-ray diffraction studies were obtained by slow crystallization from acetonitrile solutions at 20°C. Anal. Calc. for C$_{18}$H$_{27}$NP$_2$Pt: C, 42.0; H, 5.3; N, 2.7. Found: C, 42.2; H, 5.3; N, 2.7%. IR (KBr): ν(Pt–H), 2147 cm^{-1} (vs). NMR spectra in (CD$_3$)$_2$CO: ^{1}H δ, 8.02 (m, C*H*), 7.60 (m, CH), 7.23 (m, CH), 6,88 (m, CH), 1.26 (pseudo t, C*H*$_3$, $^2J_{\mathrm{PH}}\approx{}^4J_{\mathrm{PH}}=3.5$ Hz; Pt sat, $^3J_{\mathrm{PtH}}=33.5$ Hz), -14.29 (t, Pt*H*, $^2J_{\mathrm{PH}}=17.8$ Hz; Pt sat, $^1J_{\mathrm{PtH}}=1001$ Hz). ^{13}C{^{1}H}, δ 17.0 (dd, Me, $^1J_{\mathrm{PC}}=19$ Hz, $^2J_{\mathrm{PtC}}=52$ Hz), 114.3 (s, CH), 115.1 (s, CH), 120.1 (s, CH), 123.8 (s, CH), 125.5 (s, C), 150.8 (s, C). ^{31}P{^{1}H} δ -12.2 (s; Pt sat, $^1J_{\mathrm{PtP}}=2604$ Hz).

Complex **3a** was poorly soluble in CHCl$_3$, THF, MeOH, hexane, and ether, but soluble in hot acetone and in acetonitrile.

3.2. The X-ray structure determination of [HPt(PMe$_3$)$_2$(C$_{12}$H$_8$N)] **3a**

Crystal data and details of the structure refinement for complex **3a** are given in Table 1. Key bond lengths and angles are in the caption to the Fig. 1. Full details including Tables of atomic coordinates and bond length and angle data have been deposited at the Cambridge Crystallographic Data Centre.

3.3. Preparation of [HPt(C$_{12}$H$_8$N)(PEt$_3$)$_2$] **3b**

Complex **3b** was prepared in 95% yield by adding carbazole (0.90 g, 5.5 mmol) to a solution of [Pt(PEt$_3$)$_3$] (1.5 g, 2.7 mmol) in toluene (10 ml) at 20°C under argon. The colour changed from orange to yellow; the solvent and excess phosphine were then removed in vacuo (20°C/0.2 mmHg) to leave **3b** as a solid. The complex was crystallized from toluene/hexane. Anal. Calc. for C$_{24}$H$_{39}$NP$_2$Pt: C, 48.2; H, 6.6; N, 2.3. Found: C, 48.3; H, 6.6; N, 2.2%. NMR spectra in CDCl$_3$: ^{1}H: δ -14.4 (t, Pt*H*, $^2J_{\mathrm{PH}}=17$ Hz; Pt sat, $^1J_{\mathrm{PtH}}=940$ Hz) 0.95 (m, CH$_3$), 1.5 (m, CH$_2$), 7.02 (m, H$_b$), 7.6 (m, H$_c$),7.58 (m, H$_a$) and 8.25 (m, H$_d$, carbazole). ^{13}C{^{1}H} δ: 10.3 (–CH$_3$), 20.0 (m, CH$_2$), 113.0 (s, CH), 113.5 (s, CH), 118.7 (s, CH), 122.0 (s, CH), 125.3 (s, C), 149.5 (s, C). ^{31}P{^{1}H}: δ 22.6 ($^1J_{\mathrm{PtP}}=2693$ Hz).

Table 1
Crystal data and structure refinement for complex **3a**

Identification code	6oct972
Empirical formula	C$_{18}$H$_{27}$NP$_2$Pt
Formula weight	514.44
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a=13.819(3)$ Å, $\alpha=90°$ $b=17.598(4)$ Å, $\beta=108.41(3)°$ $c=8.530(2)$ Å, $\gamma=90°$
Volume, Z	1968.2(7) Å^3, 4
Density (calculated)	1.736 Mg m^3
Absorption coefficient	7.289 mm^{-1}
$F(000)$	1000
Crystal size	$0.80\times0.40\times0.12$ mm
θ range for data collection	1.94–25.15°
Limiting indices	$-1\leq h\leq16$, $-1\leq k\leq21$, $-10\leq l\leq9$
Reflections collected	2089
Independent reflections	1721 ($R_{\mathrm{int}}=0.0681$)
Absorption correction	ψ-scans
Max and min transmission	0.591 and 0.084
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1721/0/103
Goodness-of-fit on F^2	1.041
Final R indices [$I>2\sigma(I)$]	$R_1=0.0966$, $wR_2=0.2429$
R indices (all data)	$R_1=0.1014$, $wR_2=0.2529$
Extinction coefficient	0.0007(8)
Largest diff. peak and hole	3.109 and -5.849 e Å^{-3}

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