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Platinum(IV) complexes with α,ω-bis(pyrazol-1-yl) alkanediyl and diethyl ether/thioether ligands. Crystal structures of dibromodimethyl [1,2-bis(pyrazol-1-yl)ethane]platinum(IV) and trimethyl-bis [2-(pyrazol-1-yl)ethyl]etherplatinum(IV) tetrafluoroborate

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ABSTRACT

Reactions of the flexible α,ω-bis(pyrazol-1-yl) compounds 1,2-bis(pyrazol-1-yl)ethane (**L1**), 1,8-bis(pyrazol-1-yl)-*n*-octane (**L2**), bis[2-(pyrazol-1-yl)ethyl]ether (**L3**) and bis[2-(pyrazol-1-yl)ethyl]thioether (**L4**) with precursor organometallic platinum complexes ($[(PtBr_2Me_2)_n]$, $[(PtIMe_3)_4]$ and $[(PtMe_2(cod)]/I_2$) are described herein. The spectroscopic characterization of the platinum(IV) products of these reactions $[PtBr_2Me_2\{pz(CH_2)_mpz\}]$, $m = 2$ (**1**) or 8 (**2**), $[PtI_2Me_2\{pz(CH_2)_2pz\}]$ (**3**), $[PtMe_3(pzCH_2CH_2OCH_2CH_2pz)][BF_4]$ (**4**) and $[PtMe_3(pzCH_2CH_2SCH_2CH_2pz)][CF_3SO_3]$ (**5**), where 'pz' is pyrazol-1-yl, is discussed. Furthermore, solid state structures of **1**, a complex with a seven-membered chelate ring, and **4**, a complex bearing the neutral $\kappa^2N,N',\kappa O$ ligand bis[2-(pyrazol-1-yl)ethyl]ether (**L3**) are reported.

1. Introduction

The tris(pyrazol-1-yl)borate ligand and its tripod derivatives are probably the best known ligand class incorporating the pyrazolyl ring [1]. Apart from tris(pyrazol-1-yl)borate ligands, flexible alkanediyl, ether and polyether linked bis(pyrazolyl) ligands have also been studied [2–7]. Investigations with ligands of the type bis[2-(3,5-dialkylpyrazol-1-yl)ethyl]ether and various first and second row metals have demonstrated the versatile coordination modes possible with these flexidentate ligands [8]. More recently the preparation of bis[2-(pyrazol-1-yl)ethyl]ether (**L3**) has been reported in the literature [9], although its coordination chemistry has not been examined. As part of our investigations with bis(N-heterocyclic) polyether type ligands we were interested in the reactivity of flexible α,ω-bis(pyrazol-1-yl) compounds with organometallic platinum(IV) species. Herein we report the reaction of various alkanediyl, ether and thioether type α,ω-bis(pyrazol-1-yl) compounds, some of which are reported here for the first time, with $[(PtBr_2Me_2)_n]$, $[PtMe_2(cod)]/I_2$ and $[(PtIMe_3)_4]$. The coordination modes possible with these simple compounds and the characterization of all complexes, including two crystal structures, are described.

2. Results and discussion

2.1. Synthesis

The preparation of the new compounds $pz(CH_2)_8pz$ (**L2**) and $pzCH_2CH_2SCH_2CH_2pz$ (**L4**), where 'pz' is pyrazol-1-yl, was accomplished by appropriate modification of a known procedure (see Section 4) [7]. The reaction of **L1** or **L2** with $[(PtBr_2Me_2)_n]$ furnished the mononuclear complexes $[PtBr_2Me_2(pzCH_2CH_2pz)]$ (**1**) and $[PtBr_2Me_2\{pz(CH_2)_8pz\}]$ (**2**), respectively (Scheme 1).

The reaction of **L1** with dimethylcyclooctadieneplatinum(II) in the presence of I_2 yielded $[PtI_2Me_2(pzCH_2CH_2pz)]$ (**3**) (Scheme 2), as expected since the methylene linked bis(pyrazol-1-yl) derivative of **L1** yielded an analogous product [10].

Although, bis[2-(pyrazol-1-yl)ethyl]ether (**L3**) reacted with $[(PtBr_2Me_2)_n]$ to yield a yellow powder, it was not possible to characterize the product satisfactorily. However, **L3** reacted with the Pope cluster $[(PtIMe_3)_4]$ in the presence of $AgBF_4$ to afford $[PtMe_3(pzCH_2CH_2OCH_2CH_2pz)][BF_4]$ (**4**) (Scheme 3). The thioether derivative of **L3**, **L4**, reacted with the Pope cluster in a similar way. $[PtMe_3(pzCH_2CH_2SCH_2CH_2pz)][CF_3SO_3]$ (**5**) was isolated in

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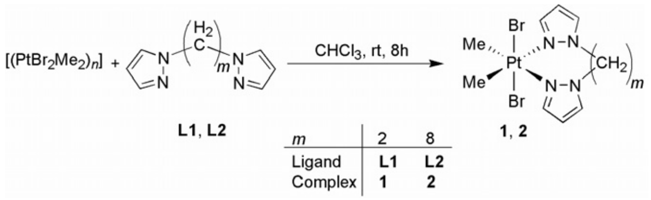
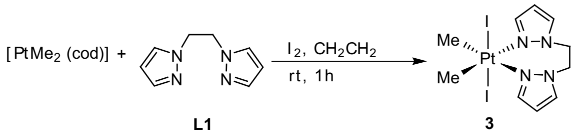
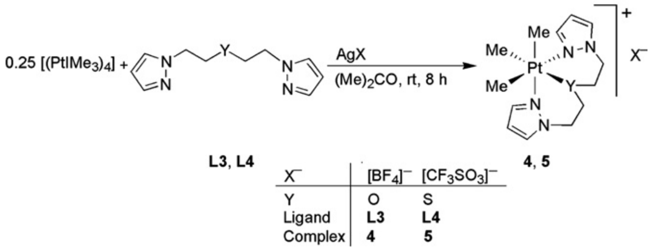


Scheme 1.



Scheme 2.



Scheme 3.

the presence of minor impurities but was fully characterized in solution as an analogue of **4**, with a triflate rather than tetrafluoroborate counterion, as discussed below.

2.2. Characterization

Complexes **1**–**5** have good solubility in common organic solvents such as acetone and chloroform and were characterized by NMR spectroscopy. As can be seen from the data given in Table 1, the ^{195}Pt NMR spectra contain a single resonance between −3409 and −2195 ppm with the diiodo substituted complex **3** the most high-field shifted, as may be expected [11]. A single resonance is found for the methyl ligands in the ^{1}H and ^{13}C NMR spectra of **1**–**3**. The $^{2}J_{\mathrm{Pt,H}}$ (70–75 Hz) and $^{1}J_{\mathrm{Pt,C}}$ (526.6 and 543.7 Hz) coupling constants confirm the *trans* coordination of the nitrogen donor ligands to the methyl ligands with the halo ligands occupying mutually *trans* positions (configuration index: *OC*-6-13), as may be expected [10,12]. In addition, the ^{1}H NMR spectrum of **2** shows a broadening of the signals assignable to the CH_2 groups of the spacer, relative to those of the free ligand, whereas the resonance of the methyl ligands are sharp.

The ^{1}H and ^{13}C NMR spectra of **4** and **5** share a number of similarities. Comparing the ^{1}H NMR spectrum of **4** to that of the corresponding free ligand **L3** (Fig. 1), the AA′XX′ spin system of the protons on the **L3** backbone ($C^6H_2C^7H_2$) becomes an ABCD spin system in **4** (δ_H 4.2–4.6 ppm; assignment by correlation spectroscopy). The three methyl ligands have two sets of resonances in a 2:1 intensity ratio and the corresponding $^{2}J_{\mathrm{Pt,H}}$ (69.9 and 80.7 Hz) and $^{1}J_{\mathrm{Pt,C}}$ (692.5 and 773.3 Hz) coupling constants confirm the coordination of two of the methyl ligands *trans* configured to the ligating nitrogen atoms and the third methyl ligand *trans* configured to the ligating oxygen atom (sulfur atom in **5**) giving a configuration index of *OC*-6-33. Due to the C_s point group symmetry of **4**, one resonance for C^6 atoms and one resonance for C^7 atoms are observed in the ^{13}C NMR spectrum. Similar findings are observed in the ^{1}H and ^{13}C NMR spectra of **5** (see Section 4).

Complexes **4** and **5** were also characterized by high resolution ESI-MS. The $[PtMe_3(pzCH_2CH_2OCH_2CH_2pz)]^+$ ($[M]^+$) cation at *m*/*z* 446.15124 is the only peak observed in the positive mode spectrum of **4** and the isotopic pattern is in satisfactory agreement with the calculated values (see Section 4). The most intensive peak in the positive mode spectrum of **5** is found to be the $[PtMe_3(pzCH_2CH_2SCH_2CH_2pz)]^+$ ($[M]^+$) cation at *m*/*z* 462.12835 (Fig. 2a). Enlargement of the peak assignable to $[M]^+$ shows an isotopic pattern consistent with the calculated values expected for a cation of this composition (Fig. 2b and Section 4). The second most intensive peak in the spectrum at *m*/*z* 1071.19950 is attributed to the dication + anion cluster ($[2M+CF_3SO_3]^+$). The signal at *m*/*z* 431.07891 agrees with the elimination of two methyl fragments from $[M]^+$.

2.3. Crystal structures

Complex **1** crystallized as **1** · $CHCl_3$ in the monoclinic space group $P2_1/c$ (Fig. 3). As the data collected in Table 2 confirm, the molecule has a distorted octahedral geometry. There is no evidence of any unusual intra- or intermolecular interactions.

The chelating ligand **L1** is *trans* configured to the methyl ligands. A large N1–Pt–N3 bite angle (97.3(1)°) is created by the chelating ligand due to geometrical constraints and is a common feature in the small number of reported platinum(IV) complexes with N,N′-bidentate ligands giving seven-membered chelate rings [13]. Although the C1–Pt–C2 bond angle is 86.4(2)° it is similar to other C–Pt–C bond angles observed for related dihalodimethylplatinum(IV) structures (86.8(4)–96.6(3)°) [10,14]. Other than the Pt–N3 bond length (2.235(3) Å) which is longer than expected for a Pt(IV)–N bond *trans* to a carbon ligator atom (median 2.163 Å; lower/upper quartile 2.142/2.198 Å; *n* = 351; *n* = number of observations) no peculiarities are found for the bond lengths of **1** [15]. Both pyrazolyl rings are twisted out of the $[PtC_2N_2]$ coordination plane (γ = 8.9(2)° and 34.5(2)°). The C6 and C7 atoms of the

Table 1
Selected ^{1}H, ^{13}C and ^{195}Pt NMR data for **1**–**5** (δ in ppm, *J* in Hz)

Complex	Solvent	δ (Pt–CH_3) ($^{2}J_{\mathrm{Pt,H}}$)	δ (Pt–CH_3) ($^{1}J_{\mathrm{Pt,C}}$)	δ_{Pt}
1	$CDCl_3$	2.31 (73.3)	−3.8 (543.7)	−2319
2	$CDCl_3$	2.31 (73.3)	−5.9 (526.6)	−2320
3	$(CD_3)_2CO$	2.66 (75.5)	−13.5[a]	−3409
4	$(CD_3)_2CO$	1.02 (69.9) (H_3C–Pt–N)	−7.1 (773.3) (H_3C–Pt–O)	−2195
		1.50 (80.7) (H_3C–Pt–O)	−6.7 (692.5) (H_3C–Pt–N)	
5	$(CD_3)_2CO$	0.95 (70.9) (H_3C–Pt–N)	−7.8 (669.5) (H_3C–Pt–N)	−2874[b]
		1.33 (66.8) (H_3C–Pt–S)	9.3 (662.0) (H_3C–Pt–S)	

[a] Coupling not observed.
[b] Measured in $CDCl_3$.