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SYNTHESIS OF BIS[2-(DIMETHYLARSINO)ETHYL]AMINE (DAEA) AND ITS COMPLEXATION WITH Rh(I) AND Pd(II)

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Abstract

The preparation of the new chelating 'HYBRID' ligand containing secondary amine and tertiary arsine donors $HN(CH_2CH_2AsMe_2)_2$ is described. The simple coordination chemistry with $[RhCl(COD)]_2$ (COD = cycloocta-1,5-diene) and Na_2PdCl_4 to give square planar complexes is also reported.

Polydentate ligands containing hard and soft donor atoms, e.g. nitrogen and arsine, with varying degrees of σ-basicity and π-acidity are of interest in the study of their affects on the magnetic and stereochemical properties of complexes[1]. We have recently established studies on the amino diphosphine ligand $HN[(CH_2)_3PMe_2]_2$ and find that with Ni(II), Pd(II) and Pt(II) metals, relatively intractable non-crystalline products predominate[2]. Presumably this behaviour will be influenced by the size of the potential chelate rings since the required six-membered rings formed with this ligand may be relatively less stable than a bridging configuration enabling polymerisation. In order to minimise this possibility we have prepared the new ligand bis[2-(dimethylarsino)ethyl]amine ($HN[CH_2CH_2AsMe_2]_2$, DAEA), and herein report its synthesis and behavioural studies of its coordination chemistry. Similar alkylarsine ligands are rare although the analogous phenyl compound $HN[(CH_2)_2AsPh_2]_2$[3] and complexes derived therefrom have been known for some time. There are also more recent studies on a related tertiary amine $PhCH_2N[(CH_2)_2AsPh_2]_2$[4].

Experimental

All manipulations of air-sensitive materials were performed under nitrogen. $[RhCl(COD)]_2$ [5] and $(CH_3)_2AsI$ [6] were prepared as described in the literature; $[NH_2(CH_2CH_2Cl)_2]^+Cl^-$ was obtained from a commercial source and used without any further purification.

Preparation of $HN(CH_2CH_2AsMe_2)_2$ (DAEA)

To a magnetically stirred suspension of fresh sodium wire (10 g, 0.43 g-atom) in THF (100 ml) in a 500 ml three-necked round-bottomed flask equipped with a nitrogen inlet and outlet, was added a solution of $(CH_3)_2AsI$ (20 g, 0.087 mol) in THF (70 ml) over a period of 1.5-2 h. A slightly exothermic reaction occurred as the solution turned bright yellow, then green with the formation of a white solid. The mixture was then refluxed (1 h) and cooled to room temperature. The solution was then separated by filtration and treated portionwise with $[NH_2(CH_2CH_2Cl)_2]^+Cl^-$ (4.75 g, 0.026 mol) during 3 h. The resultant mixture was stirred under nitrogen (20 h) with formation of a white solid. The solvent was removed *in vacuo*, and the residue treated with ether (150 ml), then filtered, dried over Na_2SO_4 and evaporated, giving 5.1 g (65% purity >90%). For further purification, it was distilled at 110°C/0.2 mmHg as a colourless air-sensitive oil.

Preparation of $PdCl_2$(DAEA)

To an ethanol solution (20 ml) of Na_2PdCl_4 (0.488 g, 1.66 mmol) was added a solution of DAEA (0.468 g, 1.66 mmol) in ethanol (3 ml). The colour changed immediately to yellow-orange. After stirring (2 h), the mixture was evaporated to dryness and the residue dissolved in CH_2Cl_2 (20 ml). The solution was filtered and concentrated to a small volume (5 ml) and the complex was precipitated by the addition of hexane (20 ml) as a yellow powder. The product was filtered, washed with hexane (10 ml), ether (10 ml) and dried *in vacuo*. Yield 74%.

Preparation of RhCl(DAEA)

To an acetonitrile solution (15 ml) of $[RhCl(COD)]_2$ (0.25 g, 0.5 mmol) was added a solution of DAEA (0.28 g, 1 mmol) in CH_3CN (2 ml), whereupon the solution became red. After stirring (6 h), the mixture was evaporated and the residue dissolved in ethanol. The ethanolic solution was filtered and the filtrate was treated as in the preparation of $PdCl_2$(DAEA) above. The red complex was obtained in 82% yield.

Preparation of $[PdCl(DAEA)]BPh_4$

To an acetonitrile solution (30 ml) of Na_2PdCl_4 (0.294 g, 1 mmol) was added a solution of DAEA (0.28 g, 1 mmol) in 3 ml of CH_3CN, with stirring, then $NaBPh_4$ (0.341 g, 1 mmol) in CH_3CN (95 ml) was added. The resultant yellow solution was stirred for further 13 h. Acetonitrile was removed *in vacuo*, the residue was extracted into dichloromethane (20 ml), filtered and evaporated to dryness, yielding a yellow powder that was washed with ether (15 ml) and dried *in vacuo*. The yield was essentially quantitative.

Results and discussions

The reaction of $[RhCl(COD)]_2$ with DAEA in acetonitrile enables the isolation of a diamagnetic red powder which analyses for RhCl(DAEA). Since both the ^1H and $^{13}C\{^1H\}$N.M.R. spectra [Table] exhibit singlets for the arsenic methyls (at 1.01 and 9.48 ppm respectively) a square

Table Elemental analyses, spectral data and physical properties of DAEA and its Pd(II) and Rh(I) complexes

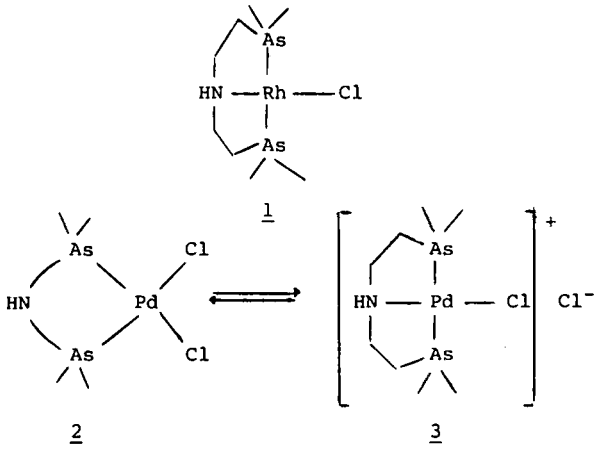
Compound	Calcd. / Found	Anal.(%) C	H	N	M	As	^1H a (ppm)	^{13}C a (ppm)	IR b (cm^{-1})	Λ_M c ($ohm^{-1}mol^{-1}cm^2$)
DAEA		34.2	7.47	4.98			0.74, s, 12H, $C\underline{H}_3As$; 1.47, t, 4H, $C\underline{H}_2As$; 2.56, t, 4H, $C\underline{H}_2N$.	8.94, $\underline{C}H_3As$; 26.6, $\underline{C}H_2As$; 46.2, $\underline{C}H_2N$.	3480, 1655, 1430, 1260, 1110, 580, 410, 320.	
		34.2	7.40	4.88						
$PdCl_2$(DAEA)		21.0	4.58	3.05	23.2	32.7	0.95, s, 12H, $C\underline{H}_3As$; 2.5, m, 4H, $C\underline{H}_2As$; 3.1, m, 4H, $C\underline{H}_2N$.	11.75, $\underline{C}H_3As$; 31.30, $\underline{C}H_2As$; 51.39, $\underline{C}H_2N$.	3390, 1260, 1160, 1090, 1040, 920, 660, 590, 420, 390, 340.	3.44 (24.05)
		21.3	4.43	2.95	23.1	32.2				
$[PdCl(DAEA)]BPh_4$		51.8	5.52	1.88	14.3	20.2	1.20, s, 12H, $C\underline{H}_3As$; 1.35-1.85, m, 4H, $C\underline{H}_2As$; 2.18-2.75, m, 4H, $C\underline{H}_2N$; 6.75-7.47, mult., 20H, $C_6\underline{H}_5$.		3180, 1575, 1150, 1170, 1035, 980, 955, 855, 655, 610.	35.0
		51.2	5.45	1.90	13.7	20.1				
RhCl(DAEA)		31.3	5.00	3.38	24.5	35.8	1.01, s, 12H, $C\underline{H}_3As$; 2.81, m, 4H, $C\underline{H}_2As$; 3.20, m, 4H, $C\underline{H}_2N$.	9.48, $\underline{C}H_3As$; 30.35, $\underline{C}H_2As$; 49.80, $\underline{C}H_2N$.	3290, 1660, 1270, 1190, 1390, 920, 880, 800, 720, 610, 380, 350.	1.86 (9.50)
		31.0	4.89	3.00	24.2	35.7				

a Relative to internal Me_4Si, in $CDCl_3$ for DAEA and in CD_3CN for Pd(II) and Rh(I) complexes.

b Neat for DAEA and in Nujol for complexes.

c Molar conductivity, conc. $1x10^{-3}$ M in acetonitrile at 298K, values in parentheses are for nitromethane solutions.

planar stereochemistry (Scheme) with trans, magnetically equivalent, dimethylarsino groups is proposed. The IR spectrum is consistent also with the nitrogen atom being coordinated, as the N-H stretch (3290 cm^{-1}) appears shifted nearly 200 cm^{-1} to lower frequency relative to the free amine (see Table) as would be expected for coordinated amine [7]. The complex is also diamagnetic and



Scheme Proposed structures of the rhodium and palladium complexes.

is essentially a non-conductor in dichloromethane. The behaviour of $[RhCl(COD)]_2$ with DAEA is then analogous to the behaviour of $[IrCl(COD)]_2$ with $PhCH_2N(CH_2CH_2AsPh_2)_2$ (DABA) where square planar IrCl(COD)(DABA) is formed [8].

The interaction of DAEA with Na_2PdCl_4 or with $PdCl_2(NCPh)_2$ in ethanol provides a yellow powder that analyses for $PdCl_2$(DAEA). Addition of sodium tetraphenylborate to solutions of the neutral complex in ethanol, causes precipitation of the salt, $[PdCl(DAEA)]BPh_4$, which is soluble in acetonitrile. For $PdCl_2$(DAEA) ^1H and $^{13}C\{^1H\}$ NMR data (singlets at 0.95 and 11.75 ppm respectively) indicate magnetically equivalent arsenic methyls. In the IR spectrum The N-H stretch occurs much closer to that in the free amine than the corresponding band in RhCl(DAEA) and may indicate that the nitrogen atom is uncoordinated to palladium. This interpretation is supported by the observation that in the salt, $[PdCl(DAEA)]^+ BPh_4^-$, the N-H stretching frequency moves to lower frequency, and for this we assign a square planar geometry around palladium with both arsenic and nitrogen atoms coordinated. Thus we assign structure 2 (Scheme) to $PdCl_2$(DAEA). Noteworthy is the conductance data for this compound; acetonitrile solutions show very low conductivity consistent with structure 2, whereas in nitromethane observed values of conductivity are intermediate between those expected for a non-electrolyte and a fully dissociated 1:1 electrolyte (comparison was made with $Bu_4N^+Br^-$: 62.5 $ohm^{-1}mol^{-1}cm^2$). This indicates an equilibrium between structure 2 and an ionic species such as structure 3 (Scheme), since the IR data is not consistent with the compound being a close ion-pair in CH_2Cl_2 that is more completely dissociated in CH_3NO_2. The same behaviour has previously been proposed for similar palladium complexes [8] and similar conductivity properties have been observed [9].

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