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COORDINATION COMPLEXES CONTAINING MULTIDENTATE LIGANDS

VI*. THE SYNTHESIS OF THE OPEN-CHAIN TETRATERTIARY ARSINE 1,3-PROPANEBIS(3-DIMETHYLARSINOPROPYLPHENYLARSINE) AND ITS REACTION WITH *trans*-CHLOROCARBONYLBIS(TRIPHENYLARSINE)-IRIDIUM(I)

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Summary

The synthesis of the open-chain tetratertiary arsine, 1,3-propanebis(3-dimethylarsinopropylphenylarsine), lqa, is described. The ligand reacts with *trans*-Ir(CO)Cl(AsPh$_3$)$_2$ to form [Ir(CO)(lqa)]Cl, from which [Ir(CO)(lqa)]-BPh$_4$ may be obtained. Other [Ir(CO)As$_4$]Cl species were formed by the reaction of *trans*-Ir(CO)Cl(AsPh$_3$)$_2$ with the bidentate chelates dae and vaa (dae = 1,2-bis(diphenylarsino)ethane; vaa = *cis*-1,2-bis(diphenylarsino)ethylene).

Introduction

Whilst the coordination chemistry of tripod tetratertiary arsine chelates has been well investigated [1,2], relatively little has been published on the preparation or reactions of open-chain tetratertiary arsines. An X-ray crystal structure of [Pd(TPAs)Cl]ClO$_4$.C$_6$H$_6$ [TPAs = *o*-phenylenebis(*o*-dimethylarsinophenylenemethylarsine)] has shown the ligand binds as a quadridentate chelate in an essentially square pyramidal complex [3], and Bosnich et al. [4] have recently separated the racemic and *meso* isomers of a disymmetric tetratertiary arsine via their cobalt(III) complexes. We wish to report here the preparation of a new open-chain tetratertiary arsine, 1,3-propanebis(3-dimethylarsinopropylphenylarsine), lqa, and its reaction with *trans*-chlorocarbonylbis(triphenylarsine)-iridium(I). This is an extension of our investigation of the reactions of *trans*-Ir(CO)X(EPh$_3$)$_2$ (E = P, As) species with bidentate [5] and tridentate [6] Group

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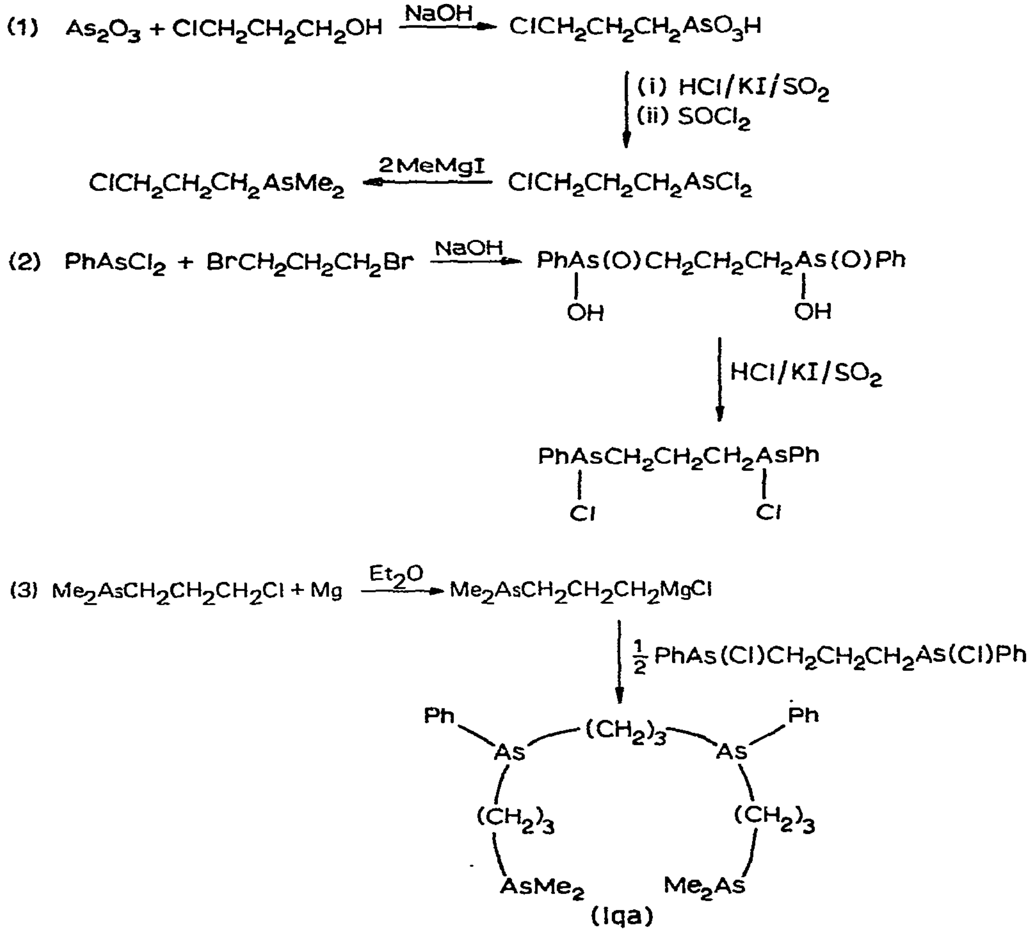
* For Part V see ref. 6.

VB ligands. Although Haines and Singleton [7] have prepared $[Ir(CO)(AsMe_2Ph)_4]BPh_4$, very few Ir^I species with more than two arsine donor groups have been reported.

Discussion

The ligand. The use by coordination and organometallic chemists of simple monodentate Group VB ligands or simple ditertiaryphosphines rather than multidentate chelating ligands reflects, to a certain extent, the difficulty of the preparation of the more complicated ligands. The method of preparation of lqa consists of three major steps (Scheme 1).

SCHEME 1



(lqa)

After stripping off the ether at the end of final hydrolysis the ligand may be distilled (200°/0.1 mm Hg) to yield a colourless oil. The ^1H NMR spectrum is interpretable thus [8,9]: phenyl τ2.63m*, 2.80m; methylene adjacent to

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* s, singlet; t, triplet; m, multiplet.

arsinophenyl τ 8.35t; methylene adjacent to arsinomethyl τ8.94; methylene τ8.56m; methyl τ9.20s. Integration Ph/Me/CH_2 10/12/18.

The complexes. As part of this study we also included the preparation of Ir^IAs_4 species involving the bidentate arsines 1,2-bis(diphenylarsino)ethane, dae, and *cis*-1,2-bis(diphenylarsino)ethylene, vaa. Previous attempts to prepare $[Ir(CO)L_2]Cl$ (L = dae, vaa) by treatment of *trans*-$Ir(CO)Cl(PPh_3)_2$ with dae or vaa were not successful, but we found that these ligands readily displaced triphenylarsine from *trans*-$Ir(CO)Cl(AsPh_3)_2$ to yield the required $[Ir(CO)L_2]Cl$ complexes.

The Nujol mull spectra of these complexes exhibit ν(CO) at 1940 (vaa) and 1920 cm^{-1} (dae). The higher CO bond order in the vaa complex indicates that vaa has a greater tendency than dae to delocalise metal π-electrons (probably arising from the presence of empty antibonding orbitals in the C=C bond or because of the more electronegative sp^2 carbon atoms). In $[Ir(CO)(vpp)_2]Cl$ [10] (vpp = *cis*-1,2-bis(diphenylphosphino)ethylene) ν(CO) appears at 1955 cm^{-1}, which may be taken to indicate that of the two vinylic ligands vpp and vaa, the former is the better π-acceptor.

The linear tetratertiary arsine, lqa, reacts with *trans*-$Ir(CO)Cl(AsPh_3)_2$ in deoxygenated benzene to yield the pale yellow [Ir(CO)(lqa)]Cl complex. Further reaction of this species with sodium tetraphenylborate led to the isolation of $[Ir(CO)(lqa)]BPh_4$. Both of these complexes are 1/1 electrolytes in nitromethane, and exhibit ν(CO) at 1910 cm^{-1}, very close to the ν(CO) value of $[Ir(CO)(dae)_2]Cl$. Unfortunately insufficient solubility in suitable solvents prohibited ^1H NMR measurements on the lqa complexes.

Experimental

*1,3-Propanebis(3-dimethylarsinopropylphenylarsine)**

Stage 1: 3-Chloropropyldimethylarsine was prepared by a modification [11] of the method of Gough and King [12]. The clear oily liquid was distilled at 82-88° (at 1.0 mm Hg).

Stage 2: 1,3-Propanebis(phenylchloroarsine) was made by a method similar to that of Dutta et al. [13] Phenyldichloroarsine (48 g) was added dropwise over 1h to a well cooled (10°C) and efficiently stirred NaOH solution (37.5 g in 150 cm^3 H_2O). A little white precipitate formed towards the end of the addition. 1,3-Dibromopropane (22 g) was then added dropwise over 1 h at 10°C, and the resulting mixture was then refluxed for 5 h. After 2 and 4 h of reflux small quantities of 1,3-dibromopropane (4 cm^3) were added. The clear solution was cooled to 5°C and acidified with conc. HCl to Congo Red (pH 3-4). The resulting white gelatinous mixture was stirred for 1 h at 10°C and left overnight to warm to room temperature. After decanting the liquid the gelatinous white material was suspended in water (50 cm^3) and conc. HCl (150 cm^3) was added, followed by more water (200 cm^3). The solution was cooled to 5°C and treated with KI (1 g in 10 cm^3 H_2O) and the brown mixture was stirred at 5°C while sulphur dioxide was passed through for 2 h. The resulting yellow mixture was allowed to

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* All reactions performed under nitrogen.

stand overnight, the lower layer separated and dissolved in ether and dried over anhydrous magnesium sulphate. After stripping off the ether a yellow viscous oil was obtained (29.7 g). (Found: C, 43.3; H, 4.1; Cl, 16.7. $C_{15}H_{16}As_2Cl_2$ calcd.: C, 42.9; H, 3.8; Cl 16.9%.)

Stage 3: 1,3-Propanebis(3-dimethylarsinopropylphenylarsine). A Grignard reagent was prepared from 3-chloropropyldimethylarsine (18.3 g; 0.1 mole) according to the method of Meek et al. [11]. To this solution, at 10°C, was added an ether solution (50 cm^3) of 1,3-propanebis(phenylchloroarsine) (22 g; 0.05 mole) with stirring over a period of 1 h. The initial heavy white/gray precipitate which formed gradually disappeared, and after completion of addition two layers were seen on standing. The mixture was hydrolysed with saturated ammonium chloride solution (100 cm^3), and the ether layer separated and dried over anhydrous magnesium sulphate. After stripping off the ether the resulting oil was distilled (200°C, 0.1 mm Hg) to yield the ligand as a colourless oil. Yield 23.7 g (74%). (Found: C, 47.0; H, 6.4. $C_{25}H_{40}As_4$ calcd.: C, 46.9; H, 6.4%.)
Infrared spectrum*: 3060 m,s, 3045 m,s, 3015 w,s, 2965 st,s, 2930 st(sh), 2900-st,s, 2840 m,s, 2800 w,s, 1940 w(br), 1868 w(br), 1800 w(br), 1578 m,s, 1480-st,s, 1445 m,s, 1430 st,s, 1415 st(sh), 1370 w(br), 1330 m,s, 1295 m(br), 1252-st,s, 1215 w(sh), 1195 w(br), 1150 w(br), 1130 w(br), 1070 st,s, 1062 st,s, 1022 st,s, 995 st,s, 950 w(br), 923 m(br), 882 st,s, 846 st,s, 795 w(br), 732 st,s, 694 st,s, 634 w(br), 577 st,s, 464 st,s, 372 w(br), 290 w(br). Absorptions at 694, 577 and 464 cm^{-1} are assignable to As—C stretching modes [14,15].

trans-Chlorocarbonylbis(triphenylarsine). This compound was synthesised according to the method of Chatt and co-workers [16]. (Found: C, 51.5; H, 3.6. $C_{37}H_{30}IrAs_2OCl$ calcd.: C, 51.3; H, 3.5%. ν(CO) 1940 cm^{-1}.)

Carbonylbis[1,2-bis(diphenylarsino)ethane]iridium (I) chloride. To a solution of *trans*-Ir(CO)Cl$(AsPh_3)_2$ (0.88 g, 1.0 mmole) in deoxygenated benzene (50 cm^3) was added dae (0.97 g; 2.0 mmole). A creamy precipitate was immediately formed and the mixture was stirred for 1 h. After filtration the solid was dried in vacuo over $CaCl_2$. Yield 9.7 g (79%). (Found: C, 51.3; H, 4.2. $C_{53}H_{48}IrAs_4OCl$ calcd.: C, 51.6; H, 3.9%.) Carbonylbis[*cis*-1,2-bis(diphenylarsino)ethylene] iridium(I) chloride was prepared similarly in 74% yield. (Found: C, 52.2; H, 4.1. $C_{53}H_{44}IrAs_4OCl$ calcd.: C, 51.8; H, 3.6%.)

Carbonyl[1,3-propanebis(3-dimethylarsinopropylphenylarsine)]iridium(I) chloride was prepared similarly in 72% yield. (Found: C, 35.5; H, 5.1. $C_{26}H_{40}OCl$ calcd.: C, 34.6; H, 4.4%.)

Carbonyl[1,3-propanebis(3-dimethylarsinopropylphenylarsine)]iridium(I) tetraphenylborate. To a solution of [Ir(CO)(lqa)]Cl (0.9 g, 1.0 mmole) in dichloromethane (25 cm^3) was added a solution of sodium tetraphenylborate (0.35 g, 1.1 mmole) in benzene (25 cm^3). After stirring for 15 min the dichloromethane was evaporated off to yield the very pale yellow solid. This was subsequently recrystallised from dichloromethane. Yield 0.76 g (69%). (Found: C, 50.1; H, 4.9. $C_{50}H_{60}IrAs_4OB$ calcd.: C, 50.8; H, 5.0%.)

Physical measurements were carried out as previously described [17].

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* s, sharp; st, strong; m, medium; (br), broad; (sh), shoulder; w, weak.

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