APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 236–238
Main Group Metal Compounds **AOC**

A ^{207}Pb NMR study of the adducts of triphenyllead chloride and diphenyllead dichloride

Lara A. Margolis[1], Charles D. Schaeffer Jr[2] and Claude H. Yoder[1]*

[1]Chemistry Department, Franklin and Marshall College, Lancaster, PA 17604-3003, USA
[2]Chemistry Department, Elizabethtown College, Elizabethtown, PA 17022-2298, USA

Received 20 July 2002; Accepted 4 December 2002

^{207}Pb NMR spectra were used to determine the structure of adducts of triphenyllead chloride and diphenyllead dichloride in CH_2Cl_2 and CH_3CN. The bases included several phosphorus donors, such as tributylphosphine, oxygen donors, such as tributylphosphine oxide, and nitrogen donors, such as pyridine. A number of bidentate bases were also studied. The ^{207}Pb spectra indicate that rapid exchange occurs in the adducts, even at temperatures of −90 °C. The magnitude of the shift relative to the lead acid indicates that all of the bases, including the bidentate bases, form five-coordinate adducts with triphenyllead chloride. Diphenyllead dichloride forms six-coordinate adducts, except for the adduct with tributylphosphine, which is five-coordinate. This is the first report of a five-coordinate adduct of diphenyllead dichloride. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: ^{207}Pb; NMR; adduct; Lewis acid; lead; triphenyllead chloride

INTRODUCTION

Because of the insolubility of organolead adducts, most studies of these compounds have been performed in the solid state. These studies have indicated that the triorganolead species form five-coordinate trigonal bipyramidal adducts whereas the diorganolead dichloride species form six-coordinate octahedral adducts in the solid state.[1–4]

Previous work from our laboratory using ^{31}P NMR and calorimetry indicated that triorganolead halides form predominantly five-coordinate adducts in solution, even with bidentate bases.[5]

The current study utilizes ^{207}Pb NMR for the investigation of adduct formation with both triphenyllead chloride and diphenyllead dichloride. The ^{207}Pb chemical shift is particularly sensitive to electronic environment and, therefore, is an excellent tool for the study of changes in coordination number.

EXPERIMENTAL

Organolead chlorides were obtained from Pfaltz and Bauer or Alfa Aesar and were used without purification. Bases and solvents were dried over Drierite and then stored over freshly activated type 4A molecular sieves. Solutions were prepared under argon using oven-dried glassware and 10 mm NMR tubes. ^{207}Pb spectra were obtained on a Varian Unity 300 at 62.7 MHz using gated proton decoupling. Spectra were obtained at both room temperature and at the lowest temperature obtainable without significant precipitation. When solubility permitted, solutions were prepared at mole ratios (acid : base) of 1 : 0.5, 1 : 1, and 1 : 2 for each acid–base pair. Reproducibility of spectra was ascertained by obtaining spectra on additional sets of solutions for most acid–base pairs. When solubility permitted, the initial concentration of acid was 0.5 M.

Conductivities were measured using either a Corning CD-55 sensor or an Oakton CON 100 Series portable conductivity meter, calibrated periodically using standard solutions. Tetrabutylammonium tetrabutylborate and tetrabutylammonium triflate were used as comparisons in methylene chloride,

---

*Correspondence to: Claude H. Yoder, Chemistry Department, Franklin and Marshall College, Lancaster, PA 17604-3003, USA.
E-mail: claude.yoder@fandm.edu

Contract/grant sponsor: Petroleum Research Fund.
Contract/grant sponsor: Dow Corning Corporation.
Contract/grant sponsor: Arnold and Mabel Beckman Foundation.
Contract/grant sponsor: Elizabethtown College Faculty Grants Committee.
Contract/grant sponsor: William and Lucille Hackman Scholar's Program.

and 0.01 M solutions gave readings of 219 μS and 144 μS respectively.

RESULTS AND DISCUSSION

^{207}Pb chemical shifts for the triphenyllead chloride systems are reported in Table 1 and are, to our knowledge, the first reports of shifts for these adducts.[6] Assignment of stoichiometry was based on the extent of the shift to low frequency relative to the shift of the free acid. For each acid–base pair, rapid exchange of base was indicated by a change in peak width upon the addition of more base and the inability to obtain tin–phosphorus coupling for most acid–base pairs even at −90 °C.

Monodentate bases included the phosphorus donor tributylphosphine (TBP), the oxygen donors tributylphosphine oxide (TBPO), triphenylphosphine oxide (TPPO), hexamethylphosphoramide (HMPA), and dimethylsulfoxide (DMSO), and the nitrogen donor pyridine. For most of these bases, the 1 : 1 and 1 : 2 mole ratio spectra were identical and the chemical shifts from the free acid at 33 ppm were upfield between 200 and 300 ppm. Even when HMPA, the strongest base used, was increased to a 1 : 30 acid to base ratio, the spectrum did not change. The consistency of the spectra at the different mole ratios and the relatively small upfield shift even at high mole ratios imply exclusive formation of a five-coordinate adduct. For TBP, a low-temperature spectrum could not be obtained at a 1 : 1 mole ratio. Conductivity measurements for 0.01 M acid–base solutions at a 1 : 1 mole ratio were less than 10 μS in methylene chloride, implying that no ionic species are formed in these reactions.

In attempts to form six-coordinate adducts, triphenyllead chloride was reacted with several bidentate ligands, *viz.*: the nitrogen donor bipyridyl (bipy); the phosphorus donors bis(diphenylphosphino)methane (DPPM), 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), and 1,4-bis(diphenylphosphino)butane (DPPB); and the oxygen donor 1,2-ethylene bis(diphenylphosphine oxide) (DPPEO). With the bidentate bases the chemical shifts were between 100 and 250 ppm upfield from the free acid, implying five-coordination. A low-temperature 1 : 1 mole ratio spectrum could not be obtained for bipy. The 1 : 1 and 1 : 2 spectra for DPPM, DPPE, and DPPEO were nearly identical. For DPPP and DPPB, however, the peaks moved upfield with increasing acid concentration, suggesting low equilibrium constants and the presence of exchanging acid and adduct. Increasing the base concentration shifts this equilibrium to the right. With DPPE, a doublet with a ^{207}Pb–^{31}P coupling constant of 464 Hz was obtained at low temperatures, indicating that only one of the two available phosphorus groups is bonded to the central tin atom. For DPPP, two peaks appeared in the spectrum, presumably due to the formation of two stereochemical isomers of the five-coordinate adduct.

Table 1. ^{207}Pb shifts for triorganolead chloride adducts in CD_2Cl_2 at −90 °C

	NMR shift (ppm)	
Base	1 : 1 mole ratio	1 : 2 mole ratio
TBP		−240
TBPO	−248	−249
TPPO	−198	−195
HMPA	−228	−228
Pyridine	−200	−207
DMSO	−180	−184
Bipy		−110
DPPM	−93	−91
DPPE	−198	−201 (d, 464)
DPPP	−130	−206
	−202	−231
DPPB	−129	−150
DPPEO	−202	−202

The ^{207}Pb chemical shifts for the diphenyllead dichloride adducts are reported in Table 2 and are, to our knowledge, the first reports of shifts for these adducts.[6] The acid is relatively insoluble in methylene chloride, but at high concentrations most of the bases produced adducts with shifts in the six-coordinate region (roughly 400 ppm upfield from the acid shift). The acid was insoluble in pyridine, triphenylphosphine, and all of the bidentate bases, and gave no indication of dissolution at high base concentrations. The chemical shift of the dichloride itself was obtained in acetonitrile as −176 ppm, indicating five-coordination in solution.

In the reaction between diphenyllead dichloride and TBP in methylene chloride the solution became clear after the addition of only one molar equivalent. Moreover, the 1 : 1 and 1 : 2 mole ratio solutions both contained a single peak around −250 ppm in acetonitrile and at slightly higher field values (−290 ppm) in methylene chloride at −70 °C. This appears to be the first reported five-coordinated adduct of diphenyllead dichloride. The relative stability of this adduct with TBP, relative to the six-coordinate adduct, is probably a

Table 2. ^{207}Pb shifts for diorganolead dichloride adducts in CD_3CN at −40 °C

	NMR shift (ppm)	
Base	1 : 1 mole ratio	1 : 2 mole ratio
TBP	−251	−251
TBPO	insoluble	−524
TPPO	insoluble	−517[a]
HMPA	insoluble	−615
DMSO	insoluble	−512[a]

[a] Mole ratio is approximate due to insolubility.

result of the steric hindrance of the large groups attached to the coordinating atom.

Acknowledgements

Support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Dow Corning Corporation, the Arnold and Mabel Beckman Foundation, the Elizabethtown College Faculty Grants Committee, and Franklin and Marshall College's William and Lucille Hackman Scholar's program is gratefully acknowledged.

REFERENCES

1. Shier GD, Drago RS. *J. Organomet. Chem.* 1966; **6**: 359.
2. Yatsenko AV, Aslanov LA, Schenk H. *Polyhedron* 1995; **14**: 2371.
3. Matwiyoff NA, Drago RS. *Inorg. Chem.* 1964; **3**: 337.
4. Das VGK, Kitching W. *J. Organomet. Chem.* 1968; **13**: 523.
5. Eppley HJ, Ealy JL, Yoder CH, Spencer JN, Rheingold AL. *J. Organomet. Chem.* 1992; **431**: 133.
6. Wrackmeyer B. *Annu. Reports NMR Spectrosc.* 2002; **47**: 1.