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# TRIPHENYLLEAD ISOCYANATE AND ADDUCTS WITH SOME O- AND N-DONOR LIGANDS: SYNTHESES AND SPECTROSCOPIC STUDIES

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## Summary

The preparation and properties of triphenyllead isocyanate have been reinvestigated and its synthesis (68% yield) by the reaction of triphenyllead acetate with potassium cyanate in boiling methanol is reported. The first 1/1 adducts of triphenyllead isocyanate with the ligands: hexamethylphosphoramide (HMPA), dimethyl sulphoxide (DMSO), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), triphenylphosphine oxide (TPPO), trimethyl phosphate (TMP), and pyridine (py), have been prepared and characterised by infrared, Raman, and $^{31}P$ NMR spectroscopy. The adducts are white solids with melting points in the range 78—143°C; the TMP and py adducts dissociate slowly on standing at room temperature and only the HMPA and TPPO adducts could be recrystallized from benzene. The infrared and Raman spectra of solid $Ph_3PbNCO$ are consistent with a polymeric structure, with $Ph_3Pb$ groups joined by cyanate bridges so that each lead has a distorted trigonal-bipyramidal coordination. Adduct formation by $Ph_3PbNCO$ probably involves the breaking of cyanate bridges at the weaker Pb—O bonds followed by formation of lead—ligand bonds so that each lead retains five coordination in a molecular structure.

## Introduction

Phenyl-tin and -lead thiocyanates ($Ph_3MNCS$ and $Ph_2M(NCS)_2$ where M = Sn or Pb) form stable adducts with a variety of ligands [1], but the Lewis acid capabilities of other pseudohalides ($Ph_3MX$ and $Ph_2MX_2$ where X = $N_3$, NC, NCO, etc.) have not yet been explored. We have continued our studies of adducts of phenyl-tin and -lead halides and pseudohalides [2,3] by preparing

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$Ph_3PbNCO$ and studying its interaction with some O- and N-donor ligands. While the corresponding fulminate is well-characterised [4], few details are available for the isocyanate, although some results have been reported privately [5]. Curiously, however, the crystal structure of $Ph_3PbNCO$ has been determined [6].

## Experimental

All solvents and liquid ligands were stored over molecular sieves before use while solid ligands were used as received. Triphenyllead acetate was recrystallized from acetonitrile before use. Microanalyses for C, H, and N were done by Galbraith Laboratories, Knoxville, Tennessee, and Guelph Chemical Laboratories, Guelph, Ontario. Lead was determined gravimetrically as lead sulphate. Molecular weights were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee. Spectroscopic measurements (infrared, Raman, $^{31}P$ NMR) were carried out as described elsewhere [3]. Mass spectra were measured by the McGill University Biomedical Mass Spectrometry Unit, using an LKB 9000 instrument at an electron potential of 70 eV, 60 μamp electron current, and a source temperature of 290°C.

## Preparations

### *Triphenyllead isocyanate*

Triphenyllead acetate (10.0 g) and potassium cyanate (1.7 g) were refluxed

TABLE 1

ANALYTICAL DATA FOR ADDUCTS ($Ph_3PbNCO \cdot L$)

| Ligand (L) | M.p. (°C) | Analysis (Found (calcd.) (%) | | | |
|---|---|---|---|---|---|
| | | C | H | N | Pb |
| Hexamethylphosphoramide.(HMPA) [a] | 141-2 | 45.5<br>(45.5) | 5.0<br>(5.0) | 8.4<br>(8.5) | 30.9<br>(31.4) |
| Dimethylsulphoxide (DMSO) | 92-6 | 45.2<br>(45.15) | 3.8<br>(3.8) | 2.3<br>(2.5) | 36.5<br>(37.1) |
| *N,N*-Dimethylacetamide (DMA) | 78-81 | 49.0<br>(48.7) | 4.3<br>(4.3) | 4.8<br>(4.9) | 36.0<br>(36.5) |
| *N,N*-Dimethylformamide (DMF) | 79-80 | 47.7<br>(47.7) | 3.6<br>(4.0) | 4.1<br>(5.05) | 36.7<br>(37.4) |
| Triphenylphosphine oxide (TPPO) [b] | 142-3 | 58.3<br>(58.55) | 4.0<br>(4.0) | 1.8<br>(1.8) | 27.5<br>(27.3) |
| Pyridine (py) [c] | 91-3 | — | — | — | 36.6<br>(37.0) |
| Trimethyl phosphate (TMP) | ~80 | — | — | — | 34.3<br>(33.4) |

[a] Mol. wt. (Benzene, 0.01 *M*, 37°C) 622(660); $^{31}P$ NMR (sat'd solution in $CDCl_3/CH_2Cl_2$ eutectic, 180 K, $\delta(P)$ 24.2 ppm, $^2J(Pb\text{-}P)$ 136 Hz (85% $H_3PO_4$ as external reference). [b] Mol. wt. (Benzene, 0.01 *M*, 37°C) 683(759). [c] Adduct lost ligand on standing at room temperature, thus could not be sent for microanalysis.

in methanol (1.0 l) for 10 min and then water (1.0 l) was added to the cooled reaction mixture to give a white precipitate. After further stirring for 1—2 h at room temperature, the white product was filtered off and recrystallized from benzene; yield, 68%, m.p. 174—175°C (dec). (Found: C, 47.5; H, 3.2; N, 2.9; $(C_6H_5)_3PbNCO$ calcd.: C, 47.5; H, 3.15; N, 2.9%) Mol. wt. (Benzene, 0.01 *M*, 37°C), found, 610; calcd. 481; *m/e*, 481 (vw).

### *Adducts with liquid ligands (1/1)*

Triphenyllead isocyanate (~1 g) in benzene (50 ml) and liquid ligand (0.5—1 ml, 3-fold excess of HMPA, DMSO, DMA, DMF, TMP, or py) were mixed to give a clear solution. After standing 3 h at room temperature benzene was removed by rotary evaporation leaving an oil. Addition of pentane (or ether/pentane) gave the white crystalline adduct (sometimes with difficulty); yields, 65—75%. Adducts were dried in vacuum at room temperature.

### *Triphenyllead isocyanate-mono(triphenylphosphine oxide)*

Triphenyllead isocyanate (1.0 g) and triphenylphosphine oxide (0.7 g) were dissolved in benzene (55 ml) and the solution allowed to stand at room temperature for 5 h. Removal of benzene by rotary evaporation gave a residue which crystallized slowly on addition of pentane. The crude product was recrystallized from toluene and dried in a vacuum at room temperature; yield, 55%. Analytical data for all adducts prepared are given in Table 1.

## Results and discussion

### *Triphenyllead isocyanate*

Triphenyllead isocyanate is a stable white solid soluble in many organic solvents, e.g. alcohols, benzene, dichloromethane, etc., but only slightly soluble in alkanes. A preliminary mass spectral study showed $Ph_3Pb^+$, $Ph_2PbNCO^+$, $PhPb^+$, $PbNCO^+$, and $Pb^+$ to be the principal ions observed while $PhPb(C_6H_4)^+$, $C_6H_4PbNCO^+$, and $Ph_2^+$ were less abundant. The transitions $Ph_3Pb^+ \rightarrow PhPb^+$, and $Ph_2PbNCO^+ \rightarrow PhPb^+$ were confirmed by observation of metastable ions at $m^*$ 439 and $m^*$ 404, respectively.

Triphenyllead isocyanate is not stable in solution in contrast with its tin analogue [7] which was recovered unchanged after being refluxed in anhydrous butanol for 24 h. For example, $Ph_3PbNCO$ decomposed extensively when refluxed in 30—60 petroleum ether for 16 h. Thin layer chromatography showed essentially complete disappearance of $Ph_3PbNCO$ after it was refluxed in methanol or ethanol for 2 days. The decomposition products differ in melting points (from MeOH, 145°C; from EtOH, 130—135°C) and in their infrared spectra (1700—400 cm$^{-1}$). The properties of the methanol product are not consistent with those reported earlier for $Ph_3PbOMe$ [8].

The white solid obtained when water is added to a methanol solution of the $Ph_3PbNCO$ decomposition product is identical with the by-product of the preparation of the isocyanate if long reflux times (2—4 h) are used. The same by-product is obtained regardless of whether methanol or ethanol is the reaction solvent. The white solid (m.p. 192—194°C) is soluble in hot benzene and has an elemental analysis (C, 48.4; H, 3.8; N, 0.0%) consistent with the formula, $[(C_6H_5)_3Pb]_2O$ (calcd.: C, 48.4; H, 3.4%) for this compound. This is supported by mass spectral data (predominant ions, $Ph_3Pb^+$ and its disintegration products) and the lack of $\nu$(O—H) absorptions in the infrared spectrum of the white solid. In the region 1700—400 $cm^{-1}$, in addition to bands associated with the $Ph_3Pb$ group, an absorption at 777 $cm^{-1}$ (wm(br) is observed which may be assigned to an overtone of a $\nu$(Pb—O) mode. Unfortunately for comparison purposes, triphenyllead oxide is incompletely characterized in the literature [9].

*Adducts of triphenyllead isocyanate (1/1)*

Of the adducts with liquid O-donor ligands reported here, only that with HMPA could be recrystallized from benzene while the TMP adduct lost ligand on standing at room temperature. The DMSO, DMA, and DMF adducts are stable in the solid state at room temperature but cannot be recrystallized. No adduct was obtained when $Ph_3PbNCO$ was crystallized from a tetrahydrofuran (THF) solution. This apparent qualitative stability order for the adducts, $Ph_3PbNCO \cdot L$, is consistent with the base strength order given be the Gutmann donor number (DN) concept [10], the respective DN values being: HMPA, 38.8; DMSO, 29.8; DMA, 27.8; DMF, 26,6; TMP, 23.0; THF, 20.0. An adduct formed with TPPO, the only solid O-donor ligand used in this work, but molecular weight values in benzene solution show $Ph_3PbNCO \cdot$ TPPO to be a weaker adduct than its HMPA counterpart, again consistent with the relative donicities of these two ligands as given by Gutmann [11].

The properties of $Ph_3PbNCO \cdot$ HMPA can be compared with those of the adducts $Ph_3PbX \cdot$ HMPA (X = Cl, Br, I, NCS) [2]. Molecular weight measurements indicate an effect of change in X increasing the $Ph_3PbX$ acceptor strength, of $I < Br < Cl << NCO \leq NCS$. No solid HMPA adduct with $Ph_3PbOAc$ was obtained by using the procedure described above. Although it is perhaps not surprising for the NCO and NCS groups to have a similar effect on central atom acceptor power, a quite different situation was observed by Graddon et al. when studying calorimetrically the interaction of $Bu_2SnX_2$ with pyridine in toluene. Here the order of change in X increasing the acceptor power of $Bu_2SnX_2$ is: $OAc < NCO < Cl << NCS$ [12]. Clearly many more systems must be studied before a general trend can be deduced for the relative effects of halide and pseudohalide ligands on the acceptor power of the metal atom they are attached to.

The $^2J$(Pb—P) value for $Ph_3PbNCO \cdot$ HMPA is the largest observed for adducts of this series [2], the order being $NCO > NCS > I \sim Br > Cl$. As in the analogous tin series, $Ph_3SnX \cdot$ HMPA [3], where X = Cl, Br, or I, this trend in $^2J$(Pb—P) values may be correlated with the change in electronegativity of the axial halide ligand. Unfortunately, group electronegativity values for N-bonded cyanate and thiocyanate are not available to further test the above correlation.

Results with N-donor and S-donor atom ligands were disappointing; only an unstable pyridine adduct was obtained, a surprising result since pyridine has a DN value of 33.1 [10]. However, Gutmann's DN values are best used in considering the relative donor abilities of ligands with the same donor atom [11]. No adducts were obtained by reaction of $Ph_3PbNCO$ with dipyridyl, *o*-penanthroline, *N,N*-dimethylthioacetamide, or triphenylphosphine sulphide by following the method used to prepare the TPPO adduct.

TABLE 2

IR VALUES (cm$^{-1}$) OF $\nu$(CN) AND SELECTED LIGAND MODES [a] FOR $Ph_3PbNCO \cdot L$

| Assignment | L = HMPA | L = TPPO | L = TMP | L = DMSO | L = DMA | L = DMF | L = py |
|---|---|---|---|---|---|---|---|
| $\nu$(CN) | 2179vs(br)<br>2125(sh) | 2176(sh)<br>2168s(br) | 2169vs(br)<br>2059(sh) | 2170vs(br)<br>2112m | 2178vs(br) | 2192(sh)<br>2182vs(br) | 2185vs(br) |
| Ligand modes | 1189vs<br>(1210) [2] | 1156s<br>(1193) [18] | 1244s(br)<br>(1284) [19] | 973s<br>(954) [20] | 1605vs(br)<br>(1645) [20] | 1638vs(br)<br>(1653) [21] | 1591s<br>(1583) [20] |
| | $\nu$(P=O) | $\nu$(P=O) | $\nu$(P=O) | $\rho(CH_3)$ | $\nu$(C=O) | $\nu$(C=O) | 8a [20] |
| | | | | 705w<br>(698) [20]<br>$\nu_{as}(SC_2)$ | | | 415s<br>(406)<br>16b [20] |

[a] Values in parentheses are for the free ligand.

*Vibrational spectra*

Triphenyllead isocyanate shows very strong IR absorptions at 2171, 2191 $cm^{-1}$(s) and 2183 ($CH_2Cl_2$ solution) due to $\nu$(CN), actually $\nu_{as}$(NCO). Values of $\nu$(CN) for the adducts are given in Table 2. Unfortunately this parameter is not a guide to the cyanate group bonding type [13]. The potentially more diagnostic $\nu$(CO) (i.e. $\nu_s$ (NCO)) mode gives generally weak infrared absorptions in the region (1350—1050 $cm^{-1}$) and was not identified in this work due to strong overlap by ligand and $Ph_3Pb$ group absorptions. However, since $Ph_3PbNCO$ has been shown to be polymeric, with the Pb—N bond stronger than the Pb—O bond [6], and since X-ray crystal structures of all metal compounds containing terminal NCO groups show them to be N-bonded [13,14], it can be reasonably assumed that the adducts reported here are indeed isocyanates. Table 2 also includes ligand bands shifted on coordination. All other infrared absorptions in the 1700—300 $cm^{-1}$ range were assigned to either $Ph_3Pb$ group modes [15] or unshifted ligand vibrations.

Skeletal vibrational data (solid state) in the region (300—50 $cm^{-1}$) are reported in Table 3 for $Ph_3PbNCO$ and $Ph_3PbNCO \cdot L$ (L = HMPA, DMSO, and DMA). Most bands may be assigned to skeletal modes of the triphenyllead moiety [15]. For the HMPA adduct comparison with results for other adducts $Ph_3PbX \cdot HMPA$ [2] indicates that $\nu$(Pb—NCO) may be assigned to the medium infrared absorption at 279 $cm^{-1}$, with a similar assignment for $Ph_3PbNCO$ and the DMSO and DMA adducts. This value of $\nu$(Pb—X) when compared with that for $Ph_3PbNCS \cdot HMPA$ (162 $cm^{-1}$) is much higher than expected by change in mass alone, but is consistent with other isocyanate-isothiocyanate comparisons of $\nu$(M—X) frequencies, for example, $Me_3SiX$ [16]; X = NCS, 436 $cm^{-1}$; X = NCO, 521 $cm^{-1}$; and $Ph_3GeX$ [17]; X = NCS, 368 $cm^{-1}$; X = NCO, 450 $cm^{-1}$. The parent Lewis acid, $Ph_3PbNCO$, shows an additional medium infrared absorption at 213 $cm^{-1}$ which is assigned to the $\nu$(Pb—OCN) vibration expected with the presence of a strongly bridging NCO group [6]. The lead—ligand

TABLE 3

SKELETAL FREQUENCIES ($cm^{-1}$) FOR $Ph_3PbNCO$ AND SOME ADDUCTS

| $Ph_3PbNCO$ | | $Ph_3PbNCO \cdot HMPA$ | | $Ph_3PbNCO \cdot DMSO$ | | $Ph_3PbNCO \cdot DMA$ | | Assignment |
|---|---|---|---|---|---|---|---|---|
| IR | R | IR | R | IR | R | IR | R | |
| 272s | 275vw | 279m | 260w | 284s | 281m | 272s | 273s | $\nu$(Pb—NCO) |
| 251m | | 250w | | | | | | |
| 230s | 236m | 226s | 233s | 226s | 234<br>224 s | 227s | 228s | $\nu_{as}$(Pb—Ph)(t) [a] |
| 213m | 214(sh) | | | | | | | $\nu$(Pb—OCN) |
| | | 208(sh) | | | | | | $\nu$(Pb—HMPA) |
| 201vw | 198s | | 202vs | | 199vs | 200w | 195vs | $\nu_s$(Pb—Ph)(t′) [a] |
| 184m | 182(sh) | 184m | | 182vs | 190(sh) | 185w | | (u) [a] |
| 148w | 153w | 144w | 153m | 150w | 155m | 155vw | 154m | (x) [a] |
| | | | | 130m | | | | |
| 100s | 100m | 111m | | 120m | | 100s | | Deformation modes |
| | | | 70m | 105m | 85(sh) | | 85sh | |
| | | | 50m | | 58m | | | |

[a] Whiffen's notation [22].

stretching frequency was identified only for the HMPA adduct, by comparison with the previous $\mathrm{Ph_3PbX \cdot HMPA}$ results [2]. For the DMSO and DMA adducts no such comparison was possible, and thus no $\nu$(Pb—L) frequencies could be assigned.

The infrared and Raman spectra of solid triphenyllead isocyanate are consistent with the known structure of this compound [6], that is distorted trigonal "$\mathrm{Ph_3Pb}$" groups joined by cyanate bridges as shown by the presence of both $\nu$(Pb—N) and $\nu$(Pb—O) frequencies, causing each lead atom to be five coordinate. Molecular weight results show $\mathrm{Ph_3PbNCO \cdot HMPA}$ and $\mathrm{Ph_3PbNCO \cdot TPPO}$ are monomeric in benzene solution while vibrational data for the solid adducts, $\mathrm{Ph_3PbNCO \cdot L}$ (L = HMPA, DMSO, or DMA) imply these are also five-coordinate with little change in $\nu$(Pb—NCO) on adduct formation and with no $\nu$(Pb—OCN) mode. Thus, adduct formation by $\mathrm{Ph_3PbNCO}$ requires the breaking of a cyanate bridge at the weaker lead-oxygen bond followed by formation of a lead—ligand bond with the retention of five-coordination by the lead atom. A similar pattern was evident in the formation of the adducts $\mathrm{Ph_3PbX \cdot HMPA}$ (X = NCS, Cl, Br, or I) where lead retains five-coordination in the solid state [2], and in $\mathrm{Ph_2PbX_2 \cdot 2HMPA}$ (X = NCS, Cl, Br, or I) and $\mathrm{Ph_2PbX_2 \cdot HMPA}$ (X = Br or I) where lead remains six coordinate [1,2].

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