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ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

V *. A 1,2-ALKYL SHIFT FROM LEAD TO A TRANSITION METAL

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Summary

The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2PbR_3$ (R = Me and Et) have been synthesized and characterized. The trimethyllead complex is extremely labile with respect to thermal and photochemical decomposition that leads to the formation of $(Me)_4Pb$, Pb, and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$. This new type of methyl transfer from Pb to Fe does not occur for the triethyllead complex thermally, but does occur to a limited extent photochemically, and helps explain certain zinc treatments for removal of organolead compounds from industrial effluents.

Introduction

Hitchen, Holliday, and Puddephatt have made a detailed study of the decomposition of alkyllead chlorides in aqueous solution in the presence of zinc [2,3]. On the basis of their studies they have proposed a mechanism whereby, for example, trimethyllead chloride forms an adsorbed complex $[Me_3Pb\text{-}ZnCl]_{ads}$. This adsorbed species is then proposed initially to undergo elimination of Me_2Pb with formation of MeZnCl via a 1,2-methyl migration from lead to zinc [2]. The latter species may then react in a number of fashions, leading eventually to the product methane. In contrast, if the reaction involves triethyllead chloride, the major product is hexaethyldilead [3]; thus, if the formation of an adsorbed species $[Et_3PbZnCl]_{ads}$ is again involved, the implication is that in this case no 1,2-ethyl transfer from lead to zinc occurs. Possibly an adsorbed species other than $[Et_3PbZnCl]$ is formed.

Puddephatt has further illustrated that the reaction of Me_3PbCl or Me_4Pb with $[PtMe_2(bipy)]$ leads to *fac*-$[PtMe_3Cl(bipy)]$, possibly via formation of a

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* For part IV see ref. 1.

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very unstable transient Me_3PbPt complex followed by a 1,2-alkyl migration [4].

There is no precedent for such 1,2-alkyl migrations in the literature of organolead complexes of the transition metals. It has been reported that trimethyllead-pentacarbonylmanganese is thermally unstable with respect to formation of Me_4Pb and $Me_2Pb[Mn(CO)_5]_2$, thus illustrating the potential lability of the alkyl—lead bond in such systems [5]. Similar redistributions were reported by Hein and Jehn in the bis-lead tetracarbonyliron systems [6], i.e., $(R_3Pb)_2Fe(CO)_4 \rightarrow R_4Pb + [R_2PbFe(CO)_4]_2$. In each case the lead—transition metal bond is retained, with no alkyl-transition metal complexes formed.

It is the purpose of this report to illustrate for the first time a clear cut system where an isolable trialkyllead-transition metal complex may be formed, and then treated in such a manner as to promote a 1,2-alkyl migration from lead to the transition metal.

Experimental

All procedures were performed under inert atmospheres of nitrogen, all solvents used were dry and oxygen free. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and Et_3PbCl were obtained from Strem Chemicals, and Me_3PbCl was generously provided by the Ethyl Corporation.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2PbR_3$. A THF solution of R_3PbCl (2.0 g, R = Me, 7.0 mmol, R = Et 6.0 mmol) was added dropwise to 40 ml of a solution containing an equivalent of $Na^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$, cooled to 0°C. After stirring the mixture for 3 h the solvent was removed under vacuum and the resulting gum extracted with 50 ml of dry hexane, concentrated to 10 ml, and placed upon an aluminium column. The column was wrapped in aluminium foil and the yellow band eluted with hexane was collected in a similarly wrapped flask under a nitrogen atmosphere. Removal of the solvent yielded an orange-red oil, with yields in the 60% range. Analytical and spectral data are recorded in Table 1.

In the case of the trimethyllead-iron complex, after purification on the column, the column contains a broad violet band. This band can be removed by eluting with methanol to yield a presently unidentified cyclopentadienyl complex that contains no alkyllead group. We are presently investigating this complex.

TABLE 1

SPECTRAL AND ANALYTICAL DATA

Complex	$\nu(C = 0)$ [a]	NMR [b]		Analysis [c] ((calcd.) found) (%)	
		$(\eta^5\text{—}C_5H_5)$	R_3Pb	C	H
$(\eta^5\text{—}C_5H_5)\ Fe(CO)_2PbMe_3$	1944, 1987	5.25	9.83	(28.12) 28.49	(3.28) 3.10
$(\eta^5\text{—}C_5H_5)\ Fe(CO)_2PbEt_3$	1943, 1987	5.20	8.90	(33.15) 33.54	(4.24) 4.08
$(\eta^5\text{—}C_5H_5)\ Fe(CO)(Ph_3)\ PbEt_3$ [d]	1915	5.72	8.72	(51.10) 51.59	(4.96) 4.98

[a] In hexane solution. [b] In $CDCl_3$, ppm. [c] Admirably performed by Canadian Analytical Service Ltd., Vancouver, Canada. [d] Aromatic protons, 7.30 m.

Thermal treatment of (η^5-C_5H_5)Fe(CO)$_2$PbR$_3$

A hexane solution of 0.2 g (0.46 mmol) of (η^5-C_5H_5)Fe(CO)$_2$PbMe$_3$ was refluxed in hexane in an aluminium foil covered flask for 2 h. After this period of time an infrared spectrum indicated no starting material, but the appearance of two new carbonyl bands at 2032 and 1976 cm^{-1}. A considerable amount of metallic lead was apparent. The solution was concentrated to 10 ml and placed upon an alumina column. Elution with hexane yielded 36 mg (40%) of (η^5-C_5H_5)Fe(CO)$_2$Me identified by comparison of its spectral data (IR, NMR, PES) with those of an authentic sample.

A similar reaction involving (η^5-C_5H_5)Fe(CO)$_2$PbEt$_3$, with a reflux period of 48 h led to no infrared observable decomposition of the lead-iron complex.

Photochemical treatment of (η^5-C_5H_5)Fe(CO)$_2$PbR$_3$

A hexane solution containing 0.5 g of the alkyllead complex, R = Me 1.16 mmol; R = Et 1.06 mmol, with an equivalent of triphenylphosphine was irradiated in a quartz flask by a 500 watt Hanovia lamp. After 7 h the reaction was stopped and the hexane solvent removed under vacuum. The crude product was dissolved in the minimum of a 1/4 CH_2Cl_2/hexane mixture and placed upon an alumina column. Elution with hexane removed any unreacted starting materials and subsequent elution with a 1/3 CH_2Cl_2/hexane mixture brings through an orange band. Upon removal of the solvent from this eluant until approximately 25% by volume remains, and cooling the solution to —15° C, orange crystals deposit. In the case of R = CH_3 this product was shown to be (η^5-C_5H_5)Fe(CO)-(PPh$_3$)Me (57%) by comparison of its spectral data (IR, NMR) with that of an authentic sample [7]. In the case of R = Et a new complex, (η^5-C_5H_5)Fe(CO)-(PPh$_3$)PbEt$_3$, was isolated (65%). The analytical and spectral properties of this new complex are recorded in Table 1. Small amounts (5%) of the known complex (η^5-C_5H_5)Fe(CO)(PPh$_3$)Et were obtained by physical separation from the above crystalline crop [8].

Discussion

The two trialkyllead-dicarbonyliron complexes reported herein are readily available using the standard salt elimination procedure as outlined in the experimental portion. All spectral and analytical data recorded in Table 1 are in accord with proposed structures. The triethyllead complex is much less prone to oxidative decomposition both in the pure form and in solution than the trimethyllead complex. Oxidative decomposition does not seem to involve any alkyl migration products.

The thermal and photochemical treatment of the trimethyllead derivative shows that the methyl migration from lead to iron is extremely facile, the reaction being complete in a matter of hours at only moderately elevated temperatures. By performing the thermal reaction in an NMR tube we have observed that the reaction is essentially quantitative as outlined below.

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2PbMe_3 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2Me + [PbMe_2]$$

$$\rightarrow 1/2\ Pb + 1/2\ PbMe_4$$

The inability of the triethyl derivative to undergo this thermal reaction is noteworthy, but presently no explanation can be offered.

The migration of the ethyl group may, however, be effected by photolyzing the triethyllead complex, but even this observation is not without added interest. In the presence of added triphenylphosphine, formation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)PbEt_3$ is noted, with only small amounts of the "expected" $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Et$ recovered. With the trimethyllead complex only the $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Me$ complex is obtained. Clearly, the substitution of the carbonyl group by triphenylphosphine is kinetically faster than the alkyl migration reaction for the triethyl complex, and, furthermore, it seems that substitution of the phosphine for the carbonyl ligand has a stabilizing effect upon the trialkyllead-iron complex since irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)PbEt_3$ failed to produce significant yields of the alkyl transfer product.

It is interesting to speculate upon the results reported here in relation with the other decomposition pathway reported in the literature for $Me_3PbMn(CO)_5$ and $(R_3Pb)_2Fe(CO)_4$ outlined in the introduction. Clearly, the relative bond strengths of the Pb—C and Pb—M (M = Fe, Mn) become significant, and the results imply that the Pb—Fe bond is of lower bond strength in the $(\eta^5\text{-}C_5H_5)Fe(CO)_2PbR_3$ system.

Studies on related alkyllead-transition metal complexes, are in progress.

Regardless of the exact mechanism, and the factors affecting this mechanism, the present results clearly illustrate the viability of the proposed routes of zinc-based removal of organolead compounds from solution, including the differences observed for methyl- and ethyl-lead compounds.

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